Laboratory of Polymer Technology
Faculty of Science and Engineering
Åbo Akademi University

BEWiSynbra RAW Oy
Finland
Porvoo

Recycling of Polystyrene in Suspension Polymerization Process

Author:

Jani Korkiamäki

June 2020

Project Type:

Master Thesis

Supervisors:

***Carl-Eric Wilén,* Professor, Åbo Akademi**

***Päivi Julku,* Head of Quality Control, BEWi Synbra RAW Finland**

Preface

This Master's Thesis was done in cooperation between BEWISynbra Group and the Laboratory of Polymer Technology of Åbo Akademi University. BEWiSynra Raw ordered the project, and the working and the experimentation were performed in BEWiSynbra Raw's facilities. Even though the project proved to be challenging, it has been an extremely educational and a rewarding journey.

First and foremost, I want to thank Päivi Julku and Ville Nurminen for supervision, guidance and support during the project, and also Carl-Eric Wilén for guidance. The expertise these people offered was crucial for the project. I want to thank BEWiSynbra RAW for financing the project and the Laboratory of Polymer Technology of Åbo Akademi University for enabling the working in the company. I am also grateful for the valuable information and guidance Asko Ronkainen and Liisa Rousi offered during the project both in practical and theoretical matters. In addition, I want to thank both Liisa Rousi and Sini Renlund from the laboratory for the help they offered in experimentation, and in the use of laboratory equipment and analyzing equipment, and for their patient and mature attitude towards working, as well. Finally, a big thanks to the authors of the literature that was used in this Master Thesis.

Jani Korkiamäki

Abstract

Dissolution of different EPS qualities and the re-use of these qualities in a suspension polymerization process and their effect on the characteristics of EPS material characteristics were studied in laboratory scale. The studied EPS qualities were off-spec EPS qualities obtained from BEWiSynbra Raw's conventional suspension polymerization process, namely undersized and oversized off-spec EPS, and extruded recycled EPS (fish-box material). Up to 30 weight percentages of EPS were successfully dissolved into MS, and batches containing up to 20 weight percentages of reused EPS were successfully suspension polymerized in a batch reactor with the different EPS qualities.

Solubility of the different EPS qualities into MS as a function of time at different temperatures namely room temperature (c. 25°C), 50°C, and 70°C, at different EPS mass concentrations, namely 5, 10, 15, 20, 25, and 30, were experimented in laboratory scale. The solubility and the dissolution times for total dissolution were determined visually and results compared. The obtained results gave the following ranking orders for the different EPS qualities regarding the dissolution times that increase to the right: undersized off-spec EPS < extruded recycled EPS < oversized off-spec EPS.

The suspension polymerization was performed mainly by predissolving EPS into virgin MS, but dissolving EPS into MS directly in the batch reactor's suspension prior to the polymerization was experimented with batches containing 5 weight percentages of off-spec EPS, as well. The quality and properties of the beads obtained from different batches were studied by the means of sieving (PSD), residual monomer and molecular weight experimentation. In addition, some of the batches were pre-foamed and subsequently molded into slabs in order to test the foaming power, mechanical (compressive and bending strength) and thermal properties (lambda). Based on the obtained results the following ranking in the bead quality between the different EPS qualities in general was obtained: off-spec EPS > extruded recycled EPS.

Keywords: *dissolution, expanded polystyrene (EPS), monostyrene (MS), off-spec, recycling, reuse, EPS, suspension polymerization*

Abstrakt

I denna avhandling undersöktes möjligheterna att återvinna polystyren i en konventionell suspensionspolymerisationsprocess för framställning av expanderad polystyren (EPS). I första skedet kartlagdes det återvunna polystyrenets löslighet i styren vid tre olika temperaturer som funktion av upplösningstid.

De undersökta EPS-kvaliteterna bestod av två olika ”off-spec”-EPS-kvaliteter från BEWiSynbra Raws konventionella suspensionspolymerisationsprocess, nämligen under- och överdimensionerad ”off-spec”-EPS, och ytterligare av en extruderad återvunnen EPS-kvalitet (material som använts som fisklådor). Resultaten visar att upp till 30 viktprocent av cellplasten kunde upplösas i styren. Lösligheten minskade enligt följande: underdimensionerad ”off spec” EPS> extruderad EPS> överdimensionerad ”off-spec”-EPS.

I det andra skedet tillfördes det återvunna och upplösta expanderade polystyrenet i en satsreaktor för framställning av pentan impregnerade polystyrenpärlor. Resultaten visar att PS-pärlor innehållande upp till 20 viktprocent av de olika återvunna EPS-kvaliteterna kunde tillverkas framgångsrikt. Vid högre halter av återvunnen EPS uppstod problem med agglomeration av pärlorna pga. instabiliteten hos den bildade suspensionen.

Suspensionspolymerisationen utfördes huvudsakligen genom att först lösa den återvunna EPS:n i styren, och utöver detta utfördes experiment att tillföra 5 vikt procent av återvunnen EPS direkt i satsreaktorn utan att först upplösa cellplasten i styren. Kvaliteten och partikelstorleksfördelningen för de erhållna pärlorna undersöktes sedan med hjälp av sikt (fördelning av partikelstorlek, PSD), och restmonomerhalten bestämdes med gaskromatografi samt molekylvikten och dess fördelning analyserades genom att passera polymerlösningen genom en gelkolonn (SEC). Därtill konverterades de framställda PS-pärlorna till skivor för att bestämma materialegenskaper såsom skumningsstyrkan, och mekaniska (kompressions- och brytningsstyrka) samt termiska (värmeledningsförmåga, lambda) egenskaper. Sammanfattningsvis kan man säga att båda de återvunna ”off-spec” EPS-kvaliteterna gick lättare att återvinna än extruderad återvunnen EPS.

Nyckelord: upplösning, expanderad polystyren (EPS), styrenmonomer (MS), off-spec, återvinning, återan-vändning, EPS, suspensionspolymerisering

Literature Analysis

The theoretical parts of the thesis are extremely general in nature, giving general education particularly on EPS, its recycling and suspension polymerization. In addition, the basics of recycling strategies for plastics, polymers and styrenic polymers in general are briefly discussed. The thesis may work as an educating tool for inexperienced readers, but the more advanced readers should stick to the experimental parts discussing the research, the results and goals of the project. The sections of the thesis that are the most interesting that may have the most practical importance are Abstract, and chapters 2 Purpose, Goals and Guidelines, 7 Solubility Experimentation, 8 Suspension Polymerization Experimentation, and 9 Conclusions. Still, chapters 3.5 and 6.4.4 may be interesting, as well. In general, the biggest issue with the literature that was used in the thesis is the fact that most of the sources are relatively old and not the most recent.

The only relevant literature regarding the research is the patents that describe incorporation of graphite into EPS particles with the help of dissolved EPS and/or PS into MS [11,12]. The patents were found by chance as they were mentioned in *Update on Mouldable Particle Foam Technology* [4] in which new modifications on EPS were discussed. These patents were relatively old and, in the future, a search for more recent graphite EPS patents could be a good direction for literature sources. Some attempt at the literature search touching the subject of the Master Thesis, EPS/PS recycling in suspension polymerization, was done, and headwords that were used included, for example:

- ‘dissolution of polystyrene’ and ‘dissolution of EPS’,
- ‘solubility of PS into styrene’ and ‘solubility of EPS into styrene’,
- ‘recycling of EPS’ and ‘recycling of PS’,
- ‘recycling of PS/EPS in suspension polymerization process’, and
- ‘EPS suspension polymerization’, to name a few.

The search engines that were used were used included Google Scholar, Google Patent, Alma (ÅA & Aalto), Scopus, Web of Science (Thomson Reuters), ScienceDirect, SpringerLink and Wiley. However, the effort in the literature search was not maximal, and the time that was scheduled for the literature search was relatively restricted. It is certainly possible that the author did not use the right headwords and did not browse thoroughly enough the search results. In addition, the spectrum of PS and EPS patents was enormous, and more beneficial patent material most certainly exists. Literature regarding dissolution of PS in other solvents than styrene and PS solvent recycling with solvents such as limonene was significantly easier to find than the use of styrene.

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Abbreviations

ABS	acrylonitrile butadiene styrene
BPO	dibenzoyl peroxide (DBPO), benzoyl peroxide or benzo peroxide
BR	batch reactor
CV	coefficient of variation
DSD	droplet size distribution
EPS	expanded or expandable polystyrene
ERE	extruded recycled EPS
GPPS	general purpose polystyrene
HBCD	hexabromocyclododecane
HIPS	high-impact polystyrene
HOF	high/upper/oversized off spec material with bead size ≥ 2.5 mm (K-110)
LCA	life cycle assessment/analysis
LOF	low/fine/undersized off-spec quality with bead size < 0.4 mm (K-1310)
MN	number average molecular weight
MS	monostyrene, styrene monomer or styrene (a.k.a. ethenylbenzene, vinylbenzene, and phenylethene)
MW	molecular weight (weight average molecular weight)
MWD	molecular-weight distribution
NaOAc	sodium acetate
PD	polydispersity index (PDI) or dispersity (Đ$_W$)
pFR	polymeric flame retardant
PS	polystyrene
PSD	particle-size distribution
RM	residual monomer
SD	standard deviation
SEC	size-exclusion chromatography
TBEC	tert-butylperoxy 2-ethylhexyl carbonate or tert-Butylperoxy 2-ethylhexyl carbonat
W	water
wt-%	weight percentage, mass fraction, weight concentration or mass concentration
XPS	extruded polystyrene

1 Introduction

The use of plastic materials and products is constantly increasing [1]. At the same time, the environmental concerns have increased, and the regulations have tightened [2]. The pressure to decrease the amount of solid waste ending up in landfills and the environment, the amount of emissions and pollutants, and the consumption of natural resources is at its all-time highest, and recycling is a preferable option for the "conventional" waste disposal [3]. All this is also true for expanded polystyrene (EPS), also known as Airpop®- engineered air in Europe, with a wide variety of applications especially in the construction, the packaging, and the automotive industry [4,5].

The impression that EPS can not be recycled is persistent [2]. While it is true that recycling EPS involve many technological challenges, the EPS is still among one of the most recycled plastics in the world [15,24]. The high cost of landfilling EPS waste (highly voluminous), high transportation cost associated with low bulk density of EPS materials, and the public opinion have been major driving forces for development of EPS recycling strategies [6]. Recycling is a crucial component in waste and pollution reduction hierarchy of EPS, which includes at least four different types of waste management strategies:

1. *reduction*; e.g., reduction of EPS content with optimized packaging designs,
2. *re-usage*; e.g., repeated use of thermo boxes for food,
3. *recycling*; e.g., re-use of material or its components in new products and applications, and
4. *recovery*; e.g., production of thermal heat and power by incineration or chemical recycling of raw materials [7].

The recycling rates around the globe have increased drastically during the last decades [8]. Still, even though the amount of the EPS waste ending up in the landfills has decreased, a significant share of the EPS "recycling" is still thermal recovery of the energy, in other words incineration. Energy recycling, in which wastes are incinerated, and mechanical recycling, in which scrap polymers are conversed into new products, are the main alternatives for treating polymer waste [9]. Dissolution of low-density PS foam waste with suitable solvents is one of the cheapest, most efficient and environmentally friendly ways for PS waste management [9,10]. Thus, the dissolution behavior of PS foams in different solvents has a crucial role in polystyrene recycling [9]. PS is also soluble into its monomer styrene, and up to this day, EPS has been to a large extent produced from monostyrene (MS) via bead suspension polymerization in batch reactors. Hence, the idea of the possibility to utilize this traditional way of producing EPS beads in recycling of PS by dissolving the waste PS or EPS into MS is extremely tempting and would be a natural direction for the EPS industry.

2 Purpose, Goals and Guidelines

The goal of this project in general was to determine how much EPS could possibly be recycled or reused in a suspension polymerization process of EPS in a batch reactor (BR). At least a couple of patents mention the possibility to dissolute 0.5-30% PS or EPS into styrene monomer and using it in suspension polymerization of EPS [11,12]. It is also stated to increase the viscosity of the reaction mixture, and presumably to help dispersion of graphite [4]. BEWi is weighing between different alternatives to recycle both EPS and PS in the future.

The fact that undersized and oversized EPS beads produced via suspension polymerization have limited technical applications make it obvious that something must be done to reduce the production of underutilized off-spec material, and reusing it directly in the suspension polymerization process is an attractive alternative for BEWISynbra Group. It is still unclear how and if the off-spec EPS and/or waste EPS and PS will be utilized in BEWiSynbra RAW's EPS suspension polymerization manufacture in the future. The two most obvious alternatives would be pre-dissolving EPS before suspension or letting it dissolve into MS directly during the suspension polymerization process. Either way, the actual polymerization with EPS content must be successfully carried out before any practical technical applications or solutions are seriously considered or planned. If the suspension polymerization process with a traditional or slightly altered manufacturing system could be carried out successfully at BEWiSynbra, it could be an asset on the highly competitive EPS market since the profitability could increase by lowering the total EPS manufacture expenses with lower consumption of virgin MS (more cheap raw material waste PS and EPS), by giving the possibility to reuse produced off-spec EPS (less waste product), and by providing a more ecofriendly high-status product attracting more customers (more sold product).

Finding approximate limits for EPS content in MS resulting in successful polymerization was the primary focus in this project rather than optimizing PSD at different EPS wt-% dissolved into MS due to the strict time schedule that was set for the project (6 months). Most of the polymerizations were carried out with pre-dissolved EPS-MS-liquid mixture to make sure that the PS has dissolved into MS properly, and supposedly, optimal process conditions are met. Defining or finding out the minimum dissolution time in suspension for different EPS concentrations would also have been very time consuming, taking into consideration that three different EPS products were tested, and less effort was placed on this due to the limited time frame. In order to determine possible dissolution times preliminary solubility tests were also done.

3 General Technical Background

3.1 Polymers, Plastics and Polymerization

3.1.1 General Overview

The ideal goal in chemical industry is to design chemical processes which follow steady-state operation conditions. However, particularly in the field of polymerization reactions, process operations are often forced to run in batch. In addition, uncertainties in measurement and process disturbances are common in real-life operation, preventing the steady-state conditions to be met. There is plenty of reasons for a dynamic behavior of polymerization plants, including for example, necessary operation policies, such as process start-up, shutdown, and grade transition, and unpredictable perturbations and failures. Thus, controllability of the process is a crucial part of the plant operation, and the aim should be in maintaining specified operation conditions despite the unknown and unwanted uncertainties and disturbances, which is not a trivial task [14]. Some classical polymerization control problems include control of reaction and of reaction temperature, monomer conversion and polymer production, molecular weight averages and MWDs, copolymer composition, and particle size and PSDs [15].

Polymers are macromolecules consisting of many monomeric covalently bonded repeating units, that can be synthetic or naturally occurring (e.g., starch, cellulose, etc.) [16], being suitable for use in a variety of products and having a wide range of applications due to among other things, their chemical inertness and optical, barrier, thermal and mechanical properties [17]. The polymeric material includes both the polymer and the additives with which it is compounded, and can be a for example, a polymer blend (copolymer) or a composite [10,11]. Monomers, or mers, are molecules possessing functional groups or elements which react with each other to form large molecules. Monomers are commonly simple organic molecules containing a double bond or a minimum of two active functional groups [18]. The size of the polymer is determined by the degree of polymerization (DP), which is the number of monomers, or more precisely the number of repetitions of the monomer [17, 18]. The total number of structural units is the polymer size, including the end groups. The polymer size is also related to both chain length and molecular weight [17]. Polymers unique chemical and physical properties can be largely attributed to their large molecular size. The common ordinary organic compounds such as alcohol, ether, chloroform, sugar etc., are made up of small molecules having molecular weights usually less than 1,000, while the molecular weights of polymeric materials vary from 20,000 to hundreds of thousands [18]. The polymers molecular and morphological characteristics depend on the formulation (e.g., monomers, catalysts, initiators, etc.), the polymerization process (e.g., reactor, polymerization technique) and the process conditions (e.g. concentrations, temperature, time) [19]. Polymers can be categorized according to one or more of the following criteria:

i. chemical nature of monomers,
ii. molecular structure of polymers,
iii. polymer chain growth mechanism, and
iv. type of polymerization process.

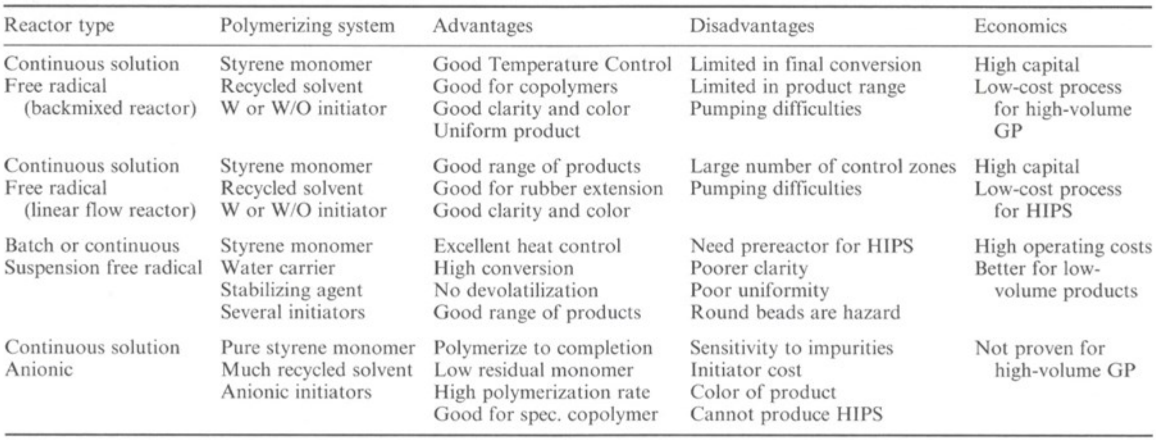
This is not a unique way of classification, though, and several other alternatives have been proposed in the literature [14].

The classes of polymerization mechanisms are classically divided into two main groups: chain-growth polymerization or addition polymerization and step-growth polymerization or condensation polymerization [3,13]. In chain polymerization, the molecule chain grows by reacting an active polymer chain with single monomer molecules, which are connected to the chain. In step-growth polymerization, the molecule chain growth involves reactions between macromolecules. Both polymerization mechanisms may produce non-polymeric byproducts [13]. A multitude of reaction mechanisms can be utilized for synthetization of polymers from monomers, and many of these can be included as subclasses in addition polymerization (e.g., free-radical, ionic, group transfer, and catalytic Ziegler-Natta polymerizations) and step-growth (e.g., polycondensation) polymerization [19]. Some newer polymerization classes such as supramolecular polymerization have been established more recently. Supramolecular polymers are a newer class of polymers in which monomeric repeating units are held together with highly directional and reversible (noncovalent) secondary interactions that result in polymeric properties in dilute and concentrated solution as well as in the bulk, in contrary to conventional macromolecules that have mainly covalent bindings [18,20]. The playground for polymer scientists has grown enormously and is no more limited to macromolecular species only [20].

The various industrial polymerization processes can be generally classified roughly into two main categories, homogeneous and heterogeneous polymerization processes. The former class (homogeneous) consists of polymerization processes that are carried out in a single phase. In the latter class either the polymer is insoluble in the monomer phase (e.g. bulk precipitation polymerization of acrylonitrile), or the polymerization involves the presence of different phases (e.g. suspension, emulsion and solid-gas catalytic polymerization). The most common polymerization processes employed to produce various polymers are

i. bulk,
ii. solution,
iii. precipitation,
iv. suspension,
v. emulsion,
vi. solid catalyzed,
vii. interfacial polycondensation, and
viii. solid state polymerization [14].

This work will mostly revolve around suspension polymerization and the expanded polystyrene (EPS) produced with it, and a description and the general features of each of these other processes is given in the Glossary & Concepts section. Especially the heterogeneous types of polymerization processes including precipitation and its subclass dispersion polymerization, and emulsion polymerization are interesting since they resemble suspension polymerization a lot. The monomer that is the most interesting in respect of this work is styrene and the PS polymers produced with it. The styrene monomer can be readily polymerized to PS via free-radical mechanism, while the polymerization is initiated either thermally or with initiators (peroxides or azocompounds). However, it is also possible to polymerize styrene via anionic and Ziegler-Natta mechanisms by using organometallic initiators. By using free-radical and anionic polymerization results in a polymer with somewhat random position of the benzene ring of the monomer units of regular polystyrene, and in this way, inhibits crystallization. On the other hand, advances in metallocene polymerization catalysts has made it possible to develop syndiotactic polystyrene with a semi-crystalline structure, a melting point of 270 °C and a great environmental stress crack resistance [21]. Different commercial polymerization methods for PS production with advantages and disadvantages are summarized in the Table 1 below [21].



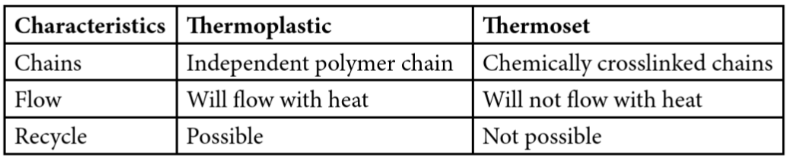
Reactor type	Polymerizing system	Advantages	Disadvantages	Economics
Continuous solution Free radical (backmixed reactor)	Styrene monomer Recycled solvent W or W/O initiator	Good Temperature Control Good for copolymers Good clarity and color Uniform product	Limited in final conversion Limited in product range Pumping difficulties	High capital Low-cost process for high-volume GP
Continuous solution Free radical (linear flow reactor)	Styrene monomer Recycled solvent W or W/O initiator	Good range of products Good for rubber extension Good clarity and color	Large number of control zones Pumping difficulties	High capital Low-cost process for HIPS
Batch or continuous Suspension free radical	Styrene monomer Water carrier Stabilizing agent Several initiators	Excellent heat control High conversion No devolatilization Good range of products	Need prereactor for HIPS Poorer clarity Poor uniformity Round beads are hazard	High operating costs Better for low-volume products
Continuous solution Anionic	Pure styrene monomer Much recycled solvent Anionic initiators	Polymerize to completion Low residual monomer High polymerization rate Good for spec. copolymer	Sensitivity to impurities Initiator cost Color of product Cannot produce HIPS	Not proven for high-volume GP

Table 1. Commercial polymerization methods for PS production [21].

In the initial state when polymers are produced, the polymers are usually viscous liquids or, in the case of a solid, are granules (powders) or flakes. It is also possible, that the granules of flakes are formed into some intermediate shape, such as for example, small pellets. Even so, these can also be called resins since they later formed into a shaped plastic part. The terms resin, plastic and polymer are often used interchangeably, although correctly used there are differences. As a summary can be stated: polymers are any material consisting of large molecular chains, plastics are synthetic, long-chain polymers that can or have been shaped, and resins are solids or liquids that are later shaped into a plastic product. [3]

Plastics, whether made by addition or condensation polymerization, can be generally divided into two groups: thermoplastics and thermosetting resins. In addition, a third group, engineering plastics has been established [3,14]. Thermoplastics are solid materials at room temperature, that can be melted or soften upon heating. This makes it possible to place them into a mold or other shaping device to be cooled, and as a result, the thermoplastic solidifies and takes the desired shape. The thermoplastics can be reshaped by reheating many times [3]. Commodity thermoplastics are manufactured in large volumes and consist of polymers such as polyethylene (low and high density), isotactic polypropylene, polystyrene, and polyvinyl chloride (PVC). The thermosetting resins harden (curing) irreversibly through chemical crosslinking, and hereby, cannot be remelted or shaped [14]. They can be either liquids or solids at room temperature and will only soften a little bit after curing [3]. Thermosets consist of phenolic resins, amino resins, epoxides, alkyd resins, unsaturated polyesters, polyurethanes, cross-linked polyethylene, etc. The engineering plastics, on the other hand, consist in general of thermoplastics with improved mechanical or thermal properties compared to commodity plastics. Polyethylene terephthalate, polyamides, polycarbonates, some modified polystyrenes (e.g., Styrene Acrylonitrile (SAN) and Acrylonitrile Butadiene Styrene (ABS)), various polyetherketones, polyamides, polysulfones, and some thermosetting resins are examples of this class of specialty plastics [14]. A short summary of the differences between thermoplastics and thermosets below in the Table 2, for example PS versus PU.

Figure 1. Thermoplastic (left) versus thermoset (right) [17].



Characteristics	Thermoplastic	Thermoset
Chains	Independent polymer chain	Chemically crosslinked chains
Flow	Will flow with heat	Will not flow with heat
Recycle	Possible	Not possible

Table 2. Thermoplastics such as PS versus thermosets such as PU [17].

3.1.2 Worldwide Demand and Production of Plastic Materials

The worldwide demand for polymeric materials is enormous. The statistics below shows the distribution of polymer demand by major polymer in 2016 (Figure 2) and the global plastic production by region in 2017. In 2016, the total demand for polymeric materials worldwide was equivalent to 243 metric tons, while the total production of plastics in 2017 was equivalent to 348 million tons [22, 23]. PP had the highest demand by a share of 26 percent of the total global demand for polymers in 2016. Regarding styrenic polymers, the highest demand was for PS (4%), ABS (2%) and EPS (2%) [22].

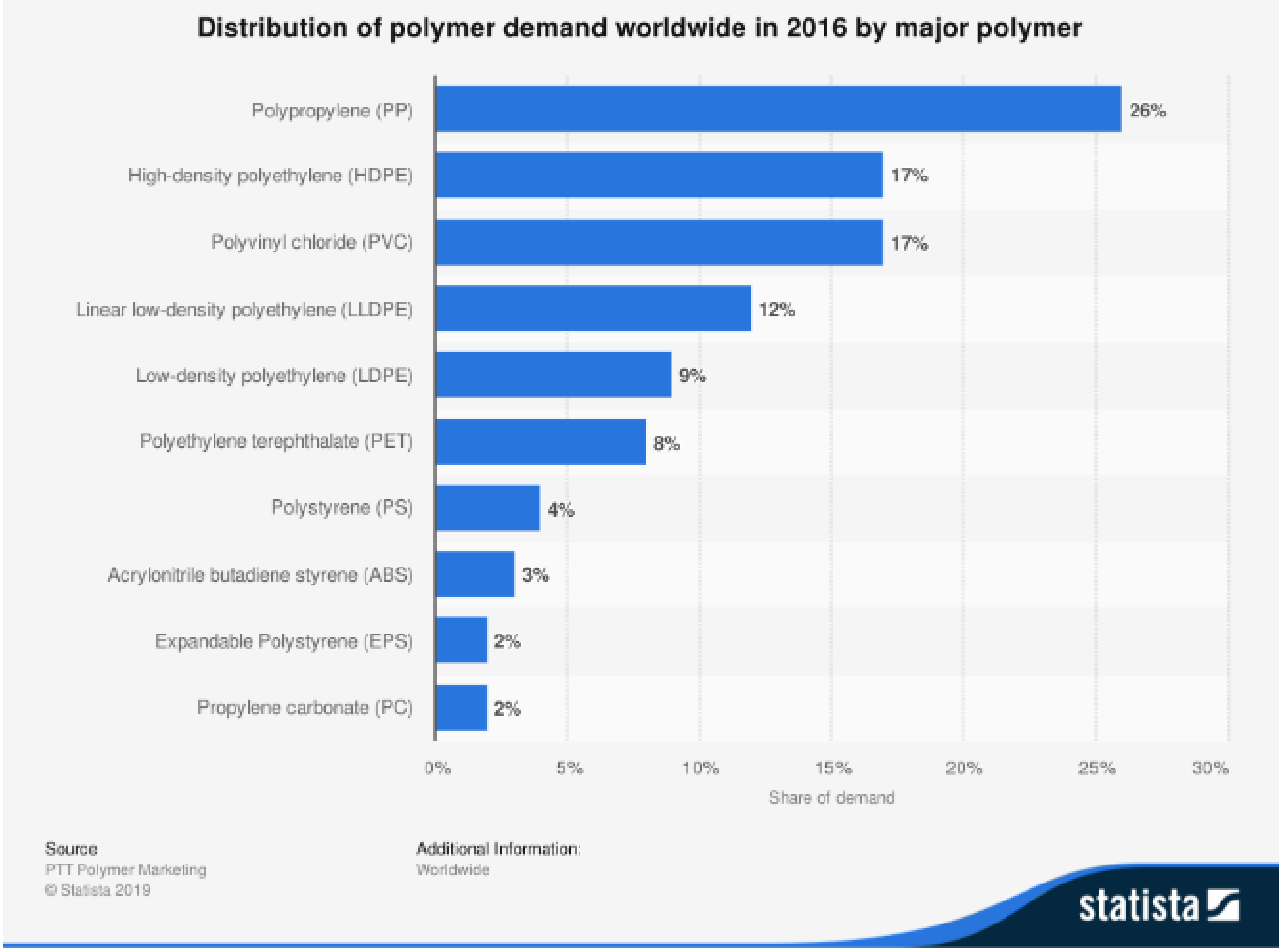
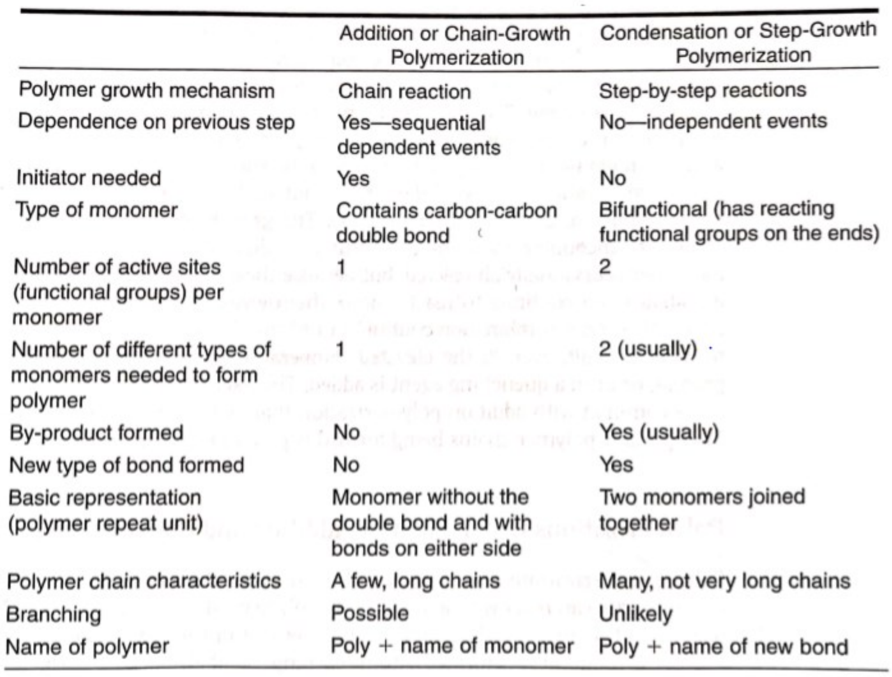


Figure 2. Distribution of polymer demand worldwide in 2016 [22].

3.1.3 Polymerization Mechanisms and Reactions

Classically, there is two fundamental polymerization reactions differentiated as addition polymerization and condensation polymerization. The important differences between these two classes are summarized below in the table below (Table 3):



	Addition or Chain-Growth Polymerization	Condensation or Step-Growth Polymerization
Polymer growth mechanism	Chain reaction	Step-by-step reactions
Dependence on previous step	Yes—sequential dependent events	No—independent events
Initiator needed	Yes	No
Type of monomer	Contains carbon-carbon double bond	Bifunctional (has reacting functional groups on the ends)
Number of active sites (functional groups) per monomer	1	2
Number of different types of monomers needed to form polymer	1	2 (usually)
By-product formed	No	Yes (usually)
New type of bond formed	No	Yes
Basic representation (polymer repeat unit)	Monomer without the double bond and with bonds on either side	Two monomers joined together
Polymer chain characteristics	A few, long chains	Many, not very long chains
Branching	Possible	Unlikely
Name of polymer	Poly + name of monomer	Poly + name of new bond

Table 3. Summary of the differences between the main polymerization mechanisms [3].

Only addition polymerization and its mechanism are discussed in detail because its relevance for this work. Of the subspecies of the main classes, the free-radical polymerization is the most essential for this work.

Step-growth Polymerization (Condensation Polymerization)

In step-growth polymerization stepwise reaction happen between functional groups of reactants. The reaction leads successively from monomer to dimer, trimer, tetramer, pentamer, and so on, finally resulting in a polymer with a large DP. The reactions occur randomly between the intermediates (e.g., dimers, trimers, etc.) and the monomer, and among the intermediates themselves. Most of the step polymerization processes involve poly-condensation (repeated condensation reactions), therefore, the terms step polymerization and condensation polymerization are used interchangeably. Condensation polymerization can be defined as polymerization in which polymers synthesis involves elimination of small molecules or the repeating unit lack certain atoms present in the monomer(s). The eliminated molecule could be water, for instance [18]. In step polymerization, the molecular weight increases continuously with time, and the formation of polymers with adequately high molecular weight for practical applications requires very high conversions of the reactive groups (over 98-99 %). This leads to strict requirements for step polymerization processes, such as the need for a favorable equilibrium and the absence of side reactions. Many of the most important step-growth polymerizations such as amidation (e.g., nylons), esterification (e.g., polyethylene terephthalate) and transesterification (polycarbonate) are reversible. In addition, the equilibrium constant decreases with temperature, since it is an exothermic process [13].

Addition Polymerization (Chain-growth Polymerization)

In addition polymerization, a simple, low-molecular-weight molecule with a double bond, ideally a monomer, is treated so that the double bond opens up, resulting in free valences to join with those of other molecules, ideally monomers, to form a polymer chain. The identical composition of repeating unit of a polymer and its monomer(s) is in most cases a strong indication that the polymer is formed by chain polymerization process [18]. Either a catalyst or an initiator generates the activity of the chain [13]. Chain-growth polymerizations can be divided to several classes according to the type of active center:

- coordination polymerization (active center is an active site of a catalyst, Ziegler-Natta catalysts),
- free-radical polymerization (active center is a radical),
- anionic polymerization (active center is an anion), and
- cationic polymerization (active center is a cation) [13].

The addition polymerization mechanism, or chain-reaction mechanism, progresses by several sequential steps. The four main steps in addition polymerization are

1) chain initiation,
2) chain propagation,
3) chain transfer, or chain branching, and
4) chain termination [18].

In the initiation step, a monomer containing a carbon-carbon double bond as an active center (π-bond), or reactive site, is attacked by free radicals. The interaction between the free radical and the monomer converts the monomer to a free radical. This newly formed unstable new radical is willing to form a bond and attacks another monomer molecule that links the atom, the carbon (active center) and the monomer to the growing chain. The most convenient source of available electrons is the π-bond of another monomer molecule, which is especially true for high monomer concentrations. This sequence of lengthening the chain with a new monomer is referred as the propagation step. The process of creation of a free radical, attack on π-bond of the new monomer molecule, and formation of new free radical can continue as long as monomers are available to react, assuming other readily available electron source does not interfere with the process by reacting with the newly formed free radicals. Thus, the chain can become very long, often growing to several thousand units of the repeating unit, the monomer. Eventually the polymer chain is ended, and this step is called the termination step [3]. There are several reactions that can result in chain termination, but the two most important termination mechanisms are termination by combination or coupling and disproportion [18]. One of the simplest of these is that the carbon free radical meets another radical, either peroxide or carbon (termination by combination). As a result, two unpaired electrons, free radicals, form a covalent bond between them. However, there is another possibility that the carbon free radical would extract an electron from a bond other than π-bond (termination by disproportionation). This is far less likely to occur because the electrons in other bonds are generally less reactive and much more tightly held. The odds are higher especially at high temperatures due to increased activity and excitement of the electrons. The most likely place for a free radical to extract another electron would be from a carbon-hydrogen bond in another polymer chain. When this occurs, a bond between the two carbon atoms in the two separate chains would form and a hydrogen free radical would be released. This process is called branching, or chain transfer, which terminates the chain, but the active center is transferred to a new chain [3]. Chain transfer may be regarded as a combination of chain termination and chain initiation [18]. The released hydrogen free radical could react with other π-bond or for any other reaction common for free radicals. It could for example, terminate some other chain. There are other possibilities resulting in termination, but these are in general of less importance [3].

3.2 Recycling and Handling of Plastic Waste

3.2.1 Introduction

Plastics have become extremely common materials in our lives, and are often used in disposable, one-time use applications that increase solid waste loads [3]. The use of plastics in disposables is considerably lower than paper-based products, but still, the use of plastic-based products grows constantly [3]. Although plastics have been major contributor in revolutionizing many technologies, applications and in creating new novel materials, the increasing volume of plastic wastes, coupled with their low biodegradability, generates a serious environmental problem [24]. Even though source reduction is not a direct recycling method, it is important to mention as a strategy to decrease the solid waste. Source reduction is defined as the reduction in amount of material used in an application, which in this way reduces the amount of discarded material when the use is completed [3]. Plastic recycling can be described as “the process of recovering scrap or waste plastics and reprocessing the material into useful products, sometimes completely different in form from their original state” [25]. The different plastic recycling methods can be classified in different levels, depending on the classification of the final product, for example, in the following way:

- *Primary recycling*: The recovered plastic can be used in a product with equivalent performance characteristics to that made using virgin plastics.
- *Secondary recycling*: The recovered plastic can be used in a product having less demands for performance than the original application.
- *Tertiary recycling*: Plastic waste can be used as the feedstock in a process generating chemicals and fuels.
- *Quaternary recycling*: Energy can be recovered from plastic waste by incineration [25].

This type of recycling, referring to material that has been discarded and used by a consumer, is called postconsumer recycle (PRC). It is opposed by recycle that is created as a normal part of normal waste (e.g. off spec) generated by production process, generally called regrind or plant recycle [3].

The reuse and various recycling of waste residues and plastics leads ideally to reduction in the use of non-renewable material and energy resources, while the energy savings are generally ranked in the following order: reuse > material recovery > energy recovery (energy from waste) [24]. Incentives for the usage of recycled plastics include for example, ecological, consumer demand, recycle-content legislation and lower cost [6]. The tree essential elements in plastics recycling are:

i. stable supply source involving adequate collection and sortation,
ii. a recycling process that is economical and environmentally sound,
iii. end-use applications/properties for the recycled polymer offering economic market values and consumer attraction [14].

Recycling of plastics or polymers can be challenging and may require greater processing than glass and metal [25]. There are 10-12 main polymer types and thousands of different resin grades and blends. On top of that, the polymers are often multicomponent systems using multi-layers, laminates and composites. Furthermore, plastics contain often one or more additive, formulant, or modifiers, such as fillers, pigments, antioxidants, and antioxidants which readily interfere with the recycling process. It is also possible that a single polymer (e.g., PE) can be found in several different melt flow indexes and thermal stabilities. As a result of all this, recycled polymers are often by their nature contaminated with foreign materials compared with virgin polymers, such as paper, metal fragments, fibers, glass and incompatible polymers [6]. This can limit the choice of applications in several ways (e.g., poor mechanical properties). The available and technically viable recycling methods can be categorized in the following groups:

I. *Mechanical recycling*, which consists of reprocessing of plastic residues into new products (different or like the original product). The origin of the raw material may be a manufacturing process or post-consumer product. The simplest way of recycling plastic material with the lowest initial investments needed.
II. *Chemical* or *feedstock recycling (tertiary recycling)*, which involves breaking down plastic material into its basic monomers or other products with the help of heat or chemical treatment, which can be recombined into polymers or used for other applications. Hydrolysis and pyrolysis are typical examples of tertiary recycling. The biggest disadvantage is the demand of huge investments, and hence, is most viable for large-scale operations with volumes (thousands of tons annually) compared to those in petrochemical industry
III. *Energy recycling* or *quaternary recycling*, which includes the recovery of energy from the plastic by combustion. The emissions of volatiles must be controlled during the processing in order to avoid environment being contaminated by other paths. This type of operation is often seen as a wasteful underutilization of the energy stored in the plastic [24].

Even though all the methods of material and energy recovery from waste plastic is technically possible, they encounter other barriers [24]. First and foremost, the recycling isn't often economically profitable, other limiting factors include for example legislative and market barriers [3,24]. The Figure 3 below presents the evolution of the amount generated plastic waste and plastic disposal practices from 1960s up to recent years.

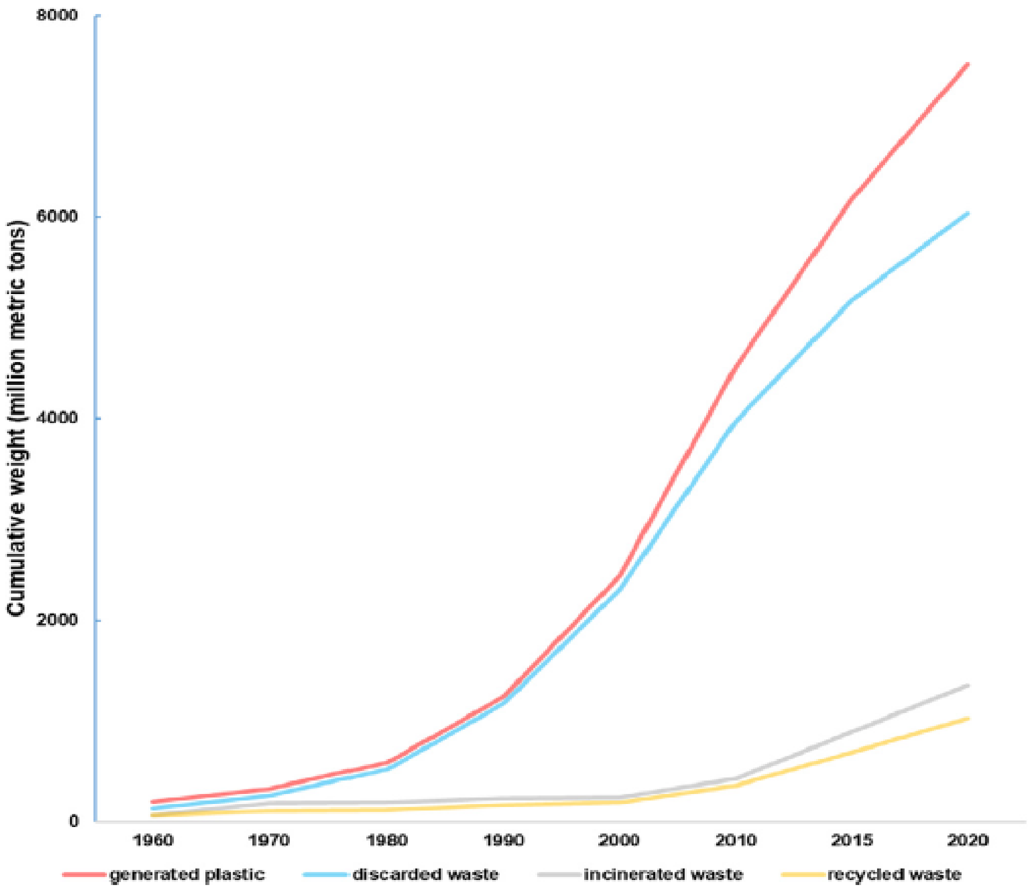


Figure 3. Global generated plastic waste and plastic disposal [1].

3.2.2 Plastic Waste Handling Strategies

Solid plastic waste can generally be handled with six different strategies or ways, which are discussed shortly below, including:

1. source reduction,
2. recycling,
3. regeneration,
4. degradation,
5. landfills,
6. incineration [3].

Each of these are important as a means of minimizing negative environmental effects. Especially recycling is a crucial method for this work as solvent recycling is applied by solving a polymer, PS, into a solvent, its monomer styrene.

Source Reduction

Some simple examples include using fewer waste causing products, choosing sizes and types of products with minimal waste, and for the manufacturers, to reduce the material requirements of the product. The most extreme case would be substituting plastics with other materials completely, for example substitution of plastic grocery sacks with paper sacks [3].

Recycling

Even if source reduction would increase drastically, materials continue to be discarded, and thus, recycling will continue to be an important way of reducing the amount of material ending up in landfills and other waste streams. The amount of recycled materials grows constantly, and according to some reasonably estimates that between 8 and 17% of all plastic product are recycled. Both PCR and plant recycle material reprocessing and refabricating requires several stages: collection, handling/sorting, reclamation/cleaning, and end-use fabrication. These steps are often expensive and challenging, and in this way, recycling is not necessarily the most tempting option. Regrind that is reused or consumed within a manufacturing process is of course not a problem, however, the unused part will most likely become a part of waste stream [3].

The ideal way to use recycled material is the same as the original or some other high-value application. The plastic can be used in the original application, if it has been thoroughly sorted. However, most plastic resins have some minor changes after the reprocessing, typically a reduction in molecular weight accompanied with drop in melt viscosity and an increase in the melt index. These changes are often minor and are not present throughout the melt, but result in in many physical and mechanical properties, including for instance yield strength and elongation. It has been noted that some products made from PCR that the small changes in molecular weight and other changes complicate the processing. A blend ratio of 20 PCR is typical regardless of that some fabricators have found that up to 50 % PCR may be used without drastic changes in processing and product performance. However, contamination and disease risk prevent the use of PCR in medical and food-contacting applications [3].

Regeneration

"Regeneration is the process of breaking down the polymer molecules in the plastic material into more basic chemicals [3]." These basic components or chemical can be used to create new polymers or materials. Regeneration is also known as chemical recycling [3]. The regeneration is done by using depolymerization and decomposition reactions [24]. Condensation polymers such as PET and nylon (most common methods glycolysis and methanolysis) are the easiest polymers to regenerate [3,24]. With the help of heat and pressure in the presence of a reacting agent the polymers can be depolymerized, also known as unzipping, monomers can be regenerated. Depolymerization of addition polymers such as PS, PE, and PP is more challenging. Much higher temperature is needed and generally the regeneration is done in large facilities a lot like oil refineries. Here cracking is used to separate large crude oil molecules into smaller units. Thermosets are the most problematic of all to regenerate. Typically, the regeneration is done with pyrolysis, which is the decomposition of a material using heat processes in the absence of oxygen [3].

Regeneration has its benefits and downsides. The advantages of regeneration compared to traditional recycling is that regeneration is typically more efficient for mixed recycle. Each of the fractions, more specifically, condensation polymers, addition polymers, and thermosets, can be selectively regenerated. This results in much higher value for the waste compared than from the conversion of a product with lower intrinsic value. The disadvantages compared to traditional recycling is the higher potential for air pollutants and the loss of thermal and chemical energy that was already expended to polymerize the monomers. Additional thermal and chemical energy is needed to break the polymers apart, and after that energy is needed to connect the structural units back together [3].

Degradation

Another strategy to reduce or eliminate especially solid waste is to use/develop biocompatible materials that are degradable. The term ‘degradable’ refers to the plastics ability to “break down into smaller molecules by natural means, usually by some biological agent or by action of something in the environment (e.g., sunlight) “[3]. The timing for degradation of a plastic is crucial. Neither should it take too long to degrade, like in the cases of many conventional plastics, nor should it degrade too rapidly for the intended use. Another crucial issue is the degradation products. Even if the plastic would decompose quickly, the degradation products can be hazardous, and hence, can damage environment. One should also take into consideration that there is no certainty that even easily decomposing materials decompose in landfills, and the permanent repository should be carefully well thought out. Achieving degradable polymers that degrade quickly, and at the same time could compete with conventional plastics with respect to cost and properties or abilities is challenging [3].

Landfills

Sanitary landfills are the most way common way of solid waste disposal. Plastics share of the total amount in landfills is about 20 % by volume and 8% by weight. For comparison, the amount of paper is largest in landfills, ca. 34 % by volume and 40 % by weight. In landfills, the waste is simply dumped and buried in the ground. The popularity of landfills is due to the low price versus the other waste disposal methods. No sorting or processing is needed. It is crucial control the landfill process in order to protect the site and its surroundings from problems of odor, fire, vermin and pollution from seepage. Plastics are relatively inert and risk-free materials in landfills. Most of the plastics are not readily degradable and do not contribute to water-soluble residues, however, but the components in them such as plasticizers may contribute. This overall inertness favors plastics since the degradation of mass is tried to prevent. Absence of air and organisms necessary for degradation to occur lack in landfills. The main issue with landfills is that the capacity is limited, and available space for landfills is dwindling. [3]

Incineration

Incineration refers to controlled burning. This strategy is used for disposal of a large percentage of municipal waste. This method makes it possible to use plastics along other flammable materials, such as paper. The plastics and other flammable materials are separated from the rest of the waste stream. The easily sorted high value plastics, such as PET bottles, are manually separated. The flammable materials are chopped into flakes and later on pressed into pellets in order to ease the handling and economical transportation to the from the recycling center to the burning facility. The general purpose for burning, in addition to the elimination of solid wastes, is the generation of electricity. The efficiency of the burning of waste is related to the energy content of the materials and is often weighed against the energy content of more traditional fuels like natural gas and oil.

The main issues and disadvantages associated with incineration include the formation of hazardous emissions, the problems with as disposal, and the release of carbon dioxide gases that could accelerate the global warming. The following pollutants have been the main concern:

- particulates: heavy metals including lead, cadmium, zinc, chromium and mercury,
- acid gases leading to acid rain including trace concentrations of sulfur, chlorine and fluoride,
- NO_x,
- trace organics, especially chlorinated dioxins and furans that may be carcinogenic.

Even though experts on incineration technology are convinced that most of the hazardous components and emissions can be efficiently limited to safe levels with the existing technologies, there could be some risks associated with incineration, and source reduction and recycling are often preferred over incineration and regeneration for management of solid waste. However, incineration is often preferred over landfills. [3]

3.3 Styrenic Polymers

3.3.1 General Information

Styrenic polymers are as a group one of the economically most important plastics in the world, right behind polyolefins, PVC and polyethylene terephthalate, with an annual production capacity of approximately 25 million tonnes per year (2011) [26]. Styrene is an important feedstock in several polymer products [15]. Of the total amount of styrene produced, almost 50 % is used for manufacture of polystyrene, 20 % for elastomers, thermosetting resins and polymer dispersions, 15 % for ABS and SAN copolymers, 10 % for expanded polystyrene (EPS), and the rest for different copolymers and specialty materials (before the year 2000). These plastics majorly determine the worldwide growth in styrene production capacity and plant utilization [15]. Styrenic polymers combine effective processing with a wide variety of properties, ranging from stiff and transparent to tough and durable. In addition, the fact that styrene can be polymerized by many different polymerization mechanisms, including radical, ionic and metal catalyzed (coordination), makes this family of products unique and attractive for many applications [15].

The first representative of styrenic polymers was polystyrene, which was in fact, the first synthetic polymer to be prepared and the earliest reports of its existence are as early as 1839 [21]. The family of styrenic polymers has continued to grow to this day, and will most certainly, continue to grow in the future, too [21]. Different styrenic polymers can be made generally by copolymerization, alloying and blending or mixing (see Glossary) [3]. The key feature of polystyrene that has led to its huge commercial success is the low cost. The unwillingness of polystyrene fabricators to pay additional costs for improved performance and the intense competition on polystyrene markets has led to highly optimized and huge PS production facilities (a typical world PS plant has production capacity of 230 000 tons/year product). The costs accompanied with the introduction of new improved PS products must be low enough so that profits can be realized by the manufacturer without raising the sales price. This limitation and the trend to minimize the R&D budgets together challenges industrial polystyrene researchers. On top of that, other pressures on PS industry include environmental and regulatory issues [21].

3.3.2 Basic Structure and Properties

The term styrenics, or styrenic polymers, describes a major family of major plastic products that have styrene (see Figure 5) as the key building block. Styrene polymers can be processed with ease over a wide temperature range well above their softening point, in other words the ‘glass transition temperature' (T_g). The partly crystalline polymers, such as polyethylene (PE), polypropylene (PP), polyamides (Pa), polyesters, styrenic polymers (except syndio- and iso-tactic polystyrene) do not have a distinctive melting point. Thus, no extra thermal energy is needed for melting of polymeric crystals (melt enthalpy) is needed during processing. As a result, the processing is easier and faster under the same conditions, but at the same time, high dimensional stability and majorly constant mechanical properties up to T_g can be obtained. Relatively slow change of melt viscosity with temperature is characteristic for styrenics. This favorable rheological behavior benefits the processing, too. [15] The actual styrene monomer, around 90 %, is produced by the catalytic dehydrogenation of ethylbenzene. This reversible endothermic reaction is performed in gas-phase, resulting in conversion of ethylbenzene into styrene in the following way (Figure 4.):

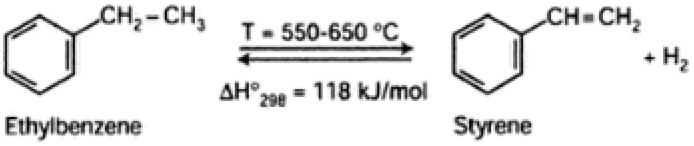


Figure 4. Conversion of ethylbenzene into styrene [26].

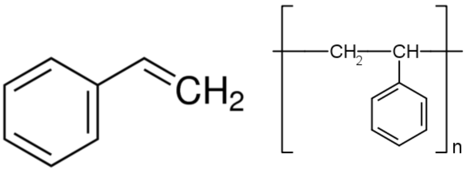


Figure 5. Molecular structures of styrene (left) and polystyrene (right).

The styrenic polymers with the most economical importance are

- polystyrene (PS) with 4% share, which is used as crystal clear, but brittle homopolymer 'general purpose polystyrene' (GPPS) or as stiff but opaque, impact modified 'high impact polystyrene' (HIPS),
- expandable polystyrene (EPS), which is GPPS beads containing pentane. EPS beads expand under heat. EPS is lightweight, strong, and us an excellent thermal insulation, which makes it an ideal material for packaging and construction industries (as insulation), and
- styrene-acrylonitrile copolymer (SAN), which is a transparent, stiff and thermoplastic polymeric material characterized by high stress cracking resistance. SAN comprises of the styrene and acrylonitrile monomer [15].

An overview of the major styrenic classes and their building blocks are presented below (Figure 6), and some of the unique value propositions of styrenic polymers as well (Table 4).

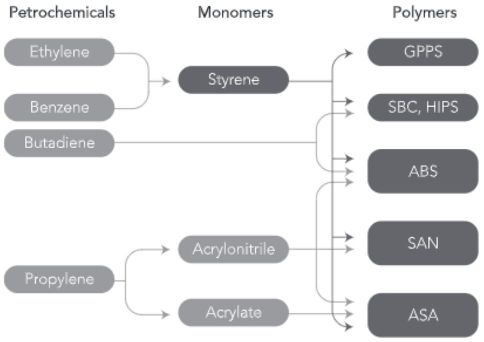
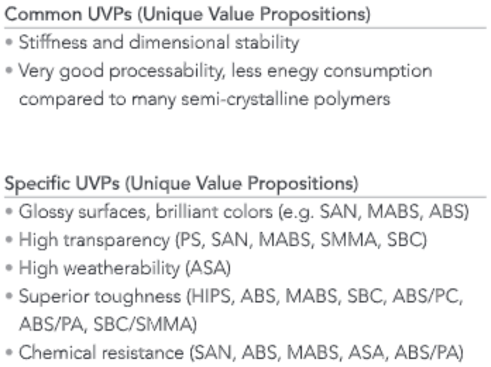


Figure 6. Major styrenic polymer classes and their connection to petrochemical value chain [27].



Common UVPs (Unique Value Propositions)

- Stiffness and dimensional stability
- Very good processability, less enegy consumption compared to many semi-crystalline polymers

Specific UVPs (Unique Value Propositions)

- Glossy surfaces, brilliant colors (e.g. SAN, MABS, ABS)
- High transparency (PS, SAN, MABS, SMMA, SBC)
- High weatherability (ASA)
- Superior toughness (HIPS, ABS, MABS, SBC, ABS/PC, ABS/PA, SBC/SMMA)
- Chemical resistance (SAN, ABS, MABS, ASA, ABS/PA)

Table 4. Some unique value proposition of styrenic polymers [28].

Styrenic polymers have many beneficial qualities that can be utilized in different kind of applications, including:

- Lightweight, water resistant, and magnificent thermal insulation.
- High strength-to-weight ratio, rigid structure offering energy-savings in transportation and a great cost performance.
- Possibility to shatterproof and transparency.
- Great electrical insulation.
- Easy processing and manufacturing in a range of different colors.
- Easy recycling [15].

Styrene based resins are used in many every day goods ranging from computer housings to food packaging. Some common applications include, for instance, extruded polystyrene (XPS) foam boards for insulation, kitchen appliances, toys, electronics, automobile parts and a wide variety of durable lightweight packaging. As summary, styrene polymers are utilized in many very demanding applications, and their strengths lie in the combination of cost efficiency, high performance and easy processing. [15]

3.4 Suspension Polymerization

3.4.1 Introduction

In this chapter the main concept and features on suspension polymerization in chemical industry is introduced. The term suspension polymerization is describing a process in which water-insoluble monomers in are dispersed as liquid droplets by combined action of steric stabilizers and vigorous stirring in order to produce polymer particles as a dispersed solid phase inside the droplets [13,21,27]. The monomer is in a liquid state in which monomer-soluble initiators for polymerization are employed. During the polymerization, the droplets are quickly transformed into sticky, viscous monomer-polymer particles, finally resulting in rigid, spherical polymer particles larger than 1 µm (smaller droplets/particles are generally known as emulsions), and the upper limit for suspension can be regarded as 1-2 mm or larger [8,29].

Suspension polymerization belongs to the class of heterogeneous polymerization. Heterogeneous polymerization processes, or particle forming processes, are typically two-phase systems. Other common commercial heterogeneous polymerization processes used in manufacture of addition polymerization of vinyl monomers are emulsion, dispersion and precipitation polymerization. In these processes the starting monomers and the formed polymers are in the form of fine dispersion in an immiscible liquid. Some general components, and their role and nature of heterogeneous polymerization can be distinguished. The monomer is normally referred to as the "monomer phase" or "dispersed phase". The liquid phase, which contains the dispersed monomer, is defined as the "polymerization medium", or just "medium". It is also common to call the polymerization medium as "continuous phase" or the "outer phase". Besides the monomer(s), the polymerizing medium and the initiator, another liquid known as "monomer diluent", or just "diluent", which must be miscible with the monomer and immiscible with the medium may be added to the system, and in addition, additives are added to the polymerization system, too, in order to emulsify the monomer and/or to stabilize the monomer droplets. Polymerization mixtures consisting of an aqueous and nonaqueous phase are classified into oil-in-water (O/W) or water-in-oil (W/O) systems [29]. Suspension, emulsion, dispersion, and precipitation polymerization can be clearly distinguished based on the following four criteria:

1) initial state of the polymerization mixture,
2) kinetics of polymerization,
3) mechanism of particle formation, and
4) shape and size of the final polymer products [29].

Suspension polymerization is the most widespread method for commercial manufacture of plastic resins both in the tonnage, and number of polymers manufactured, such as poly(vinyl chloride), poly(methyl metacrylate), a variety of ion exchange resins, and specific grades of polystyrene, namely expandable polystyrene (EPS), high-impact polystyrene (HIPS) and various styrene copolymers (e.g. SAN, ABS) [13,14,28]. For the suspension polymerization processes where particle porosity is not required, the terms pearl and bead polymerization are also used [27]. In general, there is two types of suspension polymerization that can be distinguished from one another:

- “bead” suspension polymerization in which the polymer is soluble in the monomer resulting in smooth spherical particles (e.g. EPS suspension polymerization), and
- “powder” suspension polymerization in which the polymer is insoluble in its monomer resulting in precipitation and formation or irregular grains or particles [13].

3.4.2 Main Components and Additives

The following main ingredients, or components, are present in a suspension polymerization system in general:

1) monomer(s);
    - building blocks/material for polymers dispersed in the continuous medium,
2) agitated stabilizing/dispersing medium or continuous phase;
    - usually consisting of water,
    - acts as heat-transfer medium and disperses the monomer,
3) small amount of suspension agent(s) or surface-active agent(s) or drop stabilizer(s) (0.01 to 0.50 % of the weight of monomer);
    - organic substances are commonly used, and also finely divided particulate inorganic solids are possible such as calcium phosphate or metal hydroxides are used,
    - absorption of stabilizing molecules between the monomer and the dispersing medium reduces the
    - tension, thus reduces the energy needed to form drops,
    - crucial to successful control of the polymerization process and the uniformity of the product by stabilizing monomer drops in aqueous suspension, in absence of a drop stabilizer the suspension would be unstable, and the monomer/polymer drops would coalesce and grow too large,
4) initiator(s);
    - soluble in liquid monomer, that is usually of peroxide type, but azo and ionic compounds are used in some degree, too.
    - used to initiate free-radical polymerization reactions. [13,27-31]

Other possible components or additives that may be present in a suspension polymerization system are, for example:

5) chain transfer agent(s);
    - may be restrict the average MW of the final polymer product,
6) surfactant(s);
    - may be used to reinforce stabilizers function/activity or to decrease viscosity
7) dispersant(s), or dispersion agent(s);
    - may be used to improve separation of particles, preventing coalescence
8) electrolyte(s);
    - may be used to reinforce stabilizers function/activity or to decrease viscosity
9) blowing agent(s);
    - often a volatile hydrocarbon, such as pentane for example,
    - used to form foam when the drops are subsequently heated,
10) diluents;
    - chemicals that may be used to decrease viscosity. [13,27-31]

3.4.3 Process Description

Industrial suspension polymerizations are often described as "batch" processes, but in reality, they are often semi-batch processes, and usually proceed via free-radical mechanism producing polymer beads [27,28]. The major goal in suspension polymerization is to produce as uniform as possible dispersion of monomer droplets in the continuous aqueous phase with a control over coalescence of the droplets during the polymerization process (PSD) [27]. Polymerization drops in the reactor are generally of the same size distribution to that of the polymer beads (0.1-5 mm) [13,27]. The initiator, usually of an organic peroxide type, is soluble in the monomer, and these two are insoluble in the polymerization medium, usually consisting of water. The ratio of the monomer phase to the polymerization medium is usually kept 0.01–0.5, but it can also be higher, and the typical concentration of polymer is between 30–50 % in a fully converted suspension system [14,29]. The monomer phase is suspended in the medium in the form of small droplets, "microbeads", with the help of a stirrer and a suitable droplet stabilizer, or a suspension agent. The coalescence of monomer droplets and the adhesion of partially polymerized particles during the polymerization process is hindered by suspension agents (stabilizers). The actual polymerization is initiated at the desired process temperature, usually in the range of 20–100 °C. The polymerization process is then usually allowed to proceed into completion (~100%). These conditions make possible the monomer "microdroplets" to be converted directly to the corresponding polymer "microbeads" of approximately equal size [30]. Subsequently, the yielded beads can be isolated from the continuous phase simply by filtration and/or sedimentation [27].

It is generally assumed that the kinetics in suspension polymerization are similar to those of bulk and solution polymerization, depending on the absence or presence of a monomer diluent in the monomer droplets. In this sense, suspension polymerization can be considered as "microbulk" or "microsolution" polymerization, since the individual monomer droplets act as tiny bulk or solution polymerization reactors [30]. Each droplet act as a tiny "microreactor", but with dimensions small enough so that heat removal is not an issue, and the suspension medium surrounding the "microreactors" acts as an efficient heat transfer agent. Adequate agitation of the reactor content makes sure that the heat transfer via the aqueous phase into the reactor walls is sufficient, and a two-phase dispersion is maintained. As a result, high rates of polymerization can be maintained resulting in high yields of polymers in a relatively short time. [27,29]

3.4.4 Evolution of PSD and Effect of Operating Conditions

The control of PSD is one of the most important issues in suspension polymerization [13]. Generally, both the initial monomer droplet size distribution (DSD) and the polymer PSD is dependent on the concentration of the surface-active agent, the quality of agitation (e.g. reactor geometry, impeller type, power input, etc.) and the physical properties (e.g. densities, viscosities, interfacial tension) of the continuous and dispersed phases [13]. The dynamic PSD evolution is a manifestation of the rates of two physical processes, namely the drop/particle breakage and coalescence/agglomeration [13,30]. The dispersed phase can be broken into small drops when its surface is disrupted (drop breakage) in agitated suspension and can be caused either by frictional forces (via viscous shear) or by inertial forces (via turbulence). The overall rate of drop coalescence is dependent on the collision frequency of the drops and to the coalescence efficiency [31]. Drop breakage occurs mainly in regions of high shear stress such as near the agitator blades or as a result of turbulent velocity and pressure fluctuations along the drops surface. Turbulent flow field either increasers or decreases the drop particle coalescence. However, if the concentration of surface-active agent is adequate, it can be assumed to be negligible for dilute suspensions [13]. The Figure 7 below summarizes some of the drop breakage and coalescence mechanisms.

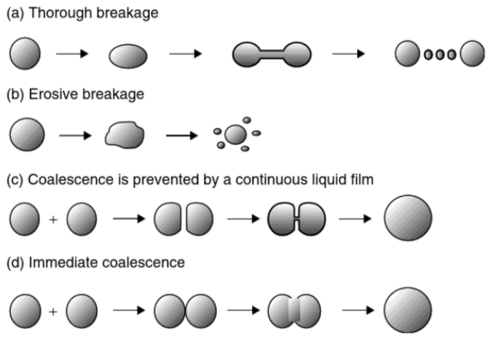


Figure 7. Drop breakage and coalescence mechanisms [13].

Suspension undergoes following developments during the polymerization, and can be divided into three different stages [13,31]:

1. An initial *low-viscosity period/stage* at low monomer conversions, in which drop breakage is the dominant mechanism and DSD shifts to smaller sizes and is generally narrow.
2. *The sticky stage* with an accelerated viscosity increase, and a decrease in breakage rate while coalescence becomes dominant mechanism. As a result, the average particle size increases, and the PSD becomes broader.
3. *Identification point*. If stability is achieved, during this stage at higher monomer conversions the particles are hard enough so that the collision between them are elastic and, hence, the particle coalescence ceases and the final shape of PSD is acquired [13,30].

The quality of polymer particles by suspension polymerization depends besides the reactor design on operational parameters that govern the overall stability of the system [29]. Efficient management of the process is as much empiricism as it is based on exact scientific principles [27,29]. A lot of empirical and theoretical studies have been published on the effect on different operating conditions and parameters on PSD. The average size of the monomer droplets, and thus, the resulting polymer particles, can be controlled by alternating operating conditions such as the stirring speed, volume ratio of the monomer to suspension medium, concentration of the stabilizer, and the viscosities of both phases according to Eq (3) [30]. The following equation gathers up most of the empirical relationships reported by Arshady and Ledwith, Hopff and coworkers, Kavarov and Bakanov, Mersmann and Grossman, and Sculles [29]:

$$\bar{d} = k \times \frac{D_v \times R \times v_d \times \varepsilon}{D_s \times N \times v_m \times C_s} \qquad (3)$$

where $\bar{d}$ = average particle size; k = parameters such as apparatus design, type of stirrer, self-stabilization etc.; D_v = diameter of vessel; D_s = diameter of stirrer; R or φ = volume ratio of the droplet phase to suspension medium; N = stirring speed (or power of mixing); v_d = viscosity of the droplet or dispersed phase; v_m = viscosity of the suspension medium; ε = interfacial tension between the two immiscible phases; and C_s = stabilizer concentration. However, Eq (3) is only a guiding equation that works as a semi-quantitative basis helping to understand particle size data of produced products. Stirring speed is by far the most practical means of controlling particle size (see Figure 8) [29].

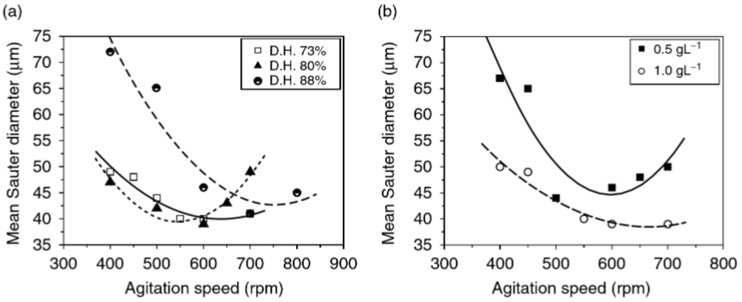


Figure 8. Dependence on Sauter mean diameter on the agitation speed for a) various PVA grades and b) concentrations [13].

By increasing power unit mass by such means as increasing agitation speed or the impeller diameter the turbulent intensity and the pressure and velocity fluctuations increase and, hence, the drop breakage rate increases leading to formation of smaller and more uniform particles. However, the increased liquid circulation rates lead to more drop collisions increasing drop coalescence rates. Depending on whether drop breakage or coalescence dominates, an increase of the input power may lead to an increase or decrease in mean particle size (see Figure 8 above). In addition, it has been noticed that the mean drop particle diameter follows a parabolic (U-shape) regarding the impeller speed or impeller diameter [13].

Increasing the dispersed phase viscosity (v_d), in general, increases both breakage and coalescence rates [13]. Generally, the increase of holdup fraction of the dispersed phase (φ) decreases the turbulent intensity (i.e., the average energy dissipation rate per unit mass) and, hence, the drop breakage rate. But then again, the coalescence rate also increases because of higher amount of monomer droplets, but the coalescence efficacy decreases because off the lower average dissipation rate. Still, the effect of φ or R affect coalescence rate more and, hence, if the input power is kept constant, as φ increases the droplet size increases [13].

3.4.5 Suspension Reactors

The most common reactor type used in industrial suspension polymerization is agitated batch reactor (see Figure 9), or possibly semi-batch, and the continuous phase is aqueous (for additional information about batch reactors see Glossary & Concepts) [28]. The reactors are generally vertical, agitated (or stirred tank) vessels, that are usually made of stainless steel or glass-lined carbon steel. They are typically equipped with agitators with a paddle or anchor-type stirrer of speed in the range 20 to 60 rpm. The stirrer can be provided with baffles to enhance dispersion since the use of baffles limits nonuniformity in turbulence and vortex formation [31,32]. Heat transfer to the aqueous phase is high because of the relatively high ratio of surface area to volume for small drops. The temperature control is crucial for the suspension polymerization process in order to keep polymer conversion rates high and is one of the most important design for the reactor. The design of the reactor must ensure a close degree of accuracy for temperature control for optimal processing conditions, and in addition, be capable of removing the heat of polymerization process, since the process is usually exothermic. In addition, suspension polymerization usually requires relatively large reactor volumes, larger than for example bulk polymerization reactors, since the vessels are usually half filled with water. Reactor geometry becomes important when large stirred vessels are used since it influences the internal liquid flow. Some other reactor types have been used for suspension polymerization, too. These include a loop reactor, an oscillatory baffled reactor and a continuous-flow tubular reactor (CFR) [28].

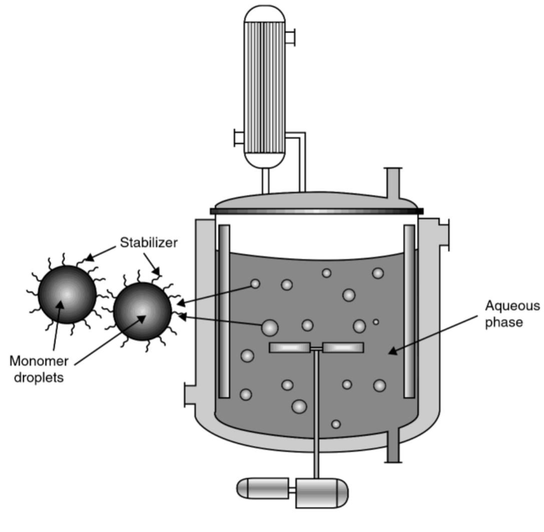


Figure 9. A scheme representing a suspension polymerization reactor (a BR or semi-BR) [13].

3.4.6 Scale-up of the Process – Laboratory → Pilot → Industrial Scale

Suspension polymerization has been studied for decades, and still, the industrial practitioners are continuously facing problems within their processes in controlling the PSD. Problematic phenomena that may cause problems and are not fully understood, include, for example, polymerization kinetics, rheological behavior of the monomer/polymer particles, interfacial properties, suspension stability, and the inhomogeneity of the vessel and mixing [27,30]. This naturally leads to a situation, where industrial practitioners overemphasize some effects, while neglecting others when process design or models are developed [27].

The step of scaling up a suspension polymerization process, or a reactor, from lab to pilot and then to industrial scape is not straightforward or well established, and much empiricism is still used in developing new products and to scale the production from pilot level up to production level, and expensive and time-consuming experimental programs are usually required [13,27]. Often it is impossible to achieve a complete dynamic, chemical and thermal similarity in a scale-up procedure, and the differences must simply be accepted at some point. This has been noted both by the researchers and the commercial manufacturers [27]. The most significant issue in scale-up is probably when different physical processes become limiting factors at different scales. An industrial-scale reactor must perform well several functions such as dispersion, reaction and heat transfer simultaneously that do not scale-up in the same manner. For example, at large scales the heat removal can become a limiting factor, while the heat removal is rarely a problem for lab-scale reactors [13].

3.4.7 Suspension Advantages and Disadvantages

Suspension polymerization has its pros and cons compared to the other common polymerization processes (e.g. bulk, solution, emulsion). Some of the advantages and disadvantages are summarized below.

Advantages

+ Easy heat removal and temperature control,
+ easily agitated,
+ low dispersion viscosity,
+ relatively easy viscosity control,
+ relatively low levels of impurities in the polymer product (compared with emulsion),
+ relatively low separation costs (compared with emulsion),
+ final product in particle form.

Disadvantages

– Relatively low productivity for the same reactor capacity compared to bulk due to the presence of the dispersing medium,
– wastewater problems since large volume of the reactor is taken by water and the need for post-treatment of dispersion medium in general,
– buildup on the reactor wall (fouling), baffles, agitators and other surfaces,
– challenging commercial continuous process operability,
– difficulty in producing homogeneous copolymers during batch suspension polymerization,
– semi-batch more difficult to operate with suspension versus emulsion,
– difficulties in controlling particle size. [13,27-32]

3.5 Solubility and Dissolution of Polymers

3.5.1 General Information

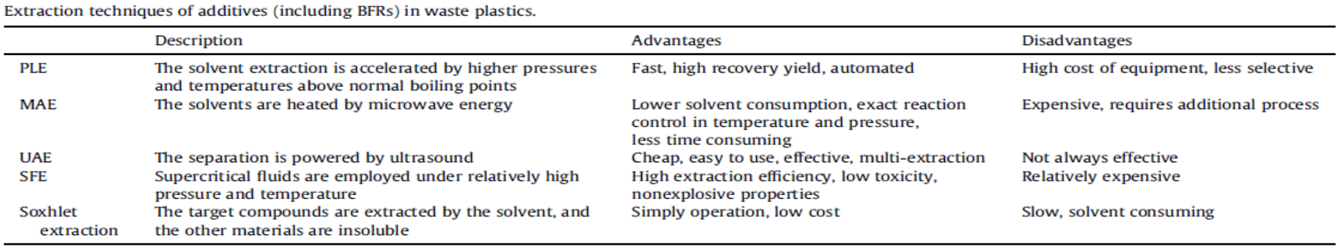
Solubility of polymers is a crucial parameter in many applications. For example, in the plastic-recycling industry large-scale processes are applied in which either one solvent is used at different temperatures to selectively dissolve different sorts of polymers or several solvents are used to selectively extract polymers from the recycled mass. In some cases, polymers are required to be insoluble, such as in fuel tanks or solvent lines [33]. Solubility is defined as "the maximum amount of an analyte that can be dissolved in a particular solvent or mixture of solvents at well-defined conditions (temperature, pressure, etc.)" [33]. Solubility describes the equilibrium state and should not be confused with the term dissolution, which is the actual kinetic process of the polymer going into the solution. The dissolution process is slow for polymers. In the beginning of the process, solvent molecules gradually diffuse into the polymer molecules and a gel is formed, which may be followed by the gel developing into a true molecular solution [33].

The solubility of polymers is affected by many chemical and physical parameters, such as temperature, nature of the solvent, average MW, PDI, degree of branching, crosslinking, crystallinity, etc. A temperature increase may either increase or decrease polymer solubility. However, the dissolution rate usually increases with increasing temperature. With increasing MW solubility and the rate of dissolution tend to decrease. Disperse polymers with a broad MW distribution will dissolve more rapidly than less disperse polymers with narrowly distributed MW. Increasing degree of cross-linking and crystallinity decrease both the solubility and dissolution rate. In general, branching of the polymer increases the solubility. As a rule of thumb, similarity in the structure between the solvent and the polymer contributes to solubility as 'like dissolves like' [33]. This is also true for PS that is soluble into its monomer, styrene [59]. Polymer solubility can be predicted with the help of solubility parameters. It is possible to estimate these quantitative parameters that are defined as the square root of the cohesive density of a solid or liquid by measuring physical properties, for example, by means of using differential scanning calorimetry, laser-light scattering or viscometry, swelling tests or from cloud-point measurements (turbidimetry) [33].

Precise and accurate studies reporting solubilities of different polymer in specified solvents or mixtures of solvents at specified temperatures, etc., is limited. Basically, the polymer solubilities can be readily measured with the help of concentration-sensitive detectors, such as differential refractometers (differential refractive index, dRI) or ultraviolet (UV) spectrometers. However, these methods are slow and may suffer from interferences (e.g. low molecular weight additives or polymers), they are only suitable for restricted solvent (e.g. non-UV active) and may be restricted by a limited range of concentrations. Still, many common methods have problem with detection, and are not suitable for only slightly soluble polymers. Pyrolysis-gas chromatography (Py-GC) is used in an increasing extent as a quantitative tool. It offers low detection limits and new opportunities for measuring physical data in the form of dissolution curves and solubilities of polymers [33].

3.5.2 Dissolution Process and Extraction with Solvents

Plastic recycling by solvent extraction generically consists of removal of impurities (e.g. SFE, MAE, ASE, and other plastic additives, see Table 5), either homogeneous or heterogeneous dissolution, and reprecipitation or devolatilization. The polymer(s) are dissolved in the solvent(s), and subsequently, each of the polymers is selectively crystallized. In an ideal situation, the solvent is able to dissolve either the target polymer or all the other polymers except the target polymer, and can be used for selective dissolution. Finding selective solvents is crucial for the dissolution process [1].



Extraction techniques of additives (including BFRs) in waste plastics.

	Description	Advantages	Disadvantages
PLE	The solvent extraction is accelerated by higher pressures and temperatures above normal boiling points	Fast, high recovery yield, automated	High cost of equipment, less selective
MAE	The solvents are heated by microwave energy	Lower solvent consumption, exact reaction control in temperature and pressure, less time consuming	Expensive, requires additional process
UAE	The separation is powered by ultrasound	Cheap, easy to use, effective, multi-extraction	Not always effective
SFE	Supercritical fluids are employed under relatively high pressure and temperature	High extraction efficiency, low toxicity, nonexplosive properties	Relatively expensive
Soxhlet extraction	The target compounds are extracted by the solvent, and the other materials are insoluble	Simply operation, low cost	Slow, solvent consuming

Table 5. A summary of some extraction techniques of additives or impurities in waste plastics [1].

The actual dissolution process is influenced by many things, such as the types of polymers and solvents, polymer size, MW, dissolution temperature, and concentration. Two thermodynamical transport processes are involded in polymer dissolution, solvent diffusion and chain disentanglement. The self diffusion of the polymer has an important role during chain distangglement. An increase in the MW of the polymer results in dissolution becoming more disenttanglement controlled instead of diffusion controlled. In general, the polymer plasticizes during dissolution and a gel-like swollen layer appears with two separate interfaces. The separate interfaces form between the gel layer and between the gel layer and the solvent. The solvent pushes the swollen polymer into the solvent, and as the solvent is further infiltrated into the polymer the swollen surface layer increases until a quasi-stability state is reached. Solvent dissolution depends kinetically on the free volume of the gel phase and the solvent size. Decrease in particle size and increase in the diffusivity of polymers result in increased mass transfer rate, and thus, decrease the dissolution times [1].

The sructure of glassy polymers and the dissolution process is illustrated in Figure 10 below. The glassy polymers consist of an infiltration layer, a solid swollen layer, a gel layer, and a liquid layer. The polymer at glassy state contains channels and holes of molecular dimensions. The empty spaces are filled with the solvent molecules annd the diffusion process is started without creating new holes.

All layers are present in “normal dissolution”, whereas the gel layer disappears as a concequence of the decrease in stress energy, which indicates a transition to cracking. The assumption is that the insoluble polymers act as an additional layer decreasing the diffusion of both solvents and polymers. Normal dissolution involves typically the penetration of the solvent, followed by swelling of the polymers and diffusion into the solvent [1].

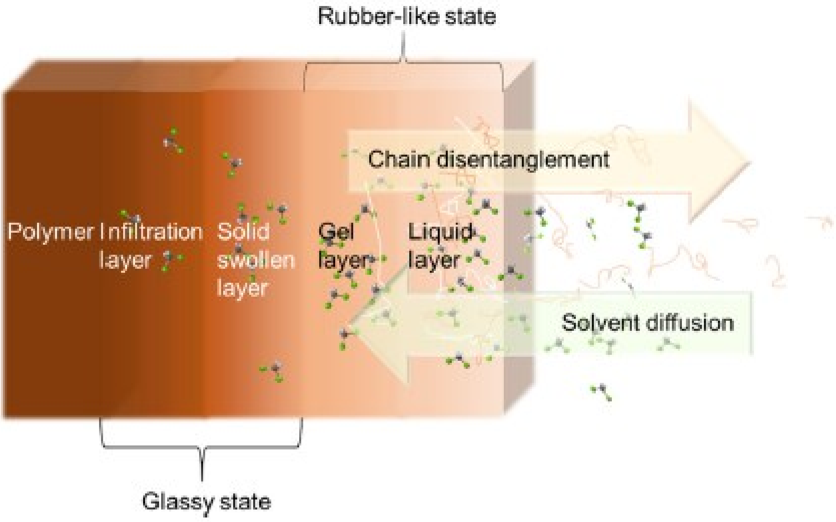


Figure 10. The different surface layers during the dissolution process [1].

The optimal solvents and non-solvents applied in the dissolution/reprecipitation method are primarily selected by the principles listed below [1].

1) ‘Like dissolves like’. Highly polar polymers are dissolved in highly polar solvents, whereas low-polar polymers are dissolved in low polar solvents. The lesser the gap in polarities between the polymer and the solvent, the easier the dissolution becomes [1].
2) Interaction between the polymer and solvent exceeds the cohesion of the polymers results in easy dissolution of the polymer into the solvent [1].
3) Solubility parameters, such as for example, δ_D (dispersion energy), δ_P (dipolar energy) and δ_H (hydrogen bonding energy), of the polymer and the solvent should be similar or equal in order to the polymer to become more readily dissolved. Several solubility parameter systems have been developed to estimate the solvation ability, such as Hansen, Kamlet Taft, Gutmann, Swain, and $E_T(30)$ systems [1,35].

4 Expanded Polystyrene – EPS

4.1 Introduction

4.1.1 General Information

Particle foams based on expanded polystyrene (EPS) are one of the most important PS applications [19]. These foams have the technical name Expanded Polystyrene, but are known with various other names, as well. For example, in Europe EPS is called Airpop®- engineered air [36]. The first processes for making EPS were developed in the 1950s using the conventional suspension polymerization process, which has been in use to this day as the predominant production route for EPS [4]. EPS is widely used for different kinds of application, including for instance, disposable drinking cups, fast-food containers, picnic plates, wall insulation, packing material for delicate instruments, etc. The wide use of foamed PS has awoken some environmental concerns since it has not traditionally been recycled to the full extent. However, other competitive materials have also met some environmental difficulties [3].

EPS foams have a closed cellular structure and the usual density range is 10-80 g/l. However, densities of 10 g/l or lower are possible but require several pre-foaming operations [21]. Unexpanded EPS beads are typically in the size range of 0.1-2 mm, while the expanded beads by heating will expand up to 20 times their original value, and subsequently with passing steam through the mold beads further expand to double the size of partially expanded size (approximately 40 times the size of the original beads) and fuse together [3,4]. The beads are charged with a volatile organic blowing agent, often a mix of isomers of pentane, in the final stage of the process before dewatering and drying. The beads are also coated with organic coating working as antistatic to prevent agglomeration and assisting in the later processes and sieved to different size fractions to suit particular application, before they are stored in silos, or filled in into gas-proof bags or octabins. Smaller bead sizes are commonly used for thinner-walled products, and correspondingly, the bigger for thicker-walled products [4].

Different EPS production plants have typically their own recipes and process settings for the polymerization. This depends partly on the designs and size of the reactors, and on the desired product. Even though EPS industry evolves in the same general direction, there is still a lot of proprietary secret information about suspending agents, bead size control and cell nucleation additives, blowing agents, bead coatings, etc. [4]

Extrusion processes have been developed more recently. These processes yield “microbeads” with more of a uniform size directly from a melt of polystyrene that may contain a blowing agent by using an underwater micro pelletizer. The PS melt is supplied form either one- or two-stage extrusion line, or directly from a polymerization reaction, which is performed in a series of static mixers and melt pumps. These extrusion processes have the advantage over suspension polymerization in the ability to efficiently incorporating additives, which may create problems during suspension polymerization. The uniform size of the beads reduces the waste or off-spec when only a specific product size fraction is desired. The subsequent processing of extruded beads is identical with polymerized beads. [4]

4.1.2 The EPS Market

The total global market value of EPS was 13 871.7 million U.S. dollars in 2016. The value was forecasted to increase to 18 797.6 million U.S. dollars by the end of 2021 (see Figure 11) [22]. The EPS market has become highly competitive since the regular grade EPS has been modified. The ‘modified’ EPS segment has been introduced by addition of additives such as flame retardants and graphite. Grey and Silver EPS are used in increasing extent (see Figure 12) and dominate the market in Europe. The grey and the silver EPS are gray to black colored products that contain graphite, which increases its refractive and reflective properties in order to provide better thermal insulation. The graphite already at low concentrations increases the refraction of IR light making the path for escaping heat less direct. The thermal conductivity is decreased by 20%, and hence, while still maintaining the same properties, reduces the board thickness by 20%. It is also possible to produce grey EPS using the same equipment used with traditional EPS. Even though the price for gray EPS is higher than for white EPS, the possibility to reduce power costs through better insulation may increase the demand for EPS gray in the construction industry even more in the future, and most probably, will lower the price for gray products (see Figure 12 and 13) [37].

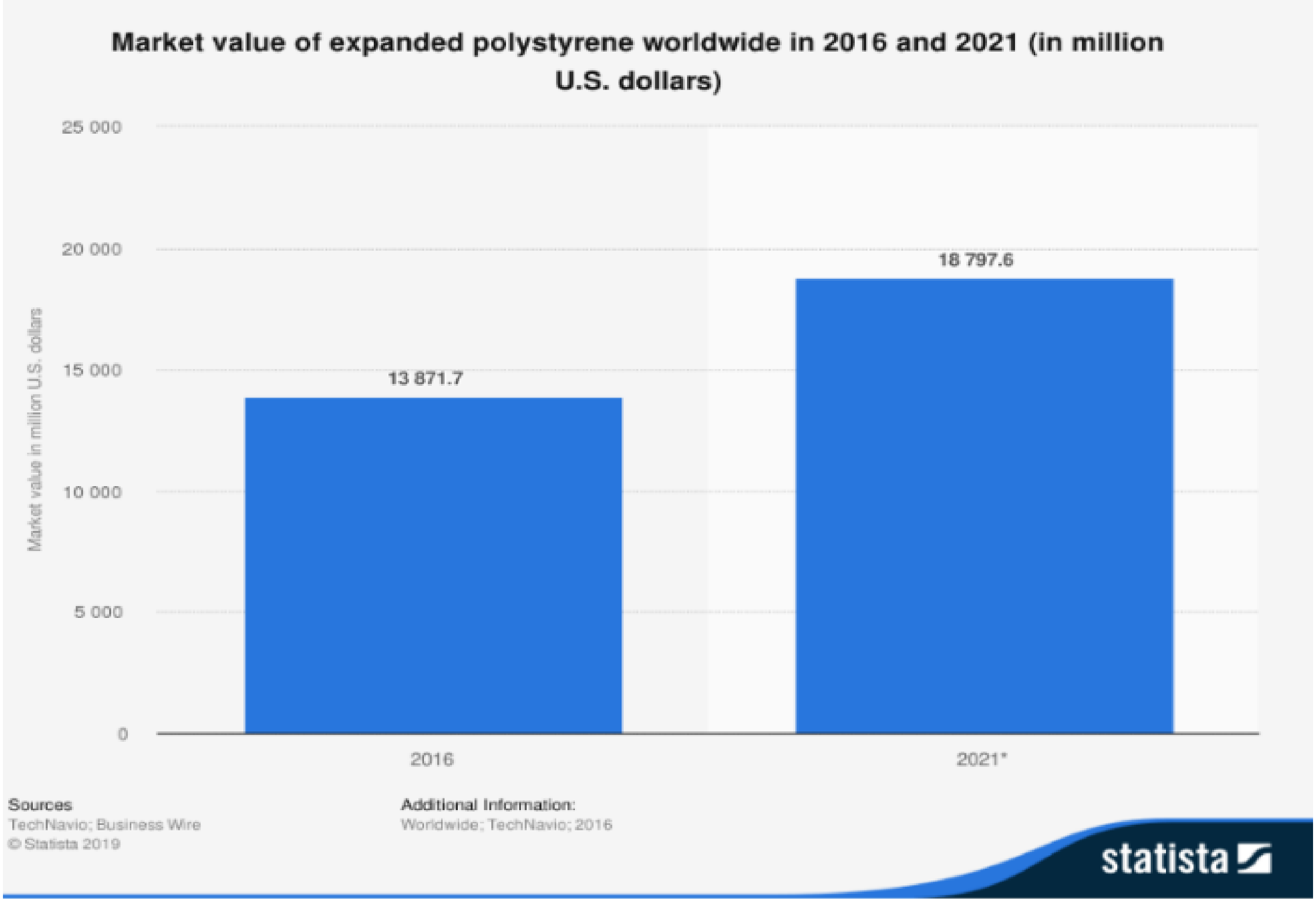


Figure 11. Market value in million U.S. dollars of expanded polystyrene worldwide in 2016 and an estimation for 2021 [22].

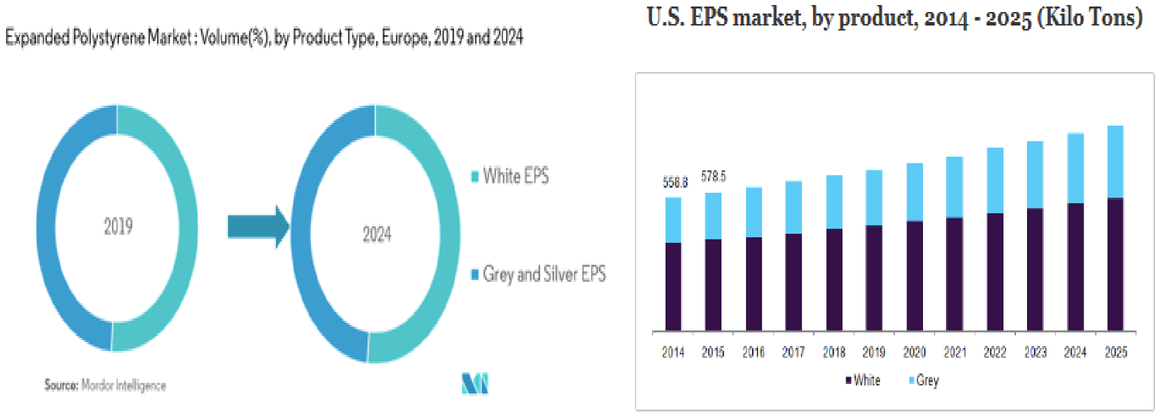


Figure 12 and 13. EPS market volumes in Europe by product type in 2019 and a forecast for 2025 (left), and U.S. EPS market in tons by product type (right) [5,37].

4.1.3 Advantages/Strengths

Some of the advantages of PS foam can be shortly summarized as follows:

- \+ low thermal conductivity (excellent insulation),
- \+ flexible mechanical properties,
- \+ good energy absorption (packaging),
- \+ high buoyancy,
- \+ moisture and chemically resistant,
- \+ proven acoustic properties (impact sound on floors and airborne sound for walls),
- \+ high-stiffness-to weight ratio (self-supporting and lightweight parts),
- \+ low cost per volume/cost-effective,
- \+ versatility in shapes, sizes and combability with a wide variety of materials,
- \+ small production capacities possible,
- \+ lifetime durability and stability (no decomposition and mold resistant)
- \+ easy to install (light, practical and safe),
- \+ easy and economical to transport in unexpanded bead form, and
- \+ relatively easily and widely recycled [3,4,8,21,23,38].

4.1.4 Disadvantages/Weaknesses

Some of the disadvantages of PS foam can be shortly summarized as follows:

- – highly flammable product (flame retardation is often required),
- – emissions,
- – limitations for blowing agents and flame retardants (additional expenses and legislative regulations), especially brominated flame retardants,
- – poor ductility and toughness, and
- – highly voluminous products taking up much space during transporting [3,4,8,21].

4.2 Applications and Properties

4.2.1 Applications

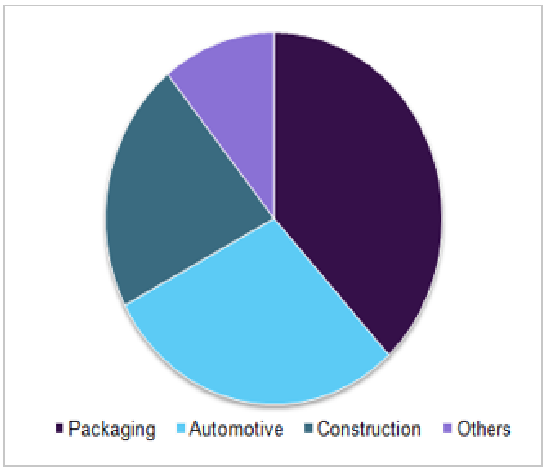


Figure 14. Global EPS market volume shares by different applications in 2016 [5].

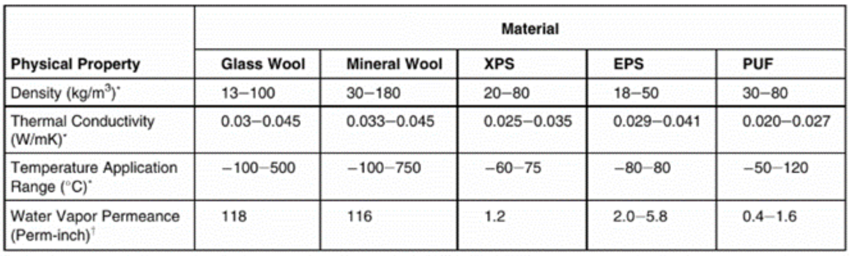
Packaging industry had the highest share of the total market, accounting for a 42.5% of the total market volume in 2016, and 46% in 2018 [5,40]. However, there are large differences regarding the main application of EPS in different regions [8]. For instance, in Europe building and construction related applications' market share accounts for approximately 70-80% [8,40,41]. The automotive industry is forecasted to grow at a volume CAGR of 32.8% from 2017 to 2025 globally. The driving factors for the growth are the strict requirements for lightweight, safe and fuel-efficient vehicles. The construction industry is forecasted to account for 21.4% of the global volume in 2025 [5]. The two conventional application areas of EPS, namely packaging and construction are shortly discussed below.

Packaging

EPS is used widely in packaging for many high-value industrial products [8]. It can provide adequate protection and safety against mechanical and thermal damage during transport, storage and handling. In general, small EPS particles (0.4-0.9 mm) are suitable for packaging best since the produced foam molding parts produced can have very complicated shapes and structures. Examples of packaging applications include packaging materials for machines and machine parts, glass, china, optical, electronical and electronic equipment, toys, pharmaceuticals, and for edge and surface protection [21]. In addition, EPS packaging is used for food packaging. The material keeps the conserve the food and provides protection against hazards, breakages and wastage in the different stages of production, transport, and in consumer usage [8]. However, this requires special type of EPS with food certification. The advantages compared to other materials include low weight, resistance to water, good shock absorption behavior, excellent heat/cold insulation and easy processing and handling [21].

Construction

EPS is used for many building projects for thermal insulation, and in increasing extent for soundproofing buildings and modernization and renovation work as well. Slabs of EPS foam are used for insulation of walls, roofs, floors and ceilings. Bigger particle size ranging from 0.9 to 1.6 mm are preferred for construction insulations [21]. EPS geofoam can also be used as an easy-handling, lightweight filler in roads, for example, in order to facilitate land drainage [8]. Foamed PU, PIR and XPS are all popular plastic foams that compete against EPS in construction as an insulation material. Both EPS and XPS are rigid, closed-cell, thermoplastic materials, while PU and PIR are thermosets. The main competing non-plastic insulation materials are fiberglass and mineral wood [42]. A comparison of thermal and vapor barrier properties of common insulation materials used in the construction industry in the Table 6 below.

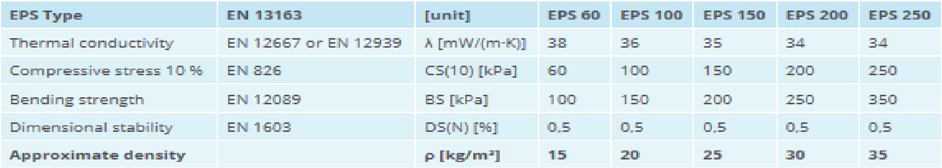


Physical Property	Material				
	Glass Wool	Mineral Wool	XPS	EPS	PUF
Density (kg/m^3)*	13–100	30–180	20–80	18–50	30–80
Thermal Conductivity (W/mK)*	0.03–0.045	0.033–0.045	0.025–0.035	0.029–0.041	0.020–0.027
Temperature Application Range (°C)*	−100–500	−100–750	−60–75	−80–80	−50–120
Water Vapor Permeance (Perm-inch)†	118	116	1.2	2.0–5.8	0.4–1.6

Table 6. Typical thermal and water vapor properties of common insulation materials used in construction industry [42].

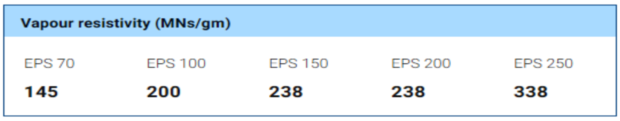
4.2.2 Properties

The primary focus in EPS development has been in the construction and packaging industries where the properties of thermal insulation and mechanical protection are of paramount importance. Insulative construction applications such as underfloor and wall insulations benefit from the very high levels of thermal insulation, while packaging of fragile goods requires high mechanical (impact) protection. For transportation applications (e.g. food transportation), both the mechanical and thermal properties are important [2]. Beneficial properties of EPS for different applications include for example good shock absorption, compressive resistance, low thermal conductivity, chemical resistance, humidity resistance, low water absorption, low weight, durability and resistance against decomposition, acoustic properties, recyclability etc. [3,4,8,43]. In the tables below an overview of a number of EPS properties per EPS type at different densities according to EN 13163 is given except for the Table 9.



EPS Type	**EN 13163**	**[unit]**	**EPS 60**	**EPS 100**	**EPS 150**	**EPS 200**	**EPS 250**
Thermal conductivity	EN 12667 or EN 12939	λ [mW/(m·K)]	38	36	35	34	34
Compressive stress 10 %	EN 826	CS(10) [kPa]	60	100	150	200	250
Bending strength	EN 12089	BS [kPa]	100	150	200	250	350
Dimensional stability	EN 1603	DS(N) [%]	0,5	0,5	0,5	0,5	0,5
Approximate density		**ρ [kg/m^3]**	**15**	**20**	**25**	**30**	**35**

Table 7. A compilation of several EPS properties at varying qualities (densities) according to EN 13163 [44].



Vapour resistivity (MNs/gm)				
EPS 70	EPS 100	EPS 150	EPS 200	EPS 250
145	**200**	**238**	**238**	**338**

Table 8. A compilation of moisture properties of EPS properties at varying qualities (densities) according to EN 13163 [45].

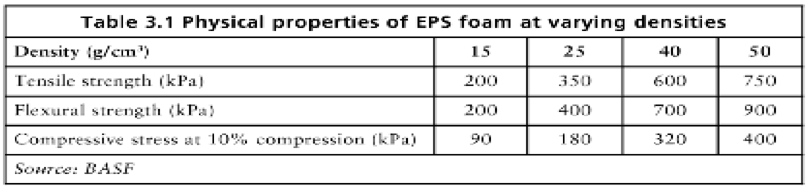


Table 3.1 Physical properties of EPS foam at varying densities				
Density (g/cm^3)	15	25	40	50
Tensile strength (kPa)	200	350	600	750
Flexural strength (kPa)	200	400	700	900
Compressive stress at 10% compression (kPa)	90	180	320	400
Source: BASF				

Table 9. A compilation of several mechanical EPS properties at varying densities [2].

The properties above are for the traditional white EPS. A grey product with an addition of graphite has a better insulation property than the traditional white EPS, more specifically, approximately a 20% better insulation value (lambda) than the traditional white EPS. This enables thinner insulation boards, savings in volume, lower transportation costs and ultimately, reduced energy consumption [46].

5 EPS Production – Processing and Processes

5.1 Introduction

There are generally two basic processes for making foamable polystyrene (EPS):

1. suspension polymerization of styrene into spherical beads containing a blowing agent, and finishing of the beads in a multi-step process (Figure 15 and 16),
2. extrusion process where incorporation of a blowing agent is incorporated in bulk PS, in which the polymer strands are quenched in a water bath to avoid foaming and the resulting strand cutting [21].

These processes result in a raw material in the form of beads or granules, which is called EPS. Usually the EPS beads or granules are produced in one location and transported to other locations for processing, that is, for expansion and molding into their final forms. This has the advantage that the cost of shipping high-volume foam is minimized, and molding can be performed directly without post-processing. The conversion of EPS particles produced with suspension polymerization into foam is done in three steps:

1. pre-foaming/pre-expansion of EPS particles,
2. maturation or temporary storage of pre-expanded beads, and
3. final foaming (molding or blocking process) [21].

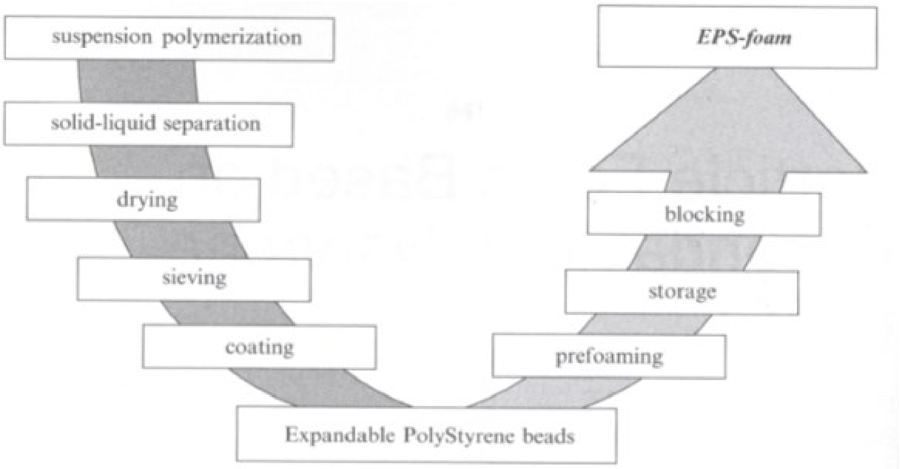


Figure 15. Schematic diagram of the manufacture of EPS particle foam [21].

5.2 EPS Manufacture Based on Suspension Polymerization Process

5.2.1 EPS Raw Material Production

EPS Suspension Polymerization

EPS suspension polymerization produces spherical beads that are expanded into foam with the help of heat or steam in the presence of blowing agent. The water in-soluble styrene monomers are dispersed as liquid droplets with suspension stabilizer(s) while vigorously stirring the suspension mixture, consisting of water and monomer, in order to produce polystyrene particles as dispersed solid phase. The actual polymerization takes place in styrene monomer droplets. The initiators (e.g., organic peroxides, azo compounds) are soluble in oil. Suspension stabilization agents are present in the suspension that help with obtaining and stabilizing the desired droplet size distribution of the dispersed phase. Commercial EPS is focused in a particle size range of 0.1-2 mm, but 0.4-1.6 mm is preferred. The monomer/water phase ratio is often kept between 40:60 and 60:40 [21]. The most important issue in suspension polymerization in general, and in EPS, is the control of the particle-size distribution (PSD) [13]. More detailed general information about free-radical suspension polymerization can be found in the Chapter 3.4 Suspension Polymerization.

Technological Steps and EPS Manufacture Procedure

The commercial suspension polymerization for EPS production is carried out in a jacket batch reactor equipped with a stirrer and often two or more baffles. The reactor volume is typically between 20 and 100 m^3.

In the beginning of the production, the water phase and monomer phase are placed in the reactor vessel. The additives are fed either before or during the polymerization into the reactor. These components are typically soluble into water or the monomer and solved or dispersed in separate vessels. The filled reactor is heated up to the desired reaction temperature, typically gradually and in steps, since the polymerization is generally carried out in two or more stages. A blowing agent, typically pentane, is added under pressure during the polymerization. Once the desired conversion of the styrene monomer droplets to EPS beads is obtained, the reactor is cooled and the suspension is transferrer, typically into a stirred mixing vessel. The following finishing process is normally continuous. Centrifuges or rotating sieves separate expandable beads from water. EPS beads may then be washed and partly pretreated with different methods. Afterwards they are dried by flash-, fluid bed-

, and/or silo dryers, and then sieved/screened in various bead size fractions and coated, depending on their size and application. Batch or continuous blenders using solid or fluid coating materials are applied for coating. The used coatings and the size of the beads affect the processing properties of the EPS foams produced from these EPS beads. Finally, the different types of EPS are packed separately, usually in octabins, IBCs or silo trucks for use by EPS foam manufacturers. [21]

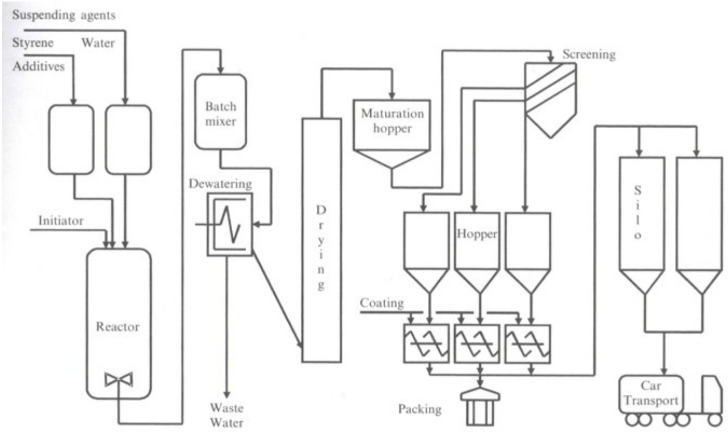


Figure 16. Technological steps for production of EPS with suspension polymerization [21].

Particle Formation and Stabilization

Particle formation starts with the dispersion of the styrene in water. Under the influence of agitation, fine drops with a definite distribution are formed. The general assumption is that the hydrodynamic forces in the turbulent field of the reactor, which is at its strongest in the stirrer region, cause droplet break-up as a result of turbulent fluctuations. If the tension available energy dissipation is adequate enough to overcome the surface tension and viscoelastic resistance of the droplets, the drops break up. Coalescence takes place if "drops collide with each other with sufficient energy to distort the drops to a degree that the liquid film between the drops can drain away before the flow field separates the drops again" [21]. Increase in stirrer speed, decrease in hold-up fraction and stabilizer concentration decrease the average drop size. In addition, the impeller type has been found to have an effect the drop size distribution (DSD) [21].

There are procedures for freezing particle size growth and DSD up to the end of the polymerization, but these particle sizes are not suitable for the target size range of EPS. Generally, by increasing conversion in the dispersed phase, the viscosity increases strongly, like do the properties of the interfacial layers as well, and the density changes a bit, and a change in equilibrium takes place between breakage and coalescence as it shifts more towards coalescence. As a result, the PSD becomes wider with a larger particle size. This phase is known as the sticky phase. During this phase a lack of suspension stabilizer leads to a total instability. For a successful EPS suspension system, it is crucial to find a suitable stabilizer system, flow conditions and procedures for shifting the particle size into right direction. [21]

Particle Size Control and PSD

Suspension polymerization yields more or less, a wide PSD [21]. Manufacturer's interest is pointed towards manipulating the PSD to satisfy the market requirements. The narrower the PSD the better [21]. Some procedures that have been invented for particle size control listed below.

- Controlling of the average diameter by using pickering stabilizer systems, such as TCP, in combination with an extender, such as ABS.
- Particle size control with the use and different timing of macromolecular suspension stabilizers, such as PVP, PVA.
- Final PSD control by geometric factors of the reactor and the hydrodynamic conditions affecting the drop break-up and coalescence during the suspension polymerization. More specifically, these include agitator type and dimensions, vessel geometry, operating parameters and the stirrer speed.
- Through sudden or stepwise reduction of stirrer speed during polymerization when pickering stabilizers are used [21].

Stabilizing Agents and Mechanism

Typical suspension stabilizers used in EPS manufacture are surface active and water-soluble macromolecules. Common stabilizers include:

- PVA (poly(vinyl alcohol)),
- HEC (hydroxyethylcellulose),
- PVP (polyvinylpyrrolidine),
- natural products, such as insoluble organic powders, such as TCP (tricalcium phosphate), also known as 'pickering stabilizer', mostly in combination with surfactants called extenders [21],

Surface-active macromolecules suit best for stabilization of large particles (e.g. PVA, PVP, gelatin, alginate, carboxy- or hydroxyethylcellulose, etc.). The reason to this is the large thickness of the adsorption layer and a multitude of good attachment points of the hydrophobic chains in the monomer drops. The scope of the forces of the macromolecular absorption layer is often larger than the effect of the electrical interactive forces. In general, the preferred macromolecules have a more or less blocky structure with one block or group has a hydrophobic nature acting as an anchoring component on the droplet surface, while the other block or group needs to be good solvate with water and provide the steric repulsion, together giving a train-loop chain arrangement. According to HVO (developed by Hesselink, Vrij, and Overbeek) theory "the steric repulsive force penetrating adsorption layers during anchoring of two particles can be essentially be attributed to the change in the volume restriction effect of macromolecules in the area of tails and the osmotic at its additional anchoring" [21]. High molecular weight chains such as gelatin, alginate and carboxy- or hydroxyethylcellulose, also known as protective colloids, give high viscosity in the water phase and a good protection against coalescence. [21]

The pickering systems consist of water soluble inorganic solid particles and an amphiphilic cosurfactant (a.k.a. extender). TCP with an average diameter in the range of 0.2-0.4 µm in the form of inorganic powder. ABS (sodium alkylbenzenesulfonate) is often used as an extender. The stabilizing mechanism is based on the ability of the solid particles to form mechanical barrier between the monomer drops that reduces the probability for coalescence [21].

Polymerization and Impregnation Process

Polymerization

The polymerization process is usually carried out in two or more stages (see Figure 17). In the first stage, the final particles are formed, and in the second stage a blowing agent that penetrates the beads is added. The residual monomer concentration that is required, normally < 1000 ppm, is preferably the determining factor for the duration of the second polymerization stage. In both stages, initiators with suitable decomposition characteristics are used to initiate the polymerization. The reaction progression probability greatly depends on the monomer conversion reactions. The viscosity of the dispersed phase is low during the first stage and the quantity of styrene is sufficiently high, the decomposition process of peroxides occurs only up to benzoyloxy radical, with the ability to start a kinetic chain reaction directly. The purely thermal initiation of chain formation with reactive dimers to styrene (Diels-Alder) reaction can be ignored in suspension polymerization due to low temperatures, in contrary to the bulk styrene processing. Two common peroxides that are used in EPS manufacture in order to complete the polymer conversion are:

1) BPO (dibenzoyl peroxide) for initiating the first stage of polymerization at a temperature of circa 90 °C,
2) TBPB (tert-butyl peroxybenzoate) for initiating the second stage of polymerization in the temperature range of 115-130 °C [1]. TBEC is very popular amongst EPS producers these days. Another possibility is TAEC (tert-amylperoxy-2-ethyl) [21].

The kinetic reaction route with constant reaction of the polymer/monomer droplet starts to dominate relatively quickly with conversion, resulting in decrease of the mobility of the polymer chain rapidly below the mobility of the monomer. This will cause a reduction of live polymer chains in the droplet, which will reduce the rate of termination of polymerization. This can be linked to drastic increase in the numbers of radicals that will cause a rapid increase in the polymerization rate. This phenomenon is known as the gel effect (Trommsdorf). The gel effect results in growth of the polymer chain length and broadening of the MWD. In order to decrease the viscosity at this stage of polymerization requires either continuous or stepped temperature increase. Addition of small amounts of bifunctional monomers or chain transfer agents ($k_{tr} > 2$) will also result in more desirable MWD (flat low M_w side and sharply decreasing high M_w flank). The preferred procedure is to add chain transfer agents later before the gel effect ends. [21]

The result of a low concentration of branched macromolecules should result in higher melt flow rate during the pre-foaming step of the EPS beads. There is literature that states that earlier addition of blowing agent reduces viscosity of the droplets. Hamielec and co-workers have pointed out that temperature increase, while simultaneously, earlier addition of blowing agent, n-pentane, with monofunctional initiators lead to a limited conversion and plasticizing effect by pentane, resulting in enhanced coalescence and total instability of suspension. They suggested that by using bifunctional initiators in which enhanced coalescence is totally overcome due to the very short duration of the particle growth and high polymerization rates. On the other hand, towards the end of the polymerization the chance for primer radical to initiate polymerization is reduced. The amount of highly reactive benoyloxy radicals that can react with the polymer chain under abstraction of hydrogen will increase with the consequent formation of benzene. This has led to substitution of tertBuPB with an initiator without aromatic groups, such as TBEC. Another interesting replacement of TBPB is TAEC (e.g. Luperox TAEC). This initiator's radicals have slightly faster decomposition rates, better diffusion into the high conversion matric of an EPS particle, and better selectivity for adding styrene monomer. [21]

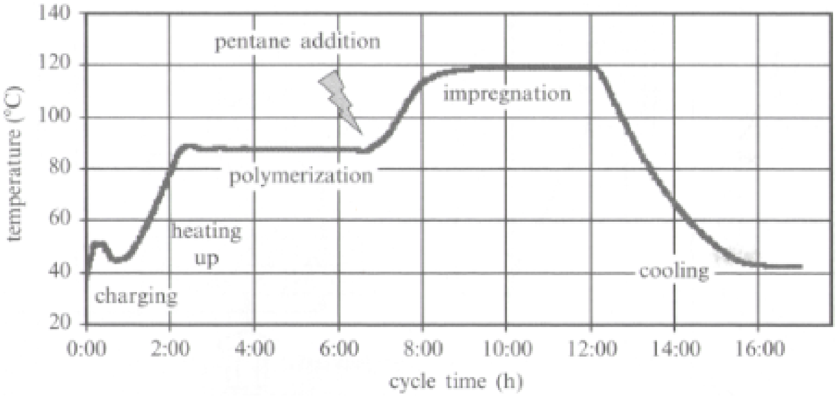


Figure 17. A traditional temperature-time regime for a two-stage polymerization process of EPS [21].

Impregnation

The process step of addition of a blowing agent is called impregnation. It is possible to add the blowing agent to the batch before or during the suspension polymerization [21]. In this work, the blowing agent, pentane, is added during the process. It is also possible to incorporate the agent into polystyrene that has been re-suspended into water [21]. Too early addition of blowing agent has the disadvantage of stunting polymerization due to a dilution effect. In practice, addition of the blowing agent after the polymerization is only used for the recycling of waste materials and side bead fraction (not for sale). Impregnation of the blowing agent at conversion between 65-85 % is currently the norm for commercial EPS production. Procedures with addition of the blowing agent at about 66 % conversion, the moment when PS particles surpasses the density of the water phase are preferred [21].

Blowing agents in use are halogen free C_nH_m compounds with n = 4-6, such as n-butane, isopentane, n-pentane, neopentane and hexane. Mixtures of iso- and n-pentane, however, are preferred for standard EPS production. Both pentane isomers have considerably different diffusion rates at a given temperature. If the content of isopentane is high, the pre-foamed beds are able to expand over a long period of time during temporary storage, but on the other hand, also longer cooling times are required for the demolding process. The correct composition of pentane mixture is always a compromise between good foamability and fast diffusion behavior [21].

The reactor’s pressure increases and its progression during impregnation depend on conversion time and the temperatures of the added pentane and the composition of the pentane mixture. Later addition of pentane leads to an asymptotic decrease of pressure which conforms with the Fickian diffusion. In the case of n-pentane, it has been shown that when it is added in suspension, the diffusion into the periphery of the beads occurs first rapidly to almost a completely pentane uptake, and stalls afterwards (depending on the degree of conversion). If the addition of pentane occurs at 60-70 % conversion, the following two effects are noticed: an increase in pressure because of arranged loss of soluble styrene with increasing conversion, and a decrease in pressure due to increased diffusion of pentane into the beads. The equilibrium pressure for the quaternary system styrene–polystyrene–isopentane–n-pentane has been calculated by Wolfart for different conversions, temperatures and n-/isopentane ratios [21].

The expansion capacity can be influenced by adjusting the pentane concentration in the beads [21]. Typically, standard EPS contains 5.5-6.5 wt-% pentane, and low-pentane types less than 4.5 % [21,47].

Additives

Either during or at the end of EPS manufacture additives are often incorporated into the beads in order to improve process and application properties. Additives that appear in EPS products include:

- nucleation agents,
- flame retardants,
- fast-cool agents,
- anti-lump and anti-static agents,
- stabilizers,
- plasticizers,
- pigments, etc. [21]

Nucleation Agents

Substances that can initiate and control cell formation and growth are called nucleation agents, and these substances are often incorporated into the polymeric structure on purpose for cell control. Still, some unwanted nucleation effects can appear from other substances such as water, suspension stabilizer or HBCD (hexabromocyclodecane). It is important that nucleation agents have the ability to control nucleation independently without disturbances of other effects and to mask the bubble initiation of other sources. Examples of nucleation agents appearing in EPS industry include paraffins, chloroparaffins, Fischer-Tropsch waxes, and also esters and amides of fatty acids. In addition, finely divided phase-incompatible polymers, such as low-molecular weight PE, are used for cell control (above its melting point, low-molecular weight PE is soluble in styrene) [21].

Flame-Retardant Agents

Small quantities of certain additives are used for fire retardation in EPS that markedly improve the behavior of the foam in the presence of mild fire sources. Traditionally bromine compounds, and in general, with at least two bromine atoms and a bromine content higher than 40 wt %, basically a suitable linear aliphatic brominated organic compound and a bromo-substituted cycloalkane. The final product should contain 0.6-3 wt % bromine. The flame retardation is intensified by using synergists, that enables usage of much less of bromine containing compounds. The most common synergist is DCP, and other alternatives include less volatile and more temperature stable -C-C initiators, such as 2,3-dimethyl-2,3-diphenylbutane [21]. HBCD was a very common bromine-based flame retardant, but as well as other bromine-containing compounds, the usage has started to become restricted due to environmental concerns. For example, in Europe, the usage of HBCD is completely prohibited [48]. A new replacement, pFR (polymeric flame retardant), was brought to the global market by Dow Global Technologies LLC (DGTL). The key advantage is that pFR is a plastic itself like EPS, is not water soluble and will not be taken up by organisms. In addition, it can maintain the reaction fire properties while other desirable properties such as thermal conductivity and mechanical strength are unchanged [46]. Currently, fire retardation is one of the most important field of studies for foams and much effort is set on finding alternative flame retardants for the existing ones.

Coatings

Poor processing characteristics would follow from untreated surface of EPS beads. A number of coating components are used to improve characteristics such as foaming, aging, blocking performance and the final application performance of the foam. PS beads and pre-foamed particles often tend to acquire various quantities of static charge. These charges are often long lasting, causing agglomeration. In order to avoid this, anti-static agents are added before or after screening. Besides to the flowability problems during the finishing steps, the static charges impact negatively the homogeneous filling of block forms and, especially, the molding equipment. Many effective anti-static agents in use include small quantities of esters of fatty acids and amines, quaternary ammonium salts, alkylphosphates, and fatty alcohol with ethylene oxide on propylene oxide. [21]

Compounds that protect against the propensity of particles to fuse together during the prefoaming process at temperatures above the transition temperature are called anti-lumping agents. Utilized anti-lumping agents include, for example, metal stearates, inorganic powders (e.g., SiO_2 and $CaCO_3$), and powders of polymeric materials (e.g. polyamide waxes). These agents can influence the fusion quality during molding, and the concentration and the composition should be adapted to in both steps in foam production. [21]

Modern EPS types have been, and are also in the future, developed to so that molding operation capacity is improved providing short aging and cooling times. External fast-cooling agents are commonly a various mixture of glyceride esters of higher fatty acids, usually with carbon chain lengths in the range of 14-20. It is assumed that the cooling effect time reduction is because of the formation of fine canals in the bead surface which allows faster diffusion of pentane out of the beads. The more rapid loss of pentane during the pre-foaming process generally leads to foamability loss with a reduction in cooling time. As a result, the balance between both properties must be matched to suit the desired application. The cooling time is more important than the increase in density and thickness of the foam. Properties of different particle sizes for different applications are provided by variating compositions and concentrations of components in a mixture. [21]

5.2.2 Pre-Foaming Process or Pre-Expansion Process

In the pre-foaming stage, the EPS beads are heated by saturated steam to above the T_g of PS, at the temperatures of between 80-100 °C, in a pre-foamer [8,21]. This causes the in the PS matrix dissolved blowing agent, typically pentane, to expand and boiling off the EPS beads, and as a result a system of spherical systems are formed [8,21]. During this stage, the EPS bead volume can increase by a factor 40-80.

5.2.3 Maturation or Conditioning

The pre-foamed beds are cooled after the pre-expansion stage. As a result, the remaining blowing agent (about 4 wt-% pentanes, and air at atmospheric pressure) in the EPS cells condenses and creates a vacuum in the beads [8,21]. In this stage the particles are very brittle. A definite time for maturation is required in order to avoid problems in the molding stage [21]. The pre-foamed are usually stored in aerated fabric silos (large fabric storage bags) [8,21]. During the maturation, process air penetrates the cells, and eventually, the internal pressure of the cells approaches atmospheric pressure [21]. The beads are also dried at the same time [8]. If the foam is heated again, the expansion will go further, and can be used for a second or third expansion process in a continuous pre-foamer, or directly in final molding process [21].

5.2.4 Final Foaming Procedures

From temporary storage the pre-foamed beads are entered molding stage [8,21]. The beads are welded into a homogeneous foam in a perforated mold by a renewed steam supply. The foaming occurs in molds, molding machines or special units (slab units, belt units). The different stages in molding can be divided into mold filling, steaming, cooling and demolding [21]. Steam is injected into the mold, and the beads are allowed to expand further, melt together and fill the mold fully. The system is cooled after a completed foaming process. The expanded beads are molded either into foam blocks or uniquely shaped products such as food boxes, waffle pods, packaging materials, etc. [8].

6 Environmental Aspects, Sustainability, and Recycling/Recovery of EPS

6.1 Environmental Aspects

Environmental legislation is constantly developing in the world, affecting EPS along many other materials. For instance, the packaging industry in Europe has been in the crosshairs of the tightening legislation (Packaging and Packaging Waste – 94/62/EC) [2]. Targets for the recycling of all packing materials have been established. However, thanks to intensive cooperation in the EPS industry and shared information on recycling and best practices, in most European countries the levels of recycling are already exceeding targets and are amongst highest of any plastic materials [2]. EPS and PS is relatively inert in landfills which is positive, but dumping it is costly and consumes a lot the landfill capacity (EPS highly voluminous) [2,6]. Regulations of volatile organic compound (VOC) are also a potential threat to EPS industry, especially since the most used blowing agent pentane for EPS has a critical global warming potential (GWP), potentially leading to extra taxes [48]. Luckily, the ozone depletion potential (ODP) is low for pentane [21], unlike for chlorofluorocarbon-based blowing agents, such as CFC and HCFC [21]. The brominated HBCD was used for decades as a proven flame retardant in EPS insulation materials but have been prohibited in Europe since 2016 due to environmental concerns [39,49]. After years of research and development a polymeric flame retardant, pFR, that was able to replace HBCD was invented. pFR is not bioaccumulative or toxic, and hence, is a sustainable option for flame retardation in EPS [50].

6.2 Sustainability and Life Cycle Assessment of EPS

Evaluating environmental impact of EPS as a packaging or insulation material include many aspects. It is necessary to take into consideration its application performance, environmental impact during itslifecycle, and end-of-life options [51]. A good environmental performance of products has become an asset for manufacturers. This is the reason for industries to investigate and find ways to operate with minimal effect on the environment. One tool that is used to measure the environmental impact of a product is life-cycle analysis or life-cycle assessment (LCA). A significant amount of time and resources have been invested in LCA by the EPS industry [52]. A number of studies and reports have been made to promote facts about EPS and its environmental implications, especially for EPS packaging and insulation. The most obvious advantage of EPS in regard of sustainability, and for making it a unique material, is its effect relative to its low material consumption (98% air, 2% PS) [29]. A typical life cycle of an EPS product (packaging) from "cradle to grave" can be seen in Figure 18.

EPS materials consume fossil fuels in the production of plastic materials and its blowing agent (pentane), in processing, finishing, and transportation. Crude oil and natural gas are also used for raw material inputs. The production and transportation processes also consume energy and emit emissions, such as greenhouse gases [53]. The manufacturing emissions can be categorized into solid wastes, airborne emissions, and waterborne emissions [54]. The energy consumed and the emissions produced can be seen as "investments". Energy savings and emission reductions can be seen as "dividends" or return on investments (ROI) of the energy used and emissions produced for the production and transportation of the product [53]. For example, the use of EPS foam insulation in walls increases the R-value of the walls drastically, and hence, saves energy and reduces greenhouse gas emissions over the total life of the building by reducing the energy needed for heating or cooling [52,53]. In fact, structural insulated panels have been estimated to have an energy payback period of less than 17 months and a recapture of greenhouse gas emissions in less than 10 months. The total return in investment is due to the long lifespan of insulation materials (e.g. in a building 50-100 years) and ability to reduce energy consumption needs [53]. In addition, insulation materials can be recycled again after use. For EPS packaging, EPS industry alliance states that:

- water and air emissions can be reduced by 2-9 % (with increasing recycling content atmospheric and waterborne emissions decrease or remain the same),
- energy use 3-14 % (with increased recycling content, energy use decreases), and
- solid waste 5-21 % net reduction (with recycling, increases in industrial waste are offset by larger decreases in post-consumer waste) [52].

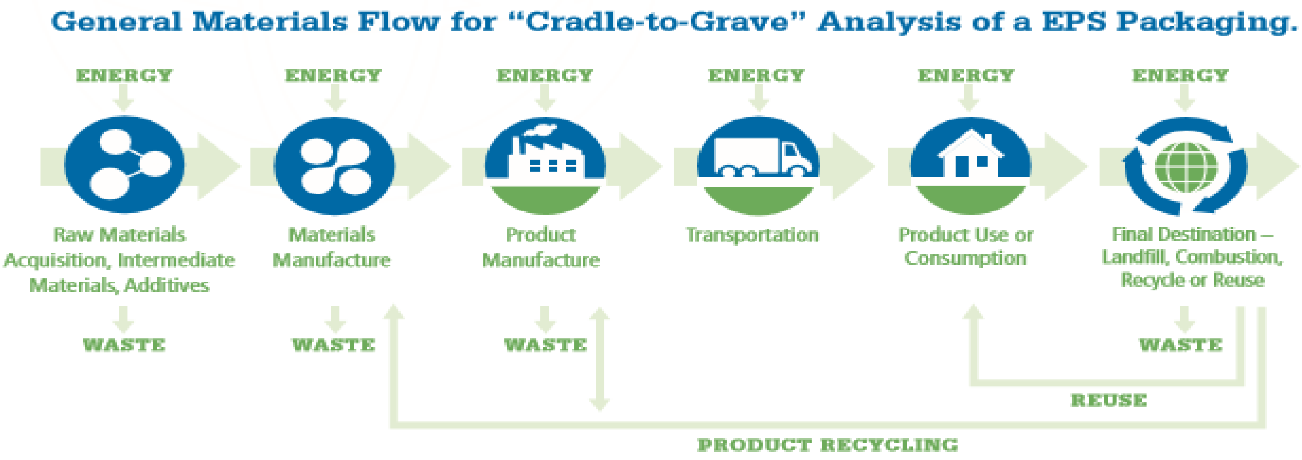
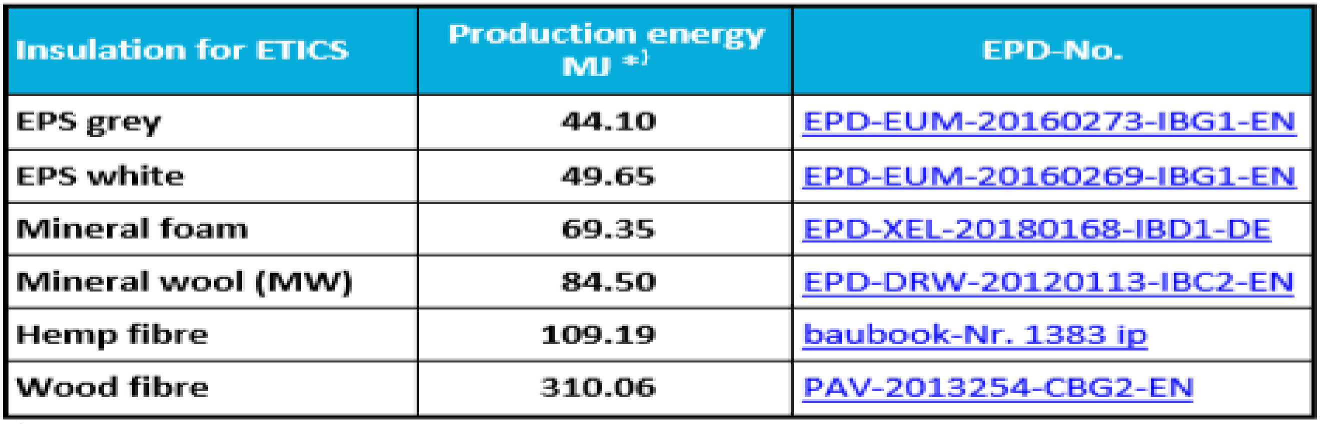


Figure 18. Lifecycle of an EPS packaging [54].

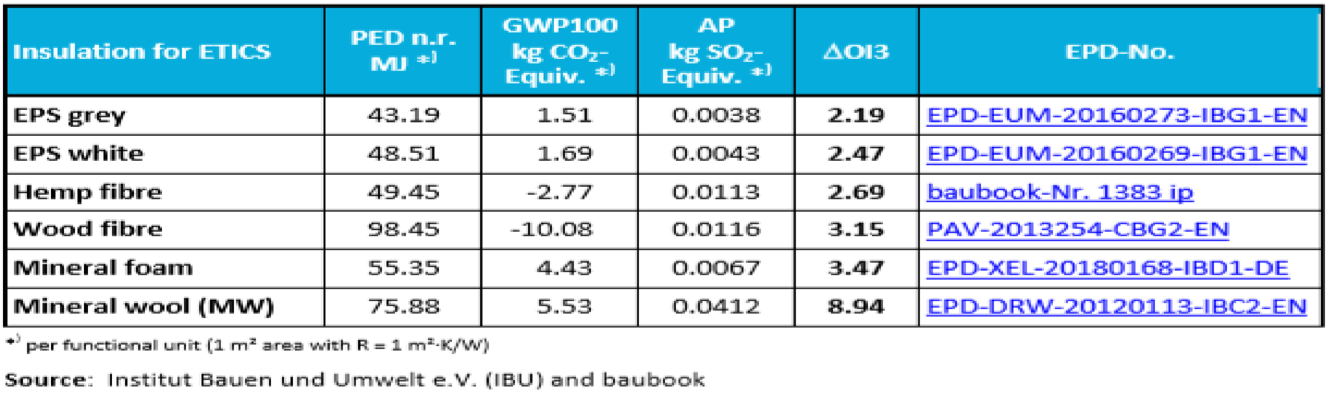
EUMEPS states that the EPS manufacturing process is energy efficient. The manufacture of EPS overall requires less energy than the manufacture of "ecological alternatives" such as mineral foam and wood fiber due to the low input of raw material (98 % air, 2 % PS) and the energy-efficient manufacturing process. A comparative table of total energy requirements in production processes of certain materials in an insulation for ETICS, including the total renewable and non-renewable ("fossil") primary as well as from secondary sources, in the Table 10 below [55].



Insulation for ETICS	Production energy MJ *)	EPD-No.
EPS grey	44.10	EPD-EUM-20160273-IBG1-EN
EPS white	49.65	EPD-EUM-20160269-IBG1-EN
Mineral foam	69.35	EPD-XEL-20180168-IBD1-DE
Mineral wool (MW)	84.50	EPD-DRW-20120113-IBC2-EN
Hemp fibre	109.19	baubook-Nr. 1383 ip
Wood fibre	310.06	PAV-2013254-CBG2-EN

Table 10. Comparative table of Environmental Product Declarations (EPD) of energy needs in production of ETICS insulation made in accordance with ISO 14025 [55].

Eco-properties of EPS are excellent. The Table 11 below summarizes an analysis of the current EPD regarding three different values “Input of Non-Renewable Primary Energy (PED n.r.)”, “Global Warming Potential (GWP100)” and “Acidification Potential (AP)” which are summarized in the ΔOI3 index (the lower the value the better) and shows that EPS is very close to the “ecological alternatives” mineral foam and wood fiber [55].



Insulation for ETICS	PED n.r. MJ *)	GWP100 kg CO_2-Equiv. *)	AP kg SO_2-Equiv. *)	ΔOI3	EPD-No.
EPS grey	43.19	1.51	0.0038	**2.19**	EPD-EUM-20160273-IBG1-EN
EPS white	48.51	1.69	0.0043	**2.47**	EPD-EUM-20160269-IBG1-EN
Hemp fibre	49.45	-2.77	0.0113	**2.69**	baubook-Nr. 1383 ip
Wood fibre	98.45	-10.08	0.0116	**3.15**	PAV-2013254-CBG2-EN
Mineral foam	55.35	4.43	0.0067	**3.47**	EPD-XEL-20180168-IBD1-DE
Mineral wool (MW)	75.88	5.53	0.0412	**8.94**	EPD-DRW-20120113-IBC2-EN

*) per functional unit (1 m^2 area with R = 1 $m^2 \cdot K/W$)

Source: Institut Bauen und Umwelt e.V. (IBU) and baubook

Table 11. Comparative table of Environmental Product Declarations (EPD) of eco-properties of ETICS insulation made in accordance with ISO 14025 [55].

6.3 Recycling of EPS – Reduction, Re-Use, Recycling & Recovery

6.3.1 Introduction

The impression that EPS can't be recycled is persistent [2]. Even though it is true that EPS recycling involve many technological challenges, EPS is these days among one of the most recycled plastics [2,6]. The low weight of EPS is an advantage during its use but can be disadvantageous for its recycling. The highly voluminous material can be difficult to transport over any distance. A typical (12 m) container with uncompacted EPS is filled with less than half a ton of material, which is not economical for transport. However, EPS industry and companies have invested in densification machinery and effective collection in order to ensure that recycling is viable [2]. The high cost of landfilling EPS waste and high transportation cost associated with low bulk density of EPS materials, and public opinion have been major driving forces for development of EPS recycling strategies [6].

EPS can be recycled several times without significant deterioration and it usually starts with grinding the EPS which can be recycled either as EPS or PS (the air is removed) [56]. However, the small margin in price between virgin and recycled EPS represses the desire for recycling [6]. Post-industrial waste consists of recycled EPS facility scrap that will never serve its planned purpose. This waste can be directly recycled by grinding and be combined with virgin material during EPS production. Any EPS material that is recycled after its planned use is referred to as post-commercial and post-consumer recycling [51].

A lot of research has been done working on recycling of EPS waste and some of the proposed available methods include melt extrusion, pyrolysis and solvent dissolution [57]. Among the first and second method there is still some significant disadvantages. In melt extrusion high temperatures up to the degradation temperature are required, and in pyrolysis, the styrene extraction from pyrolytic products is difficult, the process from polystyrene to styrene is complicated, and the cost of production is very high, and as a result, more and more attention is given to solvent dissolution [57]. Solvent recycling is also the goal in this work, in which the EPS or PS materials are recycled or re-used by directly dissolving them back into the suspension polymerization of EPS manufacturing process without any extraction and filtration steps. More specifically of different recycling activities in the Chapter 6.4 Recycling and Recovery Technologies.

6.3.2 Recycling Rates

Recycling rates of EPS around the globe have increased drastically during the last decades, while the rates continue to grow more moderately, but still steadily today. For example, in United States the post-consumer EPS recycling increased from 1.7 % in 1990 to 30 % by the end of 2012. In Japan the recycling rates of EPS grew from 12.6 % in 1991 to 87.5 % by the end of 2009 (mechanical 56.8 %, thermal 30.7 %), which is also the highest recycling rate in the world. In South Korea the rate increased from 33.1 % in 1996 to 75.1 % by the end of 2011. However, the recycling rates in some countries are still not at desired levels. For example, in Australia recycling rate during 2011-2012 was only 6.9 % (2,775 tons collected and recycled), and in Brazil recycling rate grew from only 6.7 % in 2007 to 9.3 % by the end of 2009 [8]. More recent EUMEPS (the association for European Manufacturers of Expanded Polystyrene) estimated data shows that in Europe total amount of EPS waste (construction and packaging) was 527 kilotons in 2017. Of the total amount EPS waste, energy was recovered of 40 % of the waste, 26 % was recycled, and 32 % was disposed in landfills. For comparison, the total amount of waste in 2009 was 498 kilotons, of which the corresponding rates were 35 %, 20.6 % and 43 % [56]. The recycling rates in the U.S., which have since 1991 demonstrated consistent growth, are indicated to continue an upward trend in the future thanks to newer EPS recycling technologies to facilitate EPS collection and reprocessing launched in 2018. Recycling is driven by market shifts and commodity price fluctuations, and the decline in recycling rates in 2017 was due to China's import restrictions that had severe impacts on all recyclables [42]. Comparative figures (Figure 19 & 20) below of Europe's and the Northern region's recycling situation, and the recycling development in the U.S. from 1990 to recent years below (Figure 19-23) in the Chapter 6.3.2 Recent Recycling Data.

6.3.3 Recent Recycling Data

EUMEPS (EU)

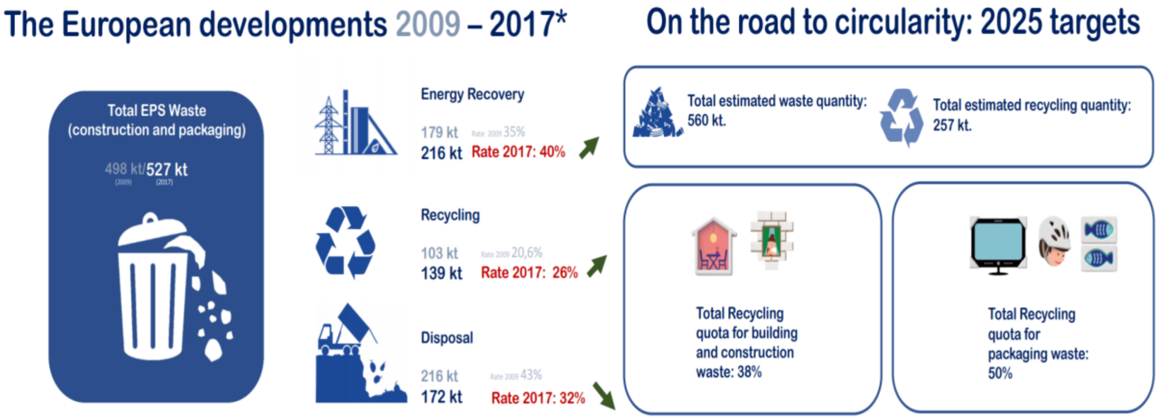


Figure 19. EUMEPS data of recycling rates in Europe in general [56].

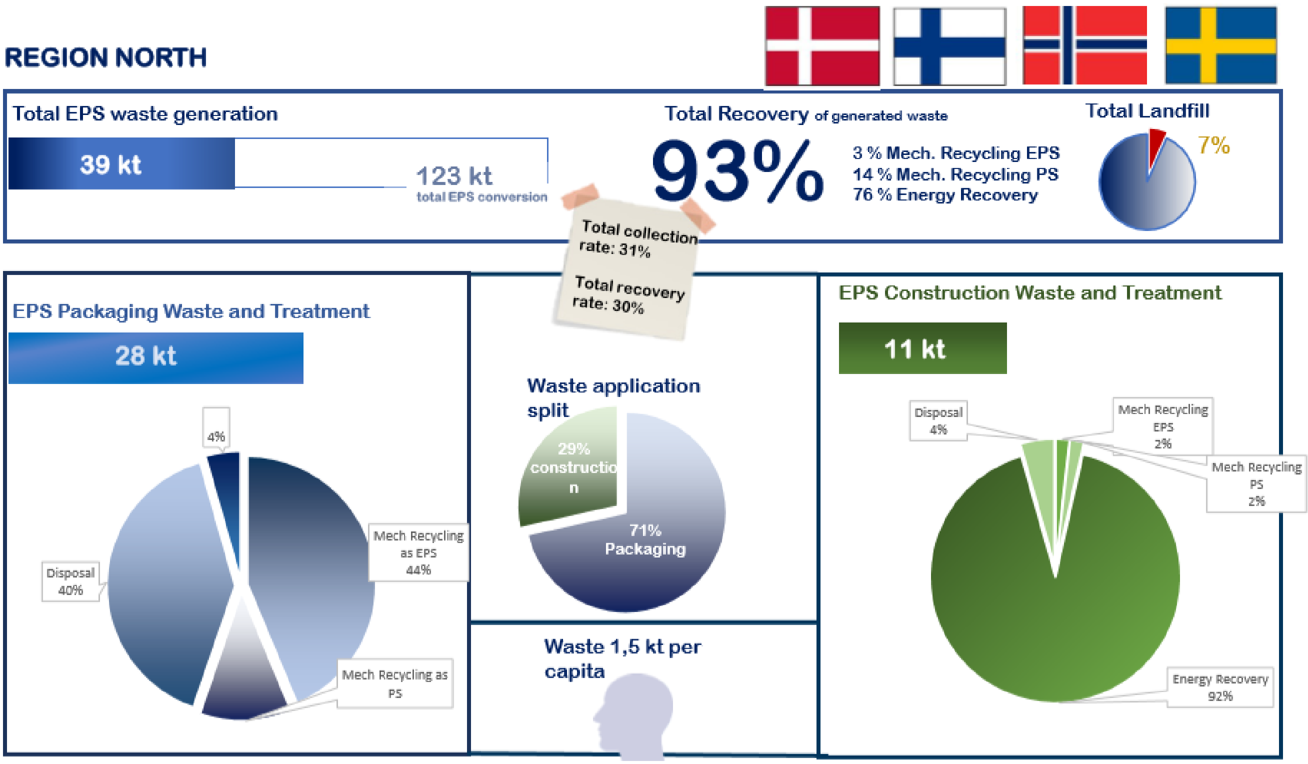


Figure 20. EUMEPS data of recycling rates in the Northern region [56].

EPS Industry Alliance (U.S.)

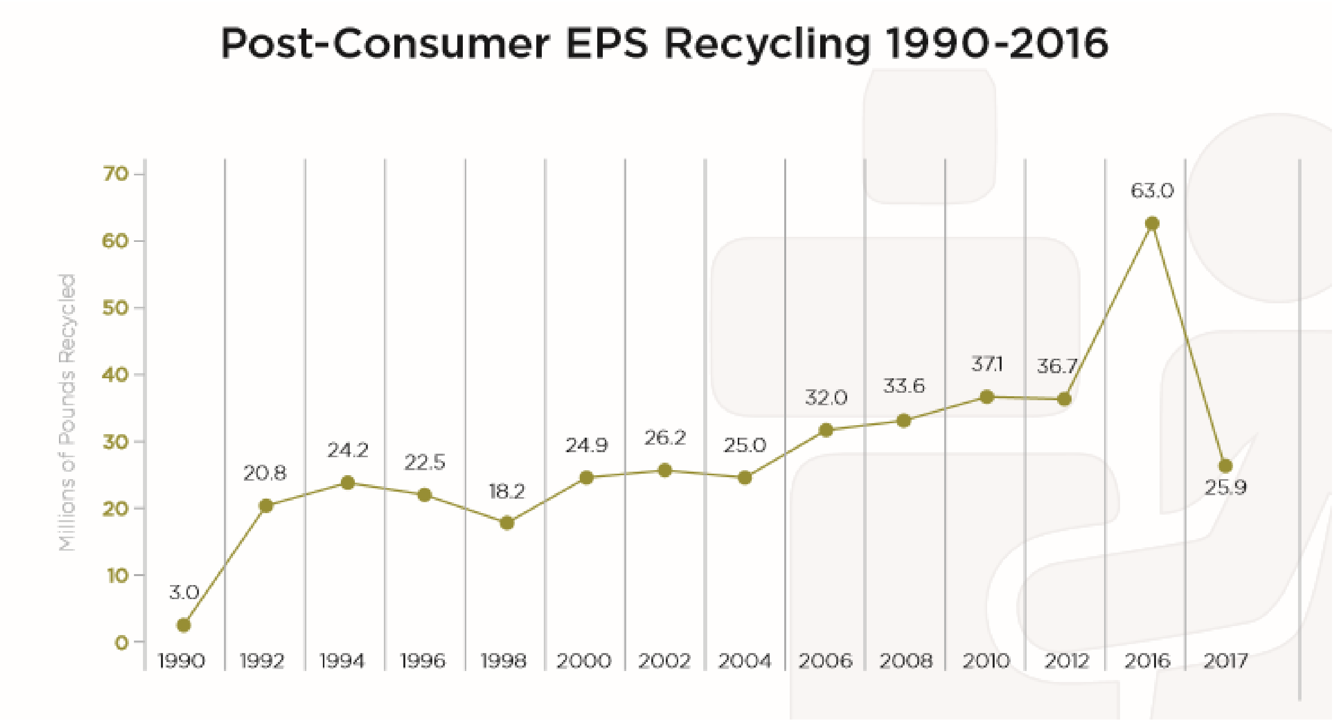


Figure 21. A diagram of the cyclical development of post-consumer EPS recycling rates in U.S from 1990 to 2017. [9]

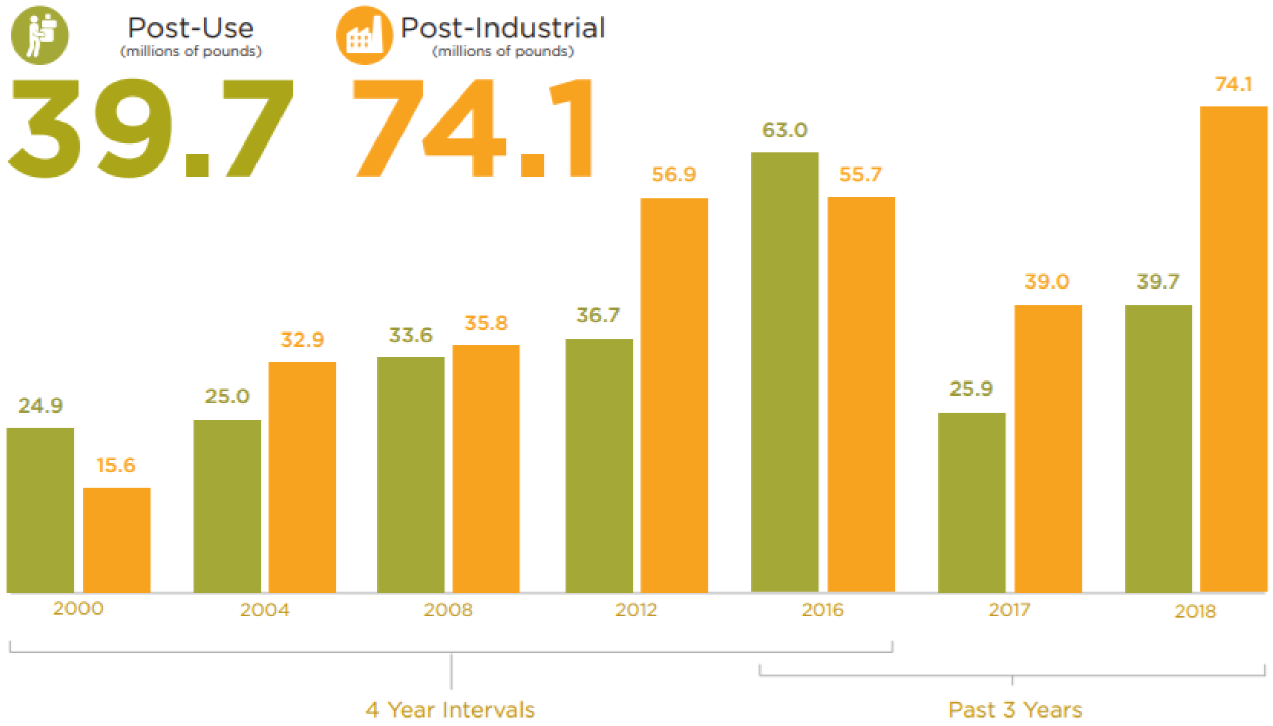
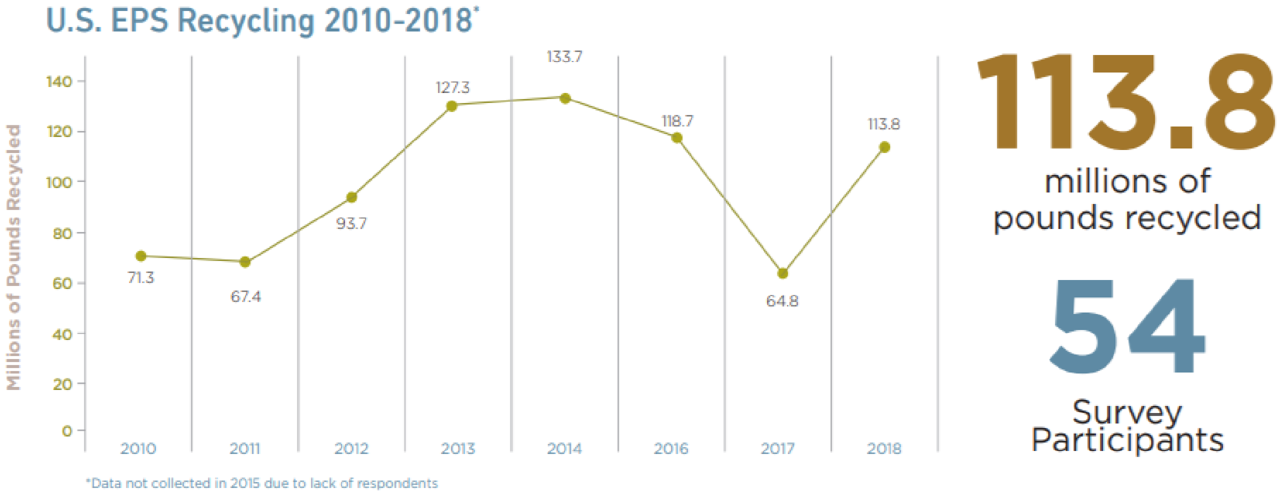


Figure 22. A diagram of the cyclical development of post-consumer and post-industrial EPS recycling rates in U.S from 2000 to 2018 [44].



*Data not collected in 2015 due to lack of respondents

Figure 23. A diagram of the cyclical development of recycling rates of EPS recycling rates in U.S. from 2010 to 2018 [44].

6.4. Recycling and Recovery Technologies

6.4.1 Densification of EPS Foam

Densification or compacting of the EPS foam is one of the most important part of the most EPS recycling processes in order to effectively transport, meter and convey it. Densification of EPS is partially or completely collapsing the cell structure. Expelling the air from the cells is crucial in obtaining the desired bulk density increase of the material. The biggest problem with densification is the polymer and property degradation. This occurs since most of the densification methods utilize melting or compression of the foam by means such as hot air, IR lamps, friction, heated rotatory drum etc. One typical example of densifications systems is a system that employ only hydraulic pressure and no heat. These systems, such as a pellet mill, can convert EPS up to densities of 400 kg/m^3 without material degradation (caused by heat). The non-thermal EPS with no applied heating result produce PS blocks in such a density range that 20 ton of densified material can be carried in a single truck. Another possibility is to use baling devices in order to increase the bulk density of EPS for protective foam packaging. The bulk density can be increased from 15 to 30 kg/m^3 with a typical downstroke baler. With horizontal baler units, however, it is possible to produce densities as high as 250-400 kg/m^3 but problems with cleaning of the recycled content can be very difficult. Hence, all contaminants should be removed before the bailing process [6].

6.4.2 Size Reduction of Waste EPS

The simplest approach in EPS recycling is to reduce the size of the foam. Size-reduction of scrap-expanded PS from packaging can be utilized in production of graded PS foam fragments. PS foam fragments produced vary between 1-50 mm depending on which type of rotary cutter is used. Different size grades are used for different applications. Typical examples with demands in different size ranges are lightweight concrete (1-4 mm), soil improvers (4-8 mm), composting aids (6-12 mm), field drainages (8-25 mm) and cladding drainage pipes (25-50 mm) [6].

6.4.3 Mechanical Recycling

Post-consumer PS foam is often shipped to mechanical recycling facilities in bags by semi-trailers. The EPS waste is first unloaded and inspected and manually sorted in order to remove contaminants such as paper, metals, other polymers and food. After this the polymer is grounded into powder and transferred to washing and drying processes. The drying of the powder is done by centrifugal drying followed by convective heat drying. Finally, an extruder is used to compress and heat the powder up to circa 205 °C. Since EPS foam consists mainly of pure PS, it may be recycled by means of compacting, melting and degassing. This is obtained with commercial rotary compacting and sintering machines. Twin screw machines are also utilized for degassing. In mechanical reprocessing of waste PS, it is crucial that the material suffers as little as possible shear (a function of the screw geometry) and short residence times. In addition, it is important to perform the degassing of the melt adequately, and to automatically filter the contaminants. Mechanically recycled PS application utilization include building insulation, egg cartons, coat hangers, etc. [6]

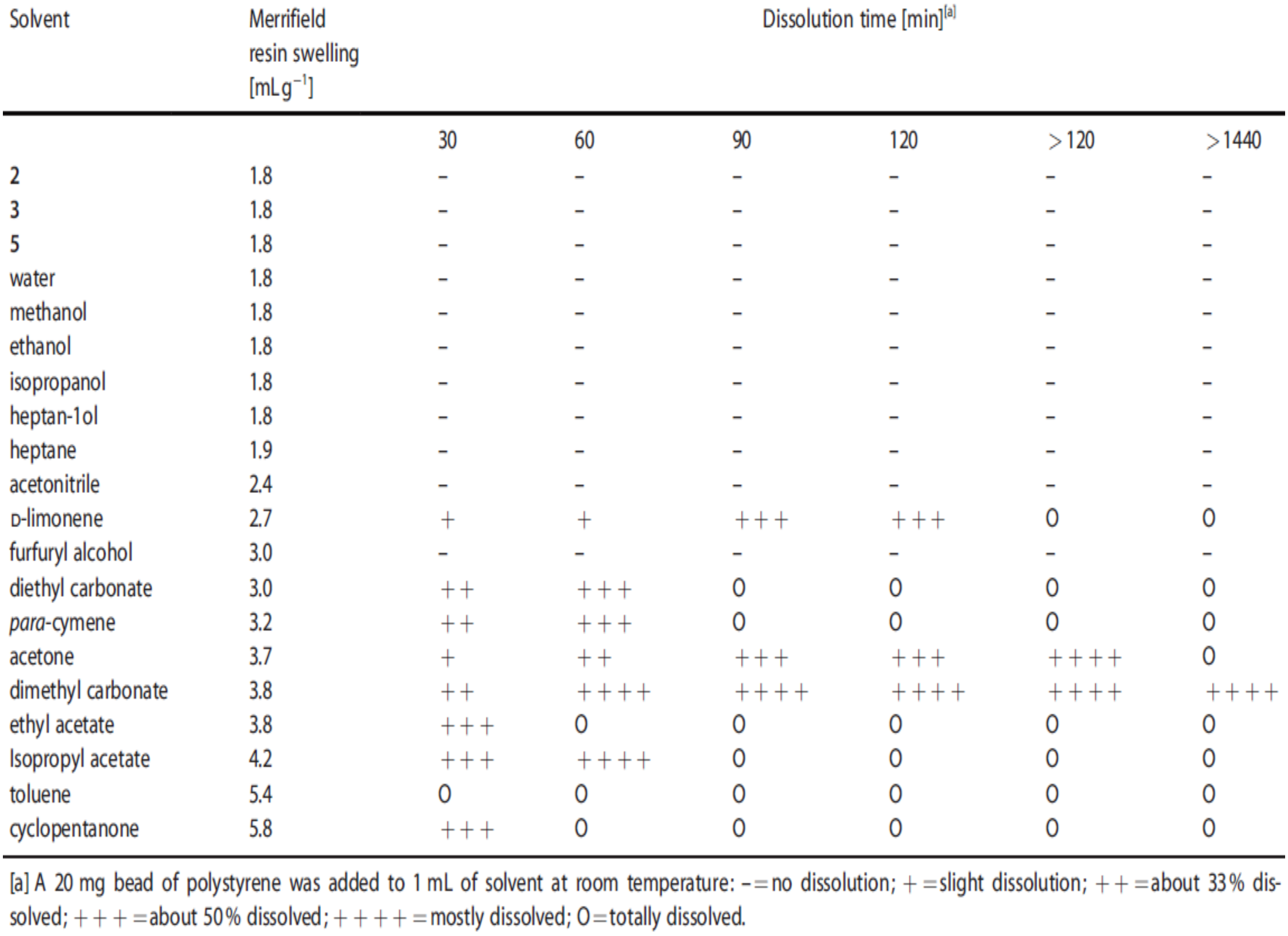
Recycling systems that directly convert EPS foam into purified, degassed granules that can be used directly in the production of new EPS (e.g., Erema systems). In the beginning, the system densifies the EPS foam in a shredder drum and meters this into a single screw vented extruder with melt filtration and degassing facilities. The molten PS is then transferred from the extruder into a dynamic mixer for degassing. These systems are especially attractive for EPS packaging and insulation [6].

Mechanical recycling is not always problem free. There is some risk for degradation of the polymer during mechanical processing due to localized over-heating in the densifying process or because of the heat histories during re-compounding. This results in discoloration (yellowing) and formation of odor due to the formation of aldehydic degradation products. Discoloration is particularly problematic with flame retardants containing EPS products. In addition, degradation and corrosion problems can occur during processing due to additives such as halogens [6].

6.4.4 Solvent Recycling

Usually in dissolution processes or solvent recycling, the polymeric material is first dissolved and afterwards different processes are applied in order to recover the polymer and the solvent. The applying of solvents in recycling of foamed polymers such as EPS offer some advantages. For example, insoluble contaminants can be removed by filtration enabling the clean polymer to be further reprocessed. In addition, selective dissolution process allows separating plastics from other types of non-soluble waste and polymers depending on their chemical nature [58]. Finally, dissolution of the foam in suitable solvent will results in remarkable volume reduction up to volume reductions of more than 100 times without degradation of polymer chains, reducing transport costs [9,58].

Dissolution of PS in several different solvents, such as toluene, xylene, benzene chloroform, acetone, cyclohexane, butyl acetate, ethyl acetate, methyl ethyl ketone, d-limonene, terpinenen, terpinolene, p-cymene, and phellandrene, has been studied [58]. It is generally well known that some aromatic compounds, such as d-limonene, are good solvents of PS foams [9]. The proposed processes for solvent/polymer separating in PS recycling include dissolution-precipitation, separation by super-critical extraction, and solvent evaporation. For solvent vaporization, there are studies reporting the use of steam distillation, vacuum evaporation, vacuum distillation, and drying in a drum dryer [58]. A couple of promising solvent recycling applications for PS or EPS are presented later in this chapter. Dissolution times and solubilities of PS in different solvents below in Table 12.



Solvent	Merrifield resin swelling [mL g^{-1}]	Dissolution time [min][a]					
		30	60	90	120	>120	>1440
2	1.8	–	–	–	–	–	–
3	1.8	–	–	–	–	–	–
5	1.8	–	–	–	–	–	–
water	1.8	–	–	–	–	–	–
methanol	1.8	–	–	–	–	–	–
ethanol	1.8	–	–	–	–	–	–
isopropanol	1.8	–	–	–	–	–	–
heptan-1ol	1.8	–	–	–	–	–	–
heptane	1.9	–	–	–	–	–	–
acetonitrile	2.4	–	–	–	–	–	–
D-limonene	2.7	+	+	+++	+++	0	0
furfuryl alcohol	3.0	–	–	–	–	–	–
diethyl carbonate	3.0	++	+++	0	0	0	0
para-cymene	3.2	++	+++	0	0	0	0
acetone	3.7	+	++	+++	+++	++++	0
dimethyl carbonate	3.8	++	++++	++++	++++	++++	++++
ethyl acetate	3.8	+++	0	0	0	0	0
Isopropyl acetate	4.2	+++	++++	0	0	0	0
toluene	5.4	0	0	0	0	0	0
cyclopentanone	5.8	+++	0	0	0	0	0

[a] A 20 mg bead of polystyrene was added to 1 mL of solvent at room temperature: – = no dissolution; + = slight dissolution; ++ = about 33 % dissolved; +++ = about 50 % dissolved; ++++ = mostly dissolved; 0 = totally dissolved.

Table 12. Comparative table of Merrifield resin swelling and rate of polystyrene dissolution times in different solvents [35].

d-limonene

EPS can be recycled by dissolving it into limonene. Limonene is a biodegradable solvent derived from citrus fruits. The solvent is sprayed on EPS foam, degassed, and converted to a gel with a higher density (volume reduces up to 90 %). D-limonene dissolves EPS safely and without significant degradation of the performance properties. In gel-like form the PS material transportation is much more efficient since larger quantities can be transported to recycling plants. The gel can be purified by filtration through screen filters that removes contaminations such as dirt particles and other polymers that are not soluble in the solvent. After filtration PS is precipitated with another solvent (a non-solvent in reality) to the mixture. Finally, centrifuging is used to separate the two solvents and PS. PS is then degassed, and the solvents are circulated back to the process. The final product can be converted back to PS or EPS by PS recyclers. Solvent recycling enables economical recycling of foamed PS boxes used in food, catering and horticultural industries [6].

Styrene

EPS can be recycled by dissolving it into its monomer, styrene [59]. There is for example patents mentioning the possibility to use PS/EPS dissolved into styrene in suspension polymerization [11,12]. EPS recycling in suspension polymerization process is also the major goal in this project. However, no filtration of the insoluble components or extraction of EPS, which is typical for solvent recycling, will be present.

PolyStyreneLooP

PolyStyreneLoop is a new physico-chemical recycling process for construction PS foam based on CreaSolv® Technology combined with the destruction of HBCD (legislated contaminant) [60,61]. A specific proprietary solvent formulation is used to selectively dissolve plastic wastes. The pretreating technology has the potential to recover high quality PS recyclate that can be used as raw material for EPS production and separate it from legislated additives (e.g. HBCD). PSLoop applies recent technology (Creacycle) and propriety solvent. In contrast to the alternatives tested in the past, the solvent is not carcinogenic or flammable. PSLoop is superior from environmental, health, safety and technical perspective compared to the alternatives in the past. These include processes such as Polystyvert and the Sony process based upon limonene. These processes have not been able to separate HBCD from PS at levels less than 100 ppm of HBCD in the recycled PS [61]. The process consists of following three steps, in which the steps 1 and 2 are pre-treatment for step 3 [60]:

1. “PS foam waste is dissolved in tanks containing a PS-specific liquid. The solid impurities (dirt, cement and the like) are separated through filtration and then incinerated.”
2. “Another liquid is added, which transforms the PS into a gel, while the additive (HBCD) stays in the remaining liquid. The PS gel is then separated from the process liquids. Once cleaned, this gel is transferred into granulated polymer and the liquid, together with the additive, is distilled and re-used in a closed loop; the additives remain as sludge”
3. “Finally, the HBCD additive within the sludge is destructed in a high temperature incineration process. During this last step the elemental bromine is recovered and can be reused to produce new products (e.g. modern flame retardants), thereby closing the loop.”

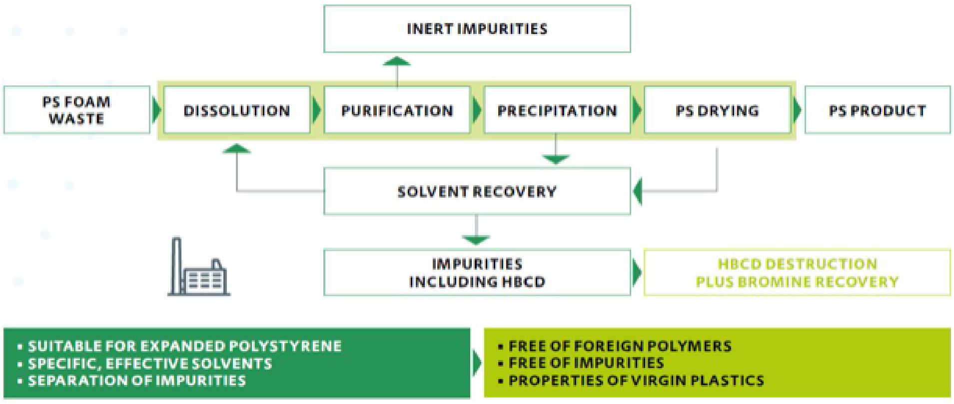


Figure 24. A schematic demonstration of PSLoop process [39].

6.4.5 Depolymerization (Pyrolysis)

Pyrolysis is the most well-known method for depolymerization of PS and EPS into styrene monomer. Still, the resulting yields are relatively low and carbonization yields are high. A large amount of coke and gas with little commercial value is produced during pyrolysis However, some techniques have been invented to make the pyrolysis recycling of PS more efficient. For example, by dissolving PS in heavy oil has been found to reduce coke and gas formation, and the yields of distillation. It has been found that waste PS decomposes completely to distillate products at 400 °C in the presence of heavy oil (Mars et al). When waste motor oil was used as a medium, the resulting distillate contained styrene monomer (52 wt-%), methyl-styrene (19.5 wt-%), toluene (13.6 wt-%), ethyl benzene (11.7 wt-%) and cumene (3.3 wt-%). These products are valuable chemical intermediates in new polymer manufacture. While dry pyrolysis of PS leads to considerable loss of PS to gas and coke formation, for example in temperature range 470-600 °C using screw-type reactor large amounts of hydrocarbon gas is produced, in heavy oil pyrolysis of PS can be done at lower temperatures resulting in lower formation of low-molecular weight gases. The heavy oil method also does not require hydrogen gas or high pressures that are crucial for hydrogenation recycling process (Anderson and Berger). Another approach is to use acid or basic catalysts to improve pyrolysis yields of styrene and to reduce carbonization from the pyrolysis of PS. Liquids composed of mostly styrene and dimer (90 %) have been managed to produce with the help of catalysts at 350 °C (Zhang et al) [6].

6.4.6 Energy Recovery

Incineration with energy recovery of PS waste is viable when volumes of PS waste are not economically profitable for mechanical recycling operations. It is also justified if the energy consumed in collection, sorting and transporting recycled PS exceeds the energy needs in virgin production. Even though burning PS in open air produces copious amounts of sooty black smoke, in modern incinerators operating at temperatures around 1000 °C the burning is complete with no significant amounts of ash or soot. PS has a caloric content of 46 000 kJ/kg beating that of heating oil (44 000 kJ/kg). In practice, this means that one kilogram of EPS foam is equivalent to 1.2-1.4 liters of fuel air. This has led to a practice where some large users of EPS use ground scrap and offcuts for steam generation. Halogenated fire retardant containing EPS foam from construction insulations have a very little effect on the composition of the exhaust gases from EPS combustion itself [6].

7 Solubility Experimentation

7.1 Purpose and Guidelines

Even though it is still unclear how and if the off-spec EPS will be utilized in suspension polymerization in BEWI Synbra Raw's EPS manufacture, the time needed for complete dissolution of EPS into MS is a very important information. Solubility experiments were done as preliminary tests as guiding EPS dissolution times for polymerization experimentation. However, as earlier stated, preliminary solubility tests in water suspension were impractical. A conclusion was drawn that the extent and time required to fully dissolve EPS in suspension could be determined more effectively directly in the suspension polymerization process. It seemed that inadequate dissolvement disturbs the polymerization and increases the particle size and oversized off spec formation (e.g. 5 % EPS dissolved in suspension for 30 minutes versus 15 min, Figure 51).

7.2 Description of the Procedure

Two different BEWI Synbra RAW's EPS qualities, namely

- standard EPS off-spec material made with traditional suspension polymerization, upper (K-110) and lower (K-1310), which are still chemically quite the same but differ in size, and
- extruded recycled EPS material (fish-box material),

solubility into styrene was studied at different temperatures, namely

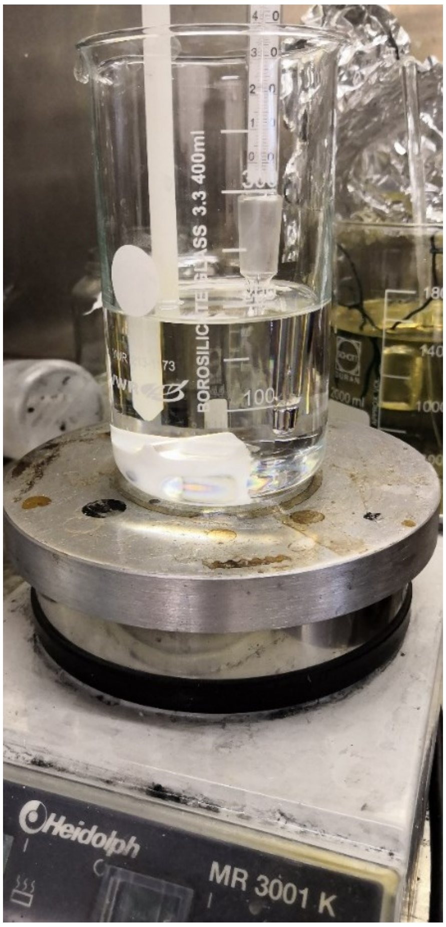
- room temperature (c. 25 °C),
- 50 °C, and
- 70 °C,

with the following EPS mass concentrations (wt-%): 5, 10, 15, 20, 25 and 30%. At least three parallel samples were made of each concentration at the different temperatures. The two-component system or mixture consisted of MS and EPS with a total weight of 180 grams. Targeted stirring speed was 500 rpm, but at higher concentrations of EPS such as over 20 %, the viscosity increase limited the stirring speed to a range of 150-400 rpm, especially at room temperature. At 70°C the solution was running enough without limitations in stirring speed, however, the mixing on the surface was non-existent at all temperatures. Regarding solubility tests in this work in general, the capacity of the magnetic stirrer was simply not adequate to stir the mixture, and the stirring magnet stagnated especially at higher EPS concentrations except for at 70 °C.

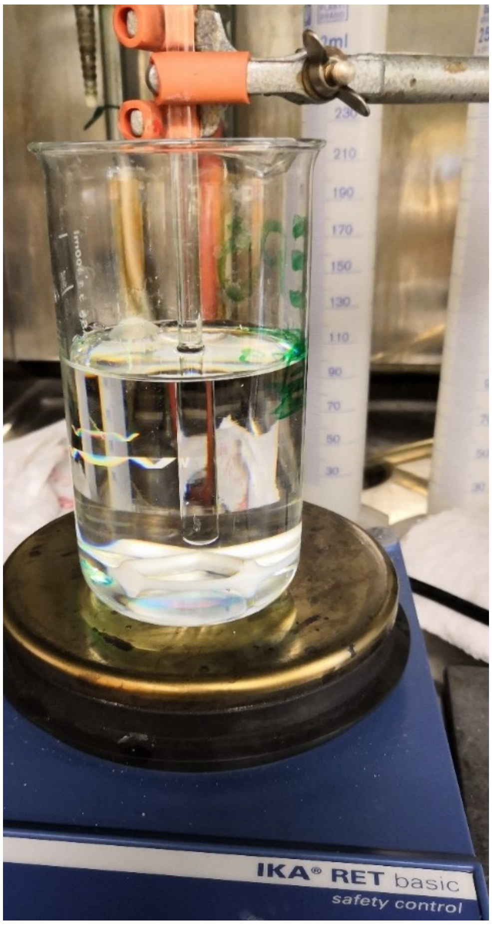
The progress of dissolvement was determined visually, which was problematic, naturally. Hence this, the obtained results were treated only as guiding results. The standard for fully dissolved state was a clear liquid/mixture without obvious EPS particles present. The solubility times were collected, and an average time of the parallel samples were calculated. A mobile phone camera was used as an accessory in order to visualize the dissolvement and to help determine the time needed to reach the fully dissolved state. The temperature was adjusted manually with the help of a thermometer and a thermostat, and heat fluctuation was impossible to avoid. An estimation for the heat fluctuation is +/-5°C of the desired temperature.

The initial plan was to test the solubility of the EPS into MS in water suspension, too, but it was practically impossible to reliably discern if EPS had been dissolved or not in the MS drops visually. The assumption was that the dissolution will take longer in water suspension's MS droplets than in pure MS. Some testing for maximum solubility of off-spec EPS into MS was also done, but the information from patents mentioning the possibility to use up to 30 % dissolved EPS in styrene were used as a base for the upper end of the test scale [11,12]. In addition, according to previous tests at BEWI Synbra Group 30% of EPS had been managed to dissolve into MS.

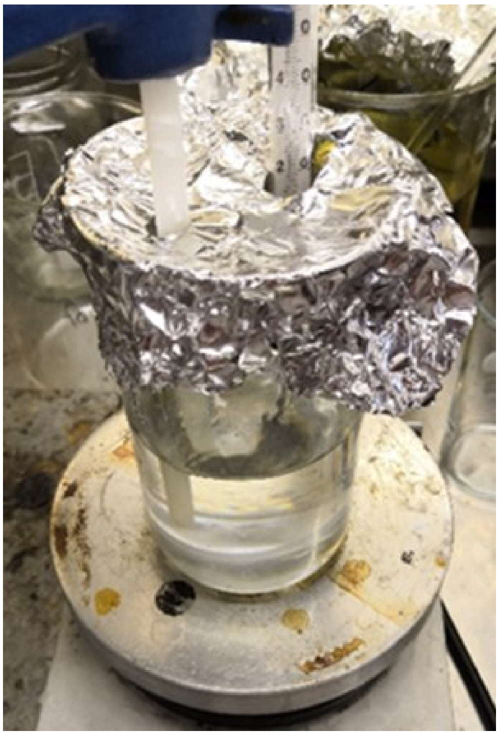
The actual dissolution system included a 400 ml beaker, a magnetic stirrer plate with a thermostat, a stirring magnet, thermometer (not at room temperature) and a baffle(s). The system was either totally open or semi-open with a folio cap, leading to evaporation of styrene especially in higher temperatures. Tests at 50 and 70 °C were carried out in a system (Picture 1, System 1) with two baffles, in which the thermometer acted as one baffle and a plastic stick as another. The tests at room temperature were carried out in a system (Picture 2, System 2) with only one baffle, a glass rod, in the middle of the beaker. A different system at room temperature was used since the tests were run parallel with the tests at 50 °C in order to save time. However, the System 2 should have been made as identical regarding reactor geometry as possible with the System 1 in order to obtain results falling in line better with the other system. It is also important to mention that the magnetic stirring plate used at room temperature was more effective than the other magnetic stirrer used for 50 and 70 °C, which was useful since the viscosity is higher for the non-warmed mixture. The main reasons for baffle installments was to mimic real batch reactors in EPS production, to gain more homogeneous and improved agitation, and to prevent air bubble formation, which would make the follow up of the dissolvement significantly harder. Finally, while the brownish extruded recycled material dissolves into MS, it will color the mixture, and in this way may complicate the follow up of dissolution.



Picture 1. Solubility system 1.



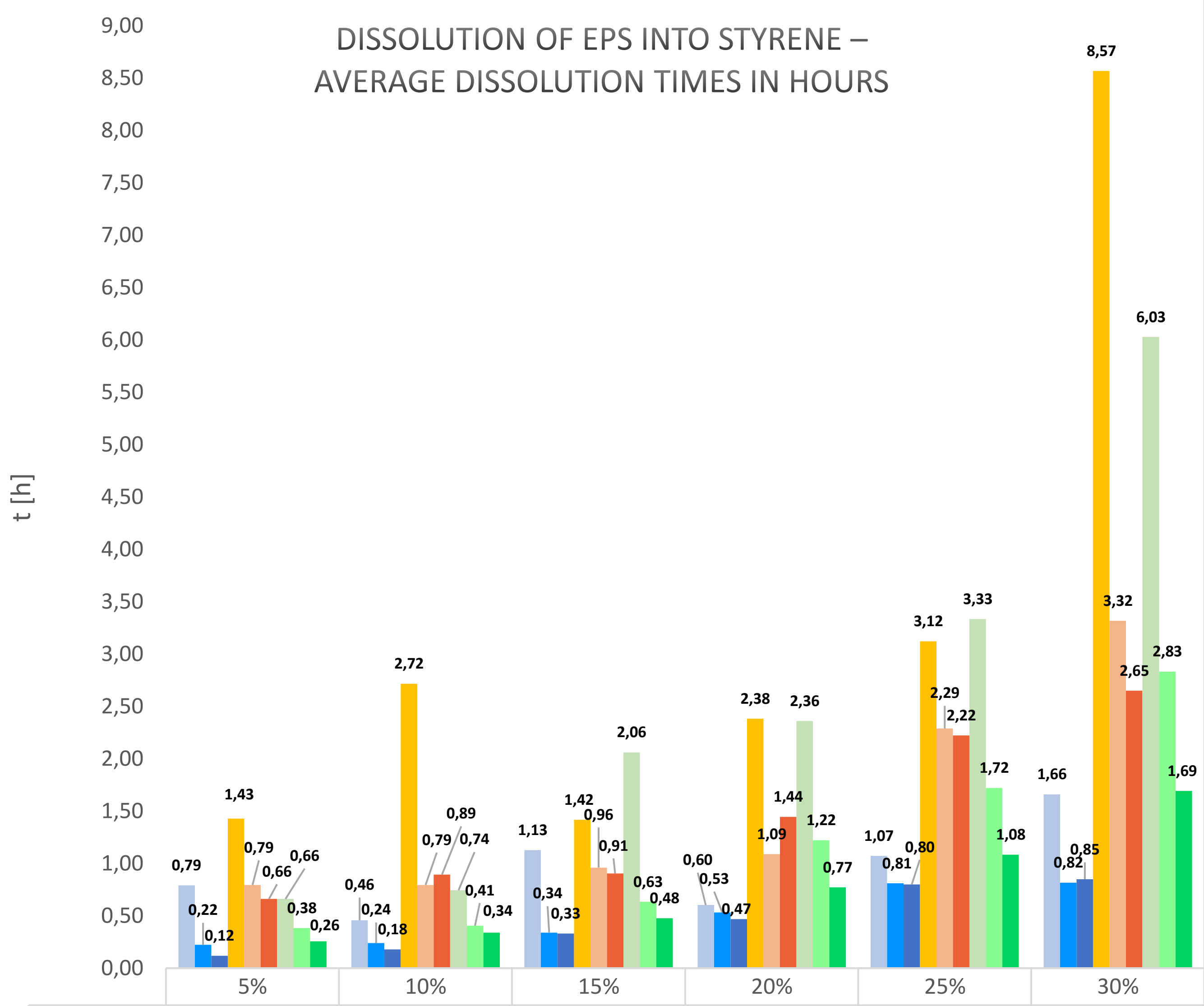
Picture 2. Solubility system 2.



Picture 3. Solubility system 1 with a folio cap.

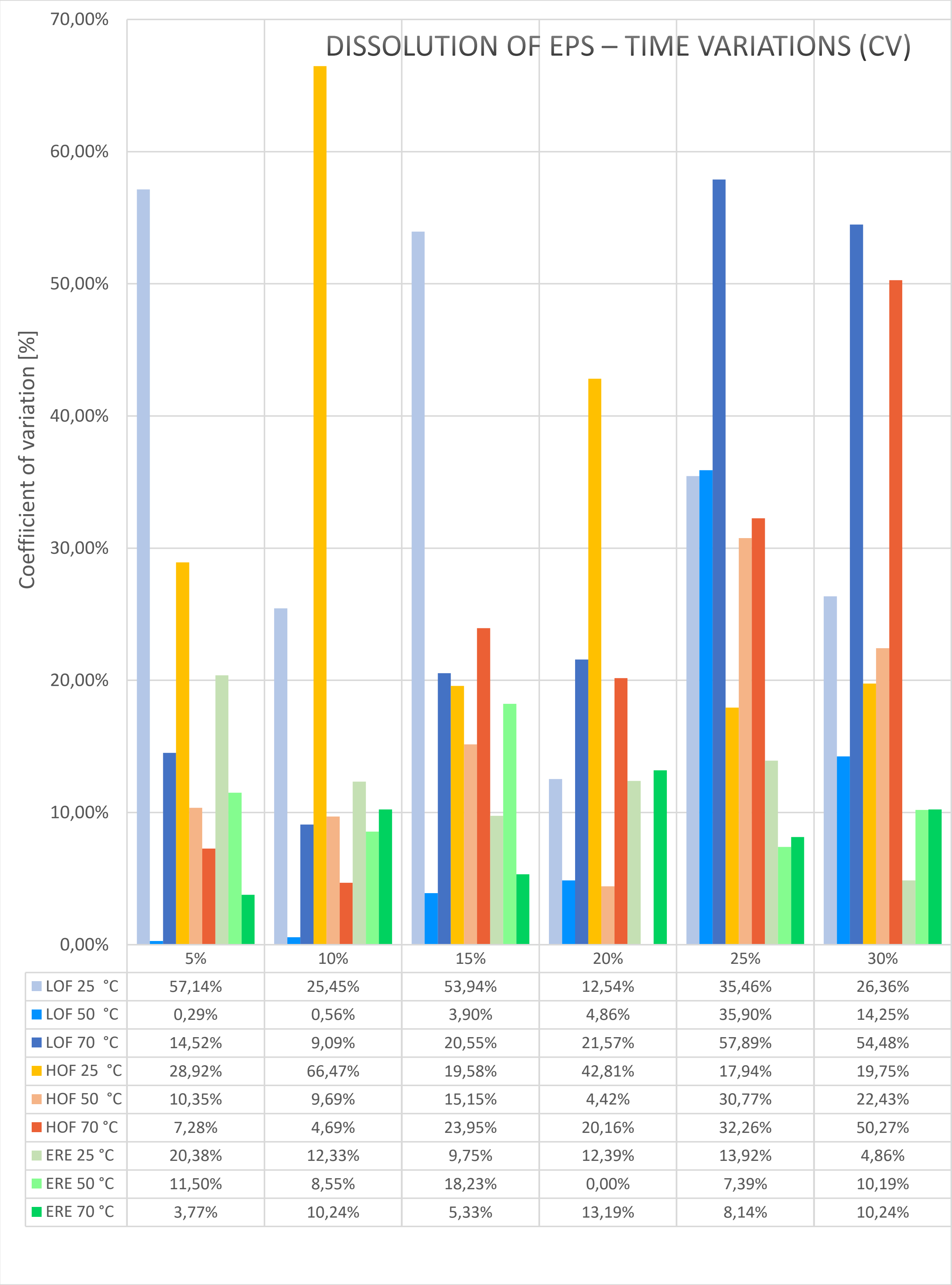
7.3 Results and Discussion

7.3.1 Result Collection



	5%	10%	15%	20%	25%	30%
LOF 25 °C	0,79	0,46	1,13	0,60	1,07	1,66
LOF 50 °C	0,22	0,24	0,34	0,53	0,81	0,82
LOF 70 °C	0,12	0,18	0,33	0,47	0,80	0,85
HOF 25 °C	1,43	2,72	1,42	2,38	3,12	8,57
HOF 50 °C	0,79	0,79	0,96	1,09	2,29	3,32
HOF 70 °C	0,66	0,89	0,91	1,44	2,22	2,65
ERE 25 °C	0,66	0,74	2,06	2,36	3,33	6,03
ERE 50 °C	0,38	0,41	0,63	1,22	1,72	2,83
ERE 70 °C	0,26	0,34	0,48	0,77	1,08	1,69

Figure 25 and Table 13. A bar chart/graph of the average dissolution times of different EPS qualities into styrene at different mass concentrations and temperatures in hours



	5%	10%	15%	20%	25%	30%
LOF 25 °C	57,14%	25,45%	53,94%	12,54%	35,46%	26,36%
LOF 50 °C	0,29%	0,56%	3,90%	4,86%	35,90%	14,25%
LOF 70 °C	14,52%	9,09%	20,55%	21,57%	57,89%	54,48%
HOF 25 °C	28,92%	66,47%	19,58%	42,81%	17,94%	19,75%
HOF 50 °C	10,35%	9,69%	15,15%	4,42%	30,77%	22,43%
HOF 70 °C	7,28%	4,69%	23,95%	20,16%	32,26%	50,27%
ERE 25 °C	20,38%	12,33%	9,75%	12,39%	13,92%	4,86%
ERE 50 °C	11,50%	8,55%	18,23%	0,00%	7,39%	10,19%
ERE 70 °C	3,77%	10,24%	5,33%	13,19%	8,14%	10,24%

Figure 26 and Table 14. Time variances in dissolution times of different EPS qualities into styrene at different mass concentrations and temperatures.

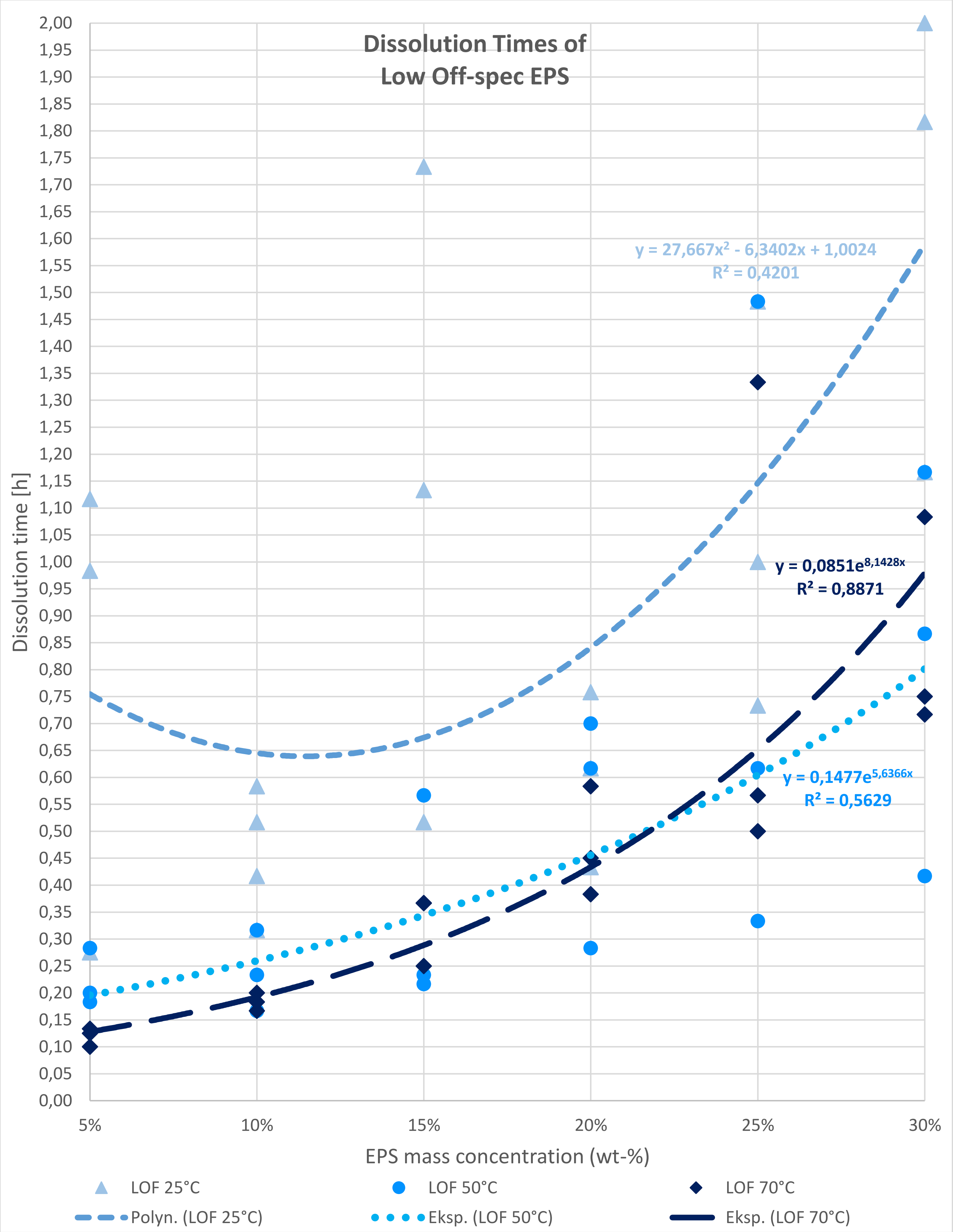


Figure 27. Dissolution times of low off-spec EPS at different temperatures and mass concentrations.

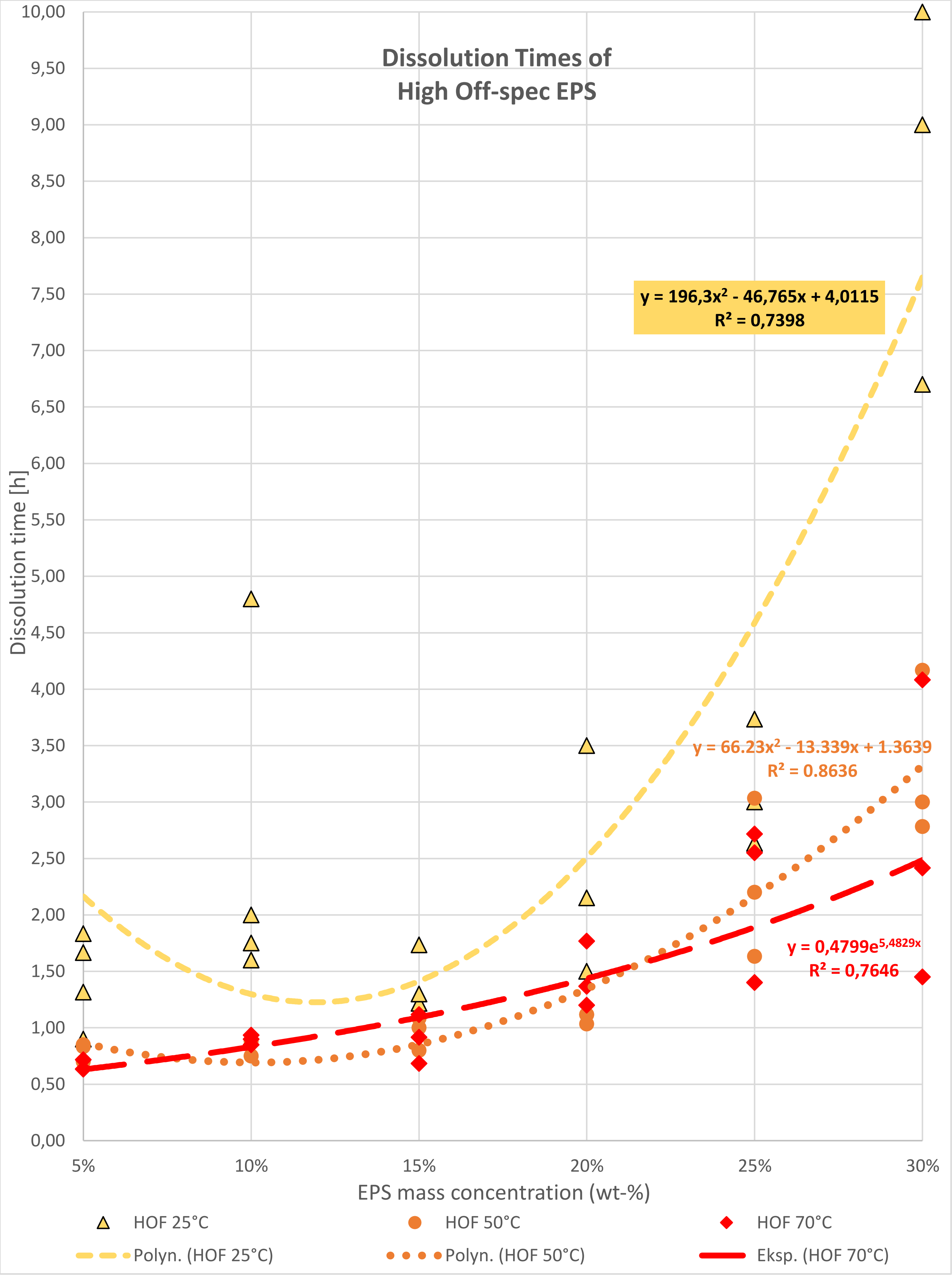


Figure 28. Dissolution times of high off-spec EPS at different temperatures and mass concentrations.

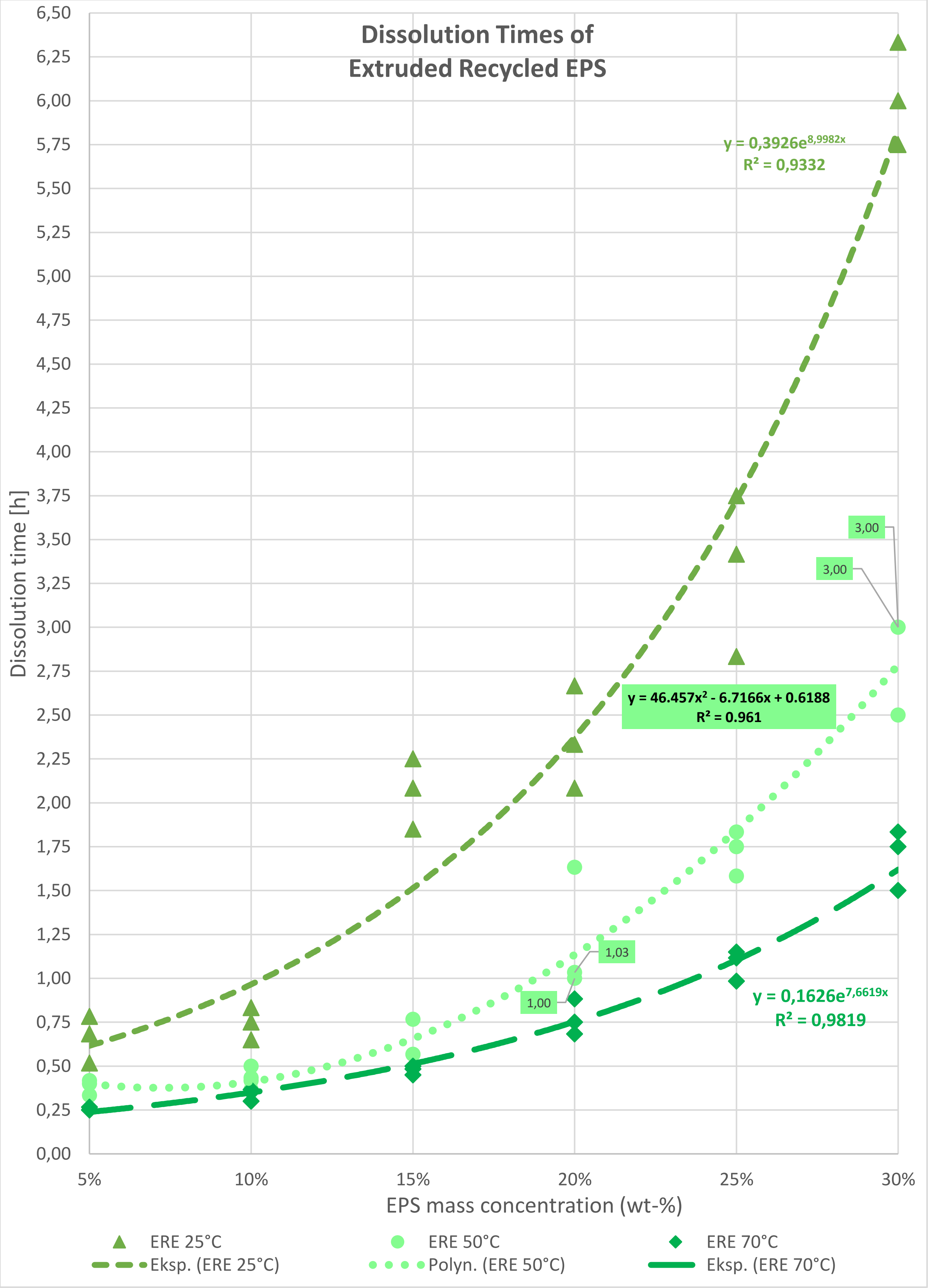


Figure 29. Dissolution times of extruded recycled EPS at different temperatures and mass concentrations.

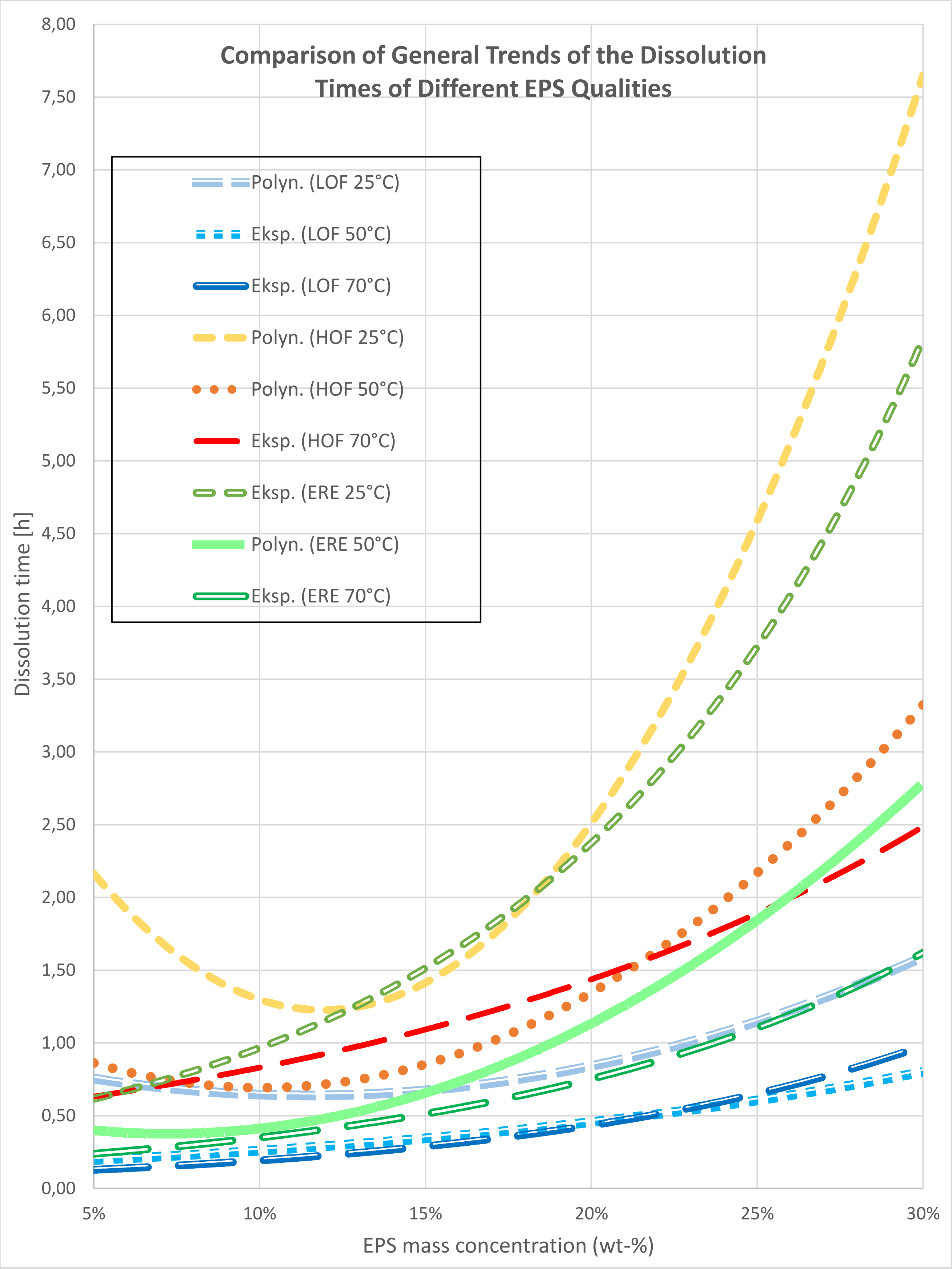


Figure 30. Comparative graph of the general trends of dissolution times of different EPS qualities

7.3.2 Discussion

Dissolution of EPS into MS results in a viscous and sticky gel-like solution. The higher the EPS content the higher the viscosity, naturally. The solution tends to make a mess, to plasticize and to form layers on surfaces and containers. The following problems may arise especially at higher concentrations of EPS such as 20 or more wt-% and low temperatures significantly slowing down the dissolution of the highly viscous and sticky mixture:

- tendency for coalescence and to stick together into lumps, and
- uneven agitation and agitation problems in general, especially at the surface and top set bed (formation of surface layer and particle float on the surface).

The points discussed above were highlighted at room temperature since the viscosity is even higher at lower temperatures. Still, up to 30% of EPS qualities were successfully dissolved into MS at room temperature, at 50°C and 70°C. All the solubility experimentation data and comparison of the proportions of the dissolution times of EPS qualities' to each other are gathered in the tables in the Appendix Dissolution data section.

The obtained results were in general somewhat consistent and logical, but not completely. The undersized off-spec EPS dissolved the fastest, which was expected since it was in a much finer, almost sand-like form, compared to oversized off-spec and extruded recycled EPS. ERE dissolved in general the second fastest and the HOF EPS the slowest. The ERE's significantly lower MW value compared to LOF and HOF EPS could explain the relatively good-natured dissolvement [59]. Figure 26 and Table 14 collect all the average dissolution times for the different EPS qualities at different EPS wt-% and temperatures. In general, as expected, an increase in temperature decreased the time needed for complete dissolution [61]. However, there were some anomalies in which the dissolvement on average was even slower at 70°C than 50°C as the Tables 21 and 22 show. According to the results the average ratio between the dissolution times at 50°C and 70°C was 1 for HOF, which is weird to say the least (see Table 22). In addition, regarding LOF and HOF EPS dissolution, there were inconsistencies with the evolution of dissolution times with increasing EPS mass concentration. In certain cases, the dissolution times were decreasing with the increase in EPS wt-% (see Figures 27 and 28), for example, LOF 5% versus 10% and LOF 10% versus 15%, and HOF 10 % versus 15 and 20 %. The amount of variation was also relatively high in LOF and HOF samples, and especially at room temperature as the Figure 26 and Table 15 shows.

There were many issues, aspects and inconsistencies in solubility experimentation that should be taken into consideration while the results are examined:

1. The dissolution system was either open or semi-open, and the evaporation most probably affected the results strongly. For example, when 30% LOF was dissolved at 70°C, during a time span of 1.58 hours (heating + dissolving) 10.54% of the total mass had vanished (18.95 g of the total mass of 180 g), or 15.04% of the total mass styrene in the system if it is assumed that all of the evaporated mass was MS. The assumption that all evaporated mass was styrene indicated that the evaporation rate of MS was 11.97 g/h and a decrease of 9.95 % in an hour. These values are only guiding but prove the fact that evaporation was significant during the solubility experimentation. On the other hand, this may be a positive sign that even more of EPS can be dissolved into styrene since the loss of styrene in the course of time resulted in higher EPS concentration, and still, the dissolvement seemed to be successful.
2. The extent of dissolution was determined visually which does not give reliable results. Many different factors make it difficult to determine the state of dissolvement such as trapped air bubbles, impurities and very fine EPS particles. There was no constant standard for a fully dissolved state other than a visually relatively clear mixture.
3. The agitation was not adequate. The magnetic stirrer stagnated at higher concentrations as a result of the highly viscous mixture, and the movement of the mass in the topset bed was nonexistent. Especially at room temperature the viscous mixture may have impacted the dissolution in a negative way.
4. The heat fluctuation was significant with an estimation of a temperature range of +/- 5 °C of the desired temperature.

Concluding remarks, and propositions regarding solubility experimentation in the future:

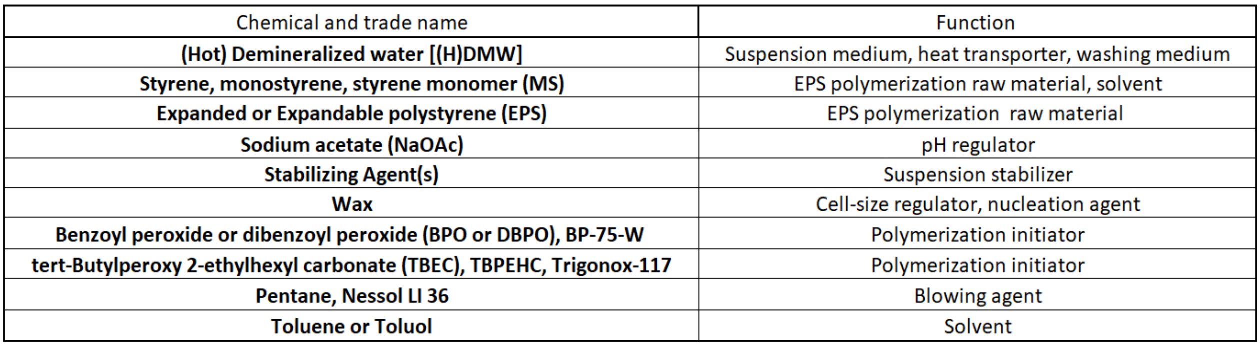
1) The experiments must be carried out in a closed vessel in order to restrict evaporation with a powerful agitation. This will most probably help with the dissolvement remarkably and better results can be achieved.
2) The evolution of dissolvement and the fully dissolved state must be monitored and defined with the help of transmittance or viscosity measurement.
3) At least 30% of EPS can be dissolved into MS. However, another important question is if the dissolution of EPS is carried out in MS-W suspension or in MS prior to suspension polymerization of EPS. Since the dissolution time in MS-W suspension will presumably take significantly longer times to occur, low concentrations of LOF EPS such as 10 wt-% or lower could be dissolved in suspension. Other EPS qualities and especially higher EPS mass concentrations may be better to predissolve in a vessel. However, it all depends on how much extra time BEWi is willing to add or invest in the production process.
4) A better automatic temperature control should be applied, probably automatic. The manual temperature control with the help of a thermometer and thermostat was not very accurate.

8 Suspension Polymerization Experimentation

8.1 Polymerization Procedure

8.1.1 Raw Materials, Chemicals and Additives

Raw materials, chemicals and additives used during EPS suspension polymerization experimentation in the Table 15 below.



Chemical and trade name	Function
(Hot) Demineralized water [(H)DMW]	Suspension medium, heat transporter, washing medium
Styrene, monostyrene, styrene monomer (MS)	EPS polymerization raw material, solvent
Expanded or Expandable polystyrene (EPS)	EPS polymerization raw material
Sodium acetate (NaOAc)	pH regulator
Stabilizing Agent(s)	Suspension stabilizer
Wax	Cell-size regulator, nucleation agent
Benzoyl peroxide or dibenzoyl peroxide (BPO or DBPO), BP-75-W	Polymerization initiator
tert-Butylperoxy 2-ethylhexyl carbonate (TBEC), TBPEHC, Trigonox-117	Polymerization initiator
Pentane, Nessol LI 36	Blowing agent
Toluene or Toluol	Solvent

Table 15. Raw materials, chemicals and additives used in the project.

8.1.2 Procedure and Operating Conditions

All the polymerizations during this project were done in laboratory scale, namely in a BR called the M-reactor (M1). The M-reactor is equipped with two baffles, an agitator, an integral heating/cooling system (oil), and a reaction vessel with a volume of 5-6 liters. The lid is tightly sealed not until the impregnation step, and until this, the development of the suspension can be monitored, and samples can be collected.

The mass relation of MS to W or MS+EPS to W, in other words polymerization medium to dispersion medium, was kept constant during this project. The added EPS was treated as virgin MS as a polymer building raw material, replacing a certain wt-% of virgin MS so that the mass of EPS+MS blend was always equal with the amount of virgin MS in the reference batch(es). Hence, the amount of peroxides was also kept constant during this project. EPS was blended into MS by means of dissolution, either directly by pre-dissolving the mixture in a glass bottle before charging the BR with ingredients, or by directly dissolving it in suspension prior to the actual polymerization stage (Polymerization stage I). The EPS qualities that were used were the same that were used in solubility testing, K-110 (HOF), K-1310 (LOF) and extruded recycled EPS (fish box, ERE). However, mostly K-1310 and ERE were used.

The process variables that were altered during this project were primarily the concentration of stabilization agents and the agitation speed. Changing the timing of the stabilizing agent A was also used as option. The reactor is washed with toluene (dissolved) and water (rinsing) if the need arises (e.g. excessive buildup, blockage, unsuccessful polymerization, etc.). The washing, and on the other hand the repeatedly carried out polymerization batches with a “dirty” reactor, however, may have an impact on the resulting beads. Still, the fact that consecutive polymerization procedures without constantly washing of the reactor between batches is the norm in industrial scale, and is thus, considered acceptable also in the laboratory scale, especially since the washing is very time consuming and the time is limited.

8.1.3 Temperature-Time profile and Production Stages

Alternative 1 – Standard Polymerization and Pre-dissolved EPS

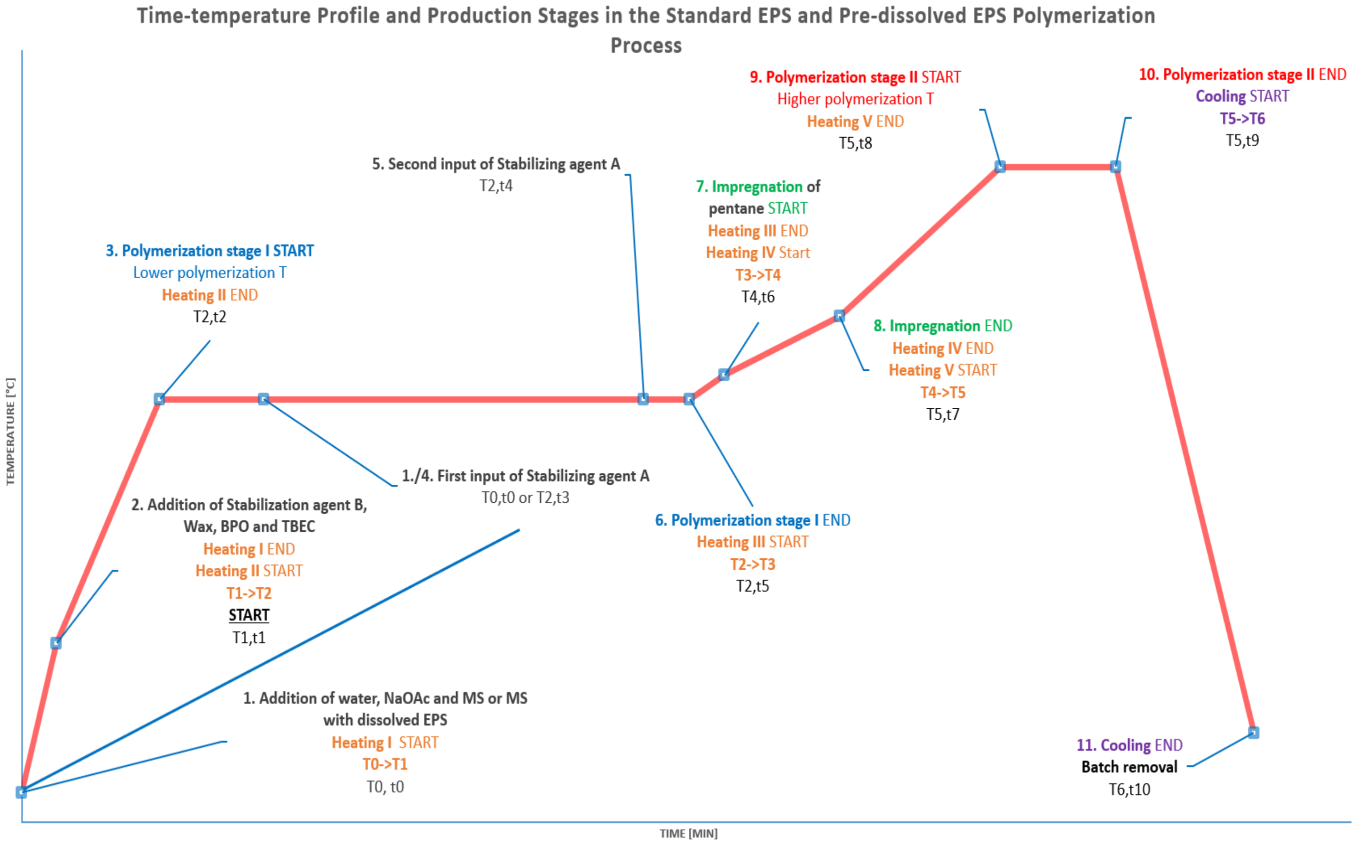
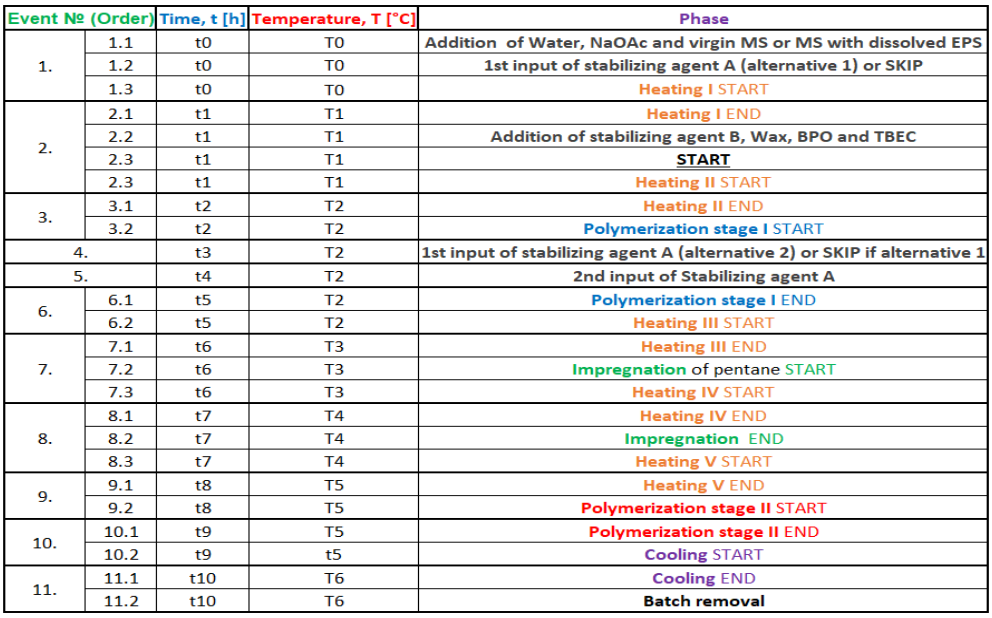


Figure 31. Temperature-time profile and production stages in suspension polymerization of EPS with dissolution in suspension.



Event № (Order)		Time, t [h]	Temperature, T [°C]	Phase
1.	1.1	t0	T0	Addition of Water, NaOAc and virgin MS or MS with dissolved EPS
	1.2	t0	T0	1st input of stabilizing agent A (alternative 1) or SKIP
	1.3	t0	T0	Heating I START
2.	2.1	t1	T1	Heating I END
	2.2	t1	T1	Addition of stabilizing agent B, Wax, BPO and TBEC
	2.3	t1	T1	START
	2.3	t1	T1	Heating II START
3.	3.1	t2	T2	Heating II END
	3.2	t2	T2	Polymerization stage I START
4.		t3	T2	1st input of stabilizing agent A (alternative 2) or SKIP if alternative 1
5.		t4	T2	2nd input of Stabilizing agent A
6.	6.1	t5	T2	Polymerization stage I END
	6.2	t5	T2	Heating III START
7.	7.1	t6	T3	Heating III END
	7.2	t6	T3	Impregnation of pentane START
	7.3	t6	T3	Heating IV START
8.	8.1	t7	T4	Heating IV END
	8.2	t7	T4	Impregnation END
	8.3	t7	T4	Heating V START
9.	9.1	t8	T5	Heating V END
	9.2	t8	T5	Polymerization stage II START
10.	10.1	t9	T5	Polymerization stage II END
	10.2	t9	t5	Cooling START
11.	11.1	t10	T6	Cooling END
	11.2	t10	T6	Batch removal

Table 16. Phases/production stages in standard and pre-dissolved EPS suspension polymerization process

Alternative 2 – Dissolution of EPS in Suspension

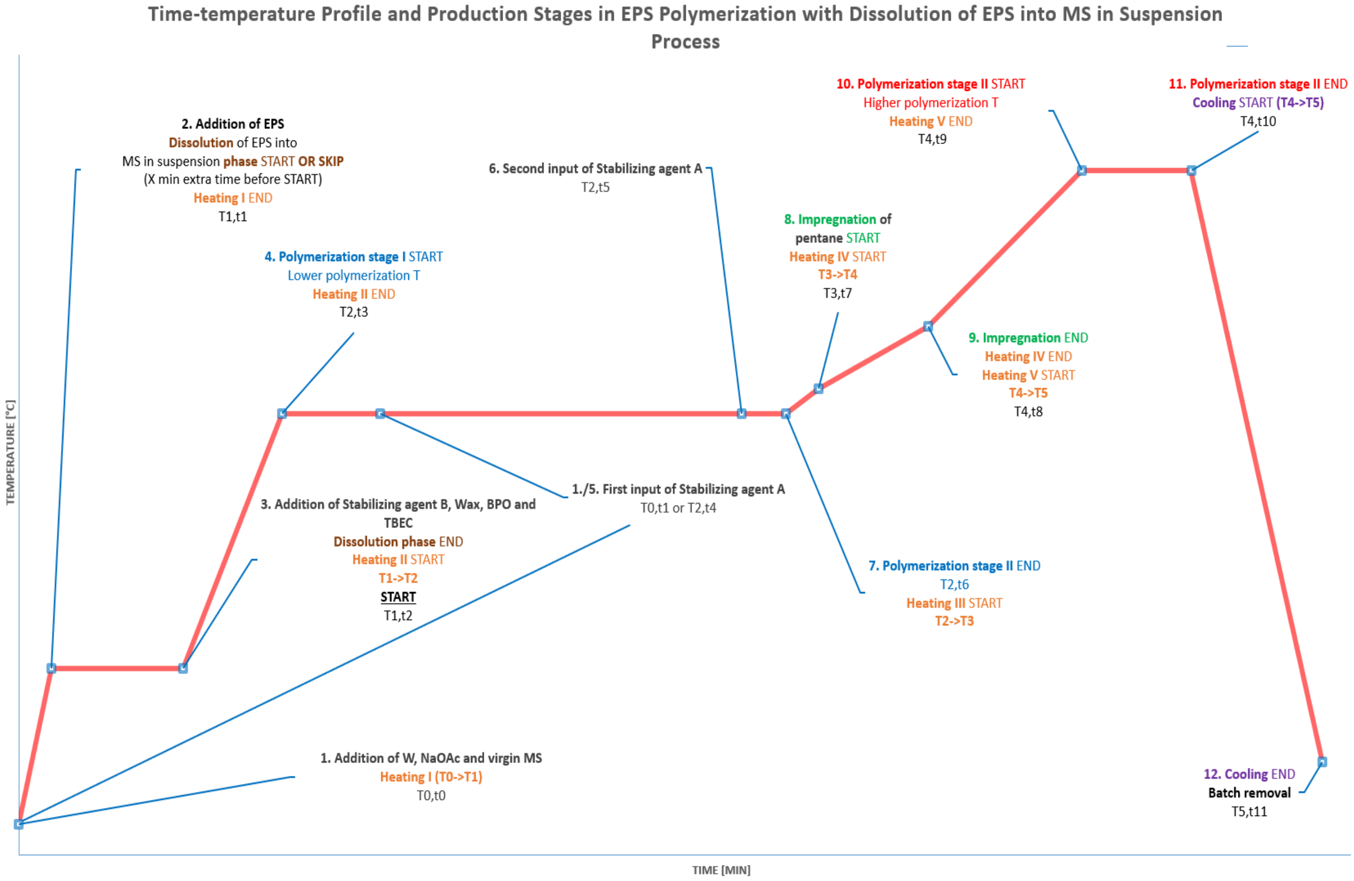
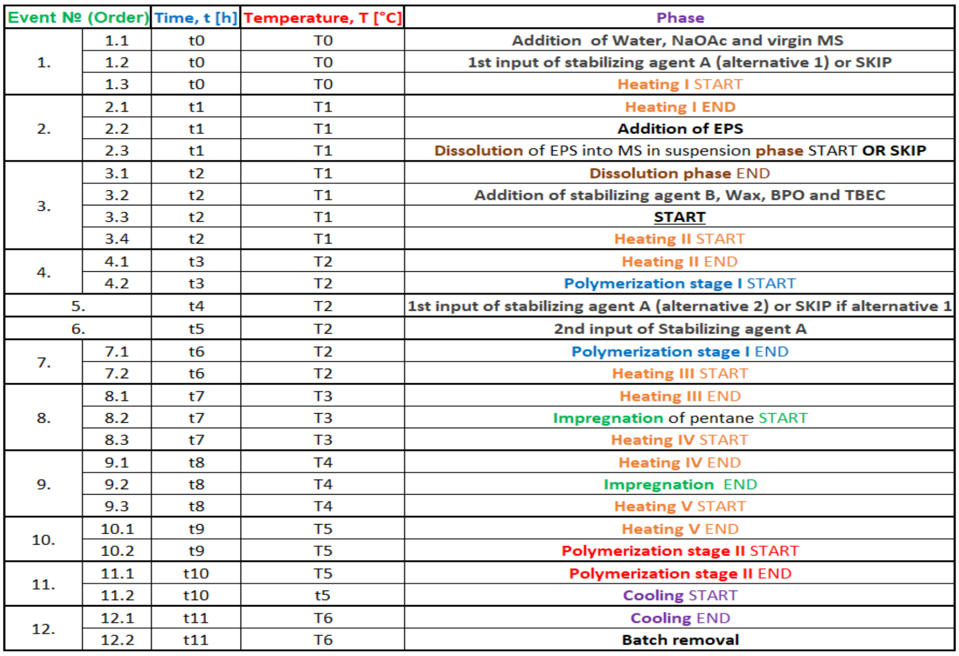


Figure 32. Temperature-time profile and production stages in suspension polymerization of EPS with dissolution in suspension.



Event № (Order)		Time, t [h]	Temperature, T [°C]	Phase
1.	1.1	t0	T0	Addition of Water, NaOAc and virgin MS
	1.2	t0	T0	1st input of stabilizing agent A (alternative 1) or SKIP
	1.3	t0	T0	**Heating I** START
2.	2.1	t1	T1	**Heating I END**
	2.2	t1	T1	**Addition of EPS**
	2.3	t1	T1	**Dissolution** of EPS into MS in suspension **phase** START **OR SKIP**
3.	3.1	t2	T1	**Dissolution phase** END
	3.2	t2	T1	Addition of stabilizing agent B, Wax, BPO and TBEC
	3.3	t2	T1	**START**
	3.4	t2	T1	**Heating II** START
4.	4.1	t3	T2	**Heating II** END
	4.2	t3	T2	**Polymerization stage I** START
5.		t4	T2	1st input of stabilizing agent A (alternative 2) or SKIP if alternative 1
6.		t5	T2	2nd input of Stabilizing agent A
7.	7.1	t6	T2	**Polymerization stage I** END
	7.2	t6	T2	**Heating III** START
8.	8.1	t7	T3	**Heating III** END
	8.2	t7	T3	**Impregnation** of pentane START
	8.3	t7	T3	**Heating IV** START
9.	9.1	t8	T4	**Heating IV** END
	9.2	t8	T4	**Impregnation** END
	9.3	t8	T4	**Heating V** START
10.	10.1	t9	T5	**Heating V** END
	10.2	t9	T5	**Polymerization stage II** START
11.	11.1	t10	T5	**Polymerization stage II** END
	11.2	t10	t5	**Cooling** START
12.	12.1	t11	T6	**Cooling** END
	12.2	t11	T6	**Batch removal**

Table 17. Phases/production stages in suspension polymerization with dissolution in suspension.

8.2 EPS Bead Analyses

Residual monomer (RM) and molecular weight (MW) analyses were done for all the successfully polymerized EPS batches. RM is an important indicator of the grade of polymerization, in other words how much unreacted MS (nonconverted) is still present in the beads. The goal is generally to reach RM values less than 1000 ppm. MW gives additional interesting information about the size of the polymer chains in the EPS beads and how it differs in samples that are partly polymerized out of reused EPS compared to the reference samples made purely out of virgin MS (tested with SEC). A sample of all the successfully polymerized batches were sieved in order to find out the PSD and the average particle size (d-50). Pentane content was also tested in samples that were potentially going to be molded.

8.3 Preparation & Molding and Mechanical & Thermal Testing

Some of the polymer batches were molded into foamed slabs or blocks in order to test the foaming power, mechanical properties/strength and insulation properties (lambda). The chosen samples were prepared by pre-foaming them and subsequently molding them into slabs. This was followed by compression stress, bending strength and lambda testing. The compression stress was measured in accordance with standard SFS-EN 826 and the bending strength with SFS-EN 12089.

8.4 Results and Discussion

8.4.1 General Overview

Besides the bead analyses, the table in Appendix (Table 26) summarizes and shows all the polymerization attempts during this project including both the successful and the failed ones. Maybe the most importance during this project was stressed on PSD, the average particle size (d-50), and the amount of formed off-spec EPS, especially undersized off-spec (LOF) EPS. Other particle sizes have more value than others, while LOF EPS is the least desirable product giving the most technical problems and having the lowest market value. The pentane content and MW related values of the different EPS qualities used as polymerization raw materials measured with a spot test are collected in the Table 27 in Appendix. The pentane content in HOF EPS was higher than in LOF EPS, 4.00% versus 2.62%, and the ERE pentane content was nonexistent, only 0.02%. The MW of ERE was lower than in LOF and HOF EPS, 156516 g/mol (ERE) versus 179286 g/mol (LOF EPS) and 181883 mg/mol (HOF EPS). As a summary can be stated, HOF and LOF EPS are chemically the same, but differ in pentane content and particle size.

The goal was to proceed to higher EPS mass fractions as quickly as possible after successful polymerizations. One major problem in the project was the lack of parallel samples. Having several parallel samples would have helped to eliminate uncertainties (e.g. reactor cleanness, possible weighing errors, etc.) and variances. As a result, the conclusions were heavily relied on assumptions. On top of all, a lot of mistakes and miscalculations were made during this project, unfortunately. The most important listed below.

1) Peroxide input miscalculations. Since the dissolved EPS was incorrectly treated as virgin MS in the process, the peroxide was fed in a surplus.
2) The reactor's air valve was not used until the sample M-172. The valve evens out pressure differences, allows gases to exit the reactor, and in this way inhibits foaming.
3) Both the agitation (rpm) and stabilization were increased simultaneously in some cases in order to improve the PSD and d-50, which complicates the conclusion which parameter had more impact on the particle formation.
4) Inadequate monitoring of the stabile point and the sticky stage in different batches.
5) Inadequate monitoring of the quality of the beads by the means of microscope pictures and foaming power testing.
6) The mass of beads (yield) that were successfully removed out of the reactor was not monitored. This would have given information about how much of the batch was lost as buildup in the reactor.

Dissolving the EPS directly in the suspension prior to the polymerization stage was experimented with 5 wt-% undersized and oversized off-spec EPS with different dissolution times based on the results obtained from solubility testing. However, based on the PSD data it seems that the dissolution time of EPS into MS is longer in water suspension compared to pure MS-EPS solution. When particle size distributions were studied, in the case of LOF EPS 30 minutes extra dissolution time seemed to give similar PSD results with batches containing either pre-dissolved LOF or HOF EPS (see Figure 51 in Appendix). However, in the case of HOF EPS even 45 minutes did not seem to be enough. In the samples in which dissolution times were not presumably long enough, the average particle size increased, and the LOF EPS formation seemed to slightly increase while HOF EPS formation slightly decreased (compare samples reference samples M-137, M-140, M-152, and M-141 - M-148 in the Table 26). Due to strict time schedule, it was decided that the rest of the batches would be done by predissolving the EPS into MS.

It seems quite clear from the results even without any graphic illustrations that in general, by increasing both the agitation (stirring speed) and the use of stabilizing agents (concentration) the average particle size decreased, and the PSD was shifted to smaller particle sizes. Another obvious observation was the fact that the agitation must be vigorous enough for maintaining a suspension. For example, the suspension was lost during the sticky phase in the reference samples when only a 240 rpm of stirring speed was applied (samples M-150 and M-151). The increase in stirring speed should at least to a certain critical point decrease the average particle size according to the literature [13] as shown in Figure 7. This phenomenon may be illustrated by the reference samples M-156 and M-157 in which the stabilization concentration was kept the same with a factor of 0.26 and the stirring speed was increased from 350 to 400 rpm, and the average particle size according to sieving results increased and the undersized EPS formation decreased. However, while M-156 was polymerized with a cleaned reactor, M-157 was not. This may also have impacted the particle evolution, and more parallel samples are needed. The increasing viscosity of the reaction mixture caused problems with the suspension, and in order to maintain the suspension the stirring speed was increased. However, increasing agitation may increase the tendency to form fines and foam, which is problematic and undesirable. Increasing the stabilization concentration did not seem to help, and in addition, may have increased foaming.

If the agitation was kept the same, an increase in the stabilization concentration decreased the average particle size in all cases except for sample M-166 (M_14%LOF_P1-370-0.38). At a mass percentage of 14% dissolved EPS, the d-50 increased and LOF EPS formation decreased compared to sample M-165 (M_14%LOF_P1-370-0.38). M-166 had a d-50 value of 1.15, 1.86% LOF EPS, 1.44% HOF EPS, while the respective values for M-165 were 0.94, 5.88%, and 0.40%. The increase in d-50 and decrease in LOF formation most probably is an indication of too low stabilization concentration. On the other hand, at a mass percentage of 20% dissolved EPS, the d-50 and LOF formation started to decrease compared to sample M-171 (M_20%LOF_P1-440-0.40). M-171 had a d-50 value of 1.06, 5.81% LOF EPS, 0.43% HOF EPS, while the respective values for M-173 were 1.04, 4.09% and 0.32%. Both the LOF and HOF formation decreased. However, M-171 was done in a cleaned reactor while M-173 was not, which may have impacted particle formation, and this may also have been normal variation. More testing and parallel samples are absolutely needed, and either higher or lower stabilization concentrations could be applied in the future. If one would like to lower the LOF EPS formation, the amount of stabilization could be lowered. Decreasing the agitation is not necessarily possible due to the increased viscosity that may lead to loss of suspension, but the possibility to do so should not be excluded.

Interestingly, regarding off-spec formation in samples containing off-spec EPS without considering the quality of the beads and the machining, the sample M-160 (M_10%HOF_P1-350-0.26) made with 10 wt-% off-spec EPS gave the best result with a mass fraction of only1.43% off-spec EPS of the total mass, even better than the best reference samples M-137 (2.89 %, M_REF1-300-0.22) and M-152 (2.94 %, M_REF_3.2-300-0.26). The LOF formation was also lower than in the references with a mass fraction of 0.75% versus 2.50% (M-137) and 2.15% (M-152). Of all the successful polymerizations, the worst result was attained with sample M-161 (M_10%LOF_P1-400-0.26) also with 10 wt-% off-spec EPS. The particle size was extremely small with high LOF formation most probably due to too powerful agitation since the stabilization factor was the same with M-160. However, there was some differences in pentane content between LOF and HOF raw material as the Table 27 in the Appendix shows.

In order to sustain the suspension in ERE containing batches the timing of stabilization agent addition was changed since the suspension was non-existent. Only one sample, M-147 (M_5%ERE_P1-300-0.26), was satisfactory carried out with the standard polymerization procedure. Increasing the concentration of stabilizing agent in the basic polymerization procedure did not seem to help, oddly, quite the contrary, and the suspension was lost already in the beginning (see failed samples M-174 and M-175 in Table 26). Still, the suspension was maintained successfully by earlier timing of stabilization addition (in the beginning). However, the early timing seemed to decrease the average the particle size significantly and increased formation of fines or LOF EPS compared to the only successful polymerization that was carried out with the basic polymerization procedure with normal stabilization timing, the sample M-147 (M_5%ERE_P1-300-0.26). This may have been a result of either too powerful agitation and too low concentration of stabilizing agents, or both. There was no time to study the use of ERE in suspension polymerization of ERE further, and the actual need for stabilization and agitation should be studied more in the future.

An important observation regarding ERE containing batches was the fact that the tendency to form rather oval shaped than spherical beads increased. However, this was also the case with the use of off-spec EPS, but the effect was not as severe. The higher the mass fraction ERE used the stronger the effect seemed to be (compare Pictures in the Appendix). Once again, this may have been a result of either too powerful agitation and too low concentration of stabilizing agents, or both. In addition, the contaminants and the chemicals that ERE may contain most probably contributed a lot and disturbed the suspension. On top of that, the brownish ERE colored the resulting beads slightly. The higher the ERE content, the more brownish the beads compared to EPS beads made with pure virgin MS and/or partly off-spec EPS beads. On the other hand, in expanded state the beads seemed to become relatively white (See Picture 40).

Studying the use of ERE in suspension polymerization of EPS is crucial since it most probably will resemble more the possible use of EPS and PS in the suspension polymerization process in the future compared to the traditional off-spec beads produced with standard suspension polymerization with pure virgin MS. Recycled EPS and PS will most probably also contain contaminants and unfamiliar chemicals that may prevent the direct use of these raw materials in suspension polymerization of EPS.

8.4.2 Mixing, Foaming and Fouling Phenomena

As earlier stated in the solubility section dissolving EPS into styrene results in a highly viscous and sticky, gel-like solution. The higher the EPS content, the higher the viscosity, naturally. The increase in viscosity caused agitation problems in the reactor, especially on the surface of the reaction mixture. The vertical agitation in M-reactor may be inadequate since the surface seemed to stagnate and the fouling or buildups of EPS and/or MS particles and clusters seemed to be emphasized in the reactor bottom and upper parts. Even though the suspension was maintained more effectively by increasing the stirring speed, the buildup problems were significant already in batches in which 10 wt-% EPS was reused, and seemed to become worse at higher mass concentrations (see Pictures 44-46). In the reference samples made with pure virgin MS, the problem did not exist. The following problems were manifested during the polymerizations:

1. excessive EPS buildups on the reactor walls and surfaces, on agitator blades, and in the bottom of the reactor,
2. blocked bottom valve,
3. stagnating surface layer,
4. excessive coalescence and formation of EPS clusters, and finally,
5. give grounds for reactor wash with toluene.

The possibility to inadequate stabilization concentration, however, should not be excluded. Still, the inadequately powerful agitation was crucial and the most effective way to obtain the suspension during this project. On the other hand, too powerful agitation itself may have been counterproductive and increased coalescence of the particles. The suspensions were typically lost by or during the sticky stage in the cases where the agitation was presumably not adequate. In addition, since the EPS-MS mixture was stickier to begin with it may have increased the tendency of particles to get stuck and to form buildups on the reactor's surfaces. As stated in the solubility experimentation section, the MS solution containing EPS made a mess, plasticized and formed layers on surfaces and containers.

Foaming was a significant problem when dissolved EPS was used in the suspension polymerization. The higher the wt-% used the higher the risk of foaming seemed to be. This was especially the case with off-spec EPS. The reaction mixture formed a layer on the surface that did not mix into the reaction mixture since the surface seemed to stagnate. The foaming seemed to be as its strongest during the sticky stage. An increase in the stabilization concentration seemed to increase the amount of foam, and on the other hand, the increased agitation may have increased the foaming, as well. The stagnated surface and foam resulted in the following problems:

1. the sticky EPS particles on the surface got stuck into the reactor walls and the stirrer's upper parts,
2. the thickening of the surface layer eventually led to total loss of suspension, and
3. the foaming was so intense that the reaction mixture started to foam out of the reactor, as the Picture 41 shows with 10 wt-% off-spec EPS (LOF).

The following reasons listed below were concluded to be possible causes for the foaming phenomena.

1) While it is difficult to say if the pentane content had any impact on the polymerization process, it should be noted that the tendency to foam between batches containing off-spec EPS versus ERE was significant. The ERE batches did not foam during the polymerization as intensively, and the mixture did not foam even once out of the reactor. Nevertheless, it should be emphasized that the role of pentane content is only speculation, and the off-spec resins (LOF and HOF) made with suspension polymerization differ in the consistency of ERE material as well. Still, even though the EPS was dissolved into MS in a closed glass bottle, the pentane should have evaporated from the reactor since the reactor was an open system until the impregnation step.
2) Another potential reason for the foaming phenomena could have been the surplus of added peroxide in the system. The acceleration in polymerization rate may have led to more drastic heat release, which in turn could promote foaming, uncontrollable cell growth and loss of suspension. In addition, the foaming started to become clearer at 10 % dissolved off-spec EPS, which would be convenient for the theory since the higher the used dissolved EPS the higher the relative surplus of peroxide added in the reaction mixture.
3) The high amount of stabilization concentration that was used may have increased the foaming. The fact that the foaming seemed to increase immediately after addition of stabilizing agents would support the theory. The amount of stabilization agents in batches containing higher wt-%

EPS was significantly higher compared to reference samples, which did not foam as strongly. In addition, the viscosity of the reaction mixture may have slightly increased due to higher concentrations of stabilizing agents.

4) The EPS itself and the additives it contains may have contributed to the foaming.

In order to solve the problems discussed above, namely agitation, foaming, and fouling problems, and to optimize the particle size distribution the following practices could possibly be applied.

1. Decreasing the viscosity by increasing the proportion of W to MS (decreasing the amount MS per batch). This could make the mass easier to agitate and the surface stagnation may be hindered. However, this too would lead to lower EPS yield per batch.
2. Decreasing the batch mass overall which could help promote agitation, especially on the surface where the problems seem most likely to occur (stagnating surface layer that may produce clusters, lumps and foam.). The blades of the stirrer are were way below the surface in the M-reactor. However, this would lead to lower EPS yield per batch.
3. Changing the structure of the stirrer with better vertical agitation.
4. Decreasing the viscosity or stickiness of the mass by some other means, such as for example, chemicals.
5. Decreasing foaming by chemicals, e.g. foam inhibitors.
6. Increasing the stabilization concentration and decreasing the agitation or the other way around. However, an increase in stabilization concentration may lead to increased foaming. Too vigorous stirring on the other hand, could lead to increased coalescence and formation of EPS clusters.
7. Either increasing or reducing the agitation suddenly or stepwise during polymerization. For example, the agitation could be increased during the sticky stage.

8.4.3 Particle-Size Distribution (PSD)

Amount of EPS Fines/LOF at Different Average Particle Sizes

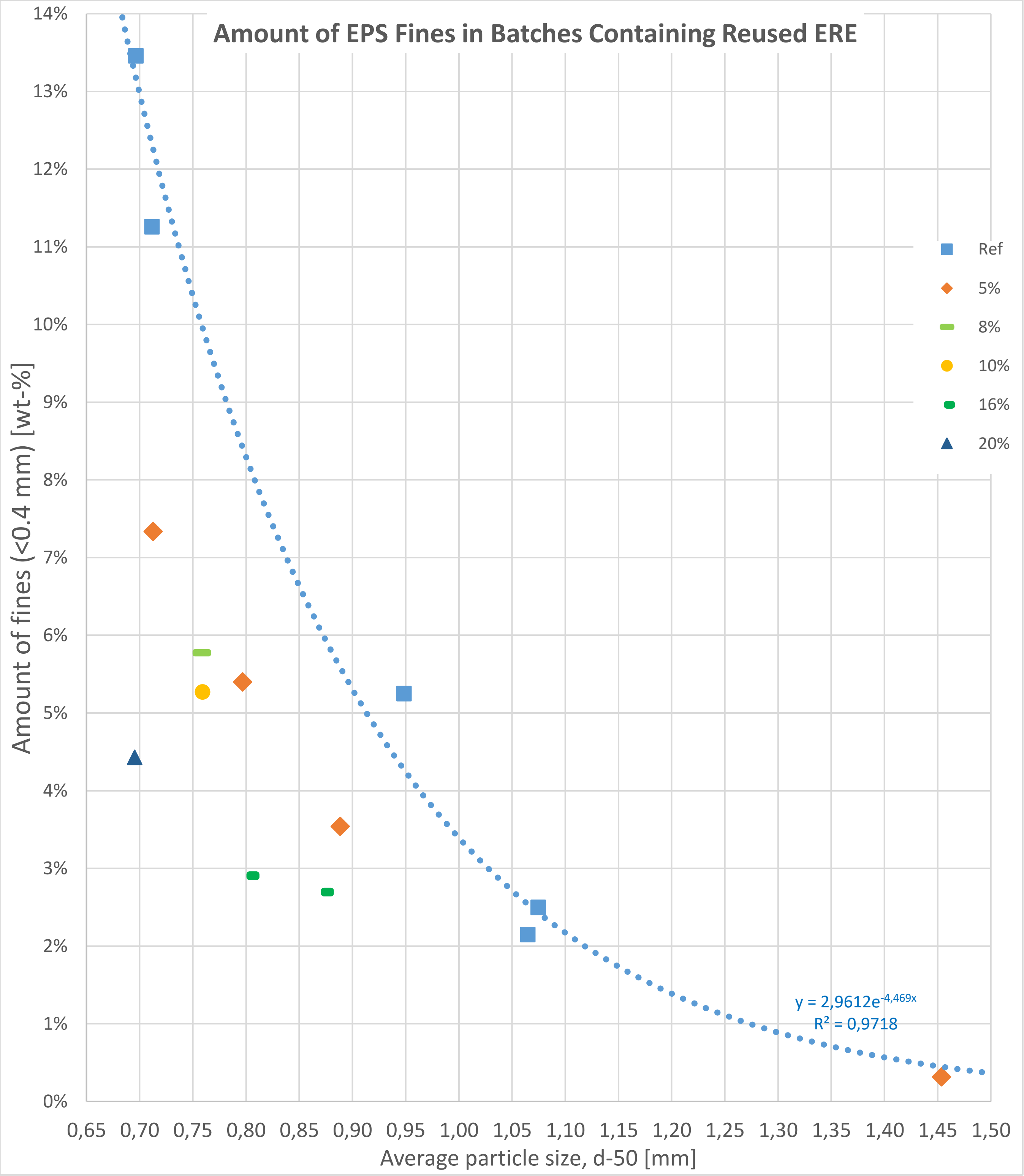


Figure 33. A collection of the formation of fines (LOF) at different average particle sizes in batches containing reused ERE.

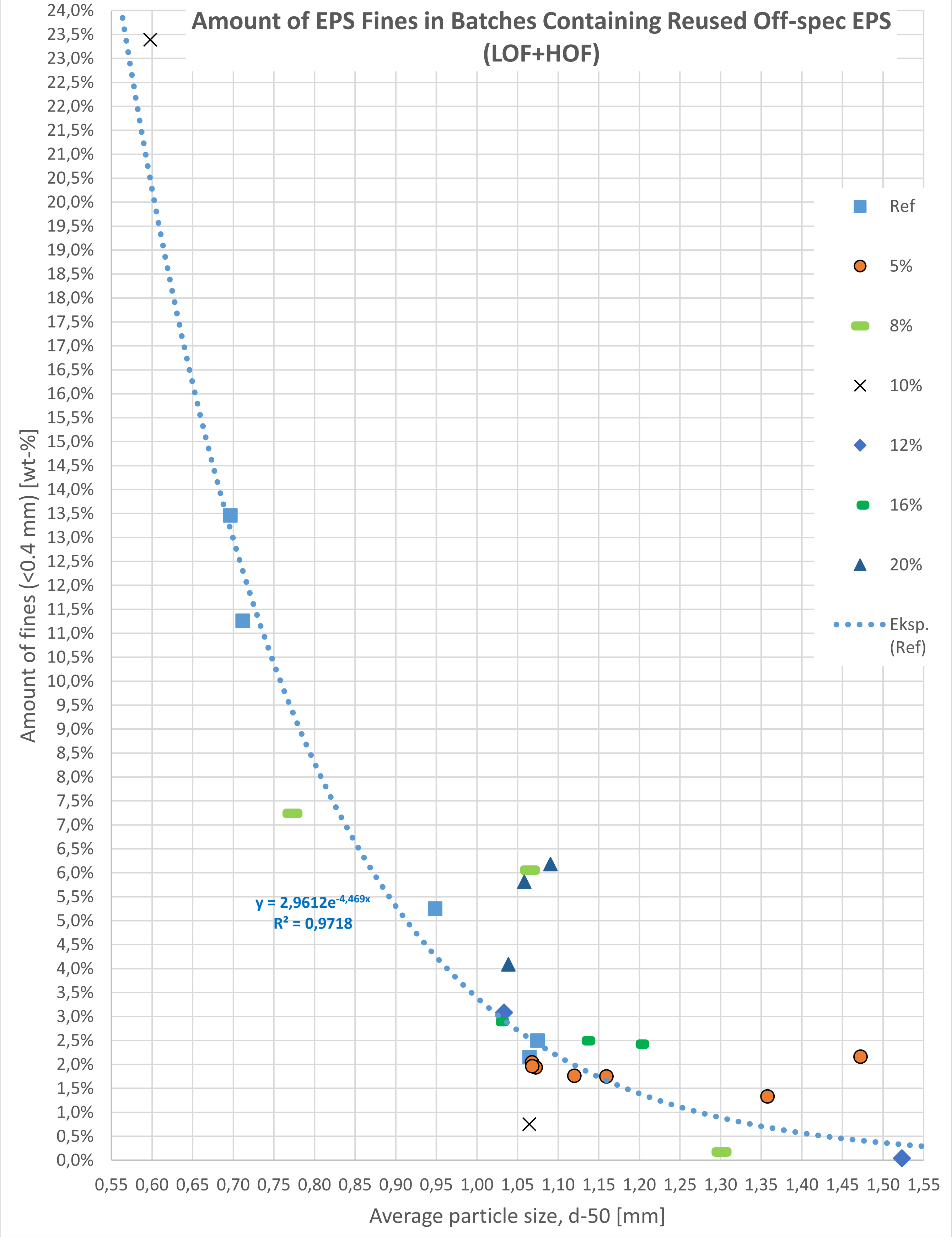


Figure 34. A collection of the fines (LOF) formation at different average particle sizes in batches containing reused off-spec EPS (LOF or HOF).

PSD Evolution at Different Reused EPS Mass Concentrations

Reuse of undersized (LOF) or oversized (HOF) off-spec EPS											
Reused EPS wt-%	Batch	Average Bead size	LOF wt-%	HOF wt-%	TOT. OFF SPEC wt-%	Agitation	Stabilization	d-50	LOF	HOF	OFF SPEC
		d50 [mm]	>0.4 mm	>2.5 mm	LOF+HOF	Increase	Increase	Change	Change	Change	Change
0%	**M-137, M_REF1-300-0.22**	**1.07**	**2.50%**	**0.39%**	**2.89%**	**START**	**START**	**START**	**START**	**START**	**START**
	M-152, M_REF_3.2-300-0.26	1.06	2.15%	0.79%	2.94%	0%	18%	-1%	**-14%**	103%	2%
5%	**M-145, M_5%LOF_P2-300-0.26**	1.07	1.94%	0.76%	2.70%	0%	18%	0%	**-22%**	95%	-7%
	M-147, M_5%HOF_S1_45-300-0.26	1.36	1.33%	1.79%	3.12%	0%	18%	27%	**-47%**	359%	8%
8%	**M-154, M_8%LOF_P1-300-0.35**	1.30	0.17%	3.29%	3.46%	0%	59%	21%	**-93%**	744%	20%
10%	**M-160, M_10%HOF_P1-350-0.26**	1.06	0.75%	0.68%	1.43%	17%	18%	-1%	**-70%**	74%	-51%
12%	**M-163, M_12%LOF_P1-350-0.35**	1.03	3.08%	0.58%	3.66%	17%	59%	-4%	**23%**	49%	27%
14%	**M-166, M_14%LOF_P1-370-0.38**	1.15	1.86%	1.44%	3.30%	23%	73%	7%	**-26%**	269%	14%
16%	**M-168, M_16%LOF_P2-370-0.35**	1.20	2.42%	0.33%	2.75%	23%	59%	12%	**-3%**	-15%	-5%
20%	**M-173, M_20%LOF_P1-440-0.42**	1.04	4.09%	0.32%	4.41%	47%	91%	-3%	**64%**	-18%	53%

Table 18. A collection of the most succesfull reference and dissolved off-spec EPS (LOF or HOF EPS) containing batches in general, and with an emphasis on EPS fines (LOF) formation.

Reuse of extruded recycled EPS (ERE)											
Reused EPS wt-%	Batch	Average Bead size	LOF wt-%	HOF wt-%	TOT. OFF SPEC wt-%	Agitation	Stabilization	d-50	LOF	HOF	OFF SPEC
		d50 [mm]	>0.4 mm	>2.5 mm	LOF+HOF	Increase	Increase	Change	Change	Change	Change
0%	**M-137, M_REF1-300-0.22**	**1.07**	**2.50%**	**0.39%**	**2.89%**	**START**	**START**	**START**	**START**	**START**	**START**
	M-152, M_REF_3.2-300-0.26	1.06	2.15%	0.79%	2.94%	0%	18%	-1%	**-14%**	103%	2%
5%	**M-148, M_5%ERE_P1-300-0.26**	1.45	0.32%	3.54%	3.87%	0%	18%	36%	**-87%**	808%	34%
	M-176, M_5%ERE_P1-300-0.26_G0	0.89	3.54%	1.28%	4.82%	0%	18%	-17%	**42%**	227%	67%
8%	**M-179, M_8%ERE_P1-350-0.35_G0**	0.76	5.78%	0.80%	6.58%	17%	59%	-29%	**131%**	105%	128%
10%	**M-180, M_10%ERE_P1-350-0.26_G0**	0.76	5.27%	1.44%	6.71%	17%	18%	-29%	**111%**	269%	132%
16%	**M-181, M_16%ERE_P1-370-0.26_G0**	0.87	2.70%	1.47%	4.17%	23%	18%	-19%	**8%**	277%	44%
20%	**M_20%ERE_P1-440-0.30_G0**	0.70	4.43%	0.55%	4.98%	47%	36%	-35%	**77%**	41%	72%

Table 19. A collection of the most succesfull reference and extruded recycled EPS containing batches in general, and with an emphasis on EPS fines (LOF) formation.

Discussion

All the PSD related data including average particle size (d-50) and the mass fraction distributions are collected in the Appendix in the PSD data section. The section also contains PSD curves and off-spec distribution graphs of all the batches. The evolution of undersized (LOF) EPS formation and the agitation and the concentration of stabilizing agents applied in the most "successful" batches at different mass concentrations of reused EPS compared to the starting point, the reference sample M-137 (M_Ref1-300-0.22) can be observed in Tables 18 and 19. The figures 33 and 34 portray the evolution of the formation of EPS fines at different d-50 for the batches containing different mass concentrations of reused EPS.

The reuse of all three EPS qualities in suspension polymerization seemed to shift EPS PSD into larger particle sizes if the process temperature-time profile and process parameters such as agitation and stabilization are identical with the standard or reference polymerization procedure, and in this way, have decreased the formation of undersized (LOF) and increase the oversized (HOF) EPS formation. For example, in the batches in which 5 wt-% off-spec EPS was reused in which same stabilization and agitation levels were applied as the reference samples (M-152 and M-141), at the same average particle sizes, the LOF formation seemed to slightly decrease and the HOF formation slightly increased compared to the references (See Figures 34, 50, and 54, and Table 18). This may partly be explained with the increasing viscosity of the reaction mixture which could reduce the grade of agitation, and hence, increase coalescence and particle size. On the other hand, without any adjustments in stabilization input timing in the batch containing 5 wt-% reused ERE (sample M-148), the d-50 was drastically increased when the same polymerization procedure with the reference sample M-152 was used, and naturally, the amount of fines dropped very low and oversized EPS formation increased (see Table 19). However, the suspension was very weak in the sample M-148. Changing the timing of stabilization addition had the opposite effect compared to the reference, and d-50 was significantly lowered, and as expected, the LOF formation increased and the HOF formation increased as the Table 19 shows.

It may be difficult to draw a straightforward conclusion if or not the reuse of EPS decreases the tendency to form EPS fines, but at least in some of the samples in which the agitation and stabilizing agent concentration was successfully applied and adjusted, at the same d-50 particle sizes less fines were formed compared to the trendline of the reference samples (see Figures 33 and 34), especially in reused ERE containing batches. The fact that the increase in viscosity of the reaction mixture was compensated with more vigorous agitation was problematic since after a certain threshold the amount of EPS fines started to increase again (see for example Table 16). In addition, the stabilization agent concentration may have been applied in abundance which may have contributed. This phenomenon is well illustrated by the Tables 18 and 19. Especially in reused ERE containing batches the Table 17 shows, however, that the right ratio between stabilization and the agitation were missing and quite randomly applied. The high amount of EPS fines may have been a result of either too high stabilization or agitation, or both. On the other hand, the amount of stabilization may have been insufficient, as well, and more systematic research is certainly needed. On top of the LOF problem, the quality of the beads was also an issue especially in batches containing reused ERE with oval-shaped beads. Another interesting aspect is that the ERE batches in general seemed to result in more narrower PSD distributions compared to only virgin MS and reused off-spec EPS containing batches (see PSD curves in the Appendix), which could be a positive thing if the particle size could be better controlled.

It seems clear from the PSD results, that when reused EPS is used in suspension is used to significant extents, most probably both the agitation and the concentration of stabilization may have to be increased in order to produce proper EPS beads both in size and quality. For example, in order to polymerize EPS containing 20 wt-% LOF EPS a 91% increase in stabilization concentration and 47% in the stirring was applied (see Table 18). Finally, the role and the effect of the surplus of polymerization initiators, peroxides, in the system on PSD remains unanswered.

8.4.4 Residual Monomer (RM)

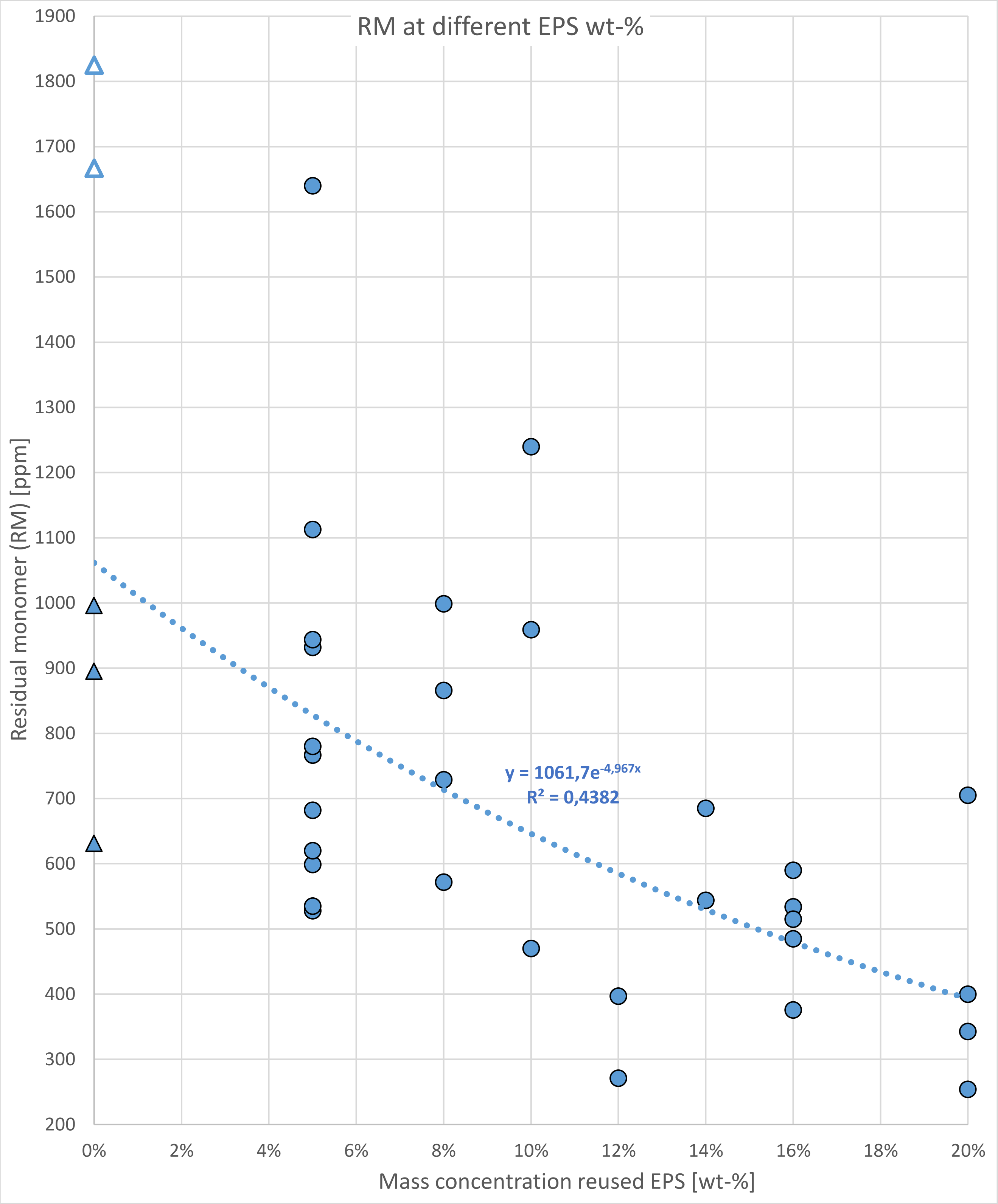


Figure 35. Residual monomer sample collection and the general trend at different EPS mass concentrations.

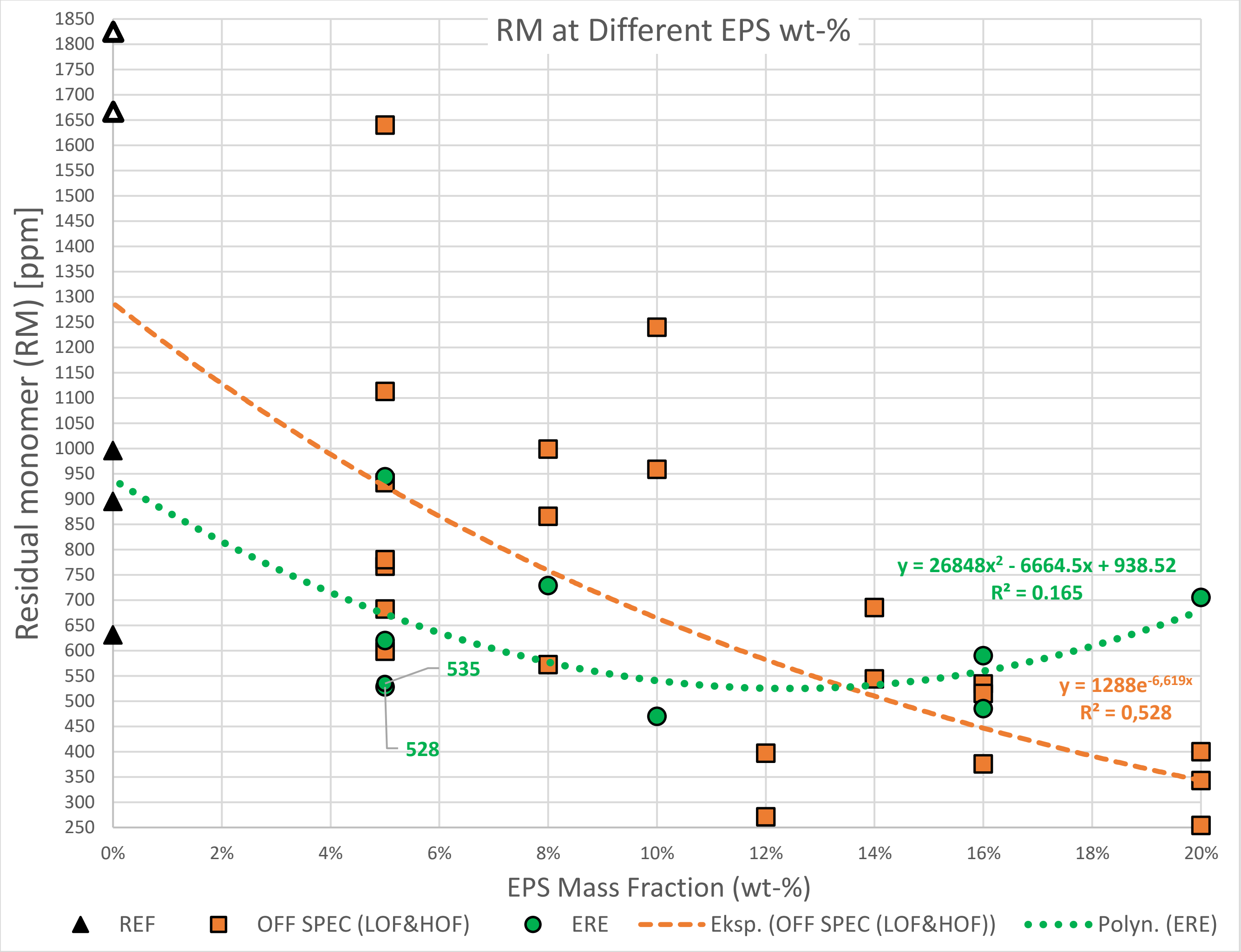


Figure 36. Residual monomer sample collection for the different qualities and the general trend at different EPS mass concentrations.

Discussion

The general trend seems to be that the residual monomer (MS concentration) decreases with increasing reused EPS content (see Figure 32). This trend would be supported by the visual observations during the polymerization. It seemed that the stabile point was obtained earlier, and the beads were harder at an earlier stage in the process. This seemed to be noticeable especially at higher EPS contents such as 16 and 20 wt-%. However, this is most probably resulting from the surplus of peroxides (BPO and TBEC) in the system. The lowest RM values were obtained with 12, 16 and 20 wt-% EPS, which also supports the theory that this was caused by the surplus of peroxide. Everything below 1000 ppm was considered acceptable**.** For some reason, the reference samples (M-156 and M-157) with powerful agitation resulted in very high RM value (see Figure 35 and 36 triangles marked with a white interior). All the RM data obtained can be found in the Appendix in the Table 29 and an additional RM graph with all in addition, the EPS qualities (LOF, HOF and ERE) differentiated in the Figure 36.

8.4.5 Molecular Weight (MW) and Polydispersity (PD)

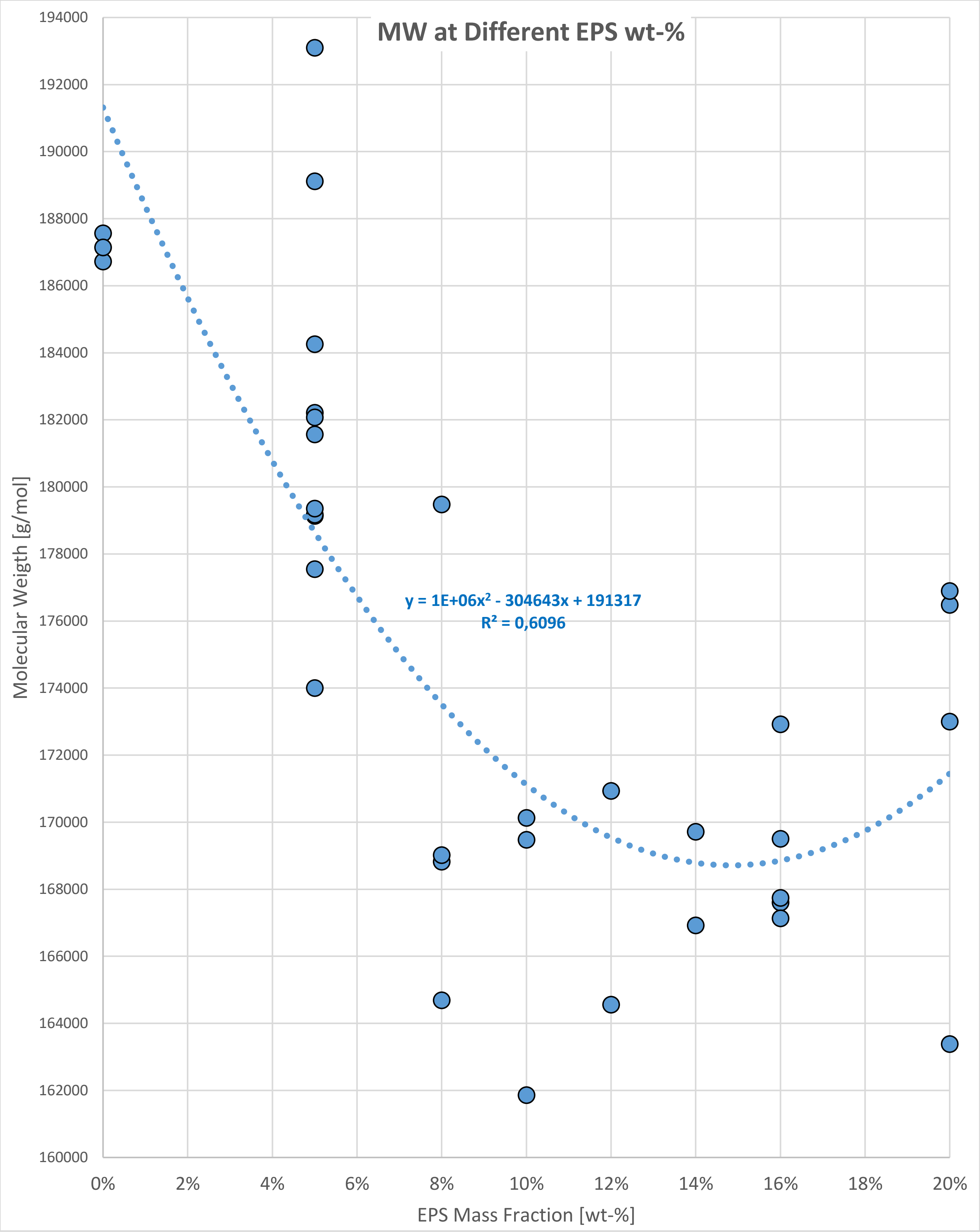


Figure 37. A general collective graph with molecular weight (MW) at different EPS mass concentrations (EPS wt-%) of all samples.

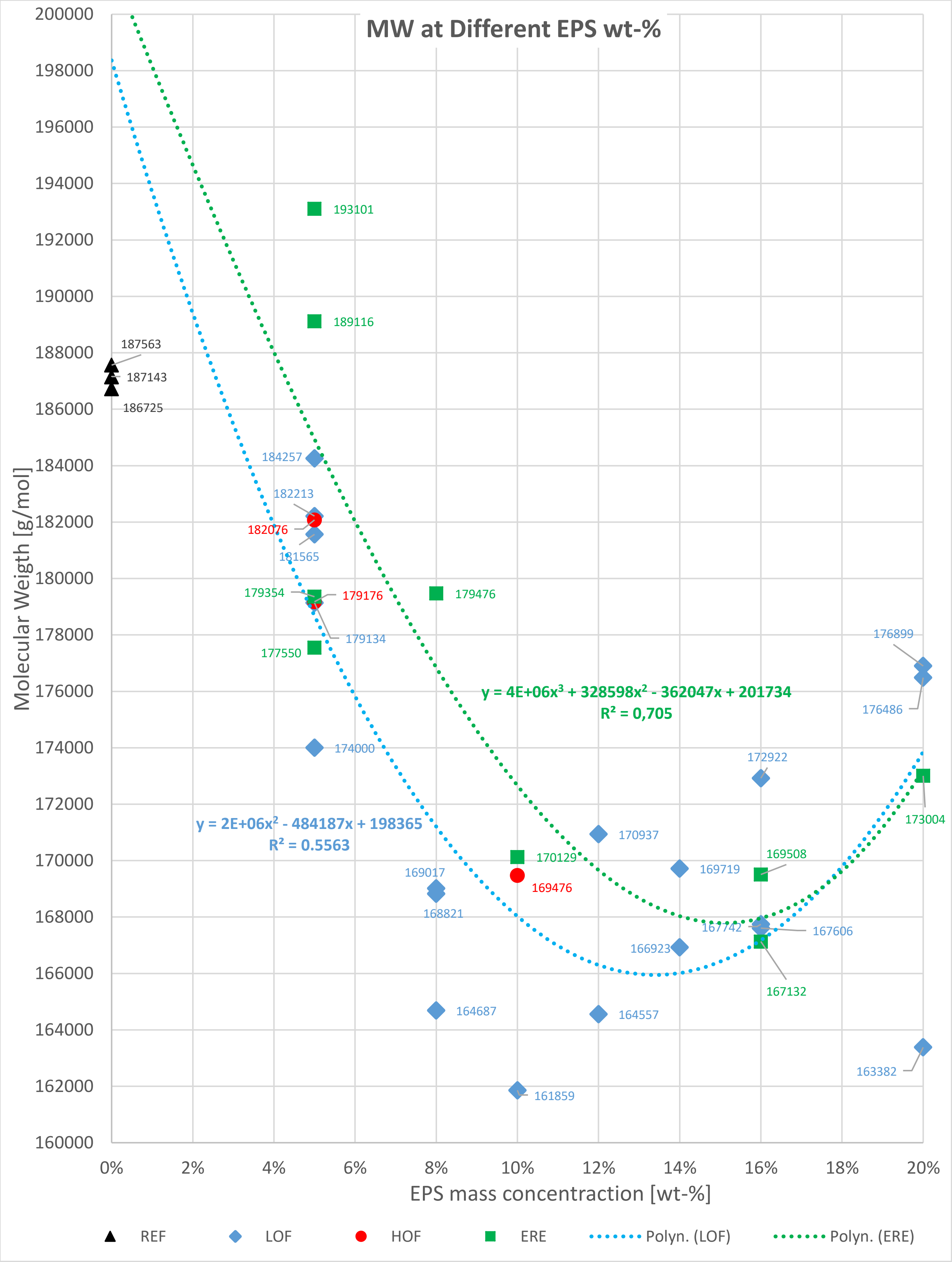


Figure 38. A graph with molecular weight (MW) at different reused EPS mass concentrations (EPS wt-%) with EPS qualities distinguished from each other.

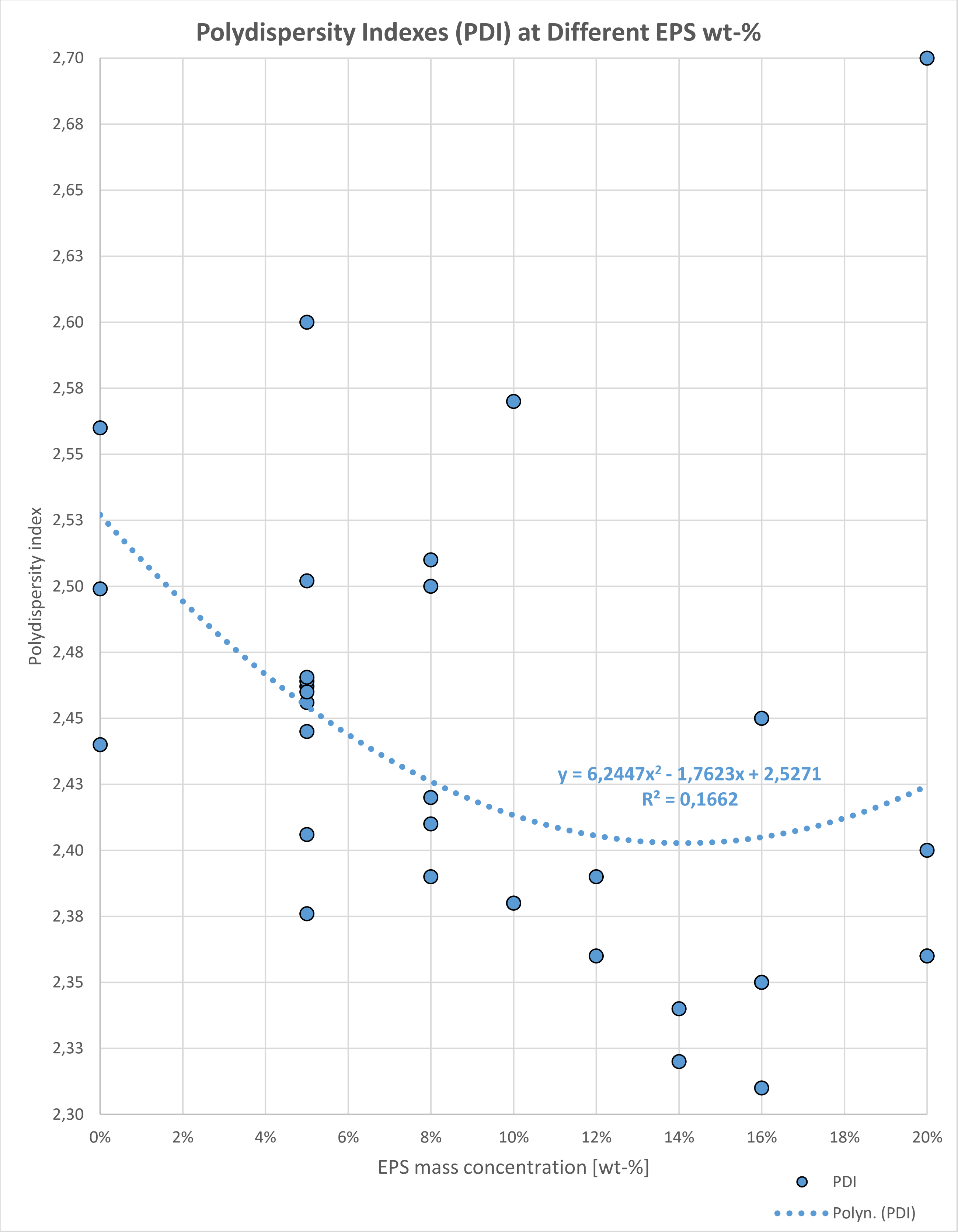


Figure 39. A collective graph with polydispersity (PDI) indexes at different EPS mass concentrations.

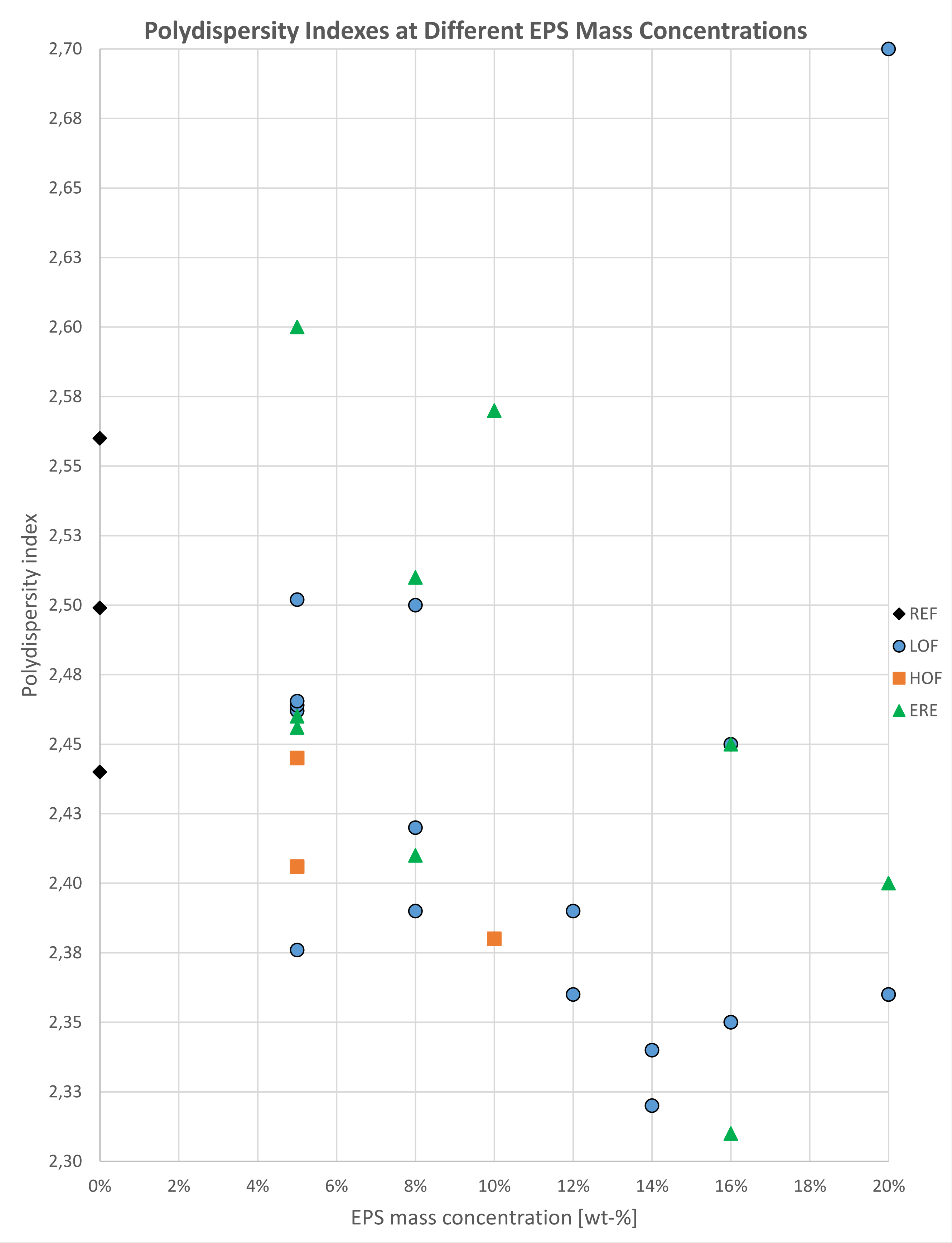


Figure 40. A collective graph with polydispersity (PDI) indexes at different EPS mass concentrations (wt-%) with EPS qualities distinguished from each other.

Discussion

All the MW value related data can be found in the Table 27 in the Appendix. The general trend in MW value development seemed to be that the values mostly decreased with increasing EPS content compared to the reference samples made purely with virgin MS (see Figure 37). On the other hand, the trendline seems to be almost parable like and starts to slowly increase after approximately 12 wt-% reused EPS both in the case of undersized off-spec (LOF) and extruded recycled (ERE) EPS. Oddly enough, extremely high MW values were obtained in batches containing 5 wt-% reused ERE with lower stabilization values (M-176 and M-177 in Tables 27 and 29 in the Appendix), even higher than the reference samples. The question that was presented earlier in Chapter 8.4.1 General Overview that does the ERE material itself lower the need for stabilization is repeated here. Another observation is the fact that predissolved LOF and HOF with the same recipe had identical MW values. This seems to support the presumption that LOF and HOF EPS are chemically quite the same time, and the HOF EPS had only a slightly higher MW value compared to LOF EPS (compare M-145 and M-146). However, there is a significant difference in MW values between the parallel samples M-143 (M_5%LOF_P1-300-0.26) and M-145 (M_5%LOF_P2-300-0.26). The fact that M-143 was done in a cleaned reactor and M-145 not, seems to support the presumption that the cleanliness of the reactor impacts results. Nevertheless, the variation in raw materials, both in styrene and reused EPS qualities may also contribute

First and foremost, in order to measure and to take into consideration the effect of the surplus of peroxides theoretical MW values were roughly estimated with the following formula (4):

$$MW_{Theoretical} = wt\%_{MS} \times MW_{average\ References} + wt\%_{reused\ EPS\ quality} \times MW_{reused\ EPS\ quality}$$

The MW values obtained were slightly on the low end. This can partly be explained with the lower MW values of the reused EPS qualities compared to reference samples, especially ERE, that were expected to sink the MW value of the end products. Interestingly, however, the ERE did not seem lower the MW more than LOF EPS, quite the contrary even in some cases. Even though the peroxide was added in a surplus in the batches, the MW values obtained in general were still relatively close to the calculated theoretical MW values.

The polydispersity index (PDI), or just the dispersity, in general, despite a couple of anomalies, seems to decrease with increasing reused EPS content (see Figure 39). This was expected, as well, since the PD indexes for LOF, HOF and ERE were significantly lower than the PD indexes of the reference samples, and the higher the concentration of the reused more uniform EPS qualities in the batches, namely off-spec and extruded recycled EPS, the more uniform the final product presumable becomes, hence, having a lower PDI.

8.4.6 Mechanical and Thermal Properties

Compressive Strength

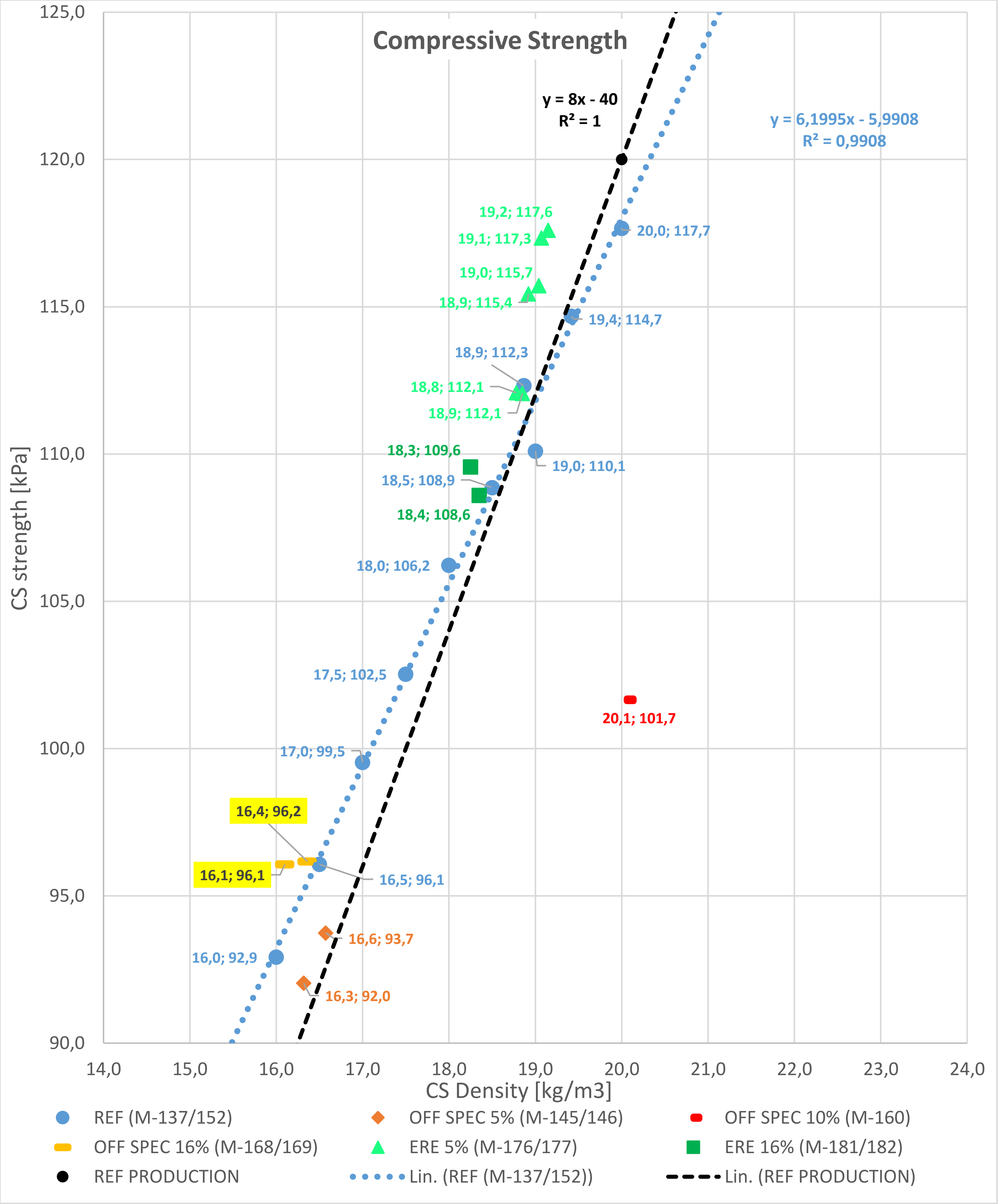


Figure 41. Compressive strength at different densities.

Bending Strength

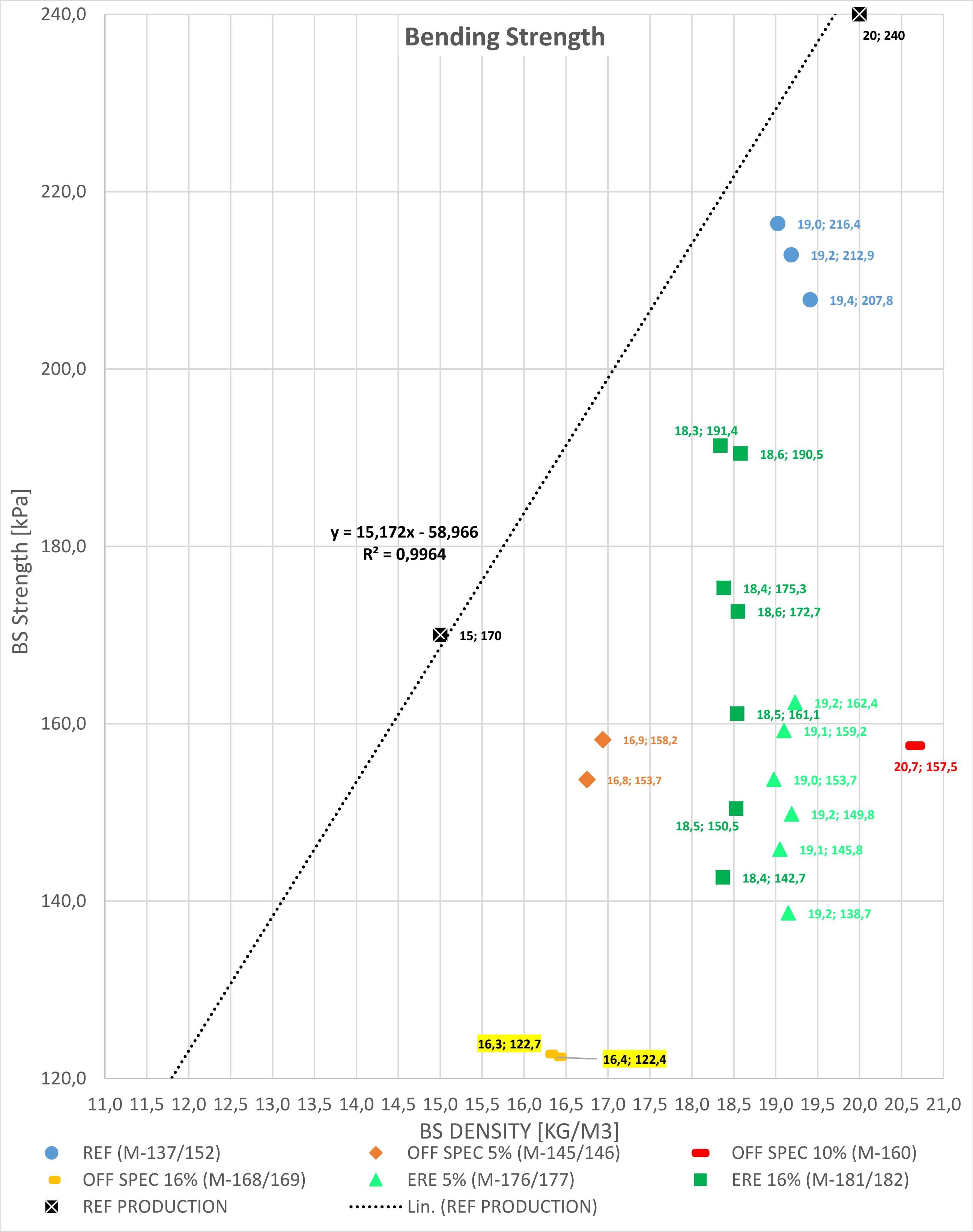


Figure 42. Bending strength at different densities.

Lambda – λ

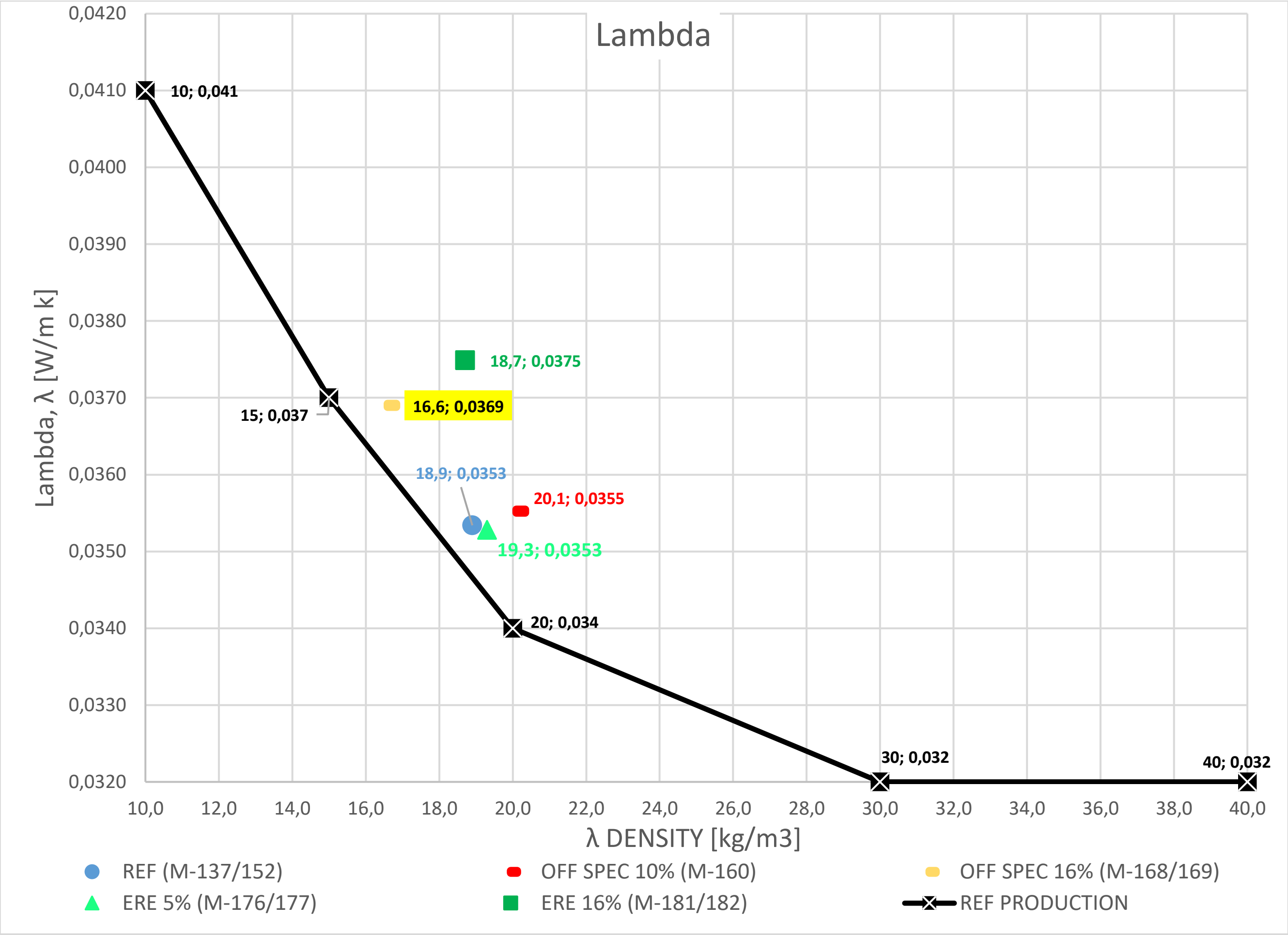


Figure 43. Lambda (thermal conductivity) at different densities.

Discussion

The three different compressive strength values at different densities obtained from the reference sample comprising of M-137 (M_REF1-300-0.22) and M-152 (M_REF_3.2-300-0.26). However, linear forecasting with such a limited data may not be trustworthy, and the reference for production was also used. Figure 41 shows that the compressive strength might even slightly increase in batches containing dissolved EPS. However, M-160 with 10 % HOF did not manage that well, most probably due to very low pentane content (3.15 wt-% versus REF 4.38% and 4.51 OFF SPEC 5%). The bending strength was also very weak. The bending strength seems to decrease in batches containing dissolved EPS (see Figure 42). It was impossible to make a linear forecast with the bending strength reference data, and the production reference was used. It should also be noted that higher steam pressure was used for the preparation of batches containing dissolved EPS, which should improve results in mechanical strength. The lambda value compared to production reference seems to increase, which is not desirable (See figure 43). More testing is absolutely needed, and more parallel samples should be included.

9 Conclusions

The solubility tests of EPS into MS gave relatively consistent results as up to 30 wt-% of three different EPS qualities was successfully dissolved at three different temperatures in laboratory scale. Clear differences between the different EPS qualities were distinguished and the contributing effect to the dissolution of the temperature increase was confirmed. However, there was some anomalies and according to the obtained results there is not a very drastic difference between the dissolution times between 50°C and 70°C. My personal conclusion based on the results overall is that a separate EPS dissolution tank would be the most practical solution in industrial scale if EPS or PS is reused in the suspension polymerization of EPS, especially at higher dissolved EPS concentrations. This on the other hand, could possibly cause some technical problems due to stickiness and highly viscous mass. Small amounts of EPS fines could possibly be dissolved directly in the suspension prior to the polymerization based on the polymerization results. Still, the fact that the dissolution times were determined visually decreases the reliability of the results significantly. As earlier stated in Chapter 7, in the future if dissolution of the PS or EPS into MS is studied further, the following suggested improvements should be taken into consideration:

1) The dissolution container must be a closed system, and preferably with automatic temperature control.
2) The dissolution container must be equipped with an adequate stirrer, for example a mechanical stirrer.
3) The extent of dissolution must be monitored and defined with the help of transmittance or viscosity measurement.

Possibly, with a closed system preventing evaporation, applied with better temperature control and vigorous stirring the dissolution times could be significantly lowered.

Suspension polymerization experimentation gave varying results as up to 20 wt-% EPS was reused in a laboratory-scale BR (M1-reactor). In general, the reused off-spec EPS, mostly undersized off-spec EPS fines, containing batches gave better results both regarding bead quality and the amount of produced EPS fines than ERE containing samples. There was no time to study the recycling of extruded recycled EPS material in suspension polymerization comprehensively, and the stabilization and agitation levels were quite randomly applied based on the results obtained from reused LOF and HOF EPS. However, in order to maintain the suspension, the timing of the addition of stabilizing agent A had to be changed, which seemed to have a drastic effect on the particle size evolution. The average particle size was remarkably decreased, and unfortunately, the amount of EPS fines increased. In addition, the quality of the beads which seemed to decrease in both groups, both in the reused off-spec EPS (HOF and LOF) as well as ERE containing batches, was significantly worse in the ERE containing batches. The ERE beads became rather oval than the desired spherical shaped beads. Even though some relatively good results with respect to PSD were obtained in single batches containing recycled off-spec EPS, there were many other problems that must be addressed in the future. These problems that may prevent industrial application may include:

- bead quality problems,
- excess foaming,
- buildups in the reactor,
- agitation problems,
- batch removal problems,
- reactor cleaning problems, and finally,
- interruptions in production.

It may also be possible that some sort of filtration or extraction technique(s), which is typical for solvent recycling in order to remove for example additives and impurities from the polymer, must be applied for the polymer-monomer mixture (monostyrene-polystyrene mixture), at least for mixtures containing ERE material, and possibly in the future, PS or EPS waste.

The next steps for research in the attempt to recycle EPS in suspension polymerization process could be the following:

1) Decreasing and correcting the amount of peroxides added to the system tied to the amount of virgin MS.
2) Testing how 5 wt-% LOF and HOF EPS behave in a pilot-scale and in an industrial-scale reactor if any significant buildups on the reactor surfaces are present and if lower bead yields overall are achieved.
3) Finding the actual need for stabilization and concentration for ERE and optimizing the ratio between stabilization concentration and agitation, possibly first in the laboratory-scale BR (M-reactor).
4) Repeating solubility tests in a better solubility system as described above and in chapter 7.3.2.

10 Sammanfattning

10.1 Teoretisk bakgrund

Förbrukning av plastiska material och produkter växer ständigt i dagens samhälle (se Figur 3) [1]. Samtidigt har oron för plasters miljöpåverkan ökats och reglering för framställning och användning av plastprodukter blivit alltmer striktare [2]. Trycket för att minska mängden fast avfall som hamnar till soptippar och miljön, mängden av emissioner, och förbrukning av naturtillgångar är på den högsta nivån någonsin, och återvinning föredras över den ”konventionella” avfallshanteringen [3]. Allt detta är sant även för EPS, det vill säga partikelskum baserat på expanderad polystyren (EPS), eller Airpop®- engineered air i Europa, som är en av de mest viktiga polystyren (PS)-tillämpningar. EPS används brett i applikationer inom konstruktions-, förpacknings- och fordonsindustrin [4,5]. Utöver isoleringsförmågan och kostnadseffektiviteten, har EPS ett flertal fördelaktiga egenskaper såsom bra stötdämpningsförmåga, bra tryckhållfasthet, låg värmeledningsförmåga, god kemisk- samt luftfuktighetsresistivitet, låg vikt, en god hållbarhet samt resistans mot nedbrytning, och återvinningsbarhet [3,4,15,43]. Den största styrkan hos EPS-materialet som gör det unikt med tanke på hållbarheten, är dess höga effektivitet i relation till mängden konsumerat råmaterial. EPS består mellan 95–98 % av luft innehållande slutna celler och endast från 2–5 % av PS [7]. Reducering av mängden avfall och föroreningar som EPS genererar bygger på åtminstone fyra olika strategier:

1. *reducering*; t.ex. ytterligare reducering av EPS-innehållet med att optimering av förpackningsdesignens,
2. *återanvändning*; t.ex. återanvändning av termoslådor för livsmedel,
3. *återvinning*; t.ex. återanvändning av material eller dess komponenter i nya produkter och applikationer, och
4. *energiåtervinning*; t.ex. produktion av termisk värme eller kraft med hjälp av förbränning eller kemisk återvinning av råmaterial [7].

Gångbara återvinningsmetoder för polymerer kan allmänt delas i följande tre huvudgrupper som gäller även för EPS:

I. *Mekanisk återvinning* som innefattar upparbetning av plastavfall till nya produkter. Ursprunget för materialet kan vara en tillverkningsprocess eller en postkonsumentprodukt.
II. *Kemisk* eller *råmaterialåtervinning* (tertiär återvinning) som innefattar nedbrytning av plastmaterialet till monomer eller andra produkter med hjälp av värme eller kemisk behandling, till exempel hydrolys och pyrolys. Dessa komponenter kan rekombineras eller användas för andra tillämpningar.

III. *Energiåtervinning* (kvartär återvinning) som innefattar återhämtning av energin från plasten med hjälp av förbränning. Denna typ av verksamhet ses oftast som underutnyttjande eller slöseri av energin som plasten innehåller [24].

Återvinningsgraden globalt har ökat drastiskt under de senaste årtiondena [8]. Åsikten att EPS inte kan återvinnas är ihärdig [24]. Även om det är sant att EPS-återvinning innebär ett flertal tekniska utmaningar, är EPS en av de mest återvunna plaster i världen (se figurer 19–23) [2,6]. Dyra dumpningskostnader på soptippar samt höga transportkostnader för de högt voluminösa EPS-materialen, och allmänna publika opinionen har varit de drivande krafterna för utvecklingsarbete av EPS-återvinningstekniker [6]. EPS kan återvinnas flera gånger utan nämnvärd försämring i materialegenskaper, och processen börjar ofta genom att krossa materialet som kan återvinnas antingen som EPS eller PS då luften avlägsnas [56]. Emellertid, den lilla marginalen i priset mellan obehandlad och återvunnen EPS sänker motivationen för återvinning [6]. Energiåtervinning där avfallet förbränns, och mekanisk återvinning där avfallspolymerer konverteras till nya produkter, är de två huvudsakliga alternativen för polymeravfallshantering [9]. Även om mängden EPS-avfall som hamnar på soptippar har sjunkit, är en signifikant andel av EPS-återvinning fortfarande värmeåtervinning, det vill säga förbränning.

Man har forskat mycket kring EPS-återvinning, och presumtiva möjliga metoder innefattar extrudering, pyrolys och upplösning av EPS i lösningsmedel [57]. Bland den första och andra metoden finns det vissa kritiska punkter. I smält extrudering krävs det höga temperaturer upp till polymerens degraderingstemperatur, och i pyrolys, är det svårt att extrahera styren ur pyrolytiska produkter, och dessutom är priset för produktionen väldigt högt. Detta har resulterat i att alltmer uppmärksamhet har skiftats mot upplösning [57]. Upplösning av lågdensitets-EPS eller PS-skum i lämpliga upplösningsmedel är ett av de billigaste, effektivaste och miljövänligaste sätten att hantera avfall [9,10]. Sålunda har upplösningsbeteendet av PS-skum i olika slags lösningsmedel en kritisk roll i PS-återvinning [9]. Återvinningsprocess av plast via upplösningsåtervinning innehåller generiskt avlägsnande föroreningar och andra additiver, antingen homogen eller heterogen upplösning, och utfällning eller förgasning. Polymeren är upplöst i lösningsmedel, och efteråt kristalliseras den selektivt. I en ideal situation har lösningsmedlet förmågan att upplösa antingen målpolymeren eller alla andra polymerer utom målpolymeren, och kan användas för selektiv upplösning. Att hitta de rätta lösningsmedlen är kritiskt för upplösningsprocessen [1]. Tillämpning av upplösningsåtervinning för skummade polymerer såsom EPS har ett flertal fördelar. Till exempel icke-upplösbara kontaminationer kan avlägsnas via filtrering som ger möjligheten att vidareprocessera ren polymer. Ytterligare, att selektivt upplösa polymeren möjliggör avskiljning av plaster från andra icke-upplösbara avfall och polymerer på basen av deras kemiska sammansättning och löslighet. Slutligen, upplösning av skummet resulterar i en hundrafaldig reduktion i volym utan degradation av polymerkedjorna. Detta leder till reducerade transportkostnader av EPS [9,58].

Ett flertal lösningsmedel för PS såsom toluen, xylen, klorbensen, aceton, cyklohexan, butylacetat, etylacetat, metyletylketon, limonen, terpinen, terpinolen, p-cymen och phellandren har undersökts (se Tabell 12) [58]. Det är allmänt känt att vissa aromatiska föreningar, exempelvis limonen, är goda lösningsmedel för PS [9]. Dessutom löser sig PS i styren, som utgör monomeren vid framställning av PS. Sedan 1950-talet, har majoriteten av EPS framställts via suspension polymerisation i satsreaktorer. Alternativt kan man även idag framställa EPS med hjälp av mera nyligen utvecklade extruderingssprocesser (producerar mikroskopiska pärlor med jämnare storlek direkt från smält PS) [4,59]. Följaktligen, är idén om möjligheten att utnyttja det traditionella sättet att producera EPS pärlor i PS-återvinning genom att upplösa PS- eller EPS-avfallet i styren väldigt lockande, eftersom inga dyra tilläggsinvesteringar krävs i den själva suspensionsprocessen. Detta vore en naturlig väg för EPS-industrin. Målet i detta arbete var uttryckligen att fastställa hur mycket EPS man skulle möjligtvis kunna återanvända i en satsreaktors suspensionspolymerisationsprocess. Åtminstone i ett par patent nämns möjligheten att lösa från 0,5 till 30% PS eller EPS i styren och användning av denna blandning i tillverkning av EPS i suspension [12,44]. Ytterligare, eftersom faktumet är att antalet tekniska applikationer för under- och överdimensionerad (LOF respektive HOF) EPS, särskilt för underdimensionerad EPS som framställs i BEWiSynbra Raws produktion är begränsade, är det uppenbart att något måste göras för att minska mängden producerat underutnyttjat så kallad ”off-spec”-EPS (material som inte uppfyller vissa kvalitetskrav). Det är fortfarande oklart hur och när “off-spec”-EPS, eller EPS- eller PS-avfall ska utnyttjas i BEWiSynbra RAWs EPS-tillverkning med suspensionspolymerisationsprocess i framtiden. Det två självklaraste alternativen är antingen att förupplösa EPS i styren innan suspensionen eller att låta EPS upplösas i styren direkt i suspensionslösningen. I samtliga fall, måste själva polymerisationen innehållande återanvänt EPS genomföras framgångsrikt före några tekniska applikationer och lösningar planeras eller övervägs seriöst. Ifall man skulle lyckas att återanvända EPS eller PS i suspensionspolymerisationsprocessen med ursprungligt eller något ändrat tillverkningssystem framgångsrikt hos BEWiSynbra, skulle man möjligtvis förbättra konkurrenskraften på den ytterligt konkurrensutsatta EPS-marknaden eftersom lönsamheten skulle öka genom att sänka de totala tillverkningskostnaderna för EPS med lägre förbrukning av styren (mera billiga råvaror i form av EPS och PS avfall), möjligheten för återanvändning av “off-spec”-EPS (mindre avfallsprodukt), och tillhandahålla en mera miljövänlig hög-prestanda produkt som lockar mera kunder.

EPS tillverkning via suspensionspolymerisation producerar sfäriska pärlor som expanderas till skum med hjälp av värme eller ånga i närvaro av ett jäsmedel [21]. Icke-vattenlösliga styrenmonomer är dispenserade som droppar i närvaro av suspensionsstabilisatorer, medan suspensionsblandningen som består av vatten och monomer omrörs kraftigt för att producera PS-partiklar som en disperserande solid fas. Själva polymerisationen sker innanför de dispergerade styren-monomerdropparna efter tillsats av initiator. Initiatorer är oftast organiska peroxider såsom BPO, TBPC och TAEC, eller azoföreningar, är lösliga i olja (styren). Polymerisationsprocessen utförs oftast i två eller flera steg (se Figur 17). Olika suspensionsstabiliserande tillsatsämnen (t.ex. PVA, HEC, PVP, naturliga produkter så som TCP, osv.) tillförs för att erhålla önskad droppestorleksfördelningen av den dispenserade fasen. Monomer/vatten förhållandet är ofta mellan 40:60 och 60:40 [21]. Den kommersiella EPS-produktionen är fokuserad på partikelstorlek mellan 0,1–2 mm, men 0,4–1,6 mm föredras, medan de expanderade uppvärmda EPS pärlorna expanderar upp till 20 gånger deras ursprungliga storlek, och efteråt fördubblas de partiellt expanderade pärlorna i gjutformen med hjälp av passerande ånga (ungefär till 40-faldigt storlek av den ursprungliga pärlan) varvid polymerpartiklarna smälts samman [3,4,21]. Jäsmedlet är oftast en blandning av pentan. Pentanet tillförs typiskt i slutskedet av processen före avvattning och torkning. Pärlorna beläggs även med organiska antistatmedel som förhindrar agglomerationen av de bildade partiklarna i den fortsatta processen. Sedan siktas EPS-partiklarna på basen av storleken i olika storleksfraktioner, och partiklar med storleken mellan 0,1–2 mm används för framställning av EPS. Sedan lagras EPS-pärlorna i gastäta påsar och silon. EPS-pärlorna är producerade i en polymerisationsanläggning och transporteras till konverter som processar pärlorna vidare till slutliga produkter, t.ex. isoleringsskivor. Detta har fördelen att kostnaderna för att transportera de volymmässigt skrymmande skivorna är minimerad, och formgjutningen kan utföras utan postbearbetningsprocesser. Alla tekniska stegen i EPS-produktionen mera detaljerat är beskrivna och illustrerade i figurerna 15 och 16 [21]. Förvandlingen av EPS-partiklar producerade med suspensionspolymerisation till cellplast är utfört i tre olika huvudsteg:

1. preformgjutning/pre-expansion av EPS-pärlor,
2. mättning eller temporär lagring av pre-expanderade pärlorna, och
3. slutlig skumning (formgjutning eller blockprocesser) [21].

Kommersiell suspensionspolymerisation utförs typiskt i vertikala satsreaktorer eller möjligtvis i semi-satsreaktorer med reaktorvolymer mellan 20 och 100 m^3, utrustade med en omrörare av paddel eller ankare typ och med en omrörningshastighet på mellan 20 och 60 rpm [21,3132]. Omröraren kan förses med bafflar för att förbättra dispersionen eftersom användning av bafflar minskar heterogeniteten av turbulens och virvelrörelse [31,32]. Temperaturkontroll är en av de mest viktiga parametrerna och korrekt reaktordesign är även kritiskt för att uppnå höga polymerkonversionshastigheter. Det är även mycket viktigt att reaktorn tillåter effektiv bortförsel av överloppsvärmet som uppstår pga. den exotermiska polymerisationsprocessen [28].

Själva suspensionspolymerisationen framskrider via fri-radikal mekanism och suspensionspolymerisationen genomgår de följande tre huvudsteg [13,21,30]:

I. *Låg-viskositetsstadium* vid låga monomerkonversioner, där droppbrott (drop breakage) är den dominerande mekanismen och storleksdistributionen av droppen är snäv.

II. *Klibbigt stadium* med en accelererad ökning i viskositeten. Under detta stadium avtar brotthastigheten medan sammansmältning (coalescence) börjar dominera. Detta resulterar i att den genomsnittliga partikelstorleken ökar, och partikelsstorleksfördelningen blir bredare.

III. *Identifikationspunkten*. Ifall ett stadigt tillstånd uppnås, under detta stadium vid höga monomerkonversioner blir partiklarna tillräckligt hårda så att kollisioner mellan dem blir elastiska, och således upphörs sammansmältning av partiklarna och den slutliga formen av partikelstorleksfördelningen förblir konstant [13,21,30].

Det huvudsakliga målet i suspensionspolymerisation är att nå så uniform dispersion av monomerdroppar som möjligt i den kontinuerliga vattenfasen med kontroll över sammansmältning av dropparna under loppet av polymerisationsprocessen [27]. Kontroll över partikelstorleksfördelningen (PSD) är den största utmaningen i suspensionspolymerisation, och ju snävare distributionen är desto bättre [13,21]. Allmänt sätt är både den ursprungliga storleksfördelningen av monomerdropparna och slutliga polymerpartiklarna, beroende på omrörningseffektivitet (t.ex. reaktorgeometrin, typen av omrörare, effekten, osv.) och fysikaliska egenskaper (t.ex. densitet, viskositet, ytspänningar) av den kontinuerliga och dispergerade fasen [13]. Kvaliteten av de polymerpartiklarna beror alltså utöver reaktordesignen på även operativa parametrar som styr det övergripande stabiliteten av systemet [29]. Effektiv styrning av processen kräver utöver kännedom om exakta vetenskapliga principer också empiriska studier. Det finns ett otal av empiriska och teoretiska undersökningar på olika slags operativa parametrar och deras effekt på partikelstorleksfördelning (PSD). Den genomsnittliga storleken av monomerdroppar, och därmed de resulterande polymerpartiklarna, är beroende av omrörningshastigheten, volymförhållandet mellan monomer- och suspensionsmedium, koncentration av stabiliseringsämnen, och viskositeten av både den kontinuerliga och dispergerade fasen, se ekvation (3) [29]. Uppskalning av suspensionspolymerisationsprocessen är krävande, och mycket empiriska metoder används för att utveckla nya produkter och för uppskalning av processen från pilot till produktionsanläggning. För detta behövs dyra och tidkrävande experimentella program [13,27].

Den dynamiska partikelstorleksfördelningen är beroende av två fysikaliska processer, nämligen droppe- eller partikelbrott och sammansmältning eller agglomeration av partiklar [13,30]. Den dispergerade fasen kan nedbrytas i små droppar när ytan sönderfaller (droppbrott) i den omrörda suspensionen pga. av friktionskrafter (via viskös skjuvning) och via tröghet (via turbulens). Den totala droppbrottshastigheten är beroende av kollisionsfrekvensen av dropparna och sammansmältningseffektiviteten [31]. Droppbrottet sker huvudsakligen i regioner där skjuvspänningen är kraftig så som exempelvis nära omrörarbladen eller som resultat av turbulent flöde och tryckfluktuationer längs droppens yta. Turbulenta flödesfält antingen ökar eller minskar fluktuationer vid droppens yta. Däremot, om koncentrationen av ytaktiva ämnen är tillräcklig, kan effekten antas vara försumbar för utspädda suspensioner [13]. Olika slags mekanismer av droppbrott och sammansmältning är summerade i Figur 7.

10.2 Experimentell del

Avhandlingens experimentella del utfördes i laborationsskala. Till en början utfördes upplösningsexperiment för att fastställa hur mycket EPS (3 olika kvaliteter) som man kan upplösa i styren. Sedan utfördes suspensionspolymerisations i närvaro av de i styren upplösta EPS-polymererna. De undersökta EPS-kvaliteterna inkluderade två olika "off-spec EPS-kvaliteter från BEWiSynbra Raws konventionella suspensionpolymerisationsprocess, nämligen under- och överdimensionerad ”off-spec”-EPS (partikeldia-meter <0,4 mm respektive ≥2,5 mm), och ytterligare en återvunnen EPS extrudat (material för fisklådor).

Löslighetsexperimenteringen utfördes för att skaffa preliminär och vägledande information om tider och gränser för upplösningen av EPS till styren. Detta två-komponent systemet bestod av en blandning av MS och EPS. Emellertid, även om det var meningen att klargöra tiden för upplösningen även i vattensuspensionen, visade sig att vara opraktiskt och omöjligt att uppfölja pålitligt med existerande utrustningar. Lösligheten av de olika EPS-kvaliteterna undersöktes vid tre olika temperaturer, nämligen vid rumstemperatur, 50°C och 70°C grader samt vid sex olika masskoncentrationer, 5, 10, 15, 20, 25 och 30. Åtminstone tre olika parallella prov för varje masskoncentration vid de olika temperaturerna undersöktes. Upplösningssystemet bestod av ett 400 ml dekanterglas, en magnetomrörare samt ett värmeelement, en termometer och en baffel (se bilderna 1–3). Temperaturen fastställdes manuellt med hjälp av termometern och den estimerade temperaturfluktuationen var +/- 5 °C av den önskade temperaturen. Systemet var antingen öppet eller semi-öppet med ett folioomslag, vilket ledde till att en del oavsiktlig avdunstning av styren inte kunde fullständigt undvikas. Det eftersökta omrörningshastigheten var 500 rpm, men på grund av den högviskosa blandningen vid högre masskoncentrationer såsom över 20% sänktes omrörningshastigheten till 150–400 rpm, särskilt vid rumstemperaturen. Vid 70°C var lösningen tillräckligt lågviskös och kunde omröras med 500 rpm utan problem. Allmänt kan konstateras att magnetomrörarens kapacitet var otillräcklig för att blanda den högviskösa och gel-liknande blandningen effektivt längs hela massan, och särskilt ytan hade en tendens att stagnera. Lösligheten och upplösningstillståndet samt tiden för det fullständigt upplösta tillståndet var fastställda visuellt och med hjälp av en telefonkamera, vilket naturligtvis var problematiskt och ökade osäkerheten i resultaten. Standarden för en fullständig upplösning baserade sig på visuella observationer, dvs. en klar lösning utan synliga partiklar klassificerades som en fullständig upplösning.

Suspensionspolymerisationsexperimenten utfördes i laboratoriet med en satsreaktor kallad M-reaktor (M1). Satsreaktorn var utrustad med en omrörare, ett integrerat uppvärmnings/kylningssystem (olja), och ett reaktorkärl med en volym på 5–6 liter. Locket var tillslutet först vid impregneringsskedet, och utvecklingen av suspensionen kunde övervakas och prov kunde plockas tills detta. De olika produktionsstegen och temperaturprofilerna vid suspensionspolymerisationen använda i projektet finns i Figurerna 31 samt 32 och Tabellerna 16 samt 17. De använda råmaterialen och kemikalierna finns listade i Tabell 15. Massaförhållandet mellan styren (MS) och vatten eller MS+EPS och vatten hölls konstant genom hela projektets lopp. Det tillsätta EPS-materialet behandlades som identiskt råmaterial med MS så att massan EPS+MS-blandning var alltid identisk med referensprovet innehållande endast MS. Således hölls mängden inmatade peroxid konstant i alla prov. Detta antagande visade sig dock vara felaktigt. EPS var blandad i MS genom upplösning, antingen genom att direkt förupplösa blandningen i en glasflaska före laddning av satsreaktorn med diverse kemikalier, eller genom att upplösa EPS i styren (MS) direkt i suspensionen inför det aktuella polymerisationssteget (Polymerisationssteg I). Processvariabler justerades för att uppnå önskad partikelstorleksfördelning (PSD) genom att först och främst ställa in koncentrationen av de stabiliserande agenterna A samt B, och omrörningshastigheten. Förändring av inmatningshastigheten av det stabiliserande ämnet A var också ett annat alternativ som studerades. Reaktorn rengjordes vid behov, till exempel på grund av agglomeration, tilltäppning eller misslyckad polymerisation, med toluen och vatten. Denna procedur hade möjligtvis en inverkan på de erhållna resultaten eftersom de föregående data har visat sig att PSD resultaten har i någon grad förändrats efter rengöring av reaktorn.

Kvaliteten och materialegenskaper av de framgångsrikt producerade EPS-pärlorna undersöktes med hjälp av siktning (fördelning av partikelstorlek, PSD), och analyser för restmonomer (RM), pentanhalt (GC) samt molekylvikt (med SEC). Partikelgeometrin och formkvaliteten granskades visuellt. Därtill mättes för ett antal preskummade prov som formades till brickor deras skumningsstyrka, mekaniska (kompressions- och brytningsstyrka) och termiska (värmeledningsförmåga, lambda) egenskaper. Alla de uppmätta egenskaperna jämfördes med motsvarande egenskaper hos referens-EPS.

En lämplig partikelstorleksfördelning är ett av de viktigaste kriterierna för användbarheten av EPS i olika slags tillämpningar. Restmonomer (RM) är en viktig indikator på polymerisationsgraden, och målet är allmänt att nå restmonomer halter mindre än 1000 ppm. Molekylvikten inverkar på de mekaniska egenskaperna och på cellbildningen. Pentaninnehållet uppmättes också för alla prov innan formgjutning. En del utvalda polymerssatser preskummades och konverterades via formgjutning till brickor. Efteråt mättes den termiska förskumningsstyrkan, isoleringsförmågan (lambda, λ) och de mekaniska egenskaperna såsom brytnings- och kompressionsstyrkan. Kompressionsstyrkan mättes i enlighet med standard SFS-EN 826 och brytningsstyrkan med SFS-EN 12089.

10.3 Resultat och diskussion

Alla relevanta resultat av upplösningstider, partikelstorleksfördelningar (PSD), restmonomer, molekylvikter, och termiska (isoleringsförmåga, λ) samt mekaniska egenskaper (brytnings- och kompressionsstyrkan) finns samlade i tabeller (se Appendix). Ytterligare finns det bilder i Appendix bland annat av de polymeriserade EPS produkterna och agglomerationer i reaktorn.

Upplösning av EPS leder till en viskös och klibbig gel-liknande lösning. Ju högre EPS halten är desto högre blir viskositeten, naturligtvis. Lösningen har en tendens att bli klibbig och forma avlagringar på ytor. Följande allmänna observationer av problem som uppstod särskilt vid EPS-masskoncentrationer 20% eller högre i samband med låga temperaturer som höjer upplösningshastigheten av den hög-viskösa och klibbiga lösningen gjordes:

- tendens för sammansmältning och fastklistrande i klimpar, och
- ojämn omrörning och omrörningsproblem generellt, särskilt vid ytan och de ytliga delarna av lösningen (formation av ett ytlager och flytande partiklar på ytan).

Upp till 30 viktprocent av alla de tre olika EPS-kvaliteterna löstes upp i MS framgångsrikt oberoende av temperatur (25 °C, 50°C och 70°C). De erhållna upplösningsresultaten var till största delen förväntade och logiska, men inte fullständigt. Underdimensionerat ”off-spec”-EPS (LOF) löste sig snabbast, vilket var förväntat eftersom polymeren var mycket fin och nästan i sand-liknande form. Emedan överdimensionerat (HOF) och extruderad återvunnen (ERE) EPS bestod av större och grova partiklar. ERE löste sig generellt näst snabbaste och HOF krävde de längsta tiderna för upplösning. EREs betydligt lägre MW värde jämfört med LOF och HOF bidrog också till det relativt goda och snabba lösligheten av ERE i styren [59]. I allmänhet, leder en förhöjning av temperaturen till en minskning av tiden som krävs för fullständig upplösning av EPS [61]. Däremot, fanns det nog vissa undantag till den regeln i resultaten. Exempelvis i vissa fall var den genomsnittliga upplösningshastigheten lägre för 50°C än 70°C så som Tabeller 21 och 22 visar. Enligt resultaten var det genomsnittliga förhållandet mellan upplösningstiderna vid 50°C och 70°C 1, som är underligt minst sagt (se Tabell 22). Ytterligare fanns det inkonsekvenser av upplösningstider med höjda EPS-viktprocenter, det vill säga, med högre EPS-koncentrationer nådde man lägre upplösningstider (se Figurer 27 och 28). Variationen var också relativt hög i LOF- och HOF-proven, särskilt vid rumstemperatur så som Figur 26 och Tabell 15 visar. Det fanns ett flertal problem, aspekter och osäkerhetsfaktorer i upplösningsexperimentering som bör beaktas när man analyserar resultaten:

1. upplösningssystemet var antingen öppet eller semi-öppet, och eventuell avdunstning av styren under själva experimenten kunde ej uteslutas varvid den registrerade upplösningsprocenten blev lägre än i verkligheten,

2. upplösningsgraden fastställdes visuellt, vilket ger utrymme för tolkning av en fullständigt klar lösning (t.ex. luftbubblor, orenheter, och väldigt fina EPS partiklar problematiska),
3. omrörningen var inte tillräcklig, och
4. värmefluktuationen var signifikant, åtminstone +/- 5 °C grader.

Målet vid polymerisationsexperimenteringen var att nå så höga återanvändningsgrader (massfraktion) av LOF-, HOF- och ERE-EPS som möjligt i produktion av nybildad EPS med korrekt partikelstorleksfördelning. Speciellt ville man undvika formation av LOF-fraktion i den nybildade EPS:n. Utöver analyser för EPS-pärlor, sammanfattas i Tabell 26 i Appendix-delen alla polymerisationsförsök inklusive både de lyckade och misslyckade försöken. Tabell 27 listar pentanhalter (storleksordning: LOF>HOF>ERE) och molekylvikter (storleksordning: LOF>HOF>ERE) av de tre experimenterade EPS-kvaliteterna. Resultaten visar att HOF och LOF EPS är kemiskt identiska men skiljer sig i upplösningshastigheten eftersom HOF har en större partikelstorlek än LOF. HOFs långsammare upplösning jämfört med LOFs avspeglas även i polymerisationsexperimenten. Dvs. i försöken där 5 viktprocent av MS ersättas med HOF och upplöstes direkt i styrensuspensionen resulterade i en större genomsnittlig partikelstorlek och en skiftning av partikelstorleksfördelningen mot större storlek i jämförelse med LOF-experimentet under samma reaktionsbetingelser. Emedan när upplösningstiderna för HOF-proven förlängdes blev PSD-kurvorna relativt identiska med LOF-proven. De mest centrala polymerisationsresultaten är angivna i kapitel 8. De största utmaningarna vid återvinning av EPS i suspensionspolymerisation var skumbildning, att åstadkomma en tillräckligt effektiv omrörning, att undvika agglomeration i reaktorn och att uppnå korrekt PSD. De största osäkerhetsfaktorerna under projektets lopp är listade nedan.

1. Vid beräkning av peroxidkoncentrationen försummades mängden återvunnen EPS.
2. Både omrörningen (rpm) och stabiliseringen höjdes samtidigt för att förbättra PSD (därav är det svårt att fastställa vilkendera parametern som påverkade processen mera)
3. Bristfällig kontroll av det stabila tillståndet.
4. Ökad kvalitetskontroll av pärlorna med hjälp av mikroskop och ökad mängd av skumningsstyrka/expanderingen försök skulle ha gett mera information om orsak och verkan.
5. Svårigheter att fastställa den exakta mängden av producerade EPS (svårt att fastställa hur stor del av satsen var förlorat pga. agglomeration i reaktorn).

I allmänhet, framgår det av resultaten att en ökning i omrörning (varvtal, rpm) och koncentration av stabiliserande ämnen sänker den genomsnittliga partikelstorleken, och PSD skiftar till minde partikelstorlekar. De erhållna genomsnittliga partikelstorlekarna (d-50) är samlade i de jämförande graferna i Figurerna 34 och 35. Omrörningens och stabiliseringskoncentrationens inverkan på partikelstorlekarna vid olika återanvänd EPS-koncentrationer är samlade i tabellerna 18 och 19. Under det experimentella arbetet gjordes även följande observationer: för att erhålla en stabil suspension måste omrörningen vara tillräckligt kraftfull och att de stabiliserande ämnenas koncentration måste vara tillräckligt hög. Upplösning av EPS i MS höjde viskositeten i reaktionsblandningen, och för att bibehålla en stabil suspension var man tvungen att öka omrörningen, speciellt med ökande halt av återvunnen EPS. Emellertid, kan en ökad omrörning öka tendensen för bildning av väldigt fina EPS-partiklar och skum, vilket är icke önskvärt. Ökning av stabiliseringskoncentrationen ensam verkar inte att markant bidra till stabilisering av suspensionen och möjligtvis ökar det enbart skumningen.

Den mest kritiska punkten för suspensionspolymerisationen var vid det ”klimpiga stadiet” där viskositeten ökar kraftigt och tendensen för agglomeration av polymerpartiklarna är överhängande. Återanvänd-ERE innehållande prov var särskilt problematiska och för att uppnå och bibehålla en stabil suspension var man tvungen att ändra tiden för tillsatsen av det stabiliserande ämnet A och tillsätta ämnet genast i början till suspensionsblandningen, medan HOF- och LOF-EPS innehållande satser lyckades med det konventionella referensreceptet. Utmaningen med detta tillvägagångssätt var att partikelstorlekarna av ERE-försök blev för små (jämför Figurer 33 och 34 och Tabeller 18 och 19). Positivt med de mest framgångsrika försöken som innehöll återanvänd-EPS var det faktum att med identiska partikelstorlekar med referenser nådde man lägre halter av underdimensionerad EPS så som referenslinjerna i Figurerna 33 och 34 påvisar. Satserna som innehöll återanvänt EPS hade dock andra problem så som till exempel ökad bildning av överdimensionerad EPS och sämre kvalitet på polymerpärlorna. Pärlornas kvalitet särskilt i de ERE innehållande proven var snarare ovala än sfäriska, vilket sedan föranledde problem vid expandering och formgjutning. Den generella trenden verka vara att RM (styrenkoncentration) sjunker med ökande återanvänd EPS-halt (se Figur 32). Trenden verifierades även genom visuella observationer under polymerisation där den stabila punkten hade flyttats till en tidigare tidpunkt och desto högre EPS-halten var desto tidigare nåddes punkten. Den inmatade överloppsperoxiden bidrar dock även till detta fenomen. MW-värden sjönk med ökande återanvänt EPS-halt (se Figur 37), medan polydispersiteten (PD), utöver ett par undantag, sjönk med ökande återanvänd EPS-halt, vilket var förväntat eftersom PD-indexen för HOF, LOF och ERE var signifikant lägre jämfört med referensprovets. Enligt mekaniska tester, kan kompressionsstyrkan till och med växa en aning (se Figur 41), medan brytningsstyrkan minskade (se Figur 42). Lambda-värdet, det vill säga den termiska isoleringsförmågan, verka minska jämfört med referenser, vilket också är icke-önskvärt (se Figur 43).

10.4 Slutsatser

Löslighetsförsök upp till 30 viktprocent av tre olika EPS-kvaliteter i styren gav relativt tillförlitliga resultat. Alla EPS-proven kunde framgångsrikt lösas i styren (MS) vid alla de tre undersökta temperaturerna i laboratorieskala. Tydliga skillnader mellan kvaliteternas löslighet noterades i avseende på tiden för upplösning och temperaturökningens positiva inverkan på lösligheten kunde bekräftas. Min personliga slutsats på basen av resultaten är att en separat EPS upplösningstank för återvunnen EPS skulle vara den mest praktiska lösningen i industriell skala, speciellt vid höga halter av återvunnen EPS. Detta kan dock möjligtvis orsaka tekniska problem pga. klibbigheten hos den högviskösa massan. Emedan, små mängder av EPS eller PS skulle möjligtvis kunna upplösas direkt i suspension på basen av polymeriseringsresultaten. De facto, är de uppmätta tiderna för upplösnings enbart är visuellt bestämda sänker pålitligheten av resultaten något. Ifall upplösningen av EPS eller PS i MS forskas vidare kunde följande förbättringsförslag beaktas:

1. Upplösningsbehållaren bör vara ett slutet system, och helst utrustad med en automatisk temperaturkontroll.
2. Upplösningsbehållaren måste vara utrustad med en optimal mekanisk omrörare.
3. Upplösningstillståndet måste kontrolleras med hjälp av transmittans- eller viskositetsmätning.

Suspensionspolymerisationsexperimenten gav varierande resultat när upp till 20 viktsprocent av EPS var återanvänt i reaktorn (M1) i laboratoriumskala. Generellt, gav de återanvända ”off-spec”-EPS, mestadels LOF-EPS, innehållande proven bättre resultat både i avseende på pärlornas kvalitet och mängden producerade underdimensionerad EPS än proven som innehöll återanvänd extruderad EPS (ERE). Det fanns inte tillräckligt med tid för att fullständigt utreda potentialen för återanvändning av ERE, och stabiliserings- samt omrörningsnivåerna var valda på basen av resultaten erhållna ur återanvänt ”off-spec”-EPS, antingen HOF eller LOF, innehållande proven. Däremot, för att bibehålla den stabila suspensionen i ERE-satser var man tvungen att förändra tidpunkten för inmatning av stabiliserande ämnet A. Tyvärr hade det stabiliserande ämnet A en drastisk inverkan på partikelstorleken. Den genomsnittliga partikelstorleken minskade och mängden producerat LOF-EPS ökade. Utöver detta försämrades partikelformen från sfärisk till oval i de båda grupperna innehållande återanvänt ”off-spec”-EPS såväl som ERE. I ERE innehållande proven var partikelformen anmärkningsvärt sämre än i ”off-spec”-EPS.

Utmaningar för industriell produktion är:

- partikelformen,
- skumning och instabilitet av polymersuspensionen,
- förorening av reaktorn (t.ex. agglomerationer på reaktorytor) samt blockeringar,
- problem med överföring av produkten,
- inadekvat omrörning,
- rengöring av reaktorn, och slutligen,
- avbrott i produktionen.

För att förbättra PS-återvinningsprocessen via suspension polymerisation vore det på sin plats att vidare optimera partikelstorleksfördelningen (PSD) genom följande åtgärder:

1. Reduktion av peroxidmängden i samma förhållande som mängden styren i reaktorn (alltså i minus återvunnen EPS),
2. minskning av viskositeten genom att öka förhållandet mellan vatten till styren (även om producerat EPS per sats blir lägre),
3. reducering av den totala mängden monomer i reaktorn och således förbättras omrörningen,
4. optimera strukturen av omröraren, möjligtvis med förbättrad vertikal omrörning,
5. reducering av skumning med hjälp av kemikalier såsom skumdämpare,
6. höjning av stabiliseringskoncentration eller reducering av omrörningshastighet eller vice versa, och
7. optimera omrörningshastigheten enligt polymerisationens olika stadier (t.ex. förhöjning av omrörningshastigheten under klibbiga stadium).

Ifall fortsatta studier för suspensionspolymerisation skall utföras, vore det ändamålsenligt att utreda hur upplöst “off-spec”-EPS inverkar på processen i pilot- och produktionsskala. Man bör även beakta att ERE innehåller avsevärt större mängder av orenheter i jämförelse med “off-spec”-EPS (HOF och LOF). Därav borde man även utreda möjligheten att utveckla någon sorts filtrerings- eller extraktionsteknik för att avlägsna tillsatsmedel eller orenheter ur ERE, eller även för av PS- och EPS-avfall i framtiden.

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Appendix

A. Dissolution Data

Collection of all the relevant dissolution samples																										
LOF									HOF									ERE								
25°C (Room Temp.)			50°C			70°C			25°C (Room Temp.)			50°C			70°C			25°C (Room Temp.)			50°C			70°C		
t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%	t [min]	t [h]	EPS wt-%
17	0.28	5%	11	0.18	5%	6	0.10	5%	110	1.83	5%	51	0.85	5%	38	0.63	5%	31	0.52	5%	20	0.33	5%	15	0.25	5%
59	0.98	5%	12	0.20	5%	8	0.13	5%	54	0.90	5%	42	0.70	5%	38	0.63	5%	41	0.68	5%	24	0.40	5%	16	0.27	5%
67	1.12	5%	17	0.28	5%	8	0.13	5%	100	1.67	5%	50	0.83	5%	43	0.72	5%	47	0.78	5%	25	0.42	5%	15	0.25	5%
35	0.58	10%	19	0.32	10%	11	0.18	10%	79	1.32	5%	53	0.88	10%	51	0.85	10%	39	0.65	10%	30	0.50	10%	18	0.30	10%
19	0.32	10%	14	0.23	10%	12	0.20	10%	105	1.75	10%	45	0.75	10%	54	0.90	10%	45	0.75	10%	26	0.43	10%	21	0.35	10%
25	0.42	10%	10	0.17	10%	10	0.17	10%	288	4.80	10%	45	0.75	10%	56	0.93	10%	50	0.83	10%	25	0.42	10%	22	0.37	10%
31	0.52	10%	34	0.57	15%	22	0.37	15%	96	1.60	10%	48	0.80	15%	55	0.92	15%	111	1.85	15%	22	0.37	10%	29	0.48	15%
31	0.52	15%	14	0.23	15%	22	0.37	15%	120	2.00	10%	65	1.08	15%	41	0.68	15%	125	2.08	15%	34	0.57	15%	30	0.50	15%
104	1.73	15%	13	0.22	15%	15	0.25	15%	73	1.22	15%	60	1.00	15%	67	1.12	15%	135	2.25	15%	34	0.57	15%	27	0.45	15%
68	1.13	15%	42	0.70	20%	35	0.58	20%	104	1.73	15%	62	1.03	20%	106	1.77	20%	125	2.08	20%	46	0.77	15%	41	0.68	20%
26	0.43	20%	17	0.28	20%	23	0.38	20%	78	1.30	15%	67	1.12	20%	82	1.37	20%	160	2.67	20%	60	1.00	20%	53	0.88	20%
46	0.76	20%	37	0.62	20%	27	0.45	20%	210	3.50	20%	67	1.12	20%	72	1.20	20%	140	2.33	20%	98	1.63	20%	45	0.75	20%
37	0.62	20%	37	0.62	25%	30	0.50	25%	90	1.50	20%	182	3.03	25%	84	1.40	25%	225	3.75	25%	62	1.03	20%	59	0.98	25%
44	0.73	25%	89	1.48	25%	80	1.33	25%	129	2.15	20%	98	1.63	25%	153	2.55	25%	170	2.83	25%	110	1.83	25%	67	1.12	25%
60	1.00	25%	20	0.33	25%	34	0.57	25%	224	3.73	25%	132	2.20	25%	163	2.72	25%	205	3.42	25%	95	1.58	25%	69	1.15	25%
89	1.48	25%	70	1.17	30%	45	0.75	30%	180	3.00	25%	167	2.78	30%	87	1.45	30%	345	5.75	30%	105	1.75	25%	90	1.50	30%
70	1.17	30%	52	0.87	30%	65	1.08	30%	158	2.63	25%	180	3.00	30%	145	2.42	30%	360	6.00	30%	150	2.50	30%	110	1.83	30%
109	1.82	30%	25	0.42	30%	43	0.72	30%	540	9.00	30%	250	4.17	30%	245	4.08	30%	380	6.33	30%	180	3.00	30%	105	1.75	30%
120	2.00	30%							402	6.70	30%										180	3.00	30%			
									600	10.00	30%															

Vessel
400 ml beaker

EPS wt-%	Total mass [g]	MS [g]	EPS [g]
5%	180	171	9
10%	180	162	18
15%	180	153	27
20%	180	144	36
25%	180	135	45
30%	180	126	54

Table 20. A collection of the relevant dissolution results.

Low off-spec EPS (K-1310)												
25°C (room temperature)				50°C				70°C				EPS wt%
[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	
48	0.79	57.14%	0.28 1.12	13	0.22	0.29%	0.18 0.28	7	0.12	14.52%	0.18 0.28	5%
28	0.46	25.45%	0.32 0.58	14	0.24	0.56%	0.17 0.32	11	0.18	9.09%	0.17 0.2	10%
68	1.13	53.94%	0.52 1.73	20	0.34	3.90%	0.22 0.57	20	0.33	20.55%	0.25 0.37	15%
36	0.60	12.54%	0.43 0.76	32	0.53	4.86%	0.28 0.7	28	0.47	21.57%	0.38 0.58	20%
64	1.07	35.46%	0.73 1.48	49	0.81	35.90%	0.33 1.48	48	0.80	57.89%	0.5 1.33	25%
100	1.66	26.36%	1.17 2.00	49	0.82	14.25%	0.42 1.17	51	0.85	54.48%	0.75 1.08	30%

	Dissolution time at 70°C in comparison to	
	25°C	50°C
	15%	54%
	40%	77%
	29%	97%
	78%	89%
	75%	98%
	51%	104%
Average	48%	86%
SD	25%	18%
CV	52%	21%

Table 21. A collection of dissolution results of LOF (undersized off-spec EPS).

High off-spec EPS (K-110)												
25°C (room temperature)				50°C				70°C				EPS wt%
[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	
86	1.43	28.92%	0.90	48	0.79	10.35%	0.9	40	0.66	7.28%	0.63	5%
			1.83				1.83				0.72	
163	2.72	66.47%	1.60	48	0.79	9.69%	0.75	54	0.89	4.69%	0.85	10%
			4.80				0.88				0.93	
85	1.42	19.58%	1.22	58	0.96	15.15%	0.8	54	0.91	23.95%	0.68	15%
			1.73				1.08				1.12	
143	2.38	42.81%	1.50	65	1.09	4.42%	1.03	87	1.44	20.16%	1.2	20%
			3.50				1.12				1.77	
187	3.12	17.94%	2.63	137	2.29	30.77%	1.63	133	2.22	32.26%	1.4	25%
			3.73				3.03				2.72	
514	8.57	19.75%	6.70	199	3.32	22.43%	2.78	159	2.65	50.27%	1.45	30%
			10.00				4.17				4.08	

	Dissolution time at 70°C in comparison to	
	25°C	50°C
	46%	84%
	33%	113%
	64%	95%
	60%	132%
	71%	97%
	31%	80%
Average	51%	100%
SD	17%	20%
CV	33%	20%

Table 22. A collection of dissolution results of HOF (oversized off-spec EPS).

Extruded recycled EPS												
25°C (room temperature)				50°C				70°C				EPS wt%
[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	[min]	[h]	Variation (CF)	Min/Max [h]	
40	0.66	20.38%	0.52	23	0.38	11.50%	0.33	15	0.26	3.77%	0.25	5%
			0.78				0.42				0.27	
45	0.74	12.33%	0.65	24	0.41	8.55%	0.37	20	0.34	10.24%	0.3	10%
			0.83				0.43				0.37	
79	1.31	9.75%	1.85	38	0.63	18.23%	0.57	29	0.48	5.33%	0.45	15%
			2.25				0.77				0.5	
125	2.08	12.39%	2.08	73	1.22	29-16%	1.00	46	0.77	13.19%	0.68	20%
			2.67				1.63				0.88	
200	3.33	13.92%	2.83	103	1.72	7.39%	1.58	65	1.08	8.14%	0.98	25%
			3.75				1.83				1.15	
362	6.03	4.86%	5.75	165	2.75	10.19%	2.50	102	1.69	10.24%	1.50	30%
			6.33				3.00				1.75	

	Dissolution time at 70°C in comparison to	
	25°C	50°C
	39%	67%
	46%	84%
	36%	75%
	37%	63%
	33%	63%
	28%	62%
Average	36%	69%
SD	6%	9%
CV	16%	13%

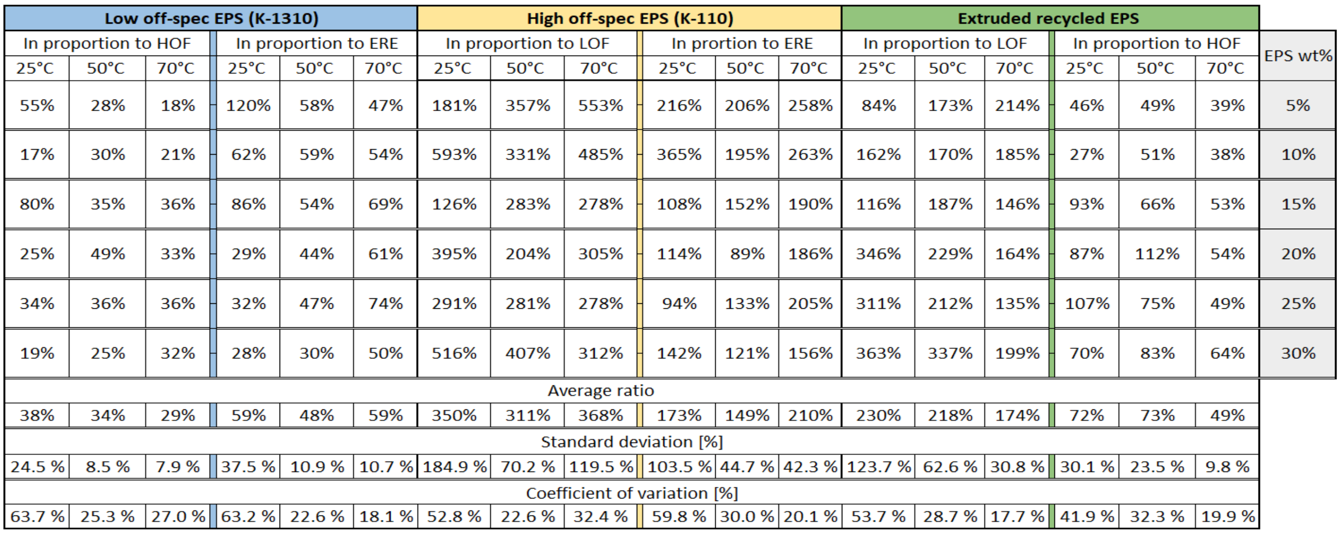
Table 23. A collection of dissolution results of ERE (extruded recycled EPS).

LOF 25°C				
Average t [min]	Average t [h]	EPS wt-%	SD	CV [%]
48	0.79	5%	0.45	57.14%
28	0.46	10%	0.12	25.45%
68	1.13	15%	0.61	53.94%
36	0.60	20%	0.08	12.54%
64	1.07	25%	0.38	35.46%
100	1.66	30%	0.44	26.36%
LOF 50°C				
13	0.22	5%	0.05	24.11%
14	0.24	10%	0.08	31.46%
20	0.34	15%	0.20	58.26%
32	0.53	20%	0.22	41.34%
49	0.81	25%	0.60	73.87%
49	0.82	30%	0.38	46.22%
LOF 70°C				
7	0.12	5%	0.02	14.52%
11	0.18	10%	0.02	9.09%
20	0.33	15%	0.07	20.55%
28	0.47	20%	0.10	21.57%
48	0.80	25%	0.46	57.89%
51	0.85	30%	0.20	54.48%

HOF 25°C				
Average t [min]	Average t [h]	EPS wt-%	SD	CV [%]
86	1.43	5%	0.41	28.92%
163	2.72	10%	1.81	66.47%
85	1.42	15%	0.28	19.58%
143	2.38	20%	1.02	42.81%
187	3.12	25%	0.56	17.94%
514	8.57	30%	1.69	19.75%
HOF 50°C				
48	0.79	5%	0.08	10.35%
48	0.79	10%	0.08	9.69%
58	0.96	15%	0.15	15.15%
65	1.09	20%	0.05	4.42%
137	2.29	25%	0.70	30.77%
199	3.32	30%	0.74	22.43%
HOF 70°C				
40	0.66	5%	0.05	7.28%
54	0.89	10%	0.04	4.69%
54	0.91	15%	0.22	23.95%
87	1.44	20%	0.29	20.16%
133	2.22	25%	0.72	32.26%
159	2.65	30%	1.33	50.27%

ERE 25°C				
Average t [min]	Average t [h]	EPS wt-%	SD	CV [%]
40	0.66	5%	0.13	20.38%
45	0.74	10%	0.09	12.33%
124	2.06	15%	0.20	9.75%
142	2.36	20%	0.29	12.39%
200	3.33	25%	0.46	13.92%
362	6.03	30%	0.29	4.86%
ERE 50°C				
23	0.38	5%	0.04	11.50%
24	0.41	10%	0.03	8.55%
38	0.63	15%	0.12	18.23%
73	1.22	20%	0.36	29.16%
103	1.72	25%	0.13	7.39%
170	2.83	30%	0.29	10.19%
ERE 70°C				
15	0.26	5%	0.01	3.77%
20	0.34	10%	0.03	10.24%
29	0.48	15%	0.03	5.33%
46	0.77	20%	0.10	13.19%
65	1.08	25%	0.09	8.14%
102	1.69	30%	0.17	10.24%

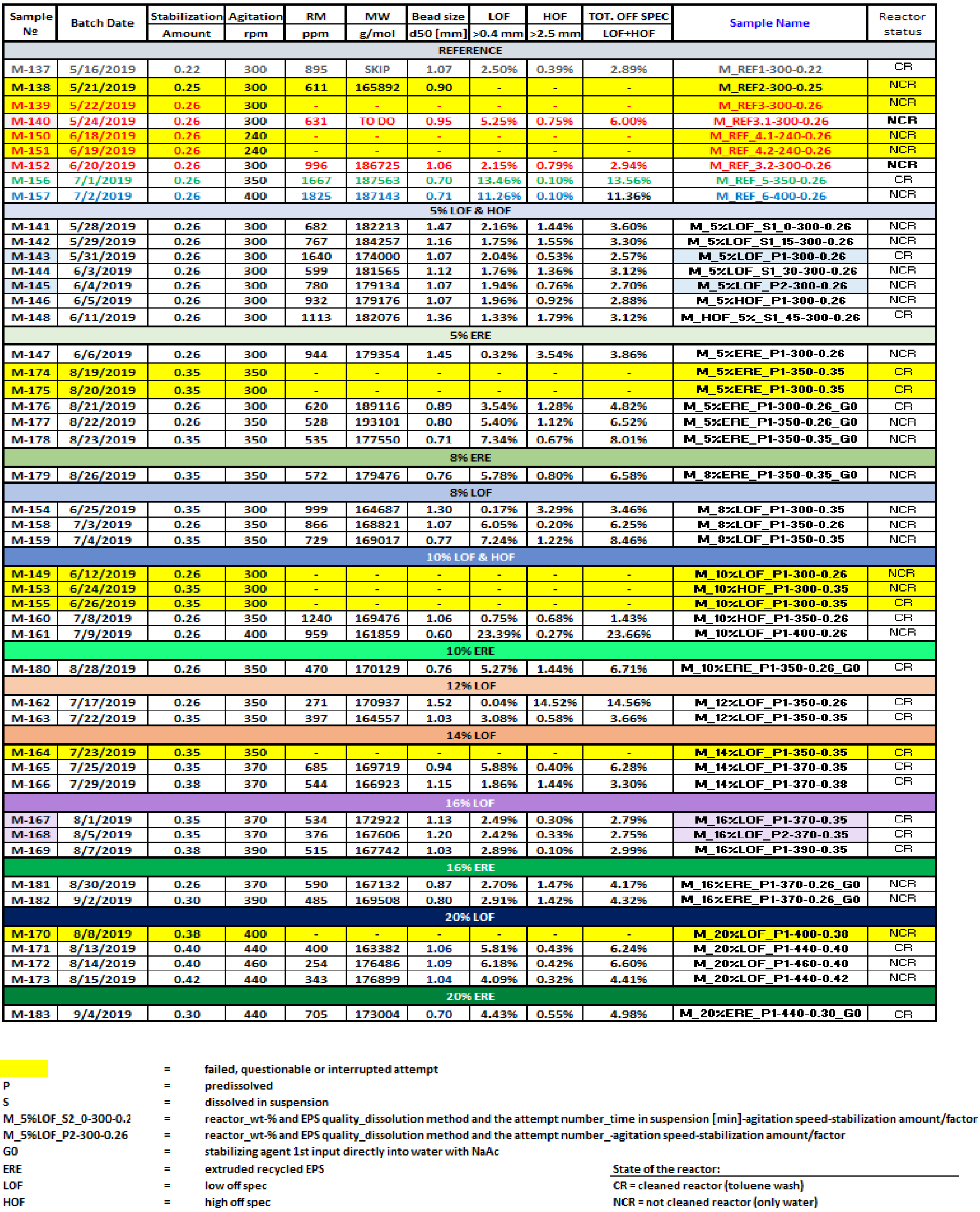
Table 24. A collection of solubility experimentation data.



Low off-spec EPS (K-1310)						High off-spec EPS (K-110)						Extruded recycled EPS						
In proportion to HOF			In proportion to ERE			In proportion to LOF			In portion to ERE			In proportion to LOF			In proportion to HOF			EPS wt%
25°C	50°C	70°C	25°C	50°C	70°C	25°C	50°C	70°C	25°C	50°C	70°C	25°C	50°C	70°C	25°C	50°C	70°C	
55%	28%	18%	120%	58%	47%	181%	357%	553%	216%	206%	258%	84%	173%	214%	46%	49%	39%	5%
17%	30%	21%	62%	59%	54%	593%	331%	485%	365%	195%	263%	162%	170%	185%	27%	51%	38%	10%
80%	35%	36%	86%	54%	69%	126%	283%	278%	108%	152%	190%	116%	187%	146%	93%	66%	53%	15%
25%	49%	33%	29%	44%	61%	395%	204%	305%	114%	89%	186%	346%	229%	164%	87%	112%	54%	20%
34%	36%	36%	32%	47%	74%	291%	281%	278%	94%	133%	205%	311%	212%	135%	107%	75%	49%	25%
19%	25%	32%	28%	30%	50%	516%	407%	312%	142%	121%	156%	363%	337%	199%	70%	83%	64%	30%
Average ratio																		
38%	34%	29%	59%	48%	59%	350%	311%	368%	173%	149%	210%	230%	218%	174%	72%	73%	49%	
Standard deviation [%]																		
24.5 %	8.5 %	7.9 %	37.5 %	10.9 %	10.7 %	184.9 %	70.2 %	119.5 %	103.5 %	44.7 %	42.3 %	123.7 %	62.6 %	30.8 %	30.1 %	23.5 %	9.8 %	
Coefficient of variation [%]																		
63.7 %	25.3 %	27.0 %	63.2 %	22.6 %	18.1 %	52.8 %	22.6 %	32.4 %	59.8 %	30.0 %	20.1 %	53.7 %	28.7 %	17.7 %	41.9 %	32.3 %	19.9 %	

Table 25. Comparison between dissolution times between different EPS qualities in proportion to each other.

B. Bead Analyses and Polymerization Data



Sample №	Batch Date	Stabilization Amount	Agitation rpm	RM ppm	MW g/mol	Bead size d50 [mm]	LOF >0.4 mm	HOF >2.5 mm	TOT. OFF SPEC LOF+HOF	Sample Name	Reactor status
REFERENCE											
M-137	5/16/2019	0.22	300	895	SKIP	1.07	2.50%	0.39%	2.89%	M_REF1-300-0.22	CR
M-138	5/21/2019	0.25	300	611	165892	0.90	-	-	-	M_REF2-300-0.25	NCR
M-139	5/22/2019	0.26	300	-	-	-	-	-	-	M_REF3-300-0.26	NCR
M-140	5/24/2019	0.26	300	631	TO DO	0.95	5.25%	0.75%	6.00%	M_REF3.1-300-0.26	NCR
M-150	6/18/2019	0.26	240	-	-	-	-	-	-	M_REF_4.1-240-0.26	NCR
M-151	6/19/2019	0.26	240	-	-	-	-	-	-	M_REF_4.2-240-0.26	NCR
M-152	6/20/2019	0.26	300	996	186725	1.06	2.15%	0.79%	2.94%	M_REF_3.2-300-0.26	NCR
M-156	7/1/2019	0.26	350	1667	187563	0.70	13.46%	0.10%	13.56%	M_REF_5-350-0.26	CR
M-157	7/2/2019	0.26	400	1825	187143	0.71	11.26%	0.10%	11.36%	M_REF_6-400-0.26	NCR
5% LOF & HOF											
M-141	5/28/2019	0.26	300	682	182213	1.47	2.16%	1.44%	3.60%	M_5%LOF_S1_0-300-0.26	NCR
M-142	5/29/2019	0.26	300	767	184257	1.16	1.75%	1.55%	3.30%	M_5%LOF_S1_15-300-0.26	NCR
M-143	5/31/2019	0.26	300	1640	174000	1.07	2.04%	0.53%	2.57%	M_5%LOF_P1-300-0.26	CR
M-144	6/3/2019	0.26	300	599	181565	1.12	1.76%	1.36%	3.12%	M_5%LOF_S1_30-300-0.26	NCR
M-145	6/4/2019	0.26	300	780	179134	1.07	1.94%	0.76%	2.70%	M_5%LOF_P2-300-0.26	NCR
M-146	6/5/2019	0.26	300	932	179176	1.07	1.96%	0.92%	2.88%	M_5%HOF_P1-300-0.26	NCR
M-148	6/11/2019	0.26	300	1113	182076	1.36	1.33%	1.79%	3.12%	M_HOF_5%_S1_45-300-0.26	CR
5% ERE											
M-147	6/6/2019	0.26	300	944	179354	1.45	0.32%	3.54%	3.86%	M_5%ERE_P1-300-0.26	NCR
M-174	8/19/2019	0.35	350	-	-	-	-	-	-	M_5%ERE_P1-350-0.35	CR
M-175	8/20/2019	0.35	300	-	-	-	-	-	-	M_5%ERE_P1-300-0.35	CR
M-176	8/21/2019	0.26	300	620	189116	0.89	3.54%	1.28%	4.82%	M_5%ERE_P1-300-0.26_G0	CR
M-177	8/22/2019	0.26	350	528	193101	0.80	5.40%	1.12%	6.52%	M_5%ERE_P1-350-0.26_G0	NCR
M-178	8/23/2019	0.35	350	535	177550	0.71	7.34%	0.67%	8.01%	M_5%ERE_P1-350-0.35_G0	NCR
8% ERE											
M-179	8/26/2019	0.35	350	572	179476	0.76	5.78%	0.80%	6.58%	M_8%ERE_P1-350-0.35_G0	NCR
8% LOF											
M-154	6/25/2019	0.35	300	999	164687	1.30	0.17%	3.29%	3.46%	M_8%LOF_P1-300-0.35	NCR
M-158	7/3/2019	0.26	350	866	168821	1.07	6.05%	0.20%	6.25%	M_8%LOF_P1-350-0.26	NCR
M-159	7/4/2019	0.35	350	729	169017	0.77	7.24%	1.22%	8.46%	M_8%LOF_P1-350-0.35	NCR
10% LOF & HOF											
M-149	6/12/2019	0.26	300	-	-	-	-	-	-	M_10%LOF_P1-300-0.26	NCR
M-153	6/24/2019	0.35	300	-	-	-	-	-	-	M_10%HOF_P1-300-0.35	NCR
M-155	6/26/2019	0.35	300	-	-	-	-	-	-	M_10%LOF_P1-300-0.35	CR
M-160	7/8/2019	0.26	350	1240	169476	1.06	0.75%	0.68%	1.43%	M_10%HOF_P1-350-0.26	CR
M-161	7/9/2019	0.26	400	959	161859	0.60	23.39%	0.27%	23.66%	M_10%LOF_P1-400-0.26	NCR
10% ERE											
M-180	8/28/2019	0.26	350	470	170129	0.76	5.27%	1.44%	6.71%	M_10%ERE_P1-350-0.26_G0	CR
12% LOF											
M-162	7/17/2019	0.26	350	271	170937	1.52	0.04%	14.52%	14.56%	M_12%LOF_P1-350-0.26	CR
M-163	7/22/2019	0.35	350	397	164557	1.03	3.08%	0.58%	3.66%	M_12%LOF_P1-350-0.35	CR
14% LOF											
M-164	7/23/2019	0.35	350	-	-	-	-	-	-	M_14%LOF_P1-350-0.35	CR
M-165	7/25/2019	0.35	370	685	169719	0.94	5.88%	0.40%	6.28%	M_14%LOF_P1-370-0.35	CR
M-166	7/29/2019	0.38	370	544	166923	1.15	1.86%	1.44%	3.30%	M_14%LOF_P1-370-0.38	CR
16% LOF											
M-167	8/1/2019	0.35	370	534	172922	1.13	2.49%	0.30%	2.79%	M_16%LOF_P1-370-0.35	CR
M-168	8/5/2019	0.35	370	376	167606	1.20	2.42%	0.33%	2.75%	M_16%LOF_P2-370-0.35	CR
M-169	8/7/2019	0.38	390	515	167742	1.03	2.89%	0.10%	2.99%	M_16%LOF_P1-390-0.35	CR
16% ERE											
M-181	8/30/2019	0.26	370	590	167132	0.87	2.70%	1.47%	4.17%	M_16%ERE_P1-370-0.26_G0	NCR
M-182	9/2/2019	0.30	390	485	169508	0.80	2.91%	1.42%	4.32%	M_16%ERE_P1-370-0.26_G0	NCR
20% LOF											
M-170	8/8/2019	0.38	400	-	-	-	-	-	-	M_20%LOF_P1-400-0.38	NCR
M-171	8/13/2019	0.40	440	400	163382	1.06	5.81%	0.43%	6.24%	M_20%LOF_P1-440-0.40	CR
M-172	8/14/2019	0.40	460	254	176486	1.09	6.18%	0.42%	6.60%	M_20%LOF_P1-460-0.40	NCR
M-173	8/15/2019	0.42	440	343	176899	1.04	4.09%	0.32%	4.41%	M_20%LOF_P1-440-0.42	NCR
20% ERE											
M-183	9/4/2019	0.30	440	705	173004	0.70	4.43%	0.55%	4.98%	M_20%ERE_P1-440-0.30_G0	CR

🟨 = failed, questionable or interrupted attempt
P = predissolved
S = dissolved in suspension
M_5%LOF_S2_0-300-0.2 = reactor_wt-% and EPS quality_dissolution method and the attempt number_time in suspension [min]-agitation speed-stabilization amount/factor
M_5%LOF_P2-300-0.26 = reactor_wt-% and EPS quality_dissolution method and the attempt number_-agitation speed-stabilization amount/factor
G0 = stabilizing agent 1st input directly into water with NaAc
ERE = extruded recycled EPS
LOF = low off spec
HOF = high off spec

State of the reactor:
CR = cleaned reactor (toluene wash)
NCR = not cleaned reactor (only water)

Table 26. A result collection of all polymerizations and bead analyses.

Raw Materials							
Quality	Pd	Mn	MW [g/mol]	Total C_5 [wt-%]	i-C_5	n-C_5	i-C_5 proportion
LOF	**2.25**	79819	**179 286**	**2.62%**	0.68%	1.94%	26.0 %
HOF	**2.27**	80028	**181 883**	**4.00%**	0.78%	3.22%	19.5 %
ERE	**2.21**	70686	**156 516**	**0.02%**	0.01%	0.01%	50.0 %

i-C_5 = isopentane
n-C_5 = pentane

Table 27. Pentane concentrations and molecular weight related values in the raw materials used in the project.

C. PSD Data

M-reactor																						
Sample	Oversized/HOF		Bead size														Undersized/LOF				<0,4 mm	>2,5 mm	TOT Off	d-50
№	Sample name	2.5	2.24	2	1.8	1.6	1.4	1.25	1.12	1	0.9	0.8	0.71	0.6	0.5	0.4	0.3	0.2	0.1	0	LOF %	HOF %	spec	mm
REFERENCE																								
M-137	M_REF1-300-0.22	0.39	0.13	0.39	0.91	2.72	9.32	17.09	13.73	14.11	12.30	7.90	6.86	6.73	3.37	1.55	1.17	0.85	0.44	0.04	2.50%	0.39%	2.89%	1.07
M-140	M_REF3.1-300-0.26	0.75	0.37	0.75	1.03	1.96	4.58	10.00	11.03	12.99	12.71	9.06	9.34	10.93	6.45	2.80	2.16	1.73	1.16	0.21	5.25%	0.75%	6.00%	0.95
M-152	M_REF_3.2-300-0.26	0.79	0.30	0.20	0.79	2.98	10.42	16.37	12.40	12.50	11.91	8.24	8.04	8.04	3.57	1.29	0.93	0.74	0.42	0.06	2.15%	0.79%	2.95%	1.06
M-156	M_REF_5-350-0.26	0.10	0.10	0.10	0.20	0.20	0.50	1.61	3.32	7.25	11.89	10.58	11.99	17.33	13.70	7.66	6.23	4.51	2.45	0.27	13.46%	0.10%	13.56%	0.70
M-157	M_REF_6-400-0.26	0.10	0.01	0.10	0.10	0.19	0.48	1.35	2.61	6.48	11.99	12.28	14.60	19.33	12.76	6.38	5.25	3.87	1.91	0.23	11.26%	0.10%	11.36%	0.71
5%																								
M-141	M_5%LOF_S1_0-300-0.26	1.44	0.29	0.38	1.72	5.84	14.46	17.81	11.58	11.30	9.67	6.61	6.13	6.22	3.06	1.34	1.05	0.80	0.30	0.01	2.16%	1.44%	3.60%	1.47
M-142	M_5%LOF_S1_15-300-0.26	1.55	1.44	3.51	9.07	18.76	24.54	16.19	7.63	5.46	3.92	2.17	1.55	1.24	0.72	0.52	0.62	0.66	0.44	0.03	1.75%	1.55%	3.30%	1.16
M-143	M_5%LOF_P1-300-0.26	0.53	0.21	0.32	1.59	6.26	13.25	13.99	9.54	9.97	10.71	8.27	8.38	9.12	4.35	1.48	0.94	0.67	0.38	0.04	2.04%	0.53%	2.57%	1.07
M-144	M_5%LOF_S1_30-300-0.26	1.36	0.39	0.58	1.66	5.26	13.25	16.57	10.92	10.62	9.65	7.41	7.70	7.99	3.61	1.27	0.88	0.61	0.26	0.01	1.76%	1.36%	3.13%	1.12
M-145	M_5%LOF_P2-300-0.26	0.76	0.19	0.29	0.86	3.82	11.47	15.87	12.04	11.85	10.61	8.03	8.22	8.79	3.92	1.34	0.90	0.75	0.29	0.01	1.94%	0.76%	2.70%	1.07
M-146	M_5%HOF_P1-300-0.26	0.92	0.31	0.31	1.23	4.70	12.05	15.42	10.62	10.31	9.70	7.86	8.68	10.01	4.49	1.43	0.91	0.73	0.32	0.01	1.96%	0.92%	2.88%	1.07
M-147	M_5%HOF_S1_45-300-0.26	1.79	0.63	1.16	4.52	12.71	23.64	19.75	9.56	7.67	5.88	3.57	3.05	2.73	1.37	0.63	0.55	0.51	0.26	0.01	1.33%	1.79%	3.12%	1.36
M-148	M_5%ERE_P1-300-0.26	3.54	1.11	1.82	5.87	16.19	29.35	22.16	9.31	5.36	2.83	1.01	0.51	0.30	0.20	0.10	0.13	0.13	0.05	0.01	0.32%	3.54%	3.87%	1.45
M-176	M_5%ERE_P1-300-0.26_G0	1.28	0.32	0.21	0.64	0.74	1.81	5.21	8.30	13.08	16.91	13.08	12.55	13.19	6.49	2.66	1.84	1.23	0.46	0.01	3.54%	1.28%	4.82%	0.89
M-177	M_5%ERE_P1-350-0.26_G0	1.12	0.34	0.34	0.45	0.79	1.35	2.59	4.50	9.22	14.96	13.84	14.51	17.44	9.34	3.82	2.69	1.84	0.84	0.02	5.40%	1.12%	6.52%	0.80
M-178	M_5%ERE_P1-350-0.35_G0	0.67	0.34	0.34	0.34	0.45	0.79	1.23	2.36	5.27	11.11	12.23	15.37	21.99	14.14	6.06	4.07	2.29	0.95	0.02	7.34%	0.67%	8.01%	0.71
8%																								
M-154	M_8%LOF_P1-300-0.35	3.29	1.49	1.91	3.29	7.53	17.50	22.81	15.06	12.73	8.06	3.39	1.59	0.85	0.21	0.11	0.08	0.05	0.02	0.01	0.17%	3.29%	3.46%	1.30
M-158	M_8%LOF_P1-350-0.26	0.20	0.10	0.20	0.61	2.73	10.63	17.01	12.96	12.25	10.73	6.78	5.97	6.78	4.35	2.63	2.38	2.07	1.41	0.20	6.05%	0.20%	6.26%	1.07
M-159	M_8%LOF_P1-350-0.35	1.22	0.51	0.41	0.41	0.51	1.32	3.56	5.70	9.46	12.61	10.88	11.49	16.07	12.51	6.10	3.86	1.99	1.19	0.19	7.24%	1.22%	8.46%	0.77
M-179	M_8%ERE_P1-350-0.35_G0	0.80	0.50	0.40	0.50	0.60	1.00	2.11	3.31	7.53	13.46	13.06	14.57	19.09	12.05	5.22	3.23	1.80	0.73	0.01	5.78%	0.80%	6.58%	0.76
10%																								
M-160	M_10%HOF_P1-350-0.26	0.68	0.23	0.23	0.80	2.73	8.88	14.68	13.89	17.07	16.05	10.47	7.74	4.78	0.80	0.23	0.26	0.33	0.15	0.01	0.75%	0.68%	1.43%	1.06
M-161	M_10%LOF_P1-400-0.26	0.27	0.18	0.18	0.18	0.27	0.55	1.55	2.74	5.11	7.76	7.12	8.67	15.07	15.98	10.96	11.50	8.64	2.78	0.47	23.39%	0.27%	23.67%	0.60
M-180	M_10%ERE_P1-350-0.26_G0	1.44	0.55	0.44	0.55	0.66	1.11	1.99	3.32	7.07	12.71	13.26	15.14	20.23	11.61	4.64	2.98	1.69	0.59	0.01	5.27%	1.44%	6.71%	0.76
12%																								
M-162	M_12%LOF_P1-350-0.26	14.52	2.33	2.54	5.83	15.37	24.59	16.85	7.74	5.09	3.07	1.17	0.53	0.21	0.11	0.01	0.01	0.01	0.01	0.01	0.04%	14.52%	14.56%	1.52
M-163	M_12%LOF_P1-350-0.35	0.58	0.19	0.19	0.58	3.99	11.00	14.30	10.61	11.87	11.87	7.98	7.69	8.66	5.06	2.34	1.51	1.02	0.54	0.01	3.08%	0.58%	3.67%	1.03
14%																								
M-165	M_14%LOF_P1-370-0.35	0.40	0.10	0.10	0.20	0.30	4.12	11.46	14.88	11.26	12.27	11.76	7.94	7.64	8.14	3.52	2.51	1.99	1.23	0.15	5.88%	0.40%	6.28%	0.94
M-166	M_14%LOF_P1-370-0.38	1.44	0.29	0.39	1.06	4.62	14.16	18.20	12.52	11.65	10.11	6.65	5.78	6.36	3.47	1.44	0.96	0.60	0.23	0.07	1.86%	1.44%	3.30%	1.15
16%																								
M-167	M_16%LOF_P1-370-0.35	0.30	0.10	0.30	1.21	4.83	14.27	18.09	12.16	11.26	9.55	6.13	5.83	6.74	4.42	2.31	1.65	0.61	0.21	0.02	2.49%	0.30%	2.79%	1.13
M-168	M_16%LOF_P2-370-0.35	0.33	0.11	0.44	2.28	8.16	17.41	17.41	10.44	9.36	8.27	5.44	5.44	6.42	4.03	2.07	1.28	0.75	0.37	0.01	2.42%	0.33%	2.74%	1.20
M-169	M_16%LOF_P1-390-0.38	0.10	0.10	0.10	0.60	2.61	9.75	15.18	11.96	12.47	11.46	7.84	7.64	8.95	5.53	2.81	1.82	0.70	0.34	0.02	2.89%	0.10%	2.99%	1.03
M-181	M_16%ERE_P1-370-0.26_G0	1.47	0.68	0.45	0.91	1.02	1.59	3.62	5.89	12.01	18.24	15.41	14.16	14.05	5.89	1.93	1.35	0.93	0.41	0.01	2.70%	1.47%	4.17%	0.87
M-182	M_16%ERE_P1-390-0.30_G0	1.42	0.54	0.54	0.87	1.09	1.52	2.50	4.03	8.16	15.13	14.69	15.67	18.18	9.36	3.37	1.75	0.78	0.35	0.02	2.91%	1.42%	4.32%	0.80
20%																								
M-171	M_20%LOF_P1-440-0.40	0.43	0.33	0.65	1.74	5.21	11.39	14.65	10.31	10.31	9.44	6.51	6.51	8.03	5.53	3.15	3.10	1.90	0.78	0.02	5.81%	0.43%	6.24%	1.06
M-172	M_20%LOF_P1-460-0.40	0.42	0.42	1.16	3.16	7.48	12.21	13.69	9.16	9.37	8.84	6.11	5.90	7.37	5.37	3.16	3.03	2.28	0.85	0.01	6.18%	0.42%	6.60%	1.09
M-173	M_20%LOF_P1-440-0.42	0.32	0.11	0.43	0.97	3.46	8.55	14.29	12.34	14.07	12.34	7.79	6.93	7.36	4.33	2.60	1.81	1.65	0.63	0.01	4.09%	0.32%	4.42%	1.04
M-183	M_20%ERE_P1-440-0.30_G0	0.55	0.11	0.22	0.44	0.44	0.99	1.43	1.54	3.09	7.05	12.01	18.41	28.00	15.65	5.62	2.87	1.23	0.32	0.01	4.43%	0.55%	4.98%	0.70

Table 28. A collection of particle size distribution data of all the samples.

Figure 44. A collection of HOF and LOF EPS formation at different average particle sizes of all the samples.

Off-spec EPS Formation

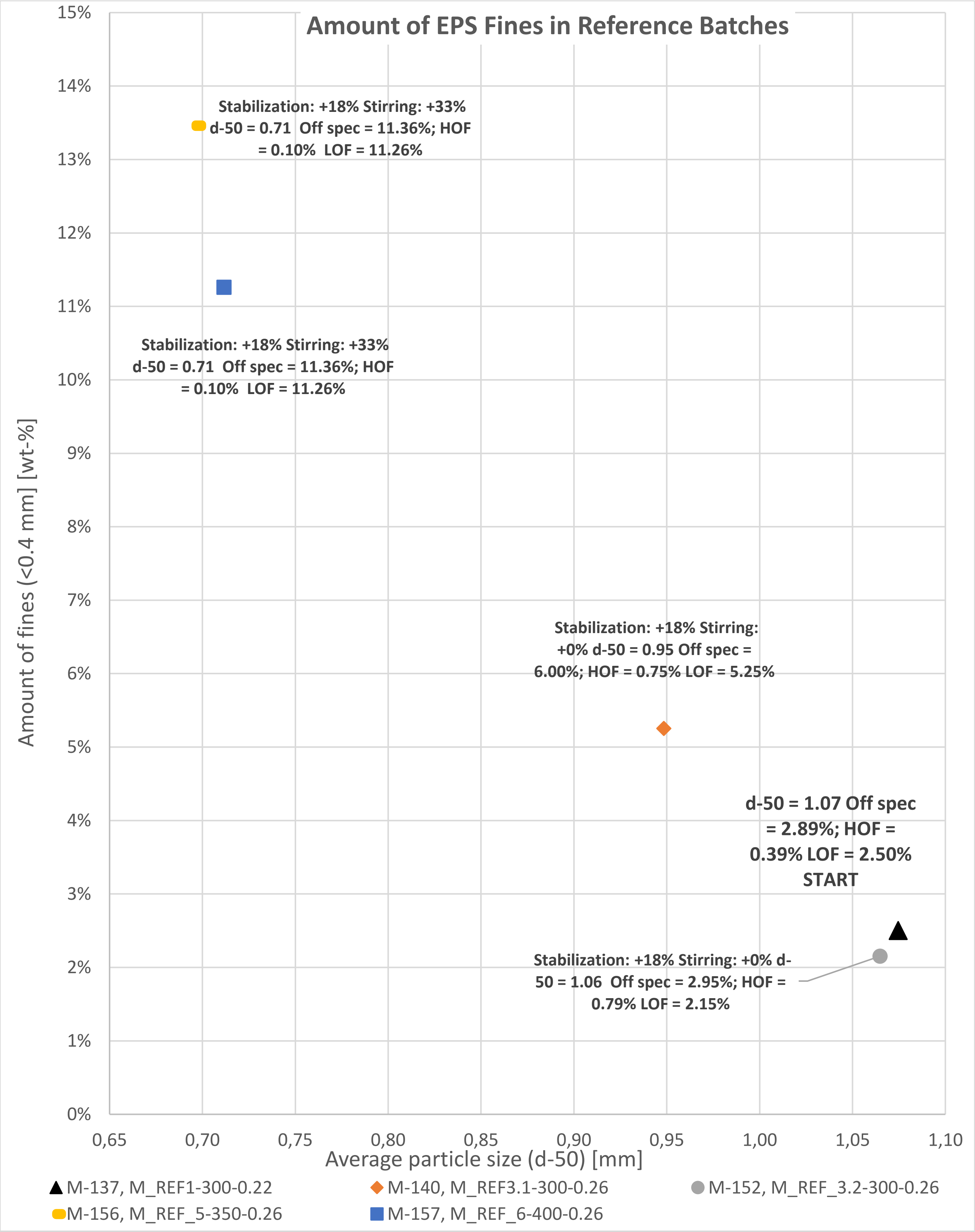


Figure 45. A collection of the EPS fines (LOF) formation at different average particle sizes in the reference samples with the level of agitation and stabilization concentration displayed.

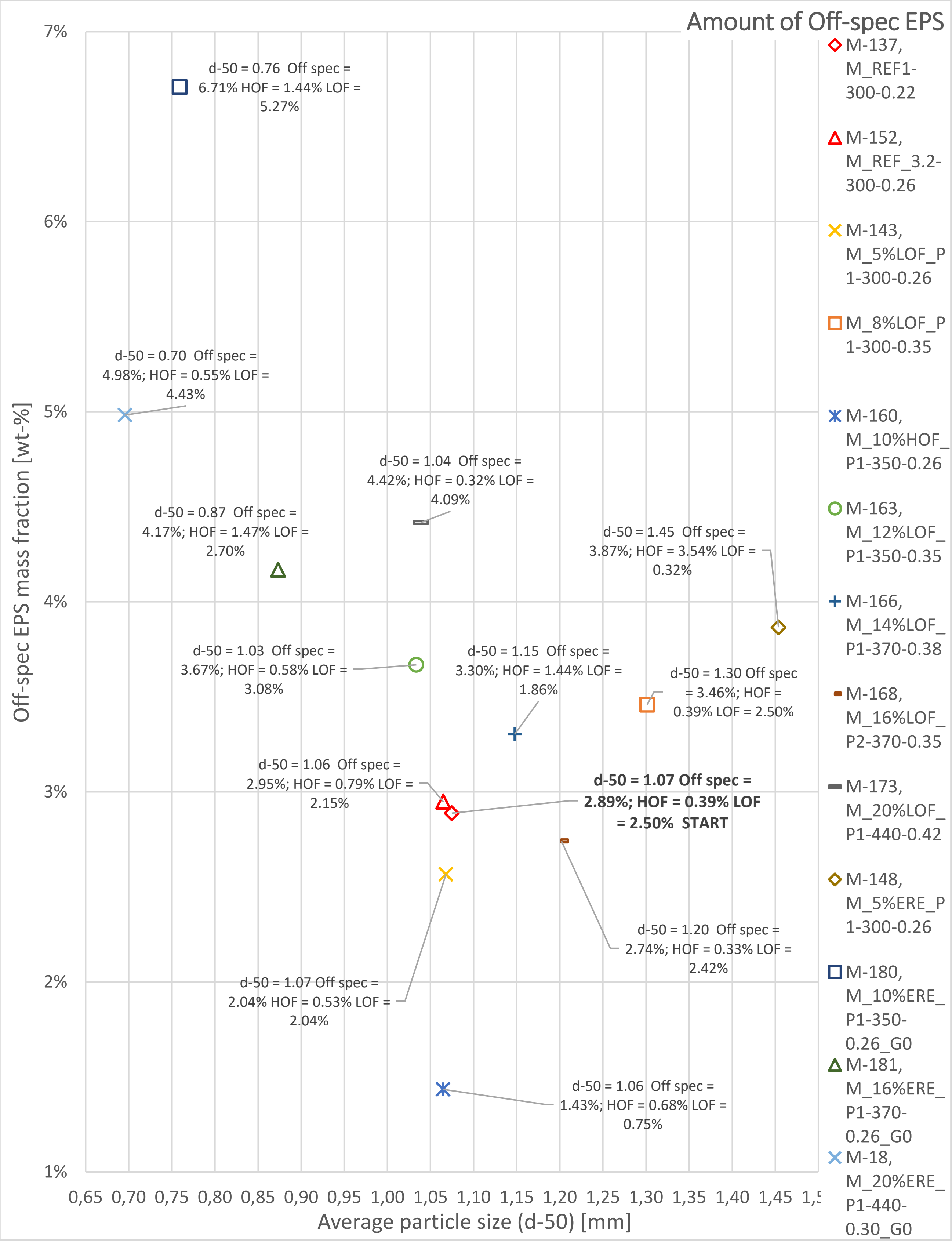


Figure 46. A collection of the most successful batches regarding off-spec EPS formation (HOF+LOF) of all the different sample qualities, references included, at different average particle sizes.

PSD, d-50 and Off-spec EPS Curves

References

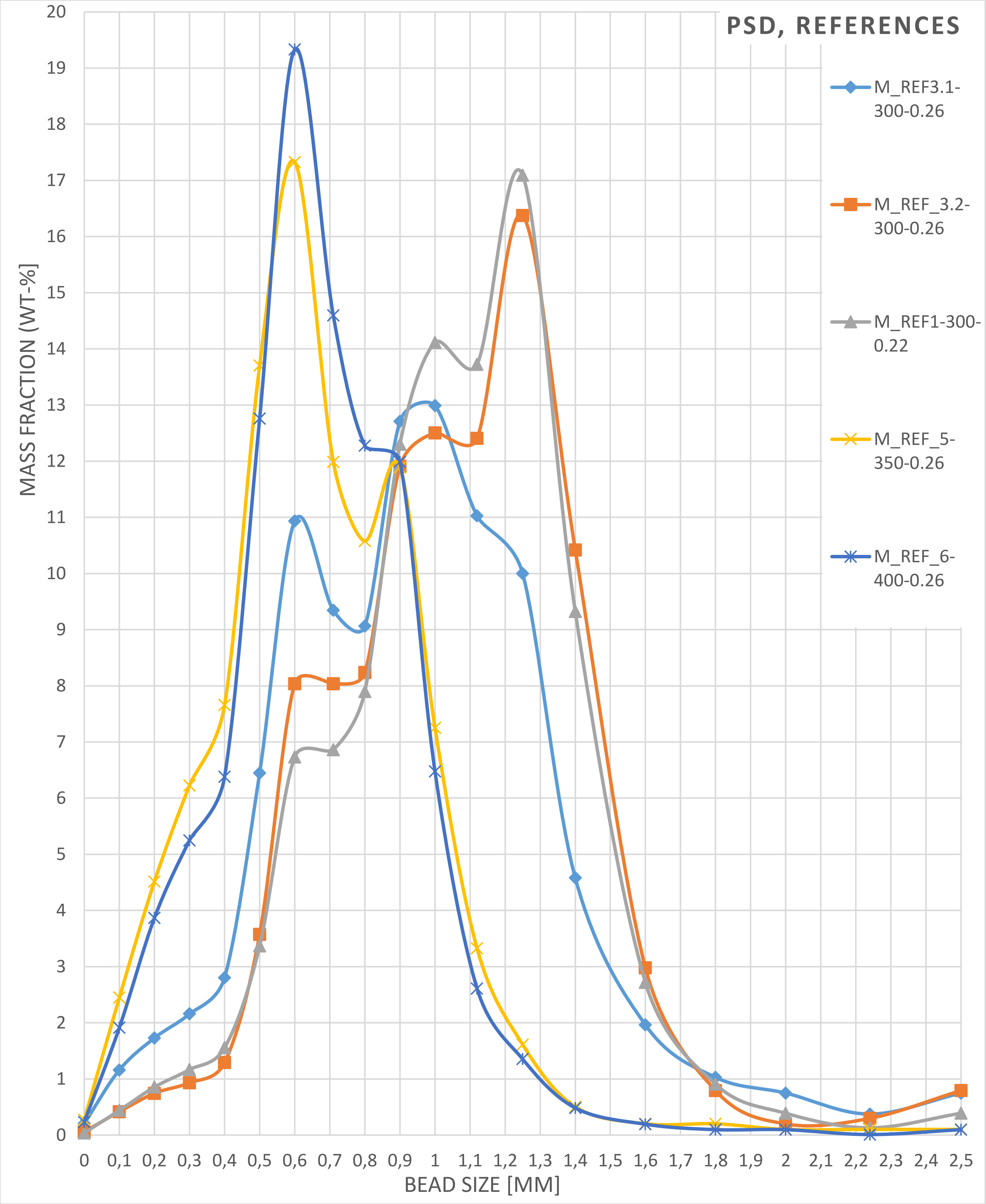


Figure 47. PSD curves of the successfully polymerized reference samples.

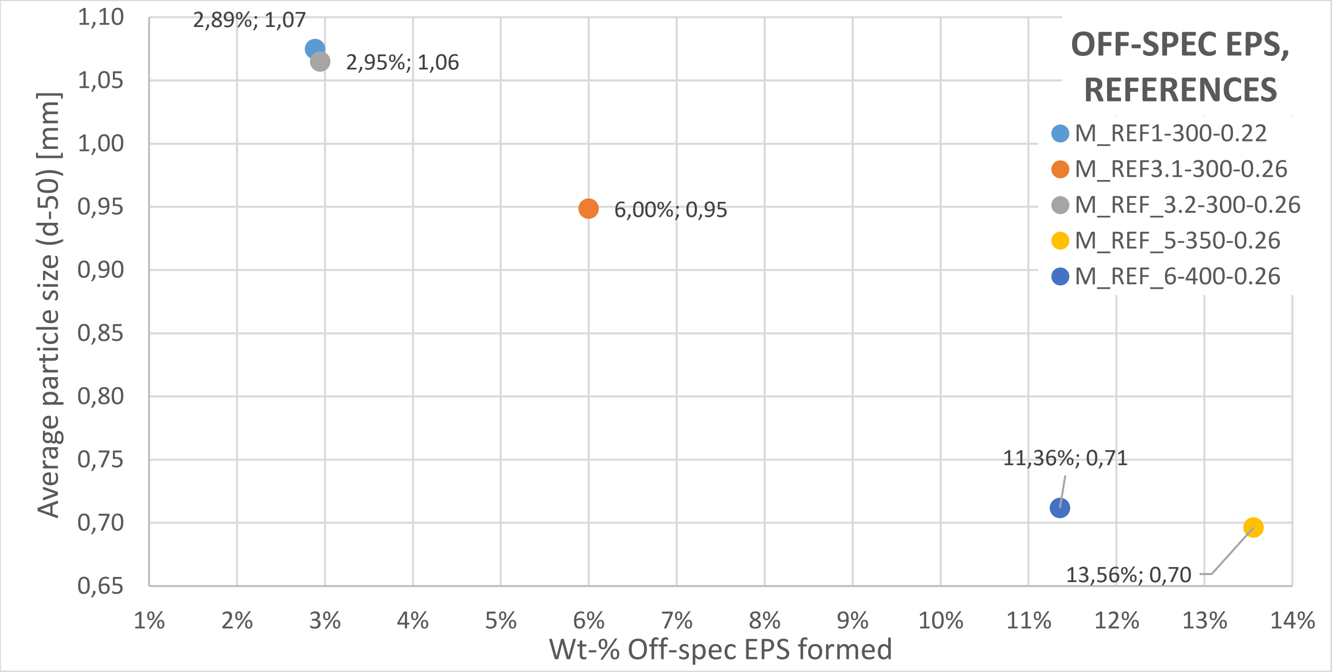


Figure 48. The total amount of off-spec EPS (HOL+LOF) in the reference samples at different average particle sizes.

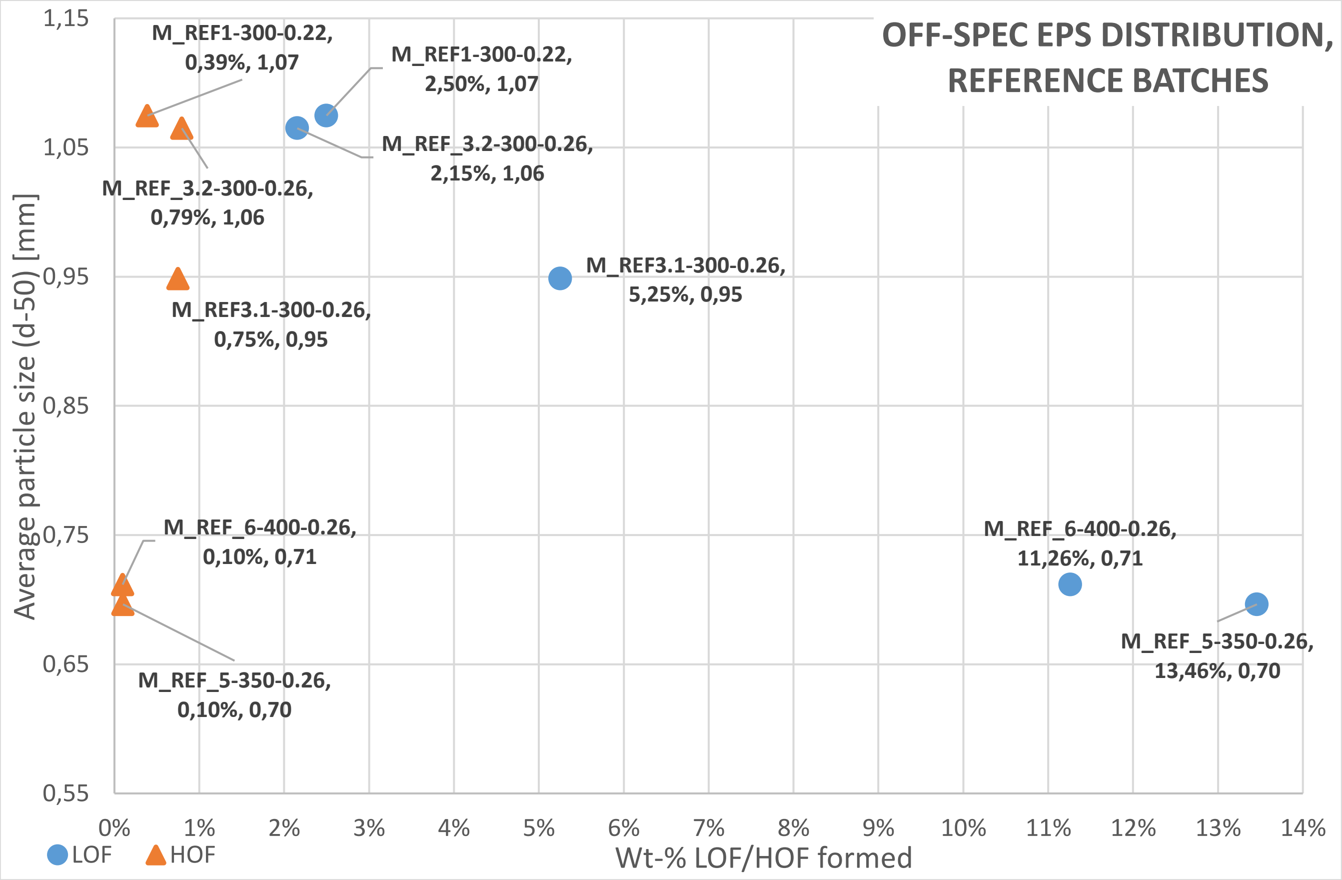


Figure 49. The off-spec distribution between LOF and HOF in the reference samples at different average particle sizes.

5%

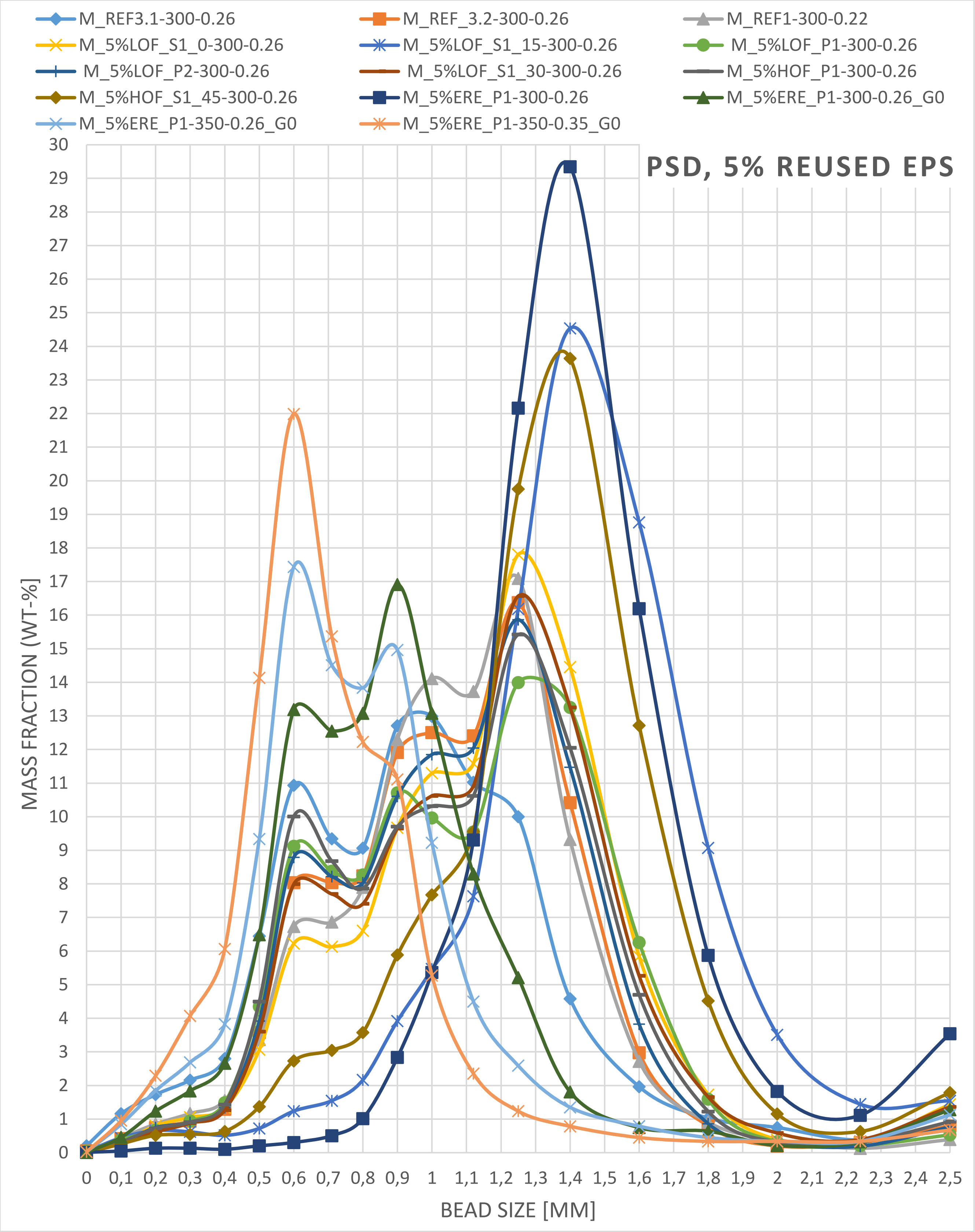


Figure 50. PSD curves of all the successful batches containing 5 wt-% reused EPS (ERE, HOF or LOF EPS).

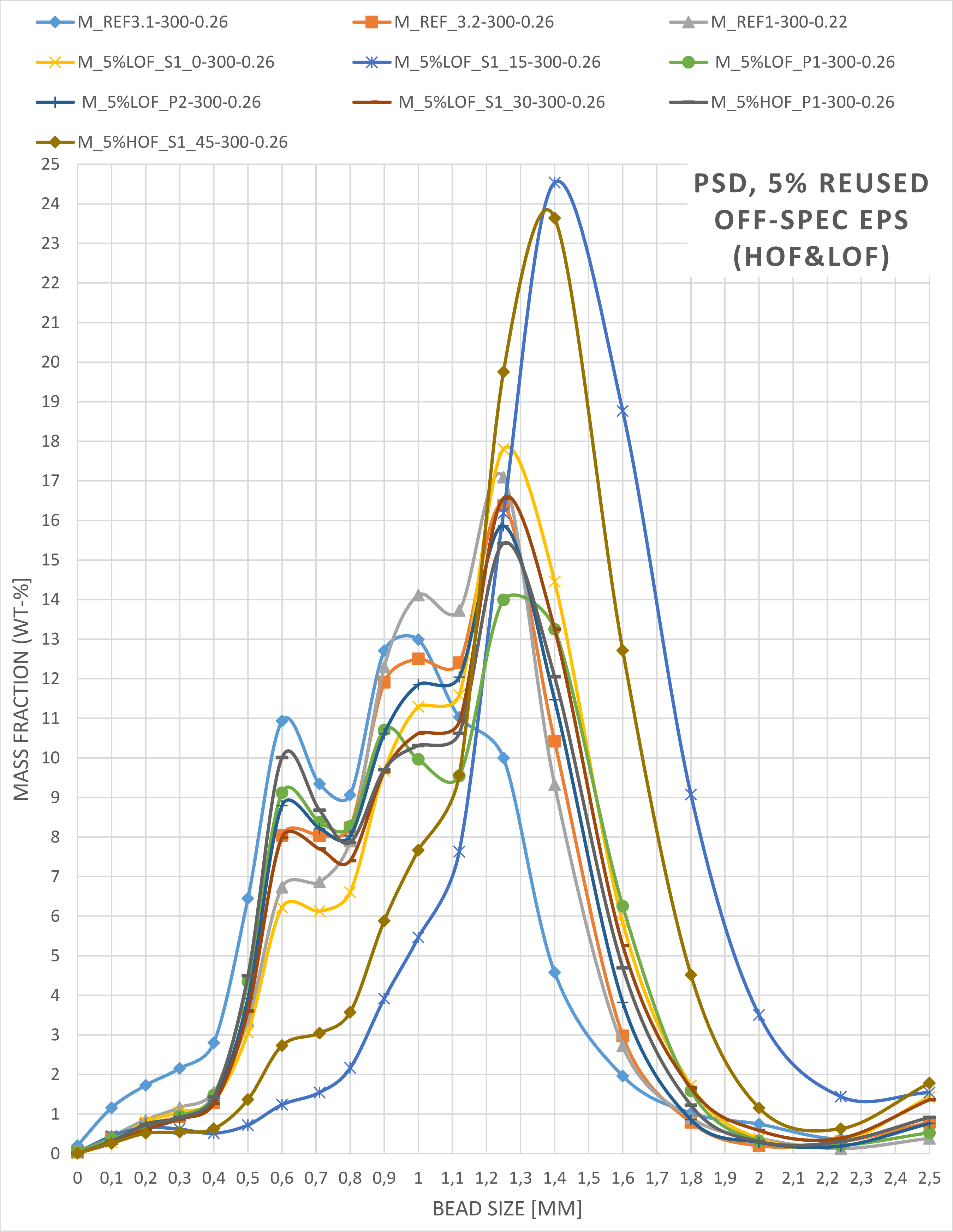


Figure 51. PSD curves of all the successful batches containing 5 wt-% reused oversized (HOF) or undersized (LOF) EPS.

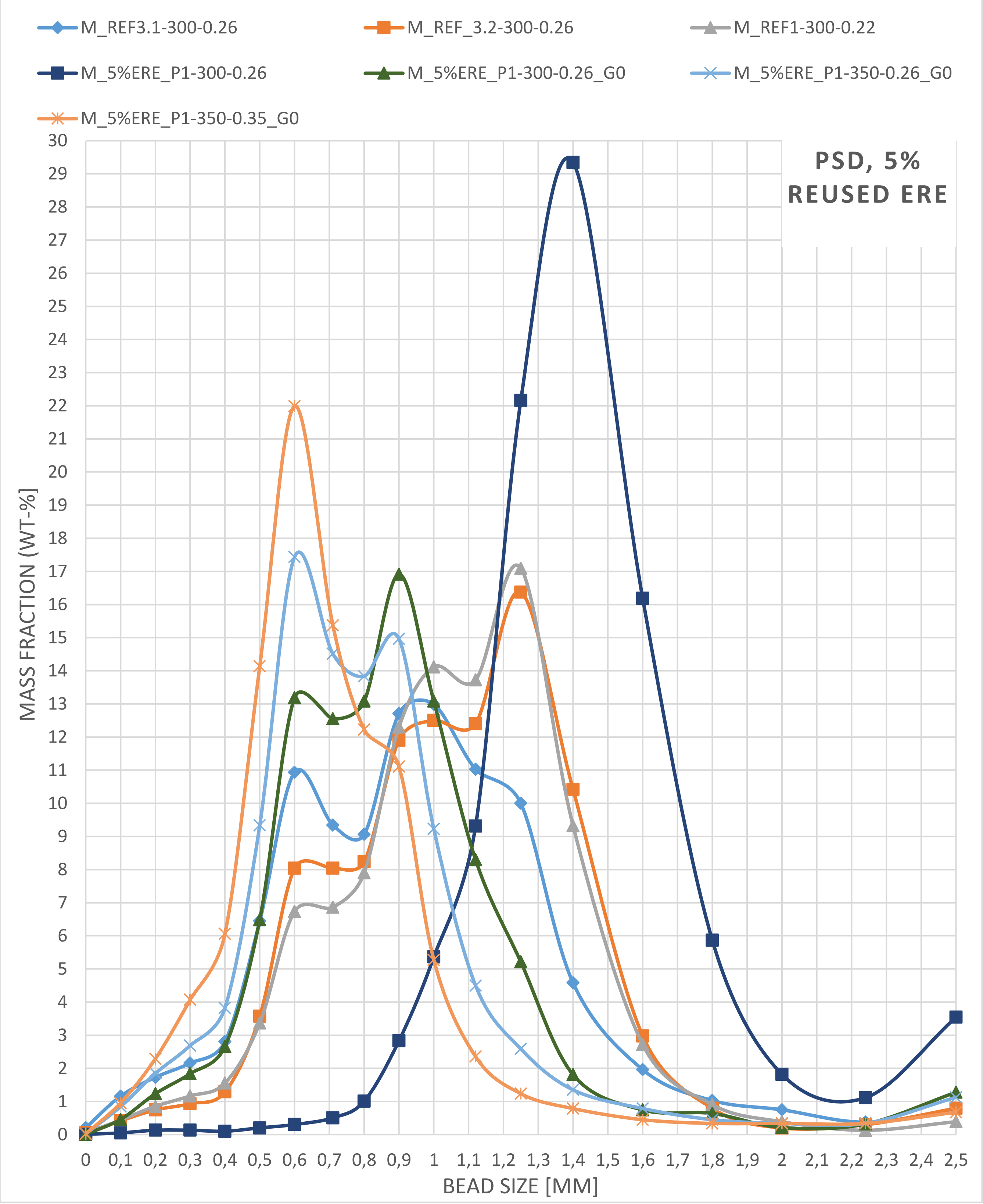


Figure 52. Particle size distribution curves of all the successful batches containing 5 wt-% reused extruded recycled EPS (ERE).

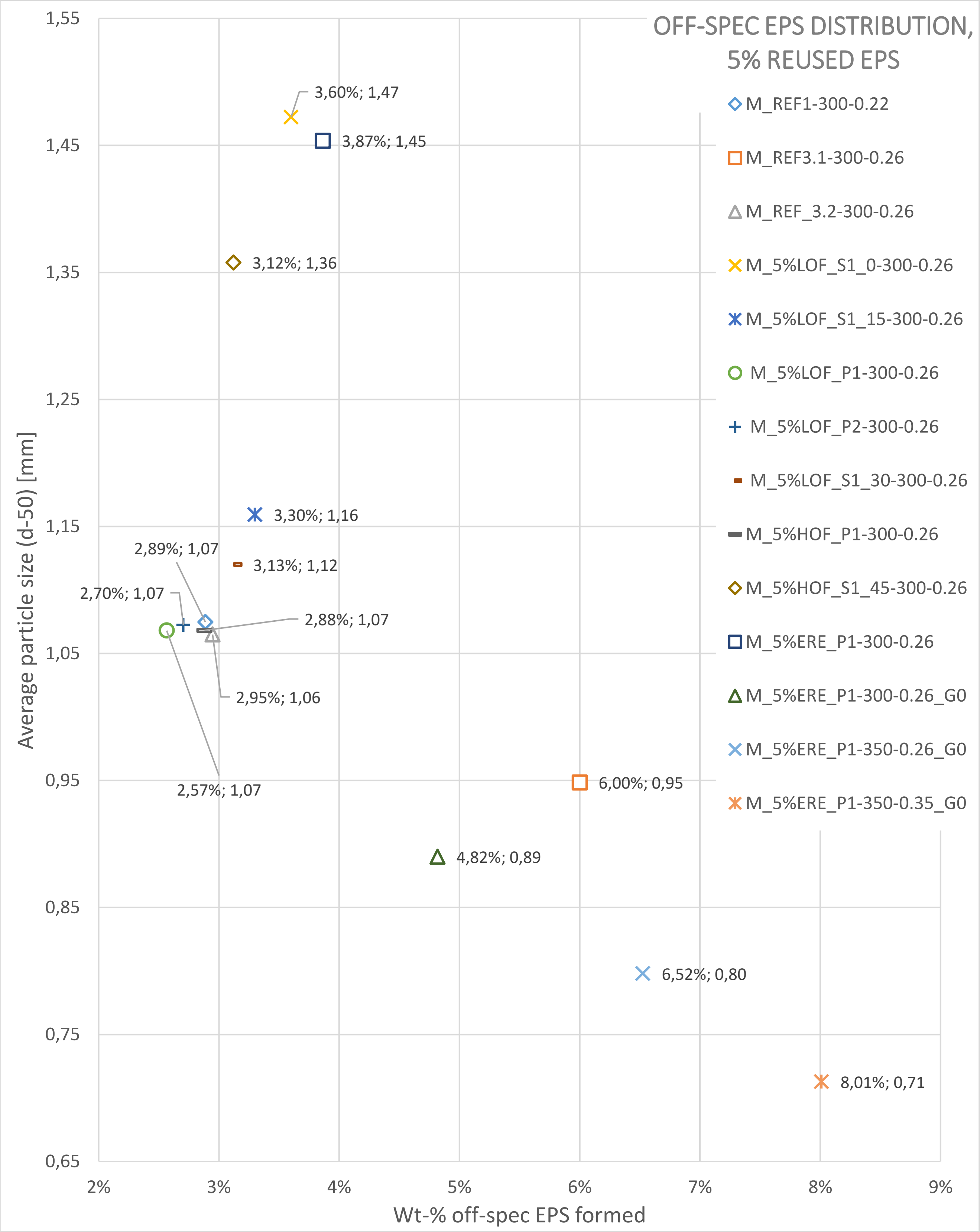


Figure 53. The total amount of off-spec EPS (HOF+LOF) in samples with 5 wt-% reused EPS (ERE, HOF or LOF) at different average particle sizes.

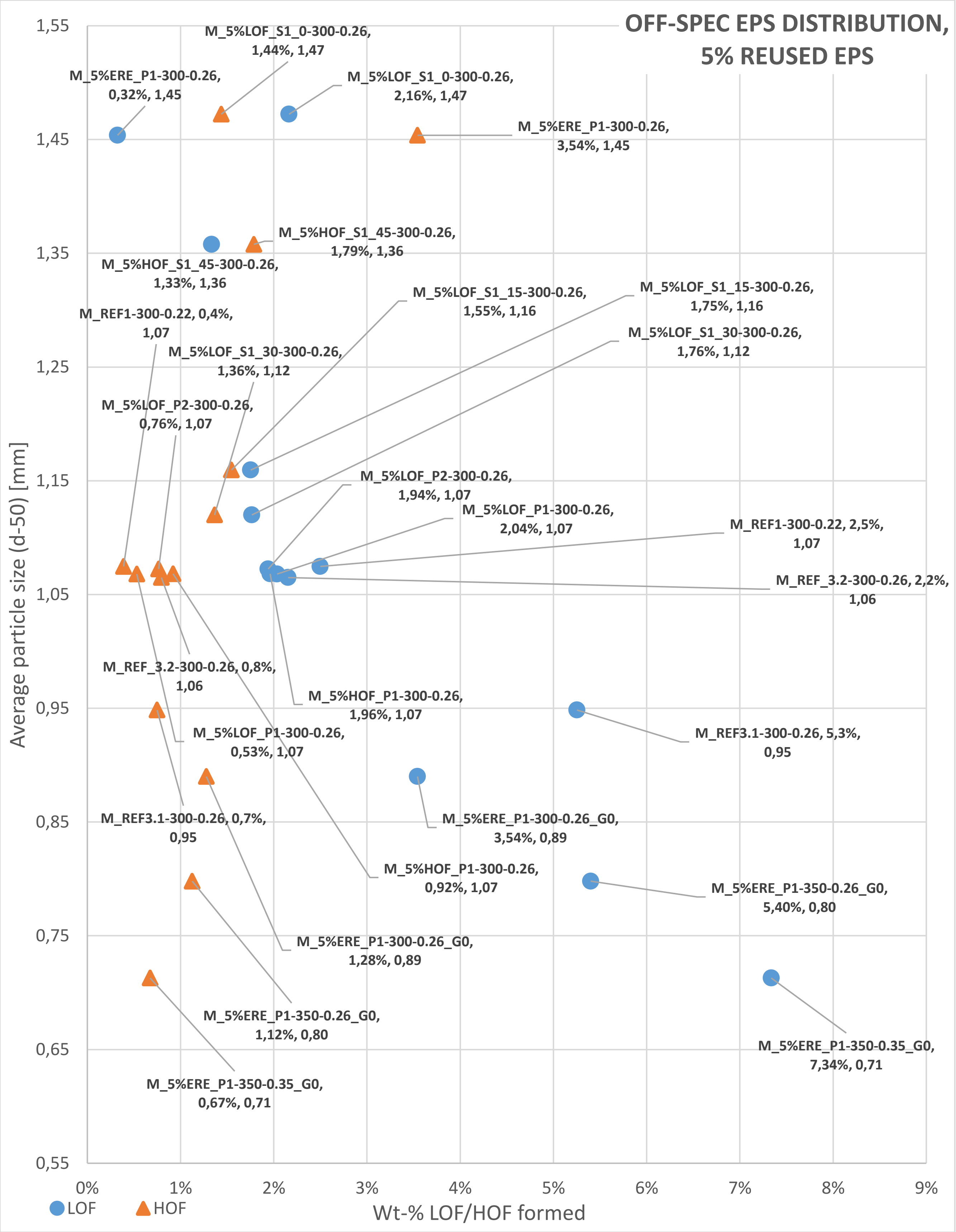


Figure 54. The off-spec distribution between LOF and HOF in the samples containing 5 wt-% reused EPS at different average particle sizes.

8%

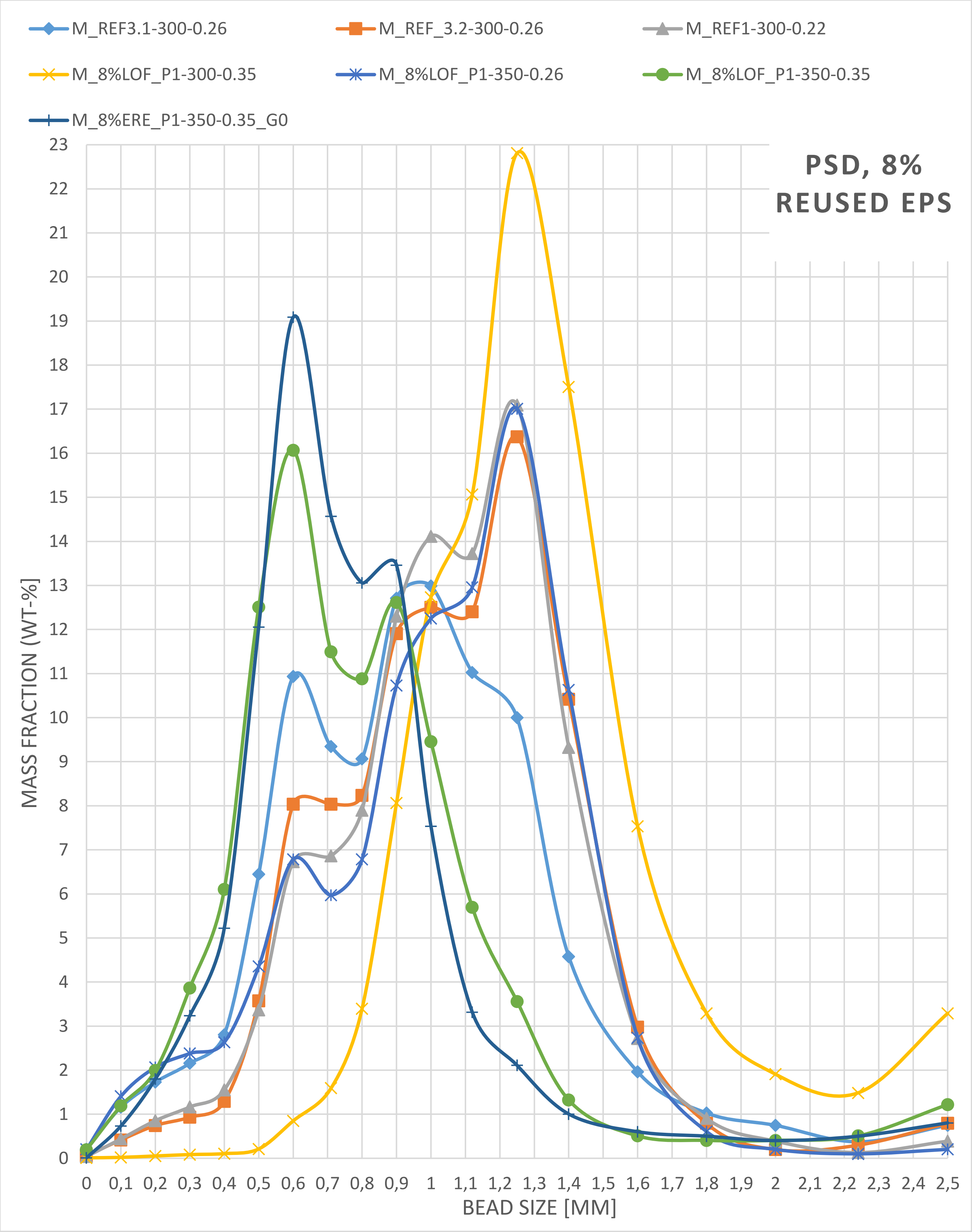


Figure 55. PSD curves of all the successful batches containing 8 wt-% reused LOF EPS or ERE.

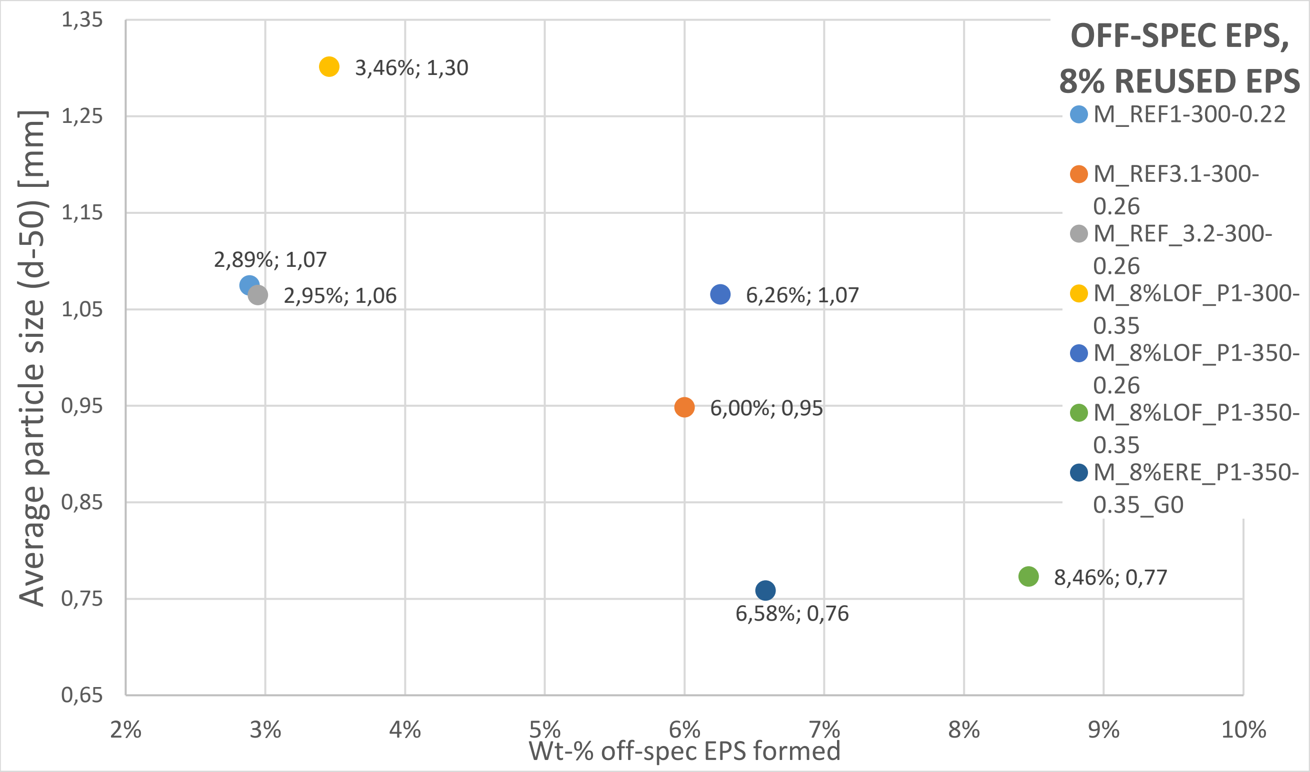


Figure 56. The total amount of off-spec EPS (HOF+LOF) in samples with 8 wt-% reused LOF EPS or ERE at different average particle sizes.

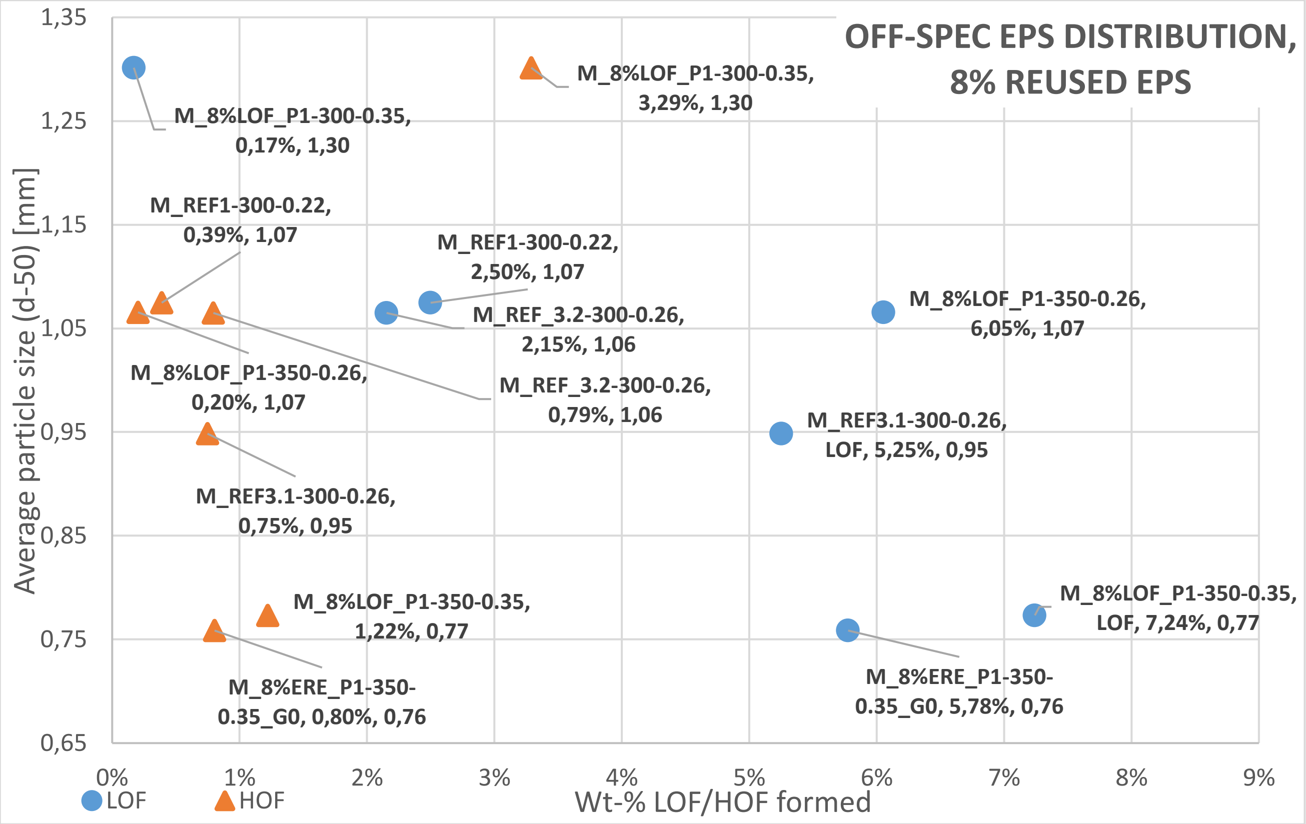


Figure 57. The off-spec distribution between LOF and HOF in the samples with 8 wt-% reused LOF EPS or ERE at different average particle sizes.

10%

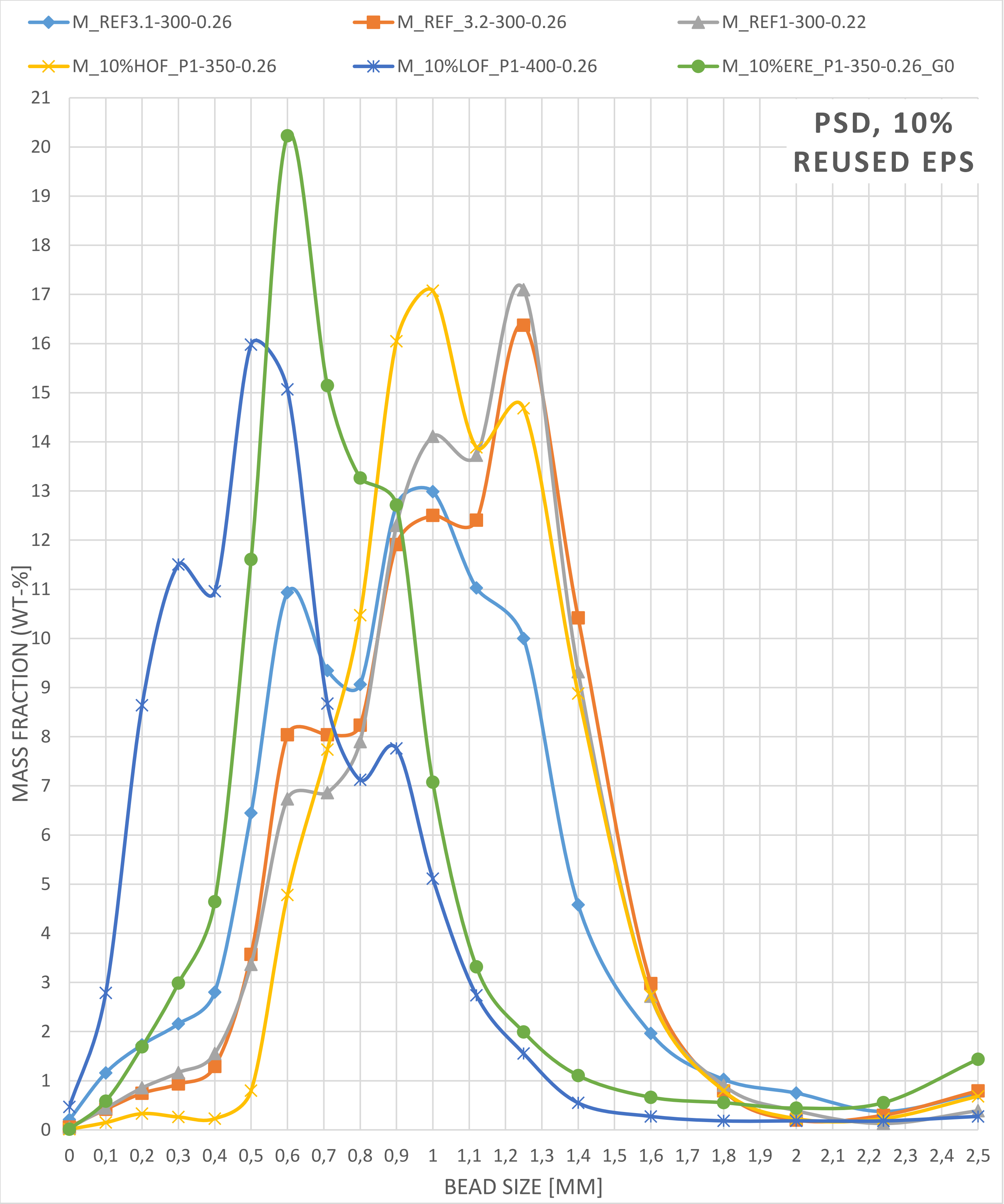


Figure 58. PSD curves of all the successful batches containing 10 wt-% reused EPS (ERE, HOF or LOF EPS).

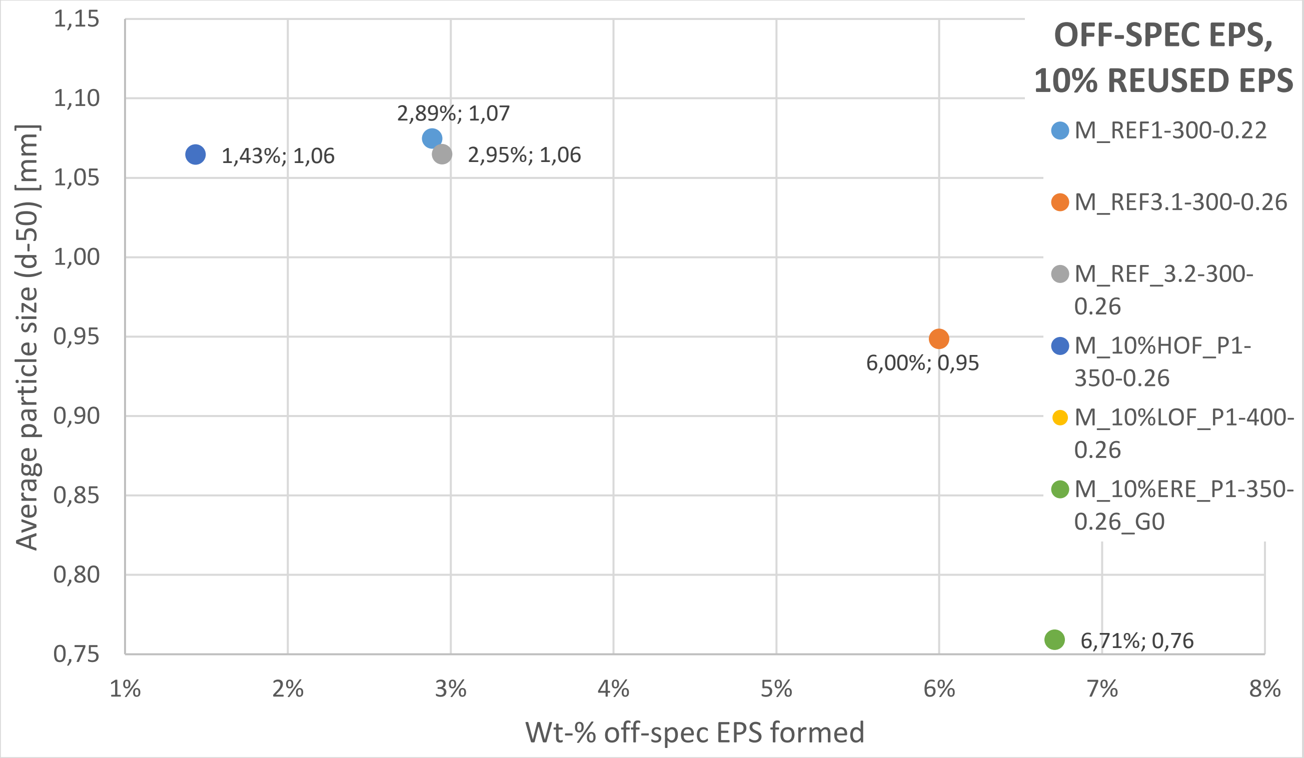


Figure 59. The total amount of off-spec EPS (HOF+LOF) in samples with 10 wt-% reused EPS (ERE, HOF or LOF EPS) at different average particle sizes.

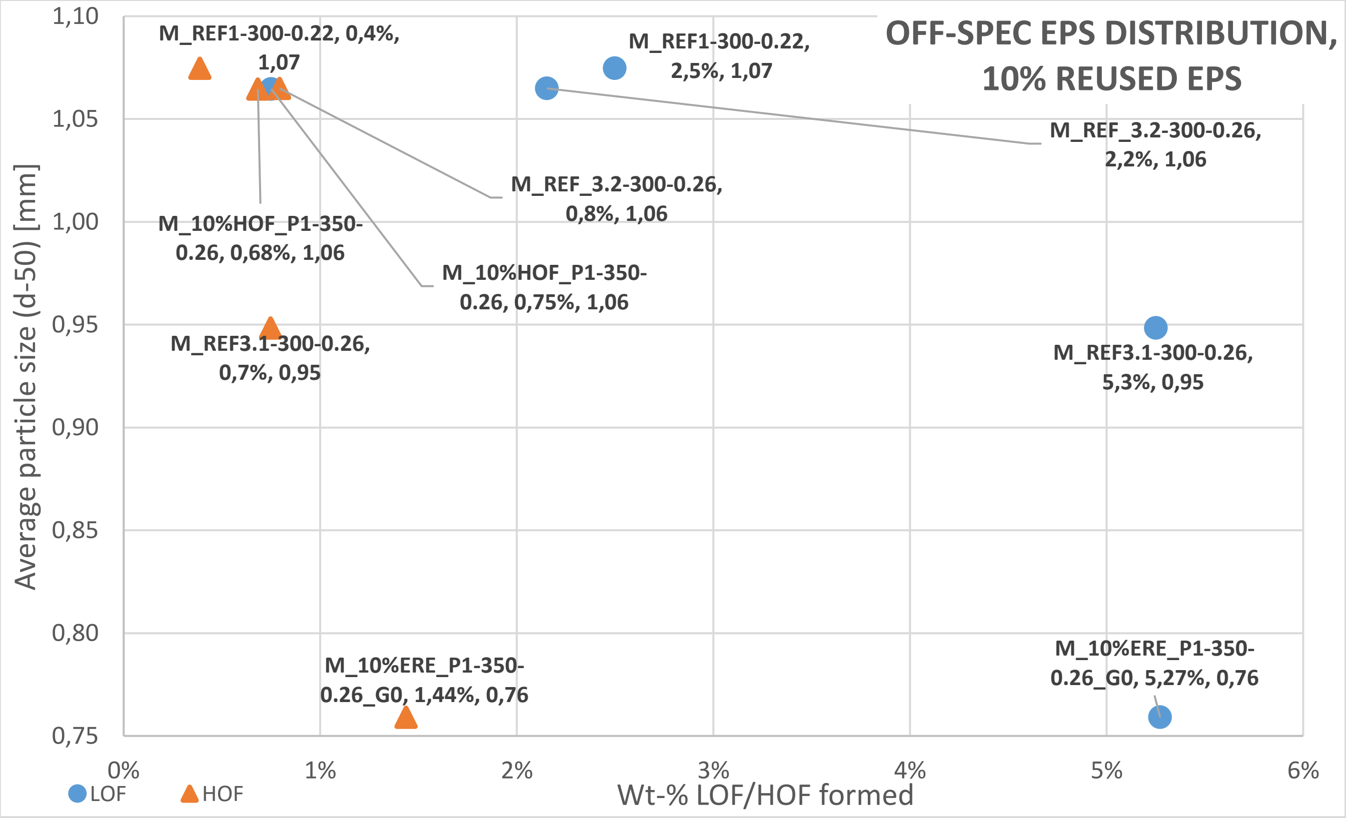


Figure 60. The off-spec distribution between LOF and HOF in the samples with 10 wt-% reused EPS (ERE, HOF or LOF EPS) at different average particle sizes.

12%

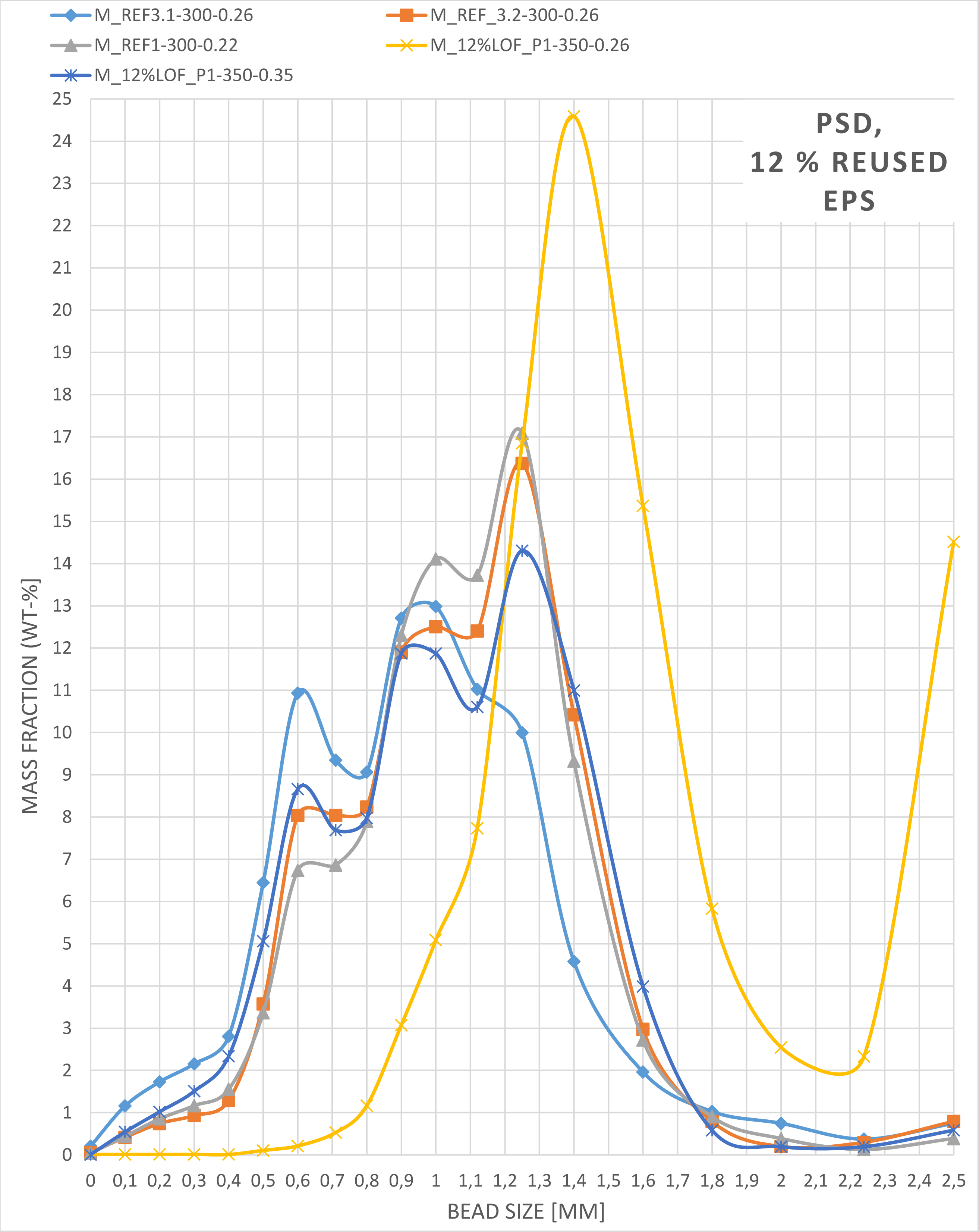


Figure 61. PSD curves of all the successful batches containing 12 wt-% reused LOF EPS or ERE.

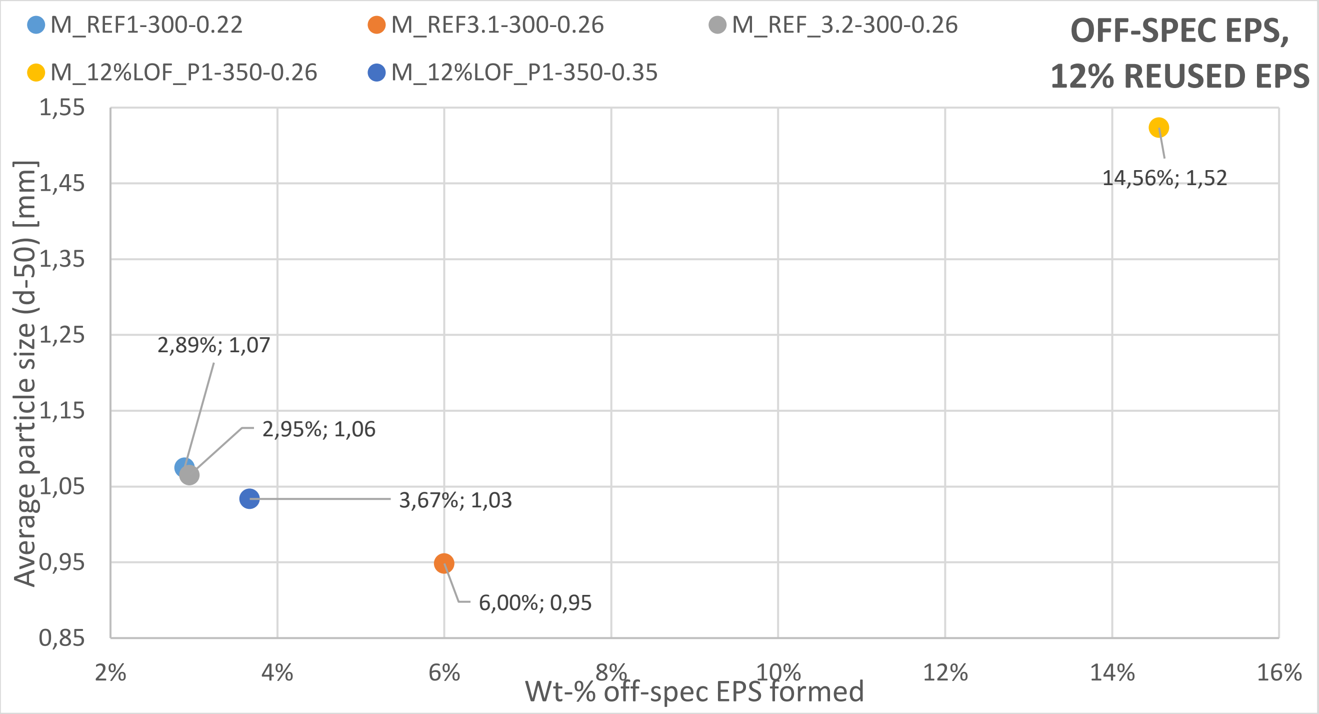


Figure 62. The off-spec distribution between LOF and HOF in the samples with 12 wt-% reused LOF EPS or ERE at different average particle sizes.

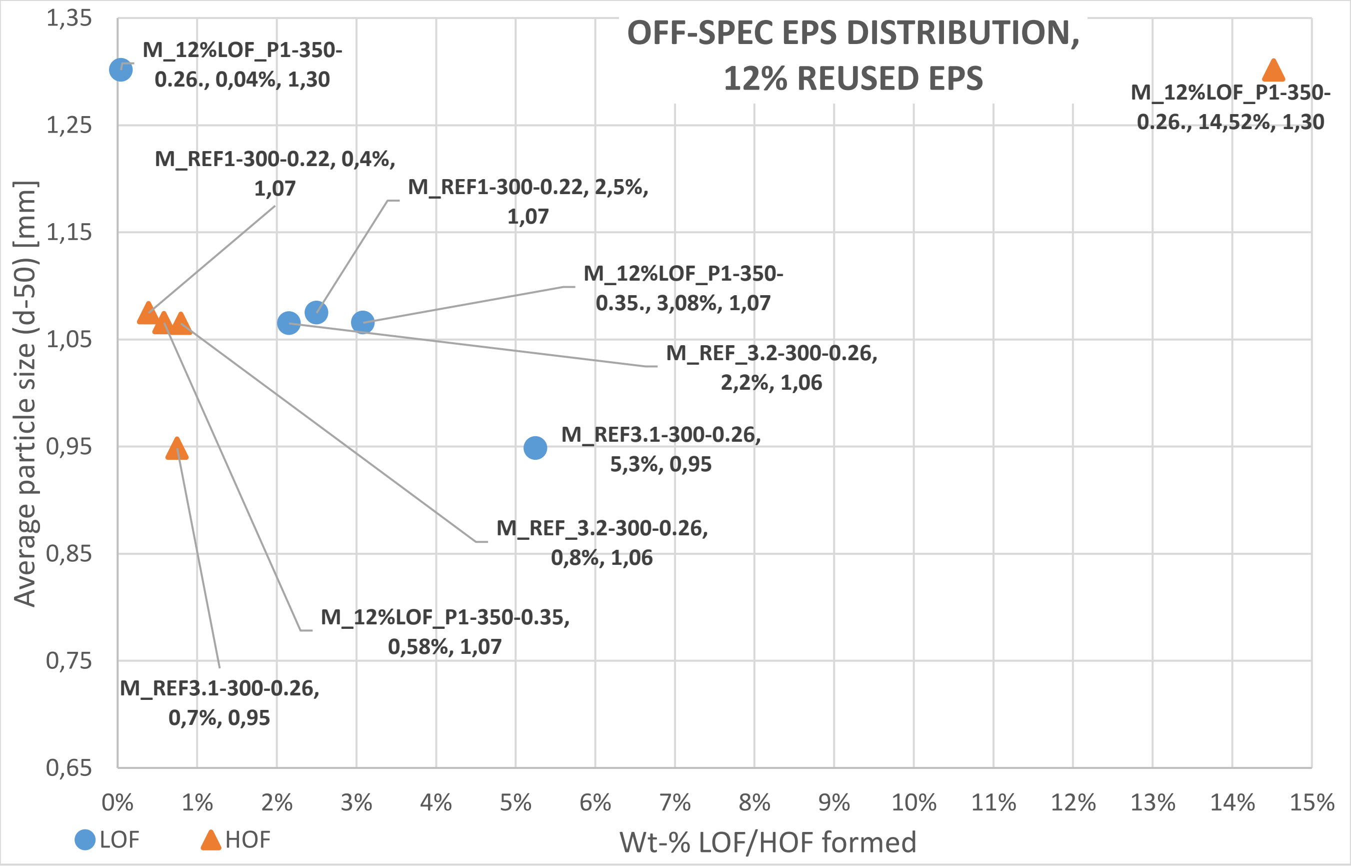


Figure 63. The off-spec distribution between LOF and HOF in the samples with 12 wt-% reused LOF EPS or ERE at different average particle sizes.

14%

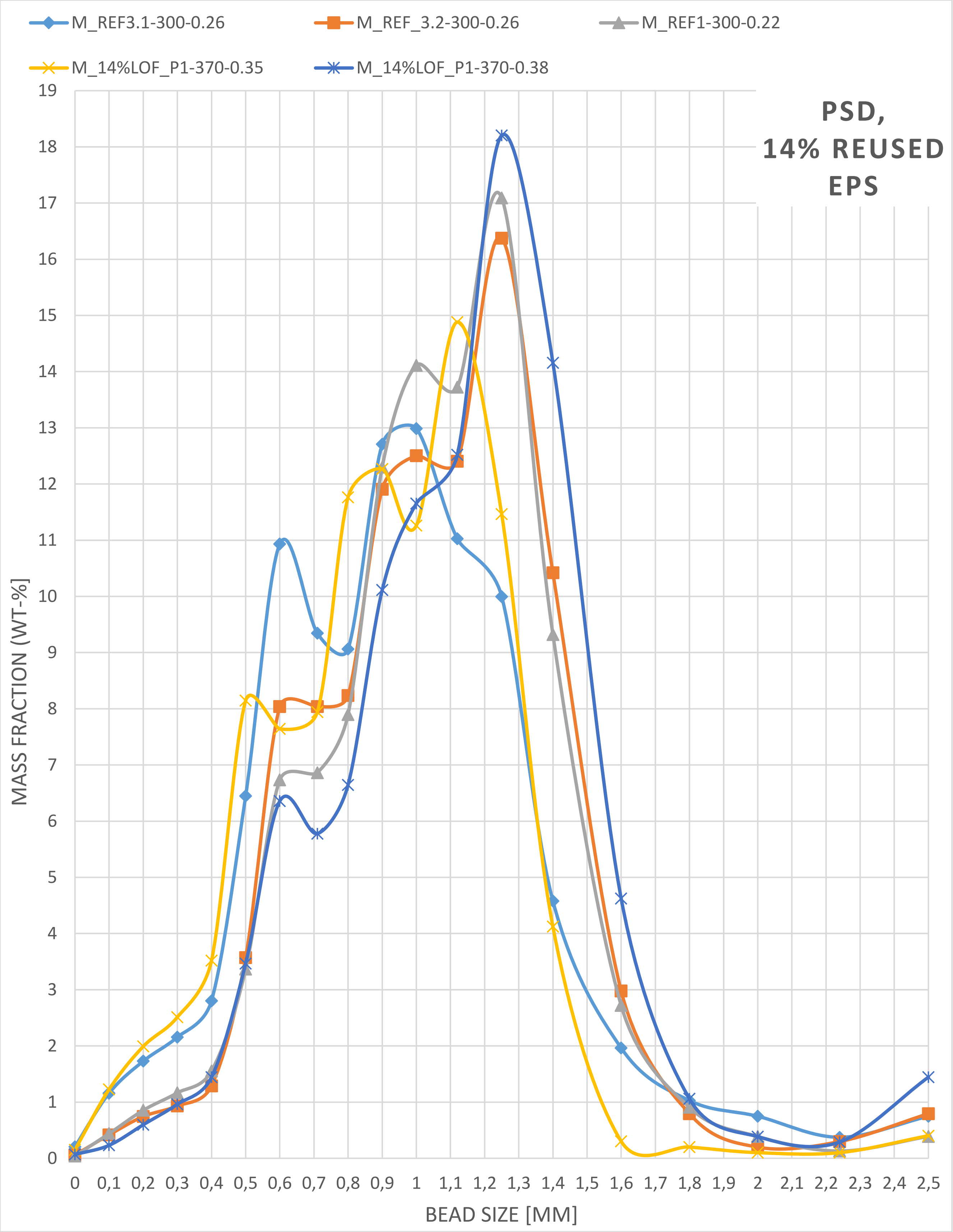


Figure 64. PSD curves of all the successful batches containing 14 wt-% reused LOF EPS.

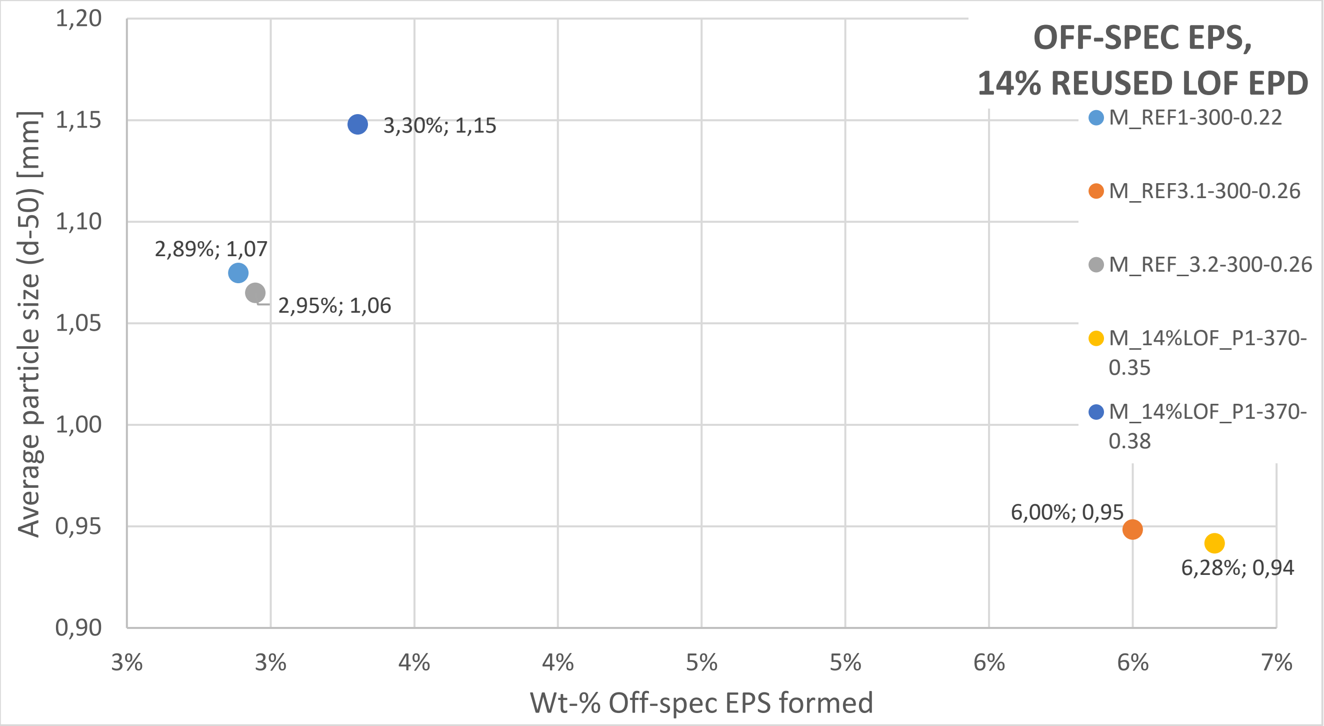


Figure 65. The total amount of off-spec EPS (HOF+LOF) in samples with 14 wt-% reused LOF EPS at different average particle sizes.

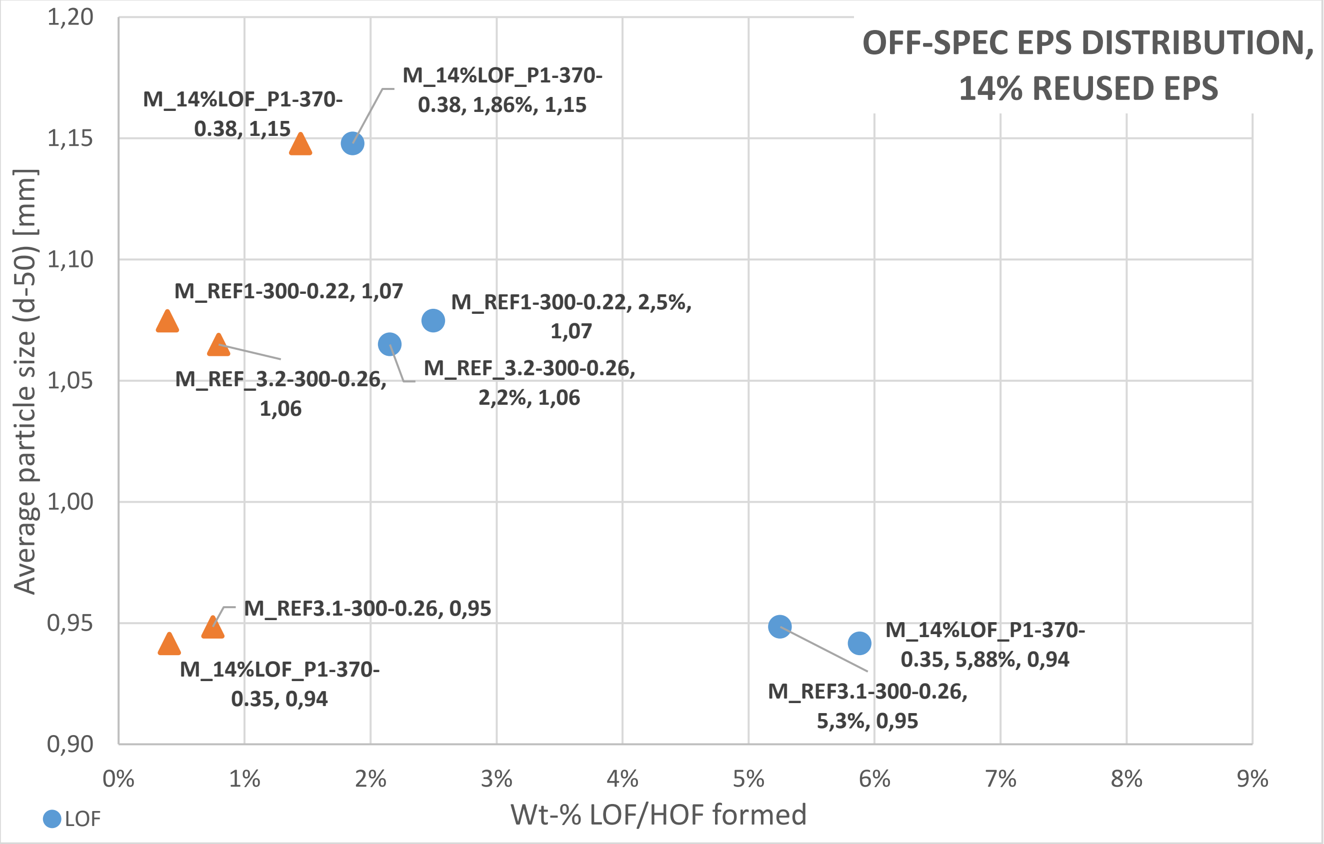


Figure 66. The off-spec distribution between LOF and HOF in the samples with 14 wt-% reused LOF EPS at different average particle sizes.

16%

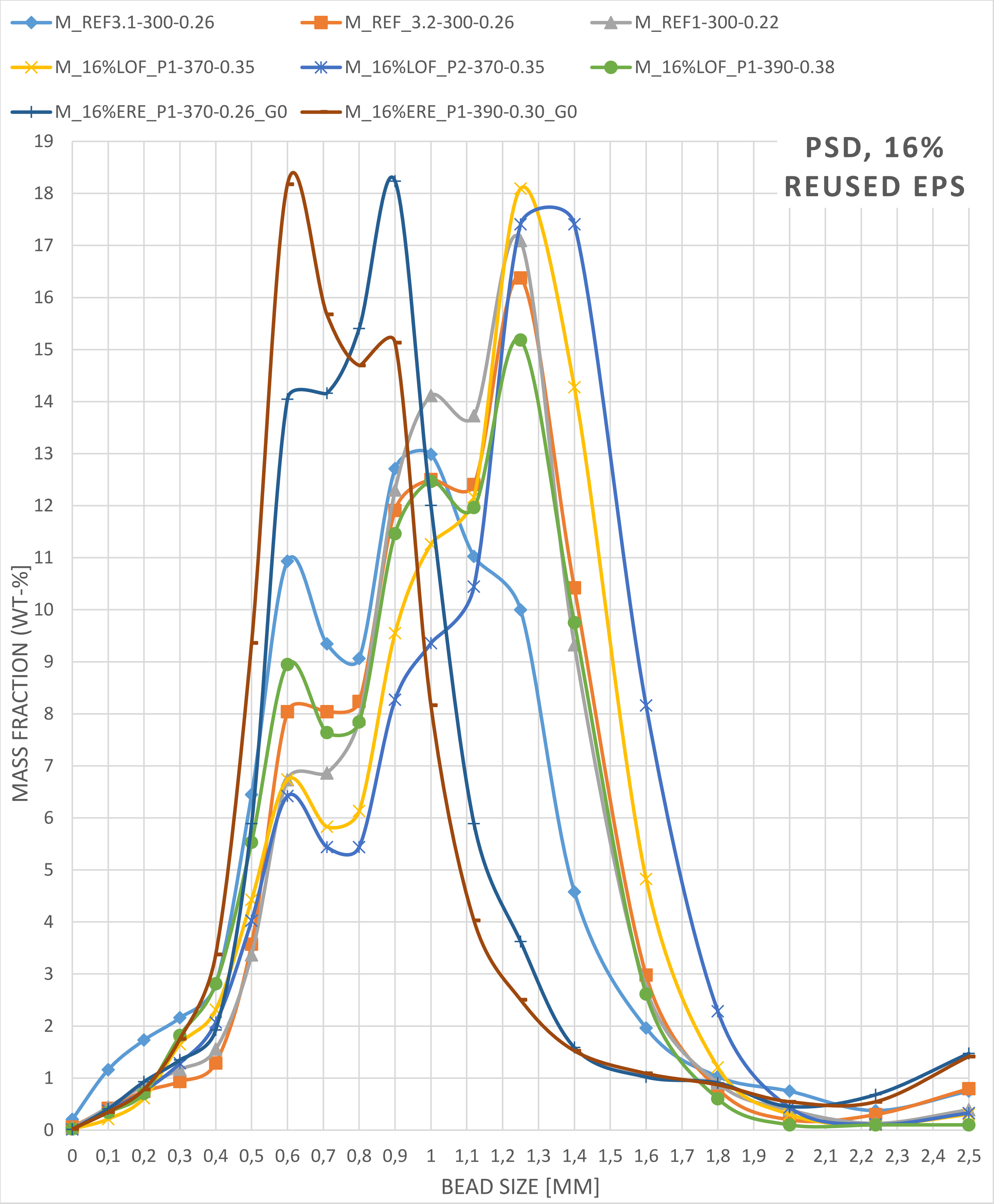


Figure 67. PSD curves of all the successful batches containing 16 wt-% reused LOF EPS or ERE.

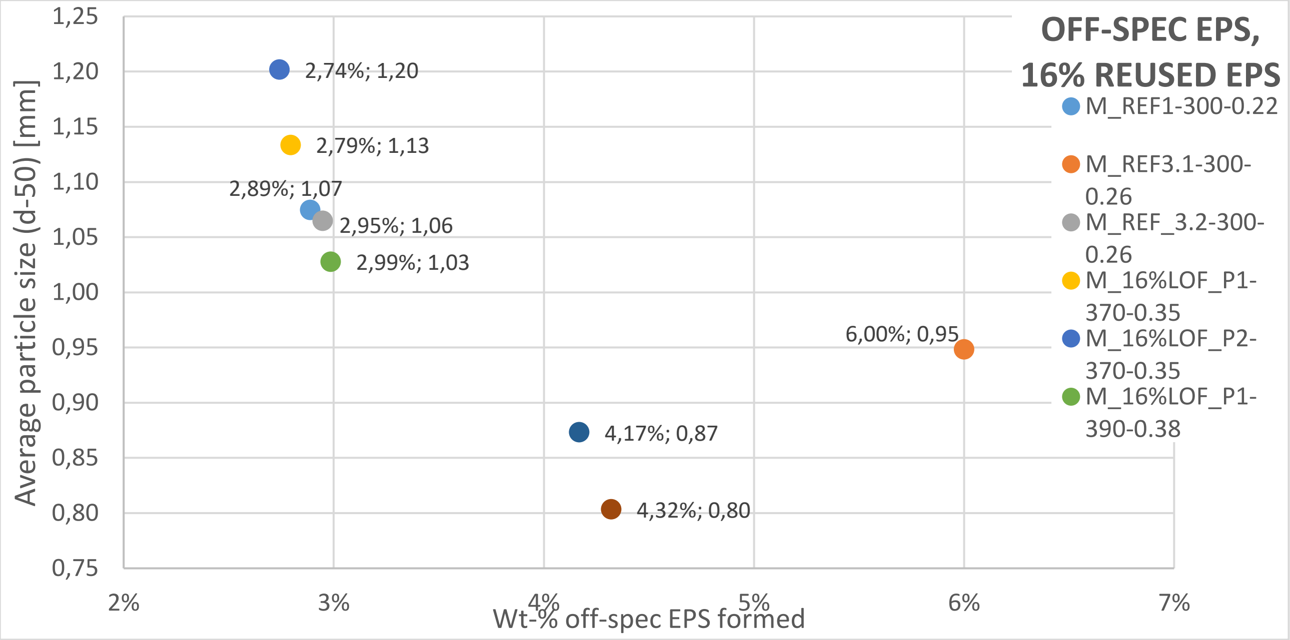


Figure 68. The total amount of off-spec EPS (HOF+LOF) in samples with 16 wt-% reused LOF EPS at different average particle sizes.

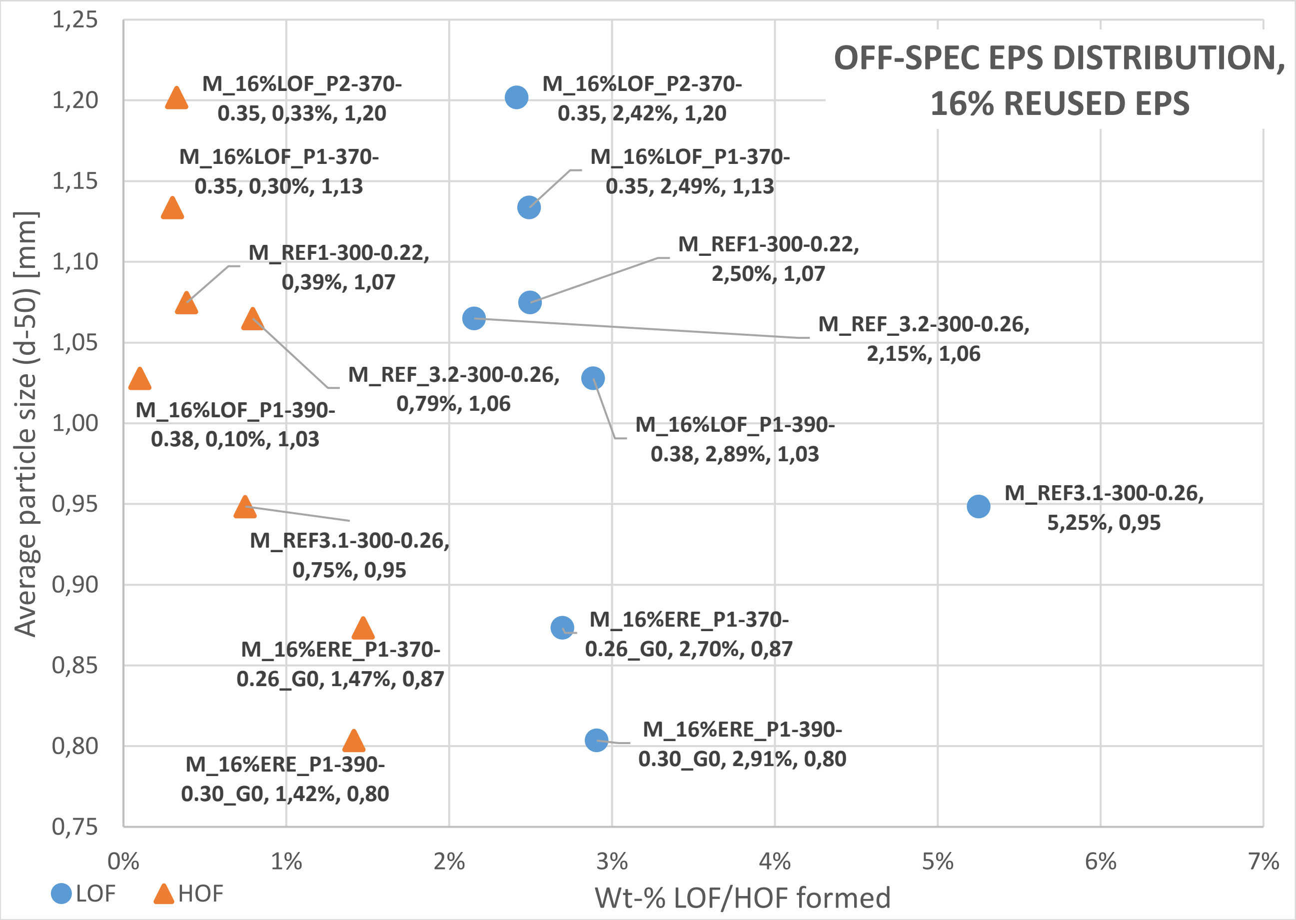


Figure 69. The off-spec distribution between LOF and HOF in the samples with 16 wt-% reused LOF EPS or ERE at different average particle sizes.

20%

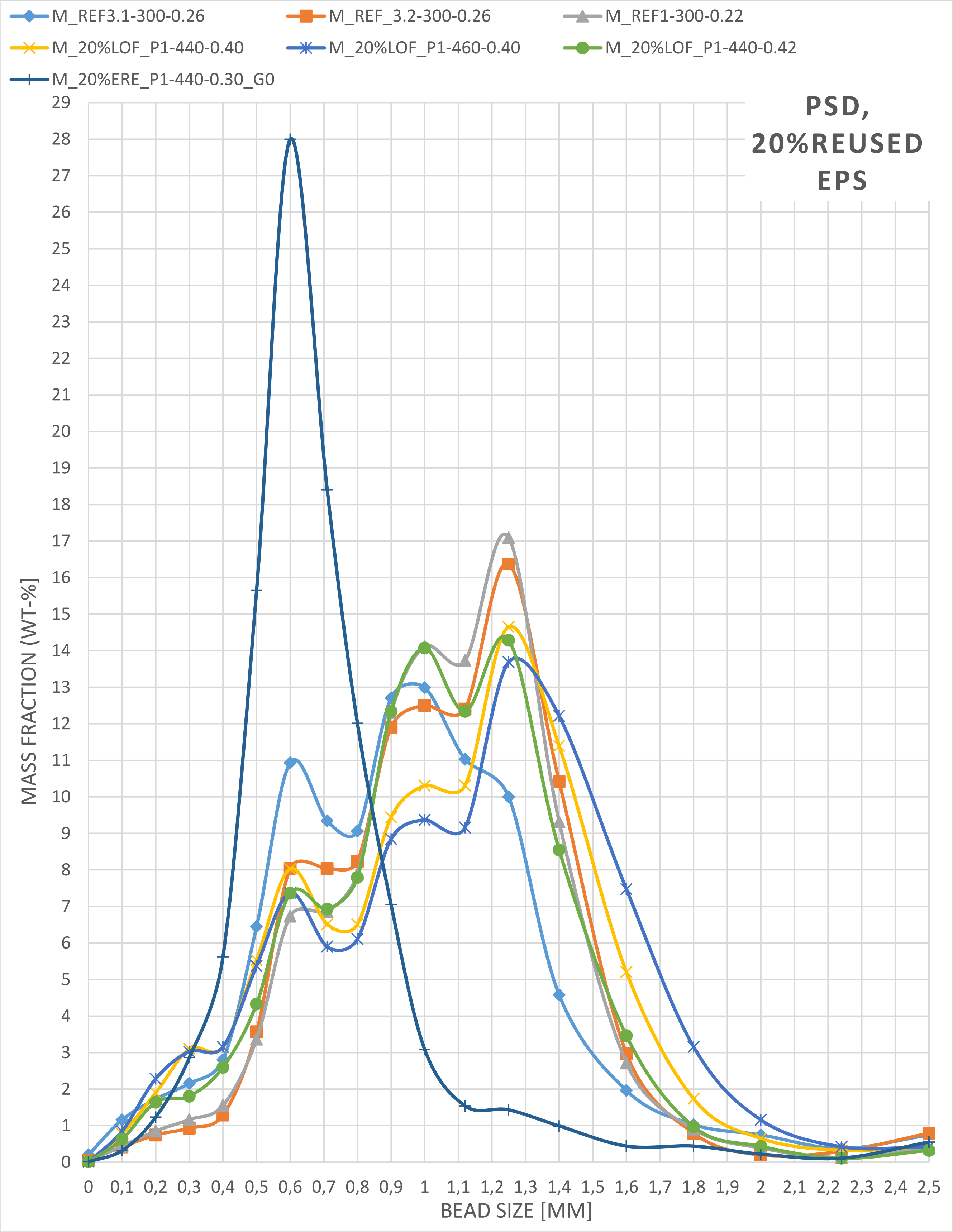


Figure 70. PSD curves of all the successful batches containing 20 wt-% reused LOF EPS or ERE.

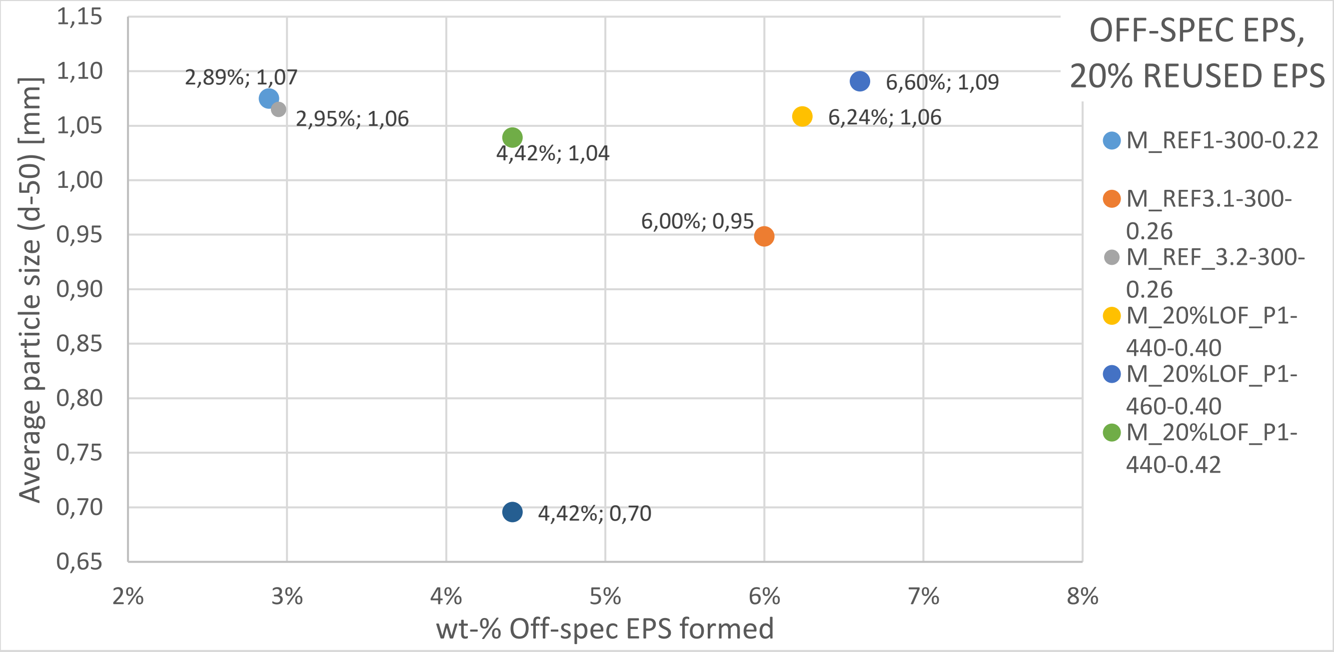


Figure 71. The total amount of off-spec EPS (HOF+LOF) in samples with 20 wt-% reused LOF EPS or ERE at different average particle sizes.

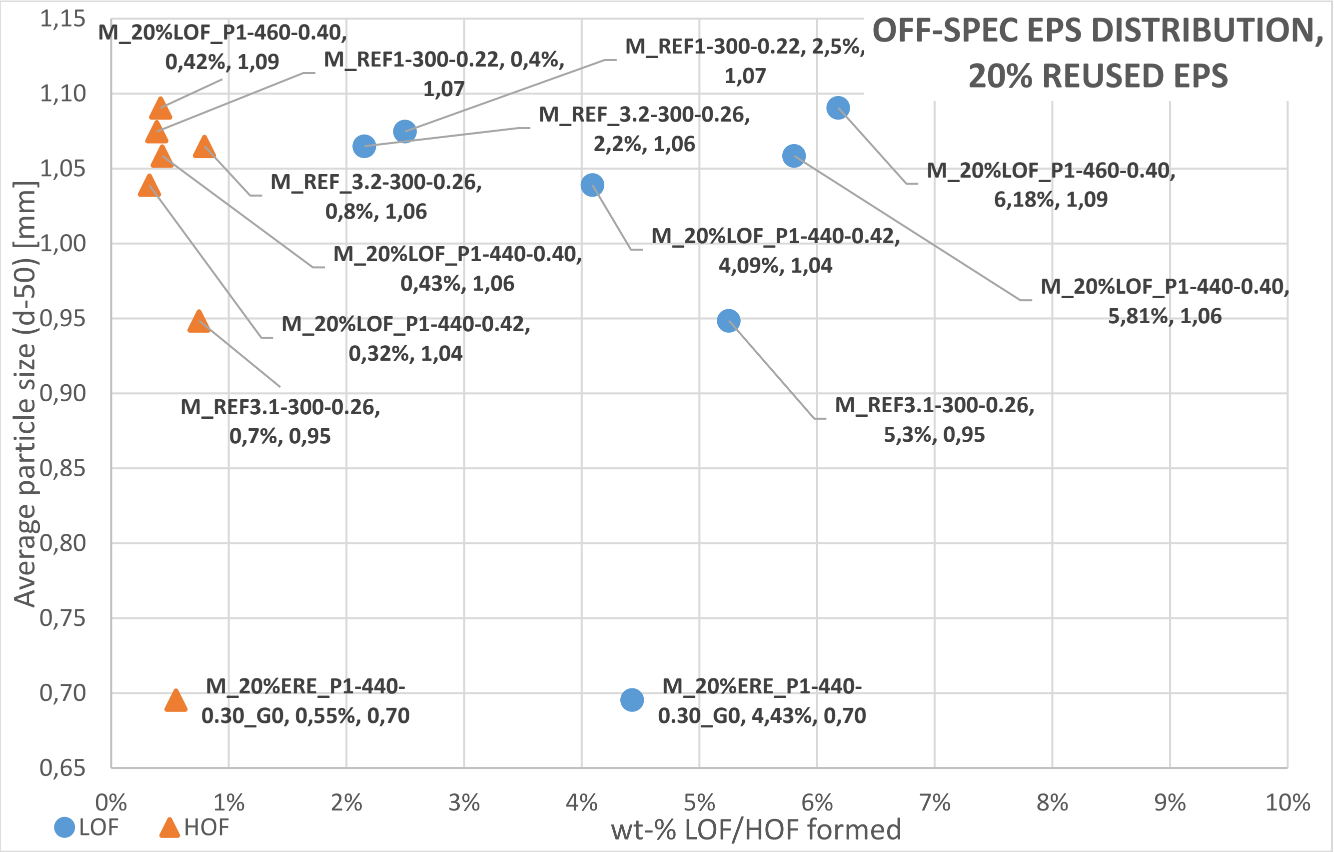


Figure 72. The off-spec distribution between LOF and HOF in the samples with 20 wt-% reused LOF EPS or ERE at different average particle sizes.

Comparative Collection

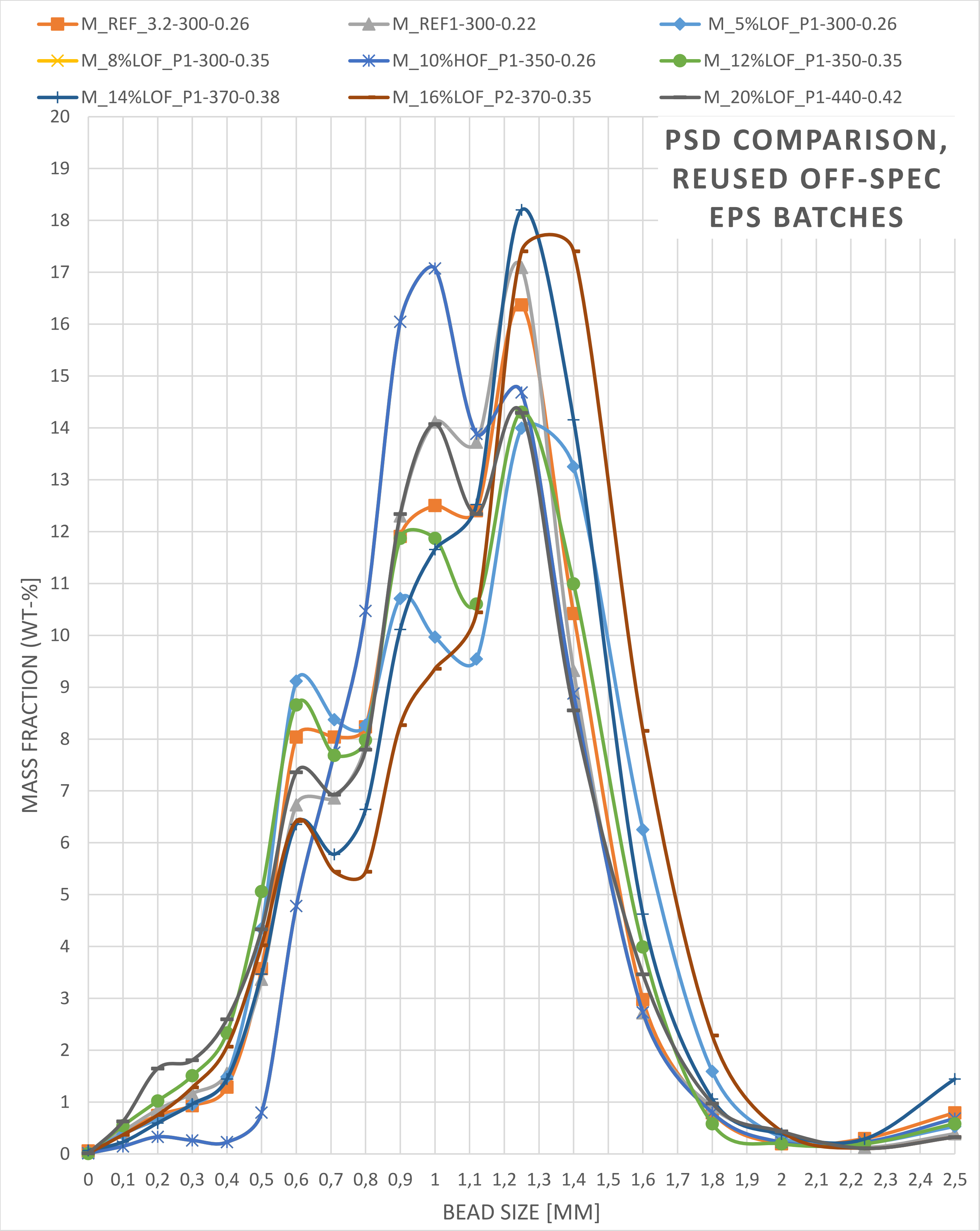


Figure 73. A collective PSD graph of successful batches containing reused LOF or HOF EPS.

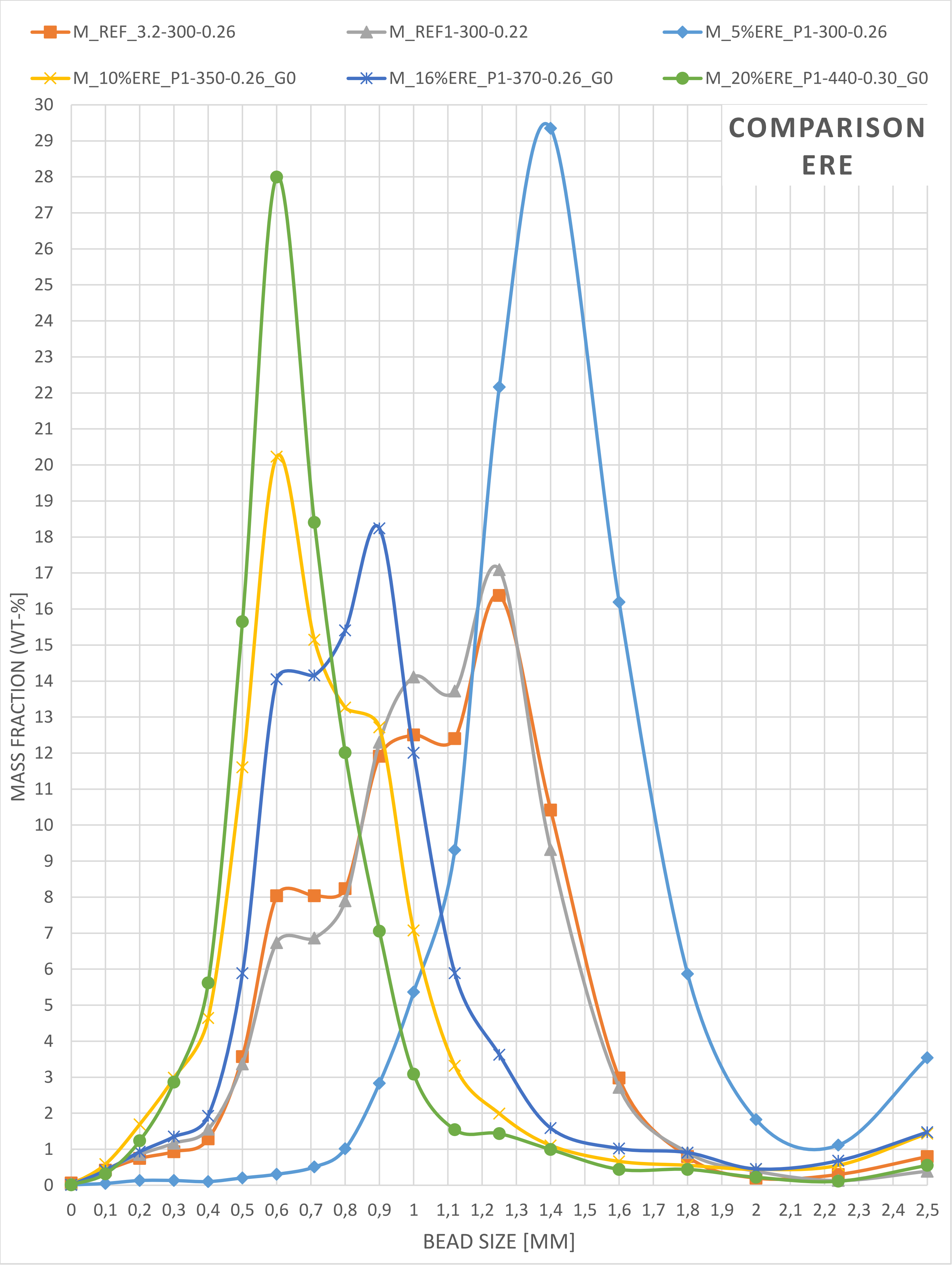


Figure 74. A collective graph for PSD curves of all the successful batches containing reused ERE.

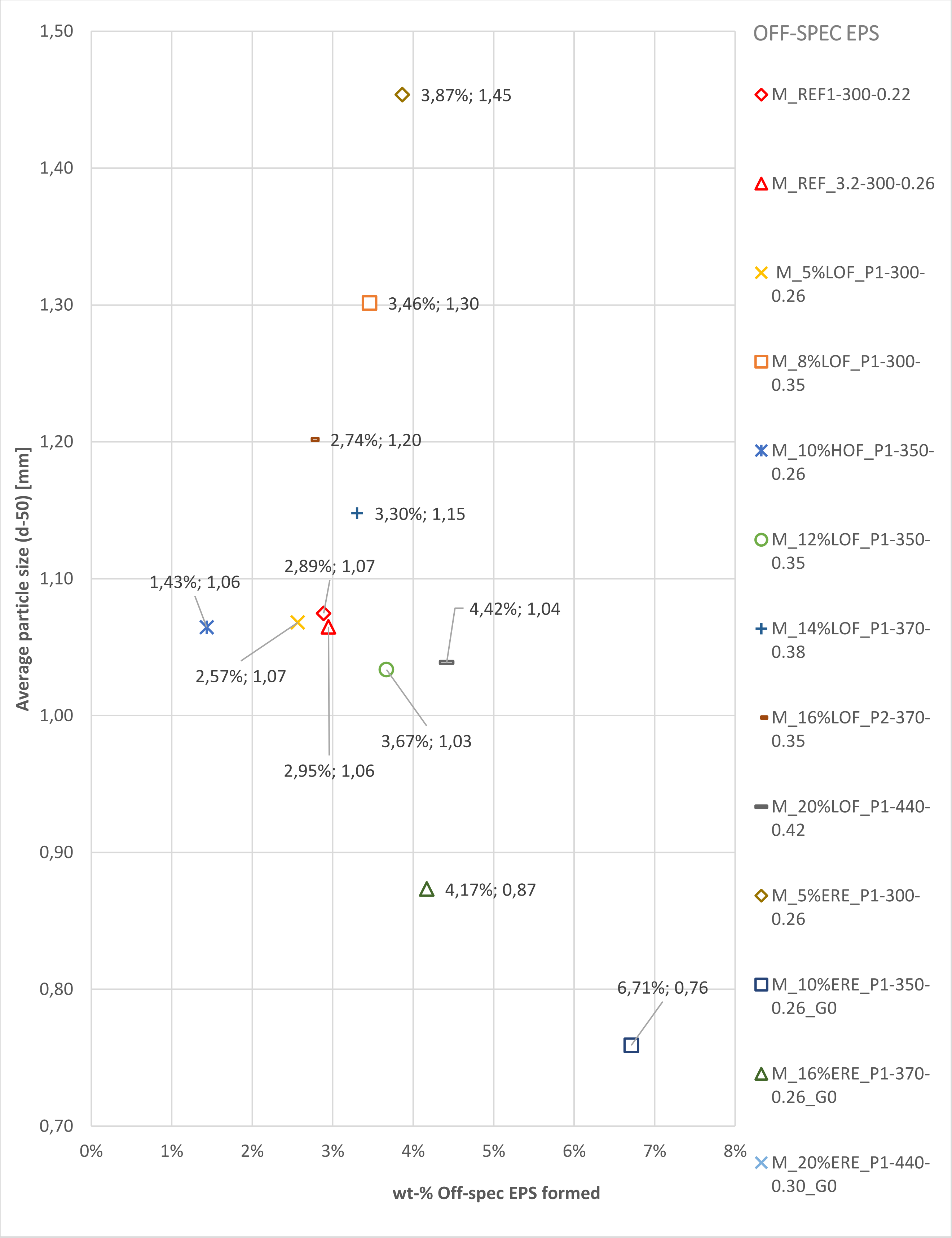


Figure 75. The total amount of off-spec EPS (HOF+LOF) in samples that were presented in Figure 69 and 70.

D. RM Data

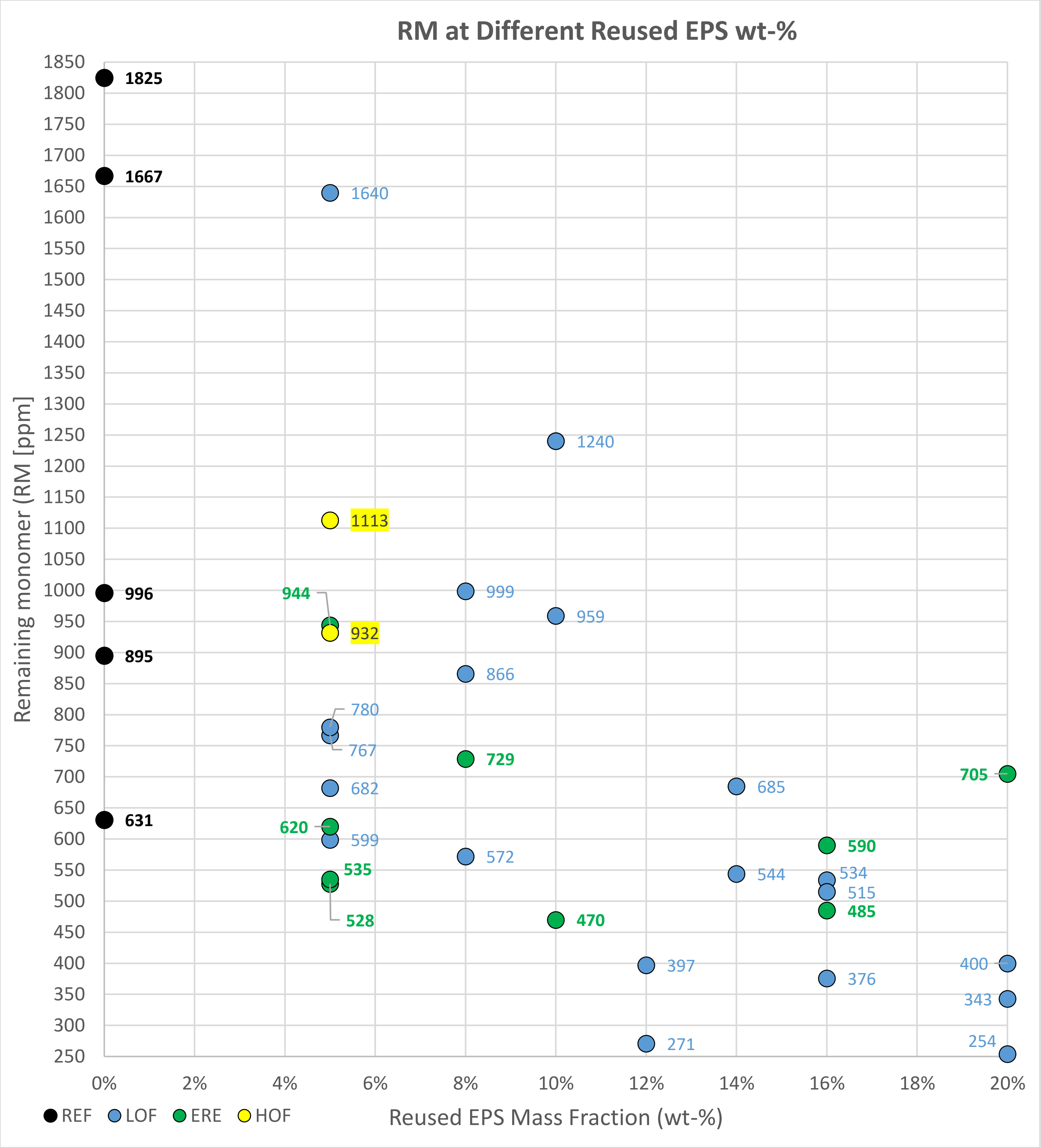


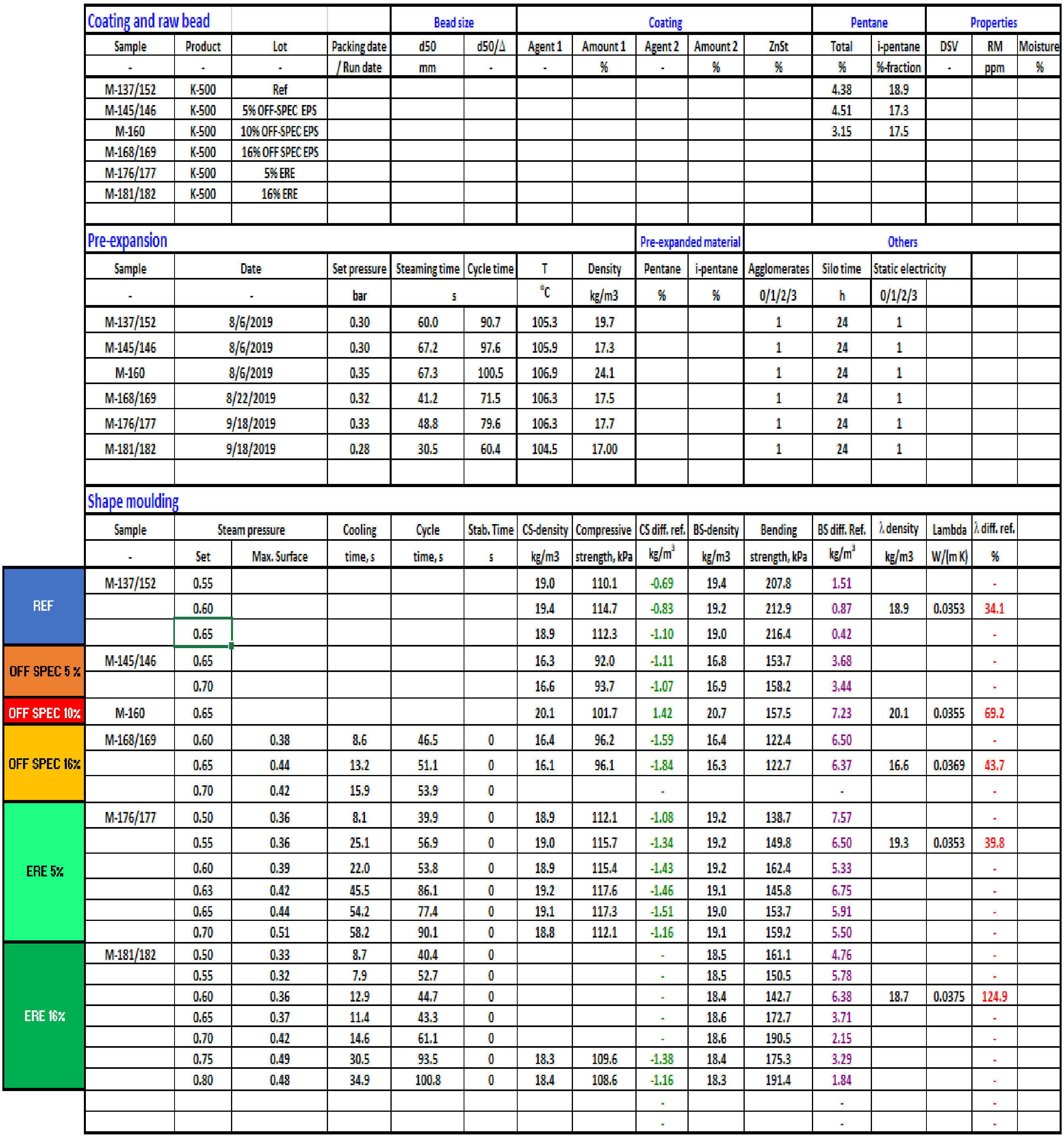
Figure 76. Residual monomer sample collection at different reused EPS qualities and the general trend at different EPS mass concentrations with EPS qualities distinguished from each other.

E. MW Data

Sample №	Sample Name	Mn	MW	Pd	Mz	Mz+1	Mz+1-Mz	stdev (Mn)	MW Theoretical	MW Difference
			g/mol	MW/MN					g/mol	Real vs. Theoretical
RAW MATERIALS										
LOF, K-1310		79819	179286	2.25	294937	400675	-	-	-	-
HOF, K-110		80028	181883	2.27	301378	411047	-	-	-	-
ERE		70686	156 516	2.21	258566	356630	-	-	-	-
REFERENCE										
M-137	M_REF1-300-0.22	-	-	-	-	-	-	-	187144	-
M-140	M_REF3.1-300-0.26	-	-	-	-	-	-	-	187144	-
M-152	M_REF_3.2-300-0.26	74774	186725	2.50	318523	438494	119970	2322.84	187144	-
M-156	M_REF_5-350-0.26	76847	187563	2.44	318694	438339	-	-	187144	-
M-157	M_REF_6-400-0.26	73204	187143	2.56	319651	441234	-	-	187144	-
5% LOF & HOF										
M-141	M_5%LOF_S1_0-300-0.26	74023	182213	2.46	308344	424291	115948	1499.38	186751	-2.43%
M-142	M_5%LOF_S1_15-300-0.26	77582	184257	2.38	310486	426012	115526	2476.27	186751	-1.34%
M-143	M_5%LOF_P1-300-0.26	69574	174000	2.50	296495	409420	112925	1683.52	186751	-6.83%
M-144	M_5%LOF_S1_30-300-0.26	73748	181565	2.46	307662	422250	113273	2755.77	186751	-2.78%
M-145	M_5%LOF_P2-300-0.26	72812	179134	2.47	304903	421438	116536	4433.96	186751	-4.08%
M-146	M_5%HOF_P1-300-0.26	73297	179176	2.45	305911	423240	117881	1245.15	186881	-4.12%
M-148	M_5%HOF_S1_45-300-0.26	75692	182076	2.41	310471	432529	-	-	186881	-2.57%
5% ERE										
M-147	M_5%ERE_P1-300-0.26	73067	179354	2.46	304532	420809	116276	1896.35	185612	-3.37%
M-176	M_5%ERE_P1-300-0.26_G0	72957	189116	2.60	327216	471791	-	-	185612	1.89%
M-177	M_5%ERE_P1-350-0.26_G0	78604	193101	2.46	337828	513976	-	-	185612	4.03%
M-178	M_5%ERE_P1-350-0.35_G0	73546	177550	2.41	303288	440088	-	-	185612	-4.34%
8% ERE										
M-179	M_8%ERE_P1-350-0.35_G0	71499	179476	2.51	311143	471816	-	-	184693	-2.82%
8% LOF										
M-154	M_8%LOF_P1-300-0.35	65809	164687	2.50	282091	394857	-	-	186515	-11.70%
M-158	M_8%LOF_P1-350-0.26	69798	168821	2.42	284400	391252	-	-	186515	-9.49%
M-159	M_8%LOF_P1-350-0.35	70652	169017	2.39	284977	393132	-	-	186515	-9.38%
10% LOF & HOF										
M-160	M_10%HOF_P1-350-0.26	71358	169476	2.38	285261	393959	-	-	186618	-9.19%
M-161	M_10%LOF_P1-400-0.26	68062	161859	2.38	274014	381713	-	-	186358	-13.15%
10% ERE										
M-180	M_10%ERE_P1-350-0.26_G0	66447	170129	2.57	299635	469640	-	-	184081	-7.58%
12% LOF										
M-162	M_12%LOF_P1-350-0.26	71522	170937	2.39	287426	395197	-	-	186201	-8.20%
M-163	M_12%LOF_P1-350-0.35	69615	164557	2.36	273557	376122	-	-	186201	-11.62%
14% LOF										
M-165	M_14%LOF_P1-370-0.35	72662	169719	2.34	283240	390864	-	-	186044	-8.77%
M-166	M_14%LOF_P1-370-0.38	71938	166923	2.32	278136	382934	-	-	186044	-10.28%
16% LOF										
M-167	M_16%LOF_P1-370-0.35	70549	172922	2.45	291878	403369	-	-	185886	-6.97%
M-168	M_16%LOF_P2-370-0.35	71396	167606	2.35	279655	384316	-	-	185886	-9.83%
M-169	M_16%LOF_P1-390-0.35	71288	167742	2.35	280565	386755	-	-	185886	-9.76%
16% ERE										
M-181	M_16%ERE_P1-370-0.26_G0	68294	167132	2.45	294002	489350	-	-	182243	-8.29%
M-182	M_16%ERE_P1-370-0.30_G0	73279	169508	2.31	302475	506171	-	-	182243	-6.99%
20% LOF										
M-171	M_20%LOF_P1-440-0.40	69363	163382	2.36	273764	378748	-	-	185572	-11.96%
M-172	M_20%LOF_P1-460-0.40	74755	176486	2.36	296217	411713	-	-	185572	-4.90%
M-173	M_20%LOF_P1-440-0.42	65595	176899	2.70	308470	495305	-	-	185572	-4.67%
20% ERE										
M-183	M_20%ERE_P1-440-0.30_G0	72248	173004	2.40	293546	430058	-	-	181018	-4.43%

Table 29. A collection of all the MW related values.

F. Molding, and Mechanical & Thermal Testing Data



Coating and raw bead				Bead size		Coating					Pentane		Properties		
Sample	Product	Lot	Packing date	d50	d50/Δ	Agent 1	Amount 1	Agent 2	Amount 2	ZnSt	Total	i-pentane	DSV	RM	Moisture
-	-	-	/ Run date	mm	-	-	%	-	%	%	%	%-fraction	-	ppm	%
M-137/152	K-500	Ref									4.38	18.9			
M-145/146	K-500	5% OFF-SPEC EPS									4.51	17.3			
M-160	K-500	10% OFF-SPEC EPS									3.15	17.5			
M-168/169	K-500	16% OFF SPEC EPS													
M-176/177	K-500	5% ERE													
M-181/182	K-500	16% ERE													

Pre-expansion							Pre-expanded material		Others		
Sample	Date	Set pressure	Steaming time	Cycle time	T	Density	Pentane	i-pentane	Agglomerates	Silo time	Static electricity
-	-	bar	s		°C	kg/m3	%	%	0/1/2/3	h	0/1/2/3
M-137/152	8/6/2019	0.30	60.0	90.7	105.3	19.7			1	24	1
M-145/146	8/6/2019	0.30	67.2	97.6	105.9	17.3			1	24	1
M-160	8/6/2019	0.35	67.3	100.5	106.9	24.1			1	24	1
M-168/169	8/22/2019	0.32	41.2	71.5	106.3	17.5			1	24	1
M-176/177	9/18/2019	0.33	48.8	79.6	106.3	17.7			1	24	1
M-181/182	9/18/2019	0.28	30.5	60.4	104.5	17.00			1	24	1

	Shape moulding														
	Sample	Steam pressure		Cooling	Cycle	Stab. Time	CS-density	Compressive	CS diff. ref.	BS-density	Bending	BS diff. Ref.	λ density	Lambda	λ diff. ref.
	-	Set	Max. Surface	time, s	time, s	s	kg/m3	strength, kPa	kg/m^3	kg/m3	strength, kPa	kg/m^3	kg/m3	W/(m K)	%
REF	M-137/152	0.55					19.0	110.1	-0.69	19.4	207.8	1.51			-
		0.60					19.4	114.7	-0.83	19.2	212.9	0.87	18.9	0.0353	34.1
		0.65					18.9	112.3	-1.10	19.0	216.4	0.42			-
OFF SPEC 5 %	M-145/146	0.65					16.3	92.0	-1.11	16.8	153.7	3.68			-
		0.70					16.6	93.7	-1.07	16.9	158.2	3.44			-
OFF SPEC 10%	M-160	0.65					20.1	101.7	1.42	20.7	157.5	7.23	20.1	0.0355	69.2
OFF SPEC 16%	M-168/169	0.60	0.38	8.6	46.5	0	16.4	96.2	-1.59	16.4	122.4	6.50			-
		0.65	0.44	13.2	51.1	0	16.1	96.1	-1.84	16.3	122.7	6.37	16.6	0.0369	43.7
		0.70	0.42	15.9	53.9	0			-			-			-
ERE 5%	M-176/177	0.50	0.36	8.1	39.9	0	18.9	112.1	-1.08	19.2	138.7	7.57			-
		0.55	0.36	25.1	56.9	0	19.0	115.7	-1.34	19.2	149.8	6.50	19.3	0.0353	39.8
		0.60	0.39	22.0	53.8	0	18.9	115.4	-1.43	19.2	162.4	5.33			-
		0.63	0.42	45.5	86.1	0	19.2	117.6	-1.46	19.1	145.8	6.75			-
		0.65	0.44	54.2	77.4	0	19.1	117.3	-1.51	19.0	153.7	5.91			-
		0.70	0.51	58.2	90.1	0	18.8	112.1	-1.16	19.1	159.2	5.50			-
ERE 16%	M-181/182	0.50	0.33	8.7	40.4	0			-	18.5	161.1	4.76			-
		0.55	0.32	7.9	52.7	0			-	18.5	150.5	5.78			-
		0.60	0.36	12.9	44.7	0			-	18.4	142.7	6.38	18.7	0.0375	124.9
		0.65	0.37	11.4	43.3	0			-	18.6	172.7	3.71			-
		0.70	0.42	14.6	61.1	0			-	18.6	190.5	2.15			-
		0.75	0.49	30.5	93.5	0	18.3	109.6	-1.38	18.4	175.3	3.29			-
		0.80	0.48	34.9	100.8	0	18.4	108.6	-1.16	18.3	191.4	1.84			-
									-			-			-
									-			-			-

Table 30. A collection of the mechanical and mechanical testing data.

G. Photographs/Pictures

Raw Materials

Picture 4. Raw materials used in polymerization and solubility experimentation (left bottom corner ERE, right upper corner LOF EPS [K-1310] and right bottom corner HOF EPS [K-110]).

Samples

REF (Virgin MS)

Picture 5. M-137 (M_REF1-300-0.22)

Picture 6. M-138 (M_REF2-300-0.22), NOT ENOUGH STYRENE.

Picture 7. M-139 (M_REF3-300-0.26), FAILED STABILIZATION TIMING.

Picture 8. M-152 (M_REF3.2-300-0.26).

Picture 9. M-156 (M_REF5-350-0.26).

Picture 10. M-157 (M_REF6-400-0.26).

Off-spec EPS (HOF & LOF)

5 %

Picture 11. M-141 (M_5%LOF_S1_0-300-0.26).

Picture 12. M-142 (M_5%LOF_S1_15-300-0.26).

Picture 13. M-143 (M_5%LOF_P1-300-0.26).

Picture 14. M-143 (M_5%LOF_P2-300-0.26).

Picture 15. M-144 (M_5%LOF_S1_30-300-0.26).

Picture 16. M-146 (M_5%HOF_P1-300-0.26).

Picture 17. M-148 (M_5%HOF_S1_45-300-0.26).

8 %

Picture 18. M-154 (M_8%LOF_P1-300-0.35).

Picture 19. M-158 (M_8%LOF_P1-350-0.26).

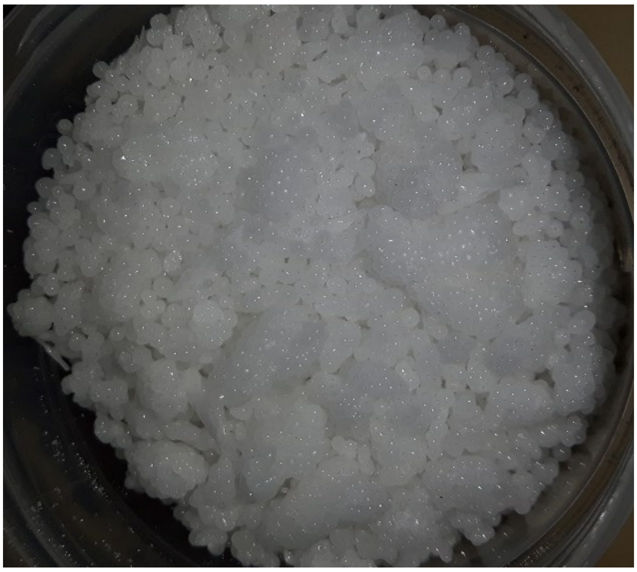
Picture 20. M-159 (M_8%LOF_P1-350-0.35).

10 %

Picture 20. M-160 (M_10%HOF_P1-350-0.26).

Picture 21. M-161 (M_10%LOF_P1-400-0.26).

12 %



Picture 22. M-162 (M_12%LOF_P1-350-0.26).

Picture 22. M-163 (M_12%LOF_P1-350-0.35).

14 %

Picture 23. M-165 (M_14%LOF_P1-370-0.35).

Picture 24. M-166 (M_14%LOF_P1-370-0.38).

16 %

Picture 25. M-167 (M_16%LOF_P1-370-0.35).

Picture 26. M-167 (M_16%LOF_P2-370-0.35).

Picture 27. M-169 (M_16%LOF_P1-390-0.35).

20 %

Picture 28. M-171 (M_20%LOF_P1-440-0.40).

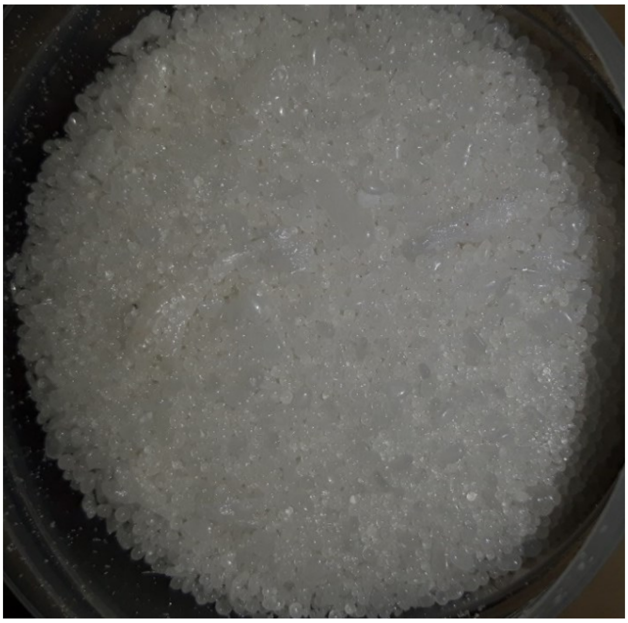
Picture 29. M-172 (M_20%LOF_P1-440-0.40).

Picture 30. M-173 (M_20%LOF_P1-440-0.42).

ERE (Fish box)

5 %

Picture 31. M-147 (M_5%ERE-P1-300-0.26)



Picture 32. M-176 (M_5%ERE-P1-300-0.26_G0).

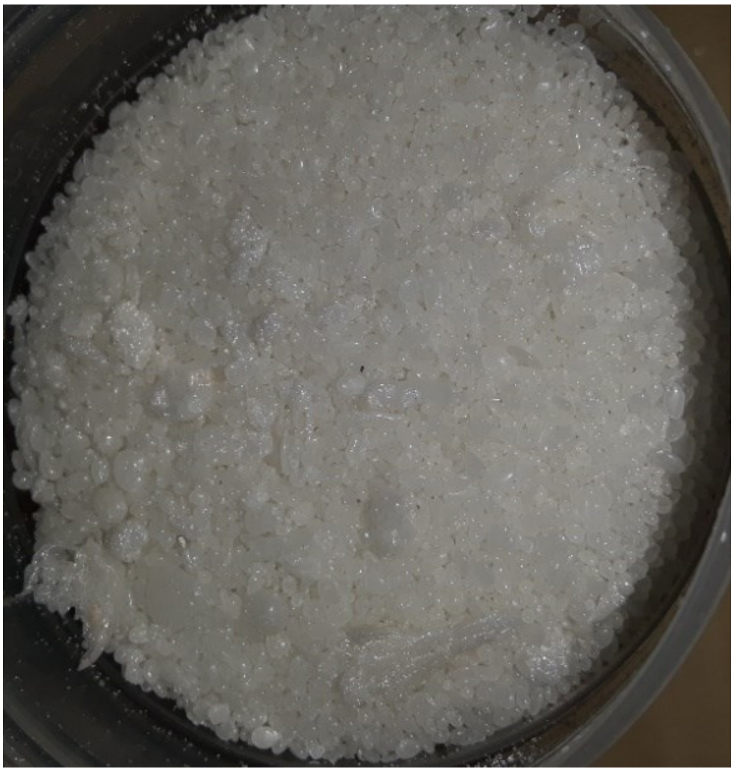
Picture 33. M-177 (M_5%ERE-P1-350-0.26_G0).

Picture 34. M-177 (M_5%ERE-P1-350-0.35_G0).

8 %

Picture 35. M-179 (M_8%ERE-P1-350-0.35_G0).

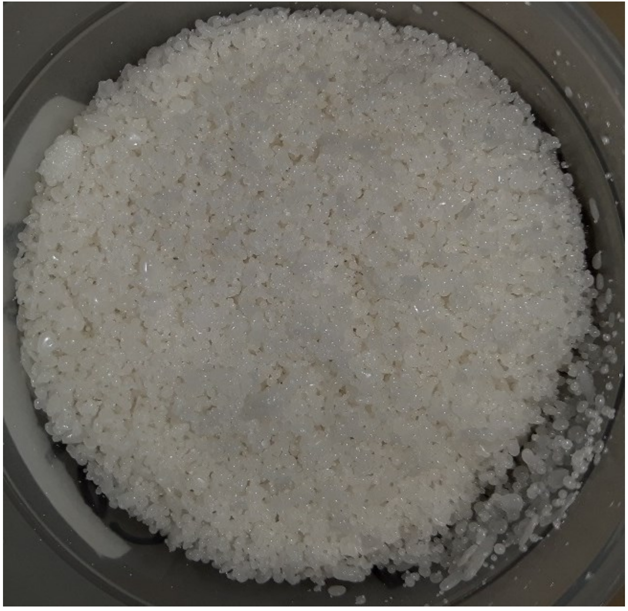
10 %



Picture 36. M-180 (M_10%ERE-P1-350-0.26_G0).

16 %

Picture 37. M-181 (M_16%ERE_P1-370-0.26_G0).

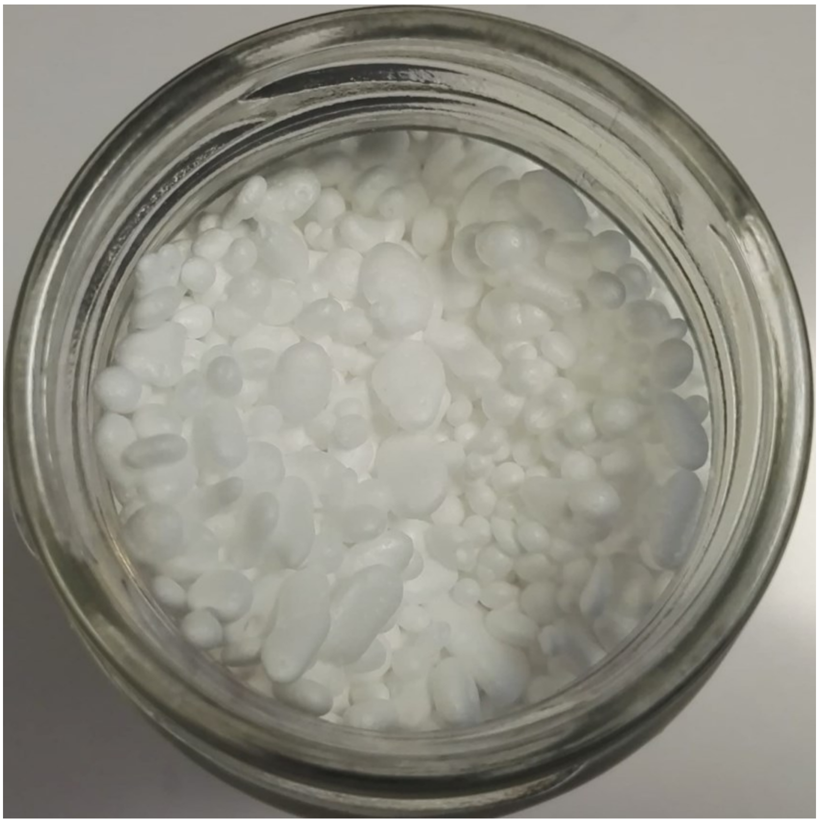


Picture 38. M-182 (M_16%ERE_P1-370-0.30_G0).

20 %

Picture 39. M-182 (M_20%ERE_P1-440-0.30_G0).

Expanded Beads

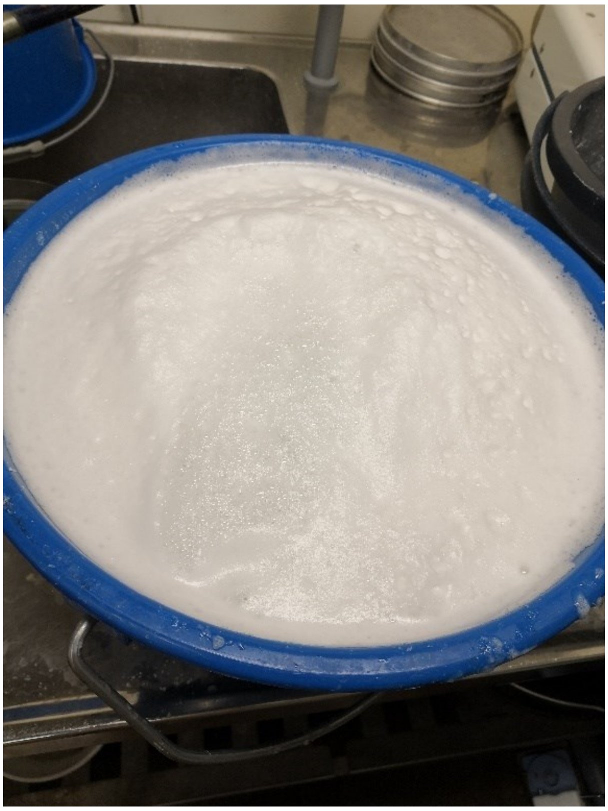


Picture 40. A sample of foamed EPS beads containing 16 wt-% ERE with oval form.

Foaming Phenomena

Picture 41. A picture of a foaming batch (10 wt-% K-1310 or LOF EPS, M-161).

Picture 42. Picture of the reactor during purification when the lid was removed after preparation of 10 wt-% reused EPS containing batches, M-161.



Picture 43. Foam surface of the batch with 14 % K-1310 with a stabilization factor of 0.38 and a stirring speed of 370 rpm (M-166) after batch removal.

Buildups

Picture 44. The M-reactor after the batch with 14 wt-% K-1310 or LOF EPS, M-166, with stabilization factor of 0.38 and stirring speed of 370 rpm (clusters and lumps on reactor walls).

Picture 45. The M-reactor after the batch 14 % K-1310 or LOF EPS, M-165, with stabilization factor of 0.35 and stirring speed of 370 rpm (clusters and lumps on reactor walls and surfaces).

Picture 46. The M-reactor after the batch 14 % K-1310 or LOF EPS, M-165, with stabilization factor of 0.35 and stirring speed of 370 rpm (clusters and lumps on reactor walls and surfaces).

Solubility Testing

Picture 47. A picture of dissolved extruded recycled EPS (ERE) after weeks of storage with sedimentation (fish-box material).

Picture 48. A picture of dissolved extruded recycled EPS after weeks of storage (fish-box material).

Glossary & Concepts

Some central and useful concepts and terms that appear in the thesis are gathered in this section in order to ease the reading and the understanding of the text and phenomenon included, and in addition, to keep the text shorter and more consistent.

Adhesion	Adhesion is the tendency of dissimilar particles or surfaces to cling to one another (cohesion refers to the tendency of similar or identical particles/surfaces to cling to one another) due to intermolecular forces [Wikipedia].
Agitation	A crucial unit operation in chemical industry and key to many heat and mass transfer operations. Movement of the components of the mass in the system in such a way that optimal physical and chemical conditions are provided, for example, by shaking or stirring.
Alloying	“The combining of polymers, after they have formed, or a polymer and a monomer into a single-phase, homogeneous polymer material. Some chemical attraction between the combined polymers is usually required to form an alloy. Alloys also form when two different metals combine [3]”.

Batch reactor (BR)

A reactor type in which all reactants are added in the beginning of the process. The reaction (polymerization) is allowed to proceed, either for a fixed time, or until some property of the product (monomer conversion, specific gravity, residual monomer etc.) is reached. The polymerization temperature may be kept constant, the reactor can be in a semiadiabatic mode in which a fixed coolant load is applied and the temperature is allowed to vary, usually due to exothermic nature of polymerization, or alternatively, a predetermined temperature trajectory is followed. The residende time distribution (RTD) is a distribution for the fraction of total material in the reactor that remains in the reactor for the same time (the reaction time or kettle time). For a BR the RTD is not a distribution at all (a spike) since all the materials remain in the reactor for the same time and there is no distribution of residence times [16]. Compare to “semi-batch reactor”.

Blending (or mixing)	“The combining of polymers, after they have formed, in such a way that resultant polymer material is in two or more phases [3]”

Bulk Polymerization

The only components of the formulation in bulk polymerization are pure monomers, the catalysts or the initiator, and molecular weight modifiers [13,14]. Both homogeneous and heterogeneous bulk polymerization are possible, depending on the solubility of the monomer to the polymer. Monomers that are miscible in their respective polymers, and in this way polymerize homogeneously in bulk include styrene, vinyl acetate and methyl methacrylate. Examples of typical heterogeneously bulk polymerized monomers are vinyl chloride and acrylonitrile [14]. In this case, the reaction mixture forms a slurry as the polymers that are insoluble in their monomers precipitate. Bulk polymerizations advantages are that very pure polymer is produced at a high production rate per unit of the reactor. The drawback is difficulties in temperature control (thermal control) because of the high viscosity of the reaction mixture associated with the high conversion of polymer [10]. This is particularly true for homogeneous bulk polymerization with high viscosity of the reaction mixture and the poor heat transfer characteristics. Especially in homogeneous free-radical polymerization the viscosity increases dramatically. Besides, the heat transfer coefficient can be further reduced due to polymer depositing on the reactor walls. Intermediate conversions often result in acceleration of the rate of heat generation with conversion due to the gel effect. This restricts the conversion to 55–65% in homogeneous bulk, while heterogeneous bulk can reach slightly higher conversion rates because of the lower increase in viscosity. The actual polymer product in bulk polymerization contains therefore residual monomer, which can be removed by flash evaporation and steam heating [14].

Coalescence	A process in which two domain phases are combined and form a larger phase domain.
Colloid	A type of homogenous mixture that contains a dispersed phase (the suspended particles) and a continuous phase (the medium of suspension). To qualify as colloid the mixture should not settle. The term emulsion is often used interchangeably with colloid, but emulsion should be used only when both phases, dispersed and continuous phases are liquids. See “emulsion”.
Copolymer	A polymer that made up of more than one species of monomers, such as HIPS: a copolymer of acrylonitrile and styrene.

Copolymerization

In copolymerization the polymer is produced by polymerizing a mixture of different monomers. The polymers of this type are called copolymers. Copolymerization is very useful for creating polymers with a combination of required properties. For example, polystyrene is brittle and polybutadiene is flexible. Hence, by combining these two monomers, a polymer that is more flexible than styrene but tougher than polybutadiene is created. The general-purpose rubber GRS (or SBR), which is a combination of styrene and butadiene, is an example of a copolymer. [18]

Compounding	“The mixing of additives into a plastic, a process often done with extrusion.” [3]
Dispersion	Material comprising more than one phase where at least one of the phases consists of finely divided phase domains, often in the colloidal size range, dispersed throughout a continuous phase. (IUPAC definition).

Dispersion polymerization

Dispersion polymerization is a form of precipitation polymerization. The term “dispersion polymerization” has come into general use because the technique replaced the process of polymer dispersion in the paint industry. In dispersion polymerization both the monomer and the initiator are soluble in the polymerization medium, but the medium is a poor solvent for the actual resulting polymer. Thus, at the onset, the reaction mixture is homogeneous, and the polymerization is initiated in homogeneous solution. Phase separation occurs at an early stage depending on the solvency of the medium for the produced macroradicals and macromolecules. This results in nucleation and the formation of primary particles. These primary particles are swollen with by the polymerization medium and the monomer. This results in formation of spherical particles in the range of about 0.1-10 µm. Typical examples of monomers polymerized with dispersion polymerization are styrene and methyl methacrylate in hydrocarbons or in C_1-C_5 alcohols. [29]

Dissolution	“The process of dissolving a solute into a solvent to make a solution.” [Wikipedia]
Emulsifier	A substance that stabilizes an emulsion by increasing its kinetic stability. See “emulsion”.
Emulsion	A mixture of two or more liquids, such as an oil-in-water emulsion, that are normally immiscible (unmixable) where one liquid is dispersed in the other, in other words the other liquid contains the other. The substances will stay mixed with the help of an emulsifier. Compare with “colloid”

Emulsion polymerization

An emulsion polymerization system converts an aqueous dispersion of monomer(s) by free-radical polymerization into a stable dispersion of polymer particles in the size range of 0.1-3 µm. Generally, an emulsion system contains the dispersing medium (e.g., water), monomer(s), a water-soluble initiator, and an emulsifying agent (e.g., sodium and potassium salts of saturated long-chain acids) as main components [16]. Typically, the monomer is insoluble, or scarcely soluble (e.g., solubility of styrene in water at 70 °C about 4 g/l), in the polymerization medium, but is emulsified into the medium by the aid of a surfactant (emulsifier or soap). The volume ratio of the monomer phase is usually in the range of 0.1-0.5 and the polymerization temperature is in the range of 40-80 °C. The initiator is, unlike in suspension polymerization, soluble in the medium, but not in the monomer [29]. Surfactant excess forms micelles (ca. 5-10 mm in diameter) that are clusters of surfactant molecules. A fractional part monomer can be found in the solution. The monomer is present partly in the form of droplets (ca. 1-10 µm or larger) and partly solubilized in the form of soap-coated micelles (ca. 50-100 Å) [29]. An emulsion system has normally 10^{18} micelles/cm^3 and 10^{10}-10^{11} monomer droplets/cm^3. The actual polymerization does not occur in monomer droplets, and neither in interior of the micelles (micellar nucleation) nor in the continuous phase (homogeneous nucleation) when the monomer is only slightly soluble. The advantages of emulsion polymerization are low viscosity of the reaction mixture, easy thermal control of the reactor, virtually 100 % conversion are achievable, high polymerization rates, and on top of that, the final latex may be directly usable. Disadvantages are the difficulties in removing emulsifier and coagulant from the final polymer (e.g., high residual impurity), and the high cost of the production compared to suspension systems. Common emulsion processing utilizing applications include copolymerization of styrene and butadiene (SBR rubber) and polymerization of chloroprene (neoprene rubber). Vinyl acetate and several acrylic monomers are polymerized in emulsion in the manufacture of latex paints, too. [14]

Endothermic	A reaction or process) accompanied by or requiring the absorption of heat. The opposite of exothermic [Oxford Dictionaries].
Exothermic	A reaction or process accompanied by the release of heat. The opposite of endothermic [Oxford Dictionaries]

Fouling	“The accumulation of unwanted material on solid surfaces to the detriment of function. Other terms used in the literature to describe fouling include: deposit formation, encrustation, crudding, deposition, scaling, scale formation, slagging, and sludge formation [Wikipedia]”.
Free radical	A.k.a. generally as radical. Radicals are reactive atoms, molecules or ions that have unpaired valence electrons. This makes radicals highly chemically reactive, and gives them the tendency for initiating chain reactions, which is extremely beneficial for producing polymer chains. Radical initiators have significant role in polymerization manufacture and industry, and can be generated in a number of ways, including redox reactions, ionizing radiation, heat, electrical discharges and electrolysis.
Heterogeneous polymerization	A polymerization process in which the produced polymer is insoluble, leading to precipitation (powder or granular) polymerization [Wikipedia].
Homogeneous polymerization	A polymerization process in which the produced polymer remains soluble [Wikipedia].
Initiator	“A source of any chemical species that reacts with monomer (single molecule that can form chemical bonds) to form an intermediate compound capable of linking successively with a large number of other monomers into a polymeric compound.” [Encyclopedia Britannica]

Interfacial polymerization

In interfacial polymerization system two phases are required, for instance, an organic phase with an acid chloride and an aqueous phase with a diamine. The actual polymerization occurs at the interface between the two immiscible liquid phases followed by a step-growth polymerization mechanism. The rate of the polymerization is high, and a high-molecular-weight polymer is produced at room temperature, which is atypical for the usual step-growth polymerization. The diffusion rates of monomers to the polymerization interface controls the rate of the polymerization [14].

Isomer	“Each of two or more compounds with the same formula but a different arrangement of atoms in the molecule and different properties”. [Oxford Dictionaries
Lambda λ	“The heat conductivity of a material is known as its lambda value [W/mK]. The thermal conductivity of a material is defined as the quantity of heat transferred in a given time through a distance L, in a direction normal to a surface area A, due to a temperature difference ΔT, and when the heat transfer is dependent only on the temperature gradient. Thus, the lower a material’s lambda value, the better its ability to insulate.“ [https://www.grundfos.com/service-support/encyclopedia-search/lambda-value.html]
Macromolecule	A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass. (IUPAC definition)
Monomer	A molecule which can undergo polymerization, thereby contributing constitutional units to the essential structure of a macromolecule. (IUPAC definition)
Octabin	“A bulk box, also known as a bulk bin, skid box, pallet box, bin box, or octabins is a pallet-size box used for storage and shipping of bulk quantities [Wikipedia]”.
Off spec	“Does not meet the specified or standard requirements.” [http://www.businessdictionary.com/definition/off-spec.html]
Peroxide	A group of compounds with the structure R−O−O−R. The O−O group in a peroxide is called the peroxide group or peroxo grous. [Wikipedia]
Petrochemicals	“Petrochemicals (also known as petroleum distillates) are chemical products derived from petroleum [Wikipedia]. Several organic and inorganic peroxides are useful as bleaching agents, as initiators of polymerization reactions, and in the preparation of hydrogen peroxide (q.v.) and other oxygen compounds.” [Encyclopedia Britannica]
Plastic	Generic term used in the case of polymeric material that may contain other substances to improve performance or reduce costs (IUPAC definition). A group of synthetic or semi-synthetic materials that can be shaped when soft and then hardened to retain a given shape. Typically, synthetic materials derived from petrochemicals with high molecular mass.
Plasticity	A general property of all materials that can be deformed irreversibly without breaking.

Plasticization	“Plasticization is the absorption of small chemically benign molecules that migrate between the macromolecular chains, thus allowing the plastic part to lose stiffness.” [62]
Polydispersity index (dispersity)	“Polydisperse systems display an array of chain lengths which broaden the molecular weight distribution. Polydispersity index (PDI) is used as a measure of broadness of molecular weight distribution. The larger the PDI, the broader the molecular weight. PDI of a polymer is calculated as the ratio of weight average by number average molecular weight. Information on PDI is required for improved selection of polymers for an application.” [63]
Polymer	A large molecule, or macromolecule, which is built of many repeated subunits, monomers. See “monomer” and “macromolecule”
Polymerization	A process of reacting monomer molecules together in a chemical reaction in order to form polymer chains.
Polystyrene	A synthetic aromatic hydrocarbon polymer produced from styrene.

Precipitation polymerization

Precipitation polymerization is heterogeneous form of solution polymerization. In precipitation polymerization the polymer is insoluble in its monomer or in the monomer-solvent solution and leads to formation of macroscopically apparent “polymer precipitates” [29]. The polymerization begins in a homogeneous phase and quickly turns into heterogeneous since the polymer precipitates as a second phase, the initial state of the reaction mixture is the same as that in dispersion polymerization (homogeneous solution) [14,29]. The overall kinetics in precipitation polymerization is assumed as the sum of independent reactions in the two different phases, that is to say, the monomer-rich phase and the polymer-rich phase. In the former phase normal solution kinetics is followed, and in the latter monomer-filled phase, all reactions (e.g., termination and propagation) may become diffusion-controlled. PVC, polyacrylenitrile, and low-density polyethylenes are some examples of well-known polymerization processes that follow precipitation polymerization kinetics under certain operating conditions [14]. See “dispersion polymerization”.

Resin	“A polymer that has not yet been formed into its final useful shape” [3].
R-value	“The R-value is a measure of resistance to heat flow through a given thickness of material. The higher the R-value, the more thermal resistance the material has and therefore the better its insulating properties.” [https://www.thegreenage.co.uk/article/thermal-conductivity-r-values-and-u-values-simplified/]
Sedimentation	The tendency of particles in suspension to be separated of the fluid against a barrier due to forces like gravity, centrifugal acceleration or electromagnetism.
Semi-batch reactor	A.k.a. a semi-continuous reactor. A reactor type in which some of the reactants are added during the process or reaction (polymerization) while others remain in the reactor for full kettle times. The added materials may be insignificant in volume, but not in effect (e.g. free radical initiators) [16]. Compare to a “batch reactor”.

Solid Catalyzed Polymerization

Production of HDPE, LLDPE, and isotactic polypropylene is done in low-pressure reactors in the presence of Ziegler-Natta catalysts. Most of the catalyst are heterogeneous, solid catalysts that can be supported or unsupported, although, some of the catalysts are used in liquid form. The monomer can be in contact with the catalyst in different forms, namely, in gaseous (the gas-phase process), pure liquid (the liquid solution process), or dissolved in a diluent (the slurry process). Whatever the case, the porous catalyst fractures and fragments of the catalyst are dispersed in the polymer and become the place for polymerization to happen. [14]

In gas-phase polymerization the system does not involve any liquid phase in the polymerization zone. Polymerization occurs at the interface between the solid catalyst and the during polymerization with monomers swollen polymer matrix. The role of the gas is to supply monomers, mix the polymer particles, and to remove the heat of the reaction. The gas-phase polymerization is also known as dry polymerization. Solution processes unique advantages include better molecular weight control, more easily controlled process variables due to homogeneous phase polymerization, and high productivity because of high temperatures. [14]

The liquid slurry polymerization has by far the most of solid catalyzed olefin polymerization technologies. The biggest advantage is the excellent temperature control of the process. The swelling of the polymer in the slurry medium can give major problems as the production rate is lowered. Manufacture of propylene in n-heptane in the presence of a solid Ziegler-Natta catalyst is one example of slurry polymerization. The growing polymer chains are attached to the solid surface. The polymer is quickly turning insoluble and precipitates forming a separate solid phase swollen with the monomer/solvent. In certain processes, every catalyst particle generates one particle (e.g., limited particle agglomeration). Many different types of homogeneous catalyst systems have been developed lately for precipitation polymerization (e.g., metallocenes). Here the polymerization starts in solution, and once the polymer chains grow enough, they become insoluble, agglomerate, and finally precipitate forming a separate solid phase. [14]

Solid-state polymerization

With solid-state polymerization it is possible to produce macroscopic single crystals, and sometimes also crystals of high optical quality. The crystal structure and the symmetry of the monomer controls the propagation reaction. Hence, sometimes propagation leads to a crystal-to-crystal transformation. Several novel polymers of perfect stereoregularity are produced by solid-state polymerization, including polydiacetylenes, crystalline 1,4-polybutadiene, ultrathin layers of vinyl polymers, and many optically active polymers in crystalline organization [14].

Solubility	"The maximum amount of an analyte that can be dissolved in a particular solvent or mixture of solvents at well-defined conditions (temperature, pressure, etc.)" [33]
Solvation	"Solvation describes the interaction of solvent with dissolved molecules. Ionized and uncharged molecules interact strongly with solvent, and the strength and nature of this interaction influence many properties of the solute, including solubility, reactivity, and color, as well as influencing the properties of the solvent such as the viscosity and density. In the process of solvation, ions are surrounded by a concentric shell of solvent. Solvation is the process of reorganizing solvent and solute molecules into solvation complexes. Solvation involves bond formation, hydrogen bonding, and van der Waals forces." [Wikipedia]

Solution polymerization

In solution polymerization the monomer is polymerized in a solution [4]. Both the polymer and the monomer are dissolved in the catalyst containing non-reactive solvent. The monomer concentration is lowered by the solvent, and hence the heat generation rate per unit volume of the reactor. The lower viscosity allows a higher heat removal rate than in bulk polymerization, and the solvent allows the use for reflux condensers. The heat of the polymerization can be removed with reflux cooling by evaporation of solvent. The condensed vapor can be recycled back to the reacting mass. On the other hand, problems may arise from remixing the condensed solvent with the viscous reacting mass. Solution processes are used for example in production of rubbers and LLDPE (linear low-density polyethylene) [13, 14]. The main disadvantages of the process are dealing with environmentally unfriendly solvent, making solvent recovery crucial [10], and in addition, the separation of polymer from the solution may become expensive. The polymerization kinetics are either homogeneous or heterogeneous (precipitation) [14].

Styrene	An organic, aromatic compound with the chemical formula C6H5CH=CH2, which is precursor for polystyrene and several copolymers. A.k.a. ethenylbenzene, vinylbenzene and phenylethane. "This derivative of benzene is a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations have a less pleasant odor." [Wikipedia]
Suspension	A heterogeneous mixture containing solid particles large enough for sedimentation. Dispersion of solid particles in a liquid (IUPAC definition). See "dispersion" and "sedimentation".
Suspension polymerization	See Chapter 3.1.2 Suspension Polymerization.
Tensile strength	Greatest strength a material can withstand without breaking.
Unit operation	A basic step in a process involving a physical change or chemical transformation such as crystallization, evaporation, filtration, polymerization, isomerization etc.
Vinyl compound	Any compound containing the vinyl group (CH2=CH-) such as styrene.