Modification of commercial poly-lactide for extrusion coated food packaging applications

Mohammad Bagher Khajeheian

Laboratory of Polymer Technology

Faculty of Science and Engineering

Åbo Akademi University

2015

Modification of commercial poly-lactide for extrusion coated food packaging applications

Mohammad Bagher Khajeheian

Academic Dissertation

Laboratory of Polymer Technology

Faculty of Science and Engineering

Åbo Akademi University

2015

Supervisor
Associated professor Ari Rosling
Åbo Akademi University
Turku, Finland

Custos
Professor Carl-Eric Wilén
Åbo Akademi University
Turku, Finland

Opponent and reviewer
Professor Mikael Skrifvars
University of Borås
Borås, Sweden

Reviewer
Associate Professor Paola Fabbri
University of Bologna
Bologna, Italy

PREFACE

The present work was carried out at the Laboratory of Polymer Technology, Center of Functional Material (FUNMAT), Åbo Akademi University, department of Materials Science, since Nov. 2010- Aug. 2015.

I would like to thank Professor Mikael Skrifvars for being my opponent, and Associate Professor Paola Fabbri for reviewing my thesis, as well as providing kind and valuable comments.

I wish to express my gratitude to my supervisor and mentor assistance professor Ari Rosling for his valuable advice and guidance during my long journey since 2008. I am greatly indebted to his wisdom, enthusiasm, and inspiration that have lightened up my path in science. I would also like to thank Professor Carl-Eric Wilén for his support, especially in recent years.

I wish to thank the Finnish Funding Agency for Technology and Innovation (TEKES) and Stora Enso Oyj for financial support. I was thrilled that I had a chance to collaborate with Stora Enso Oyj, and the Tampere University of Technology. I would especially like to thank Kimmo Nevalainen, Outi Kylliäinen, Ville Ribu from Stora Enso, and Professor Jurkka Kuusipalo, Sami Kotkamo and Sanna Auvinen from the TUT Materials Science department.

I wish to express my extreme gratitude to each and every one of the former, and current, lab members for their contribution. They shared their time creating a pleasant and innovative working atmosphere, as well as providing their warm friendship.

I wish to thank all my friends in Turku, and around the world, ''alla kära och nära'' for all fun we had together.

Finally, I would like to thank my family, for their love and support. To them I dedicate this thesis.

ABSTRACT

Poly-L-lactide (PLLA) is a widely used sustainable and biodegradable alternative to replace synthetic non-degradable plastic materials in the packaging industry. Conversely, its processing properties are not always optimal, e.g. insufficient melt strength at higher temperatures (necessary in extrusion coating processes). This thesis reports on research to improve properties of commercial PLLA grade (3051D from NatureWorks), to satisfy and extend end-use applications, such as food packaging by blending with modified PLLA. Adjustment of the processability by chain branching of commercial poly-L-lactide initiated by peroxide was evaluated. Several well-defined branched structures with four arms (sPLLA) were synthesized using pentaerythritol as a tetra-functional initiator. Finally, several block copolymers consisting of polyethylene glycol and PLLA (i.e. PEGLA) were produced to obtain a well extruded material with improved heat sealing properties.

Reactive extrusion of poly-L-lactide was carried out in the presence of 0.1, 0.3 and 0.5 wt% of various peroxides [tert-butyl-peroxybenzoate (TBPB), 2,5-dimethyl-2,5-(tert-butylperoxy)-hexane (Lupersol 101; LOL1) and benzoyl peroxide (BPO)] at 190°C. The peroxide-treated PLLAs showed increased complex viscosity and storage modulus at lower frequencies, indicating the formation of branched/cross linked architectures. The material property changes were dependent on the peroxide, and the used peroxide concentration. Gel fraction analysis showed that the peroxides, afforded different gel contents, and especially 0.5 wt% peroxide, produced both an extremely high molar mass, and a cross linked structure, not perhaps well suited for e.g. further use in a blending step. The thermal behavior was somewhat unexpected as the materials prepared with 0.5 wt% peroxide showed the highest ability for crystallization and cold crystallization, despite substantial cross linking.

The peroxide-modified PLLA, i.e. PLLA melt extruded with 0.3 wt% of TBPB and LOL1 and 0.5 wt% BPO was added to linear PLLA in ratios of 5, 15 and 30 wt%. All blends showed increased zero shear viscosity, elastic nature (storage modulus) and shear sensitivity. All blends remained amorphous, though the ability of annealing was improved slightly. Extrusion coating on paperboard was conducted with PLLA, and peroxide-modified PLLA blends (90:10). All blends were processable, but only PLLA with 0.3 wt% of LOL1 afforded a smooth high quality surface with improved line speed. Adhesion levels between fiber and plastic, as well as heat seal performance were marginally reduced compared with pure 3051D. The water vapor transmission measurements (WVTR) of the blends containing LOL1 showed acceptable levels, only slightly lower than for comparable PLLA 3051D.

A series of four-arm star-shaped poly-L-lactide (sPLLA) with different branch length was synthesized by ring opening polymerization (ROP) of L-lactide using pentaerythritol as initiator and stannous octoate as catalyst. The star-shaped polymers were further blended with its linear resin and studied for their melt flow and thermal properties. Blends containing 30 wt% of sPLLA with low molecular weight (30 wt%; Mw_{total}: 2500 g mol^{-1} and 15000 g mol^{-1}) showed lower zero shear viscosity and significantly increased shear thinning, while at the same time slightly increased crystallization of the blend. However, the amount of crystallization increased

significantly with the higher molecular weight sPLLA, therefore the star-shaped structure may play a role as nucleating agent.

PLLA-polyethylene glycol–PLLA triblock copolymers (PEGLA) with different PLLA block length were synthesized and their applicability as blends with linear PLLA (3051D NatureWorks) was investigated with the intention of improving heat-seal and adhesion properties of extrusion-coated paperboard. PLLA-PEG-PLLA was obtained by ring opening polymerization (ROP) of L-lactide using PEG (molecular weight 6000 g mol^{-1}) as an initiator, and stannous octoate as catalyst. The structures of the PEGLAs were characterized by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). The melt flow and thermal properties of all PEGLAs and their blends were evaluated using dynamic rheology, and differential scanning calorimeter (DSC). All blends containing 30 wt% of PEGLAs showed slightly higher zero shear viscosity, higher shear thinning and increased melt elasticity (based on tan delta). Nevertheless, no significant changes in thermal properties were distinguished. High molecular weight PEGLAs were used in extrusion coating line with 3051D without problems.

SVENSK SAMMANFATTNING

Bioplasten, poly-L-laktid (PLLA), som erhålls från förnybara råvaror, utgör ett hållbart och bionedbrytbart alternativ för ett antal icke-nedbrytbara petroleumbaserade plastmaterial inom förpackningsindustrin. Generellt kan det konstateras att PLLAs bearbetningsegenskaper inte alltid är fullt optimala, t.ex.vållar dess smälthållfasthet vid högre temperaturer (nödvändigt vid extruderings- beläggningsprocesser) problem. I denna avhandling studeras olika möjligheter att förbättra smältegenskaperna hos en kommersiell PLLA kvalitet (3051D), samt att tillfredsställa och utvidga materialets slutanvändningstillämpningar som livsmedelsförpackning. För att skapa lämpliga slutmaterial framställdes och blandades olika förgrenade PLLA strukturer med en linjär PLLA kvalité. Förgrenade PLLA strukturer åstadkoms snabbt och effektiv genom reaktiv extrudering i närvaro av olika peroxider. Härtill syntetiserades mera väldefinierade förgrenade PLLA strukturer med fyra armar (sPLLA) med hjälp av pentaerytritol som en tetrafunktionell initiator. Slutligen har flera sampolymerer bestående av polyetylenglykol och PLLA ändblock (dvs. PEGLA) framställts för att erhålla en extruderingsbar blandning med linjär PLLA med förbättrade värmeförseglingsegenskaper.

Reaktiv extrudering av poly-L-laktid utfördes i närvaro av 0,1, 0,3 och 0,5 vikt-% av olika peroxider [tert-butyl-peroxibensoat (TBPB), 2,5-dimetyl-2,5- (tert-butylperoxi) hexan (Lupersol 101; LOL1) och bensoylperoxid (BPO)] vid 190°C. Peroxid-behandlad PLLA uppvisade ökad komplex viskositet och lagringsmodul vid lägre frekvenser vilket leder till uppkomsten av en förgrenad/tvärbunden arkitektur. De uppkomna materialegenskaperna var beroende av använd peroxid och peroxidkoncentrationen. En analys av gelinnehållet påvisade att peroxiderna gav olika gelhalter och speciellt med 0,5 vikt-% peroxid, producerades både, en extremt hög molmassa och en tvärbunden struktur. Den höga gelhalten kan utgöra ett problem för t.ex. en vidare användning i ett smältblandningssteg. Det termiska beteende var något oväntat emedan material som framställts med 0,5 vikt% peroxid uppvisade den högsta kristallisationsförmågan samt förmåga till kallkristallisation trots betydande tvärbindning grad.

Peroxid-modifierad PLLA, (0,3 vikt-% av TBPB och LOL1 samt 0,5 vikt-% BPO) smältblandades med linjär PLLA i förhållandet 5, 15 och 30 vikt-%. Samtliga blandningar visade ökad noll skjuvviskositet, elastisk karaktär (lagringsmodul) och skjuvkänslighet. Alla blandningar förblev amorfa, men kristallisationen under anlöpningen förbättrades något. Extruderingsbeläggning på kartong testades med PLLA/peroxid-modifierad PLLA blandningar (90:10). Alla blandningar var bearbetbara, men endast PLLA med 0,3 vikt-% av LOL1 gav en slät högkvalitativ yta med förbättrad körhastighet på linjen. Vidhäftningsnivån mellan pappersfiber och plast samt värmeförseglingsprestandan minskade marginellt jämfört med ren 3051D. Vattenånga diffusionen för belagt material innehållande LOL1 visade acceptabla nivåer, vilka var något lägre än för PLLA 3051D.

Fyr-armade, stjärnformade poly-L-laktid (sPLLA) med olika armlängd syntetiserades genom ringöppningspolymerisation av L-laktid med pentaerytritol som initiator och tennoktoat som katalysator. De stjärnformiga polymererna blandades med kommersiell linjär PLLA och blandningarnas smältbeteende och termiska egenskaper undersöktes. Blandningar innehållande 30 vikt-% av sPLLA med låg molekylvikt (Mw_{total}: 2500 g mol^{-1} och 15000 g mol^{-1}) uppvisade lägre

noll skjuvviskositet och ett märkbart skjuvtunnande beteende men samtidigt också något förhöjd kristallisationsförmåga. Emellertid ökade kristallisationen signifikant hos sPLLA med den högre molekylvikten, vilket antyder på att den stjärnformade strukturen kan fungera som ett nukleeringsmedel.

PLLA-polyeten glykol-PLLA triblock-sampolymerer (PEGLA) med olika PLLA blocklängd syntetiserades och blandades med linjär PLLA (3051D) med avsikt att förbättra materialets värmeförseglings och adhesionsegenskaper hos extruderingsbelagd kartong. PLLA-PEG-PLLA erhölls genom ringöppnings polymerisation av L-laktid med PEG (molekylvikt 6000 g mol-1) som initiator och tennoktoat som katalysator. Strukturerna för PEGLA och molmassorna bestämdes med proton-kärnmagnetisk resonansspektroskopi (1H-NMR). Smältflödet och de termiska egenskaperna hos alla PEGLA och deras blandningar med linjär PLLA karakteriserades med dynamisk reologi och differentiell svepkalorimeter (DSC). Alla blandningar innehållande 30 vikt% av PEGLA visade något högre noll skjuvviskositet, kraftigare skjuvtunning och ökad smältelasticitet (baserat på tan delta). Inga signifikanta förändringar i de termiska egenskaperna kunde urskiljas. Högmolekylär PEGLA/PLLA (3051D) blandingar kunde köras vid en extruderingsbeläggningslinje utan problem.

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications:

I   Khajeheian M. B.; Rosling A. 'Rheological and thermal properties of peroxide-modified poly(L-lactide)s for blending purposes' *Journal of Polymers and the Environment.* DOI 10.1007/s10924-014-0693-4.

II   M. B. Khajeheian, A. Rosling. Rheological and thermal properties of peroxide-modified poly(L-lactide)s in the blend with commercial PLLA. Submitted.

III M. B. Khajeheian, A. Rosling. 'Preparation and Characterization of Linear and Star-shaped Poly L-lactide Blends'. Accepted at *Journal of applied polymer science* in March 2015. DOI: 10.1002/app.42231

IV   Khajeheian M. B.; Kotkamo S.; Kuusipalo J.; Rosling A. 'Synthesis and characterization of tri-block PLLA-PEG-PLLA for blending purposes with commercial PLLA'. Accepted for publication at *Polymer-Plastics Technology & Engineering*.

M. B. Khajeheian, A. Rosling. Rheological and thermal properties of peroxide-modified poly(L-lactide)s in the blend with commercial PLLA. Submitted to Journal of Open chemistry.

CONTENTS

1. INTRODUCTION

1.1. Background

Many products such as modern cars, computers, airplanes, medical implants, sport equipment, and safer food packaging are highly dependent on the developments in plastics technology. For the last few decades, packaging has been one of the rapidly growing areas for the use of plastics. Plastics are convenient, safe, and inexpensive with good aesthetic qualities, which are the major factors that make plastics useful for packaging almost anything [1]. Over the latest decades, the most frequently observed keywords in the packaging-related literature have been biodegradable, biocompatible, compostable, environmentally friendly, annually renewable, sustainable, green, and biopolymers. This manifests from the idea that, due to the high impact of plastic waste from our daily use, environmental pollution has become a great concern. Today, more than 230 million tons per year of different synthetic plastics are produced throughout the world. Packaging is the largest single market for plastics, amounting to over 12 million tons per year, about a quarter of the total U.S. plastics production [2,3]. Industrial attention is increasingly turning to paperboard and folding cartons for their product packaging solutions, due to the multitude of benefits that paperboard offers across its lifecycle [4]. However, paper has a high porosity and weak tear resistance, and is therefore usually coated, or laminated, with one or more layers of polymeric materials for its usage in food packaging. Paper–based laminates are useful for a large variety of packaging products [5,6]. Currently, most polymer packaging plastics are based on polyethylene (PE), polypropylene (PP), polystyrene (PS), poly vinyl chloride (PVC), nylon, and polyesters such as polyethylene terephthalate (PET). These polymers are mainly produced from non-renewable fossil resources, and extensively used because of their strength, inertness and ease of production. Due to their poor biodegradability, synthetic petrochemical-based polymers become a major source of solid waste, causing a global environmental problem [7]. In order to control the problem of plastic waste, two approaches have to date been used, the first being the storage of waste at landfill sites. However, due to rapidly growing plastic consumption, satisfactory landfills are limited, and burying of plastic waste in the landfills is a burden for future generations. The second approach, which embraces usage, can be divided into incineration and recycling of waste materials. Incineration converts the waste into ash, flue gases, particulates and heat that can be used to generate electricity. However, incineration produces a large amount of carbon dioxide (CO_2) and sometimes toxic gases that also contribute to global warming, and pollution. Instead, recycling can somehow solve these problems; however, this involves significant expenditure of labor and energy: collecting of plastic waste, separating according to the type of plastic, washing, grinding and eventually reprocessing to a final product. Therefore the quality of the recycled plastic is lower than the material produced directly by the primary manufacturer and packaging becomes more expensive [8]. One of the possible solutions to this problem is to replace the synthetic commodity plastics with biodegradable polymers that are readily degraded and disposed of in bioactive environments by enzymatic action of microorganisms such as bacteria and fungi [9]. Increasing oil prices, growing concern about the emission of greenhouse gases, and changes in waste economy lead to a rising interest the

development of new bio-based products, and innovative process technologies. These developments can prevent diminishing natural oil resources, reduce the dependency on fossil fuels, and move towards a sustainable biodegradable basis [10]. These materials are called green polymeric materials, which do not involve the use of toxic or noxious components in their manufacture, and degrade in the environment naturally [8]. By definition, materials that degrade in the biological environment are called biodegradable. Biodegradable polymers usually degrade through enzymatic, or non-enzymatic hydrolysis, rather than thermal oxidation or radiation. These polymers are currently used in biomedical, and ecological environmental-friendly applications. Biodegradable polymers can be also classified based on their origin into natural polymers (obtained from plants, animals and microbes) and synthetic polymers (e.g. aliphatic polyesters, polyols, polycarbonates) [11]. Different classifications of various biodegradable polymers have been proposed, however, one of the most common ways to classify them is based on their production. They can be classified into four major groups: (I) Polymers from biomass, such as agro-polymers from agro-resources [polysaccharides (starch, lingo-cellulose, chitosan/chitin), proteins and lignin], (II) Polymers obtained by microbial production such as the polyhydroxyalkanoates (PHAs) and polyhydroxy butyrate-co-hydroxyvalerate (PHBV), (III) Polymers conventionally and chemically synthesized from monomers obtained from agro-resources like polylactic acid (PLA), (IV) Polymers obtained from fossil/petrochemical resources such as polyvinyl alcohol, polycaprolactone (PCL), polyglycolic acid (PGA) and all the other aliphatic or aromatic homo- or copolyesters. Biopolymers are either biodegradable polymers or polymers (or their constituents) produced by living organisms; in other words, they are polymeric biomolecules and are often derived from plants processing atmospheric CO_2. Their polymer chains may also be broken down by non–enzymatic processes, such as chemical hydrolysis. Upon disposal in bio–bins and exposure to a bioactive environment, certain biopolymers degrade to natural substances, such as CO_2, methane, water, biomass, humic matter and various other natural substances, which can be readily eliminated. Biodegradable polymers thus naturally recycle by biological processes. New agricultural crops, using nutrients from compost and fixing CO_2, produce new polymer building blocks, monomers and polymers [9–12].

At present, the basic raw materials for producing these biodegradable polymers, such as sugar and starch, are less expensive than oil, but the complexity of the production routes and their low productivity still increase the price of these polymers [13]. After various advancements and technologies, biodegradable materials are showing a number of excellent and promising properties for many applications, including packaging, automotive, food and drinks packaging, as well as biomedical applications. As these polymers are biodegradable, they can be a solution for the solid plastic waste issue [14]. In extrusion coating of paper and paperboard, the replacing of traditional polyolefin resins with those from sustainable resources faces increasing interest. New technologies have been created through intensive R&D in order to reduce costs and improve the material properties of the sustainable resins [4]. It is noteworthy that while designing new biodegradable materials, their properties as packaging product like the ability to form films, adequate tensile strength and elongation, as well as puncture resistance and tear resistance have to be considered. In general, the important physical properties and rheological

characteristics of the main polyolefins used in packaging, such as low-density polyethylene (LDPE) or high-density polyethylene (HDPE), need to be retained [15].

1.2.   Justification

In recent years, PLLA's properties were modified for better suiting in melt extrusion coating processes [16]. PLLA is a moderately new polymer in the plastic industry, and has been intensively marketed since the end of the 1990s. In addition to extrusion coating, PLLA can also be processed by several other processing techniques such as injection molding, thermoforming and film casting. Equipment for processing polyethylene, polyvinyl chloride, polystyrene and polyamide can be useful for processing properly modified PLLA grades. The physical properties of PLLA resins can be modified by stereo-chemical purity, molecular weight and additive packages, and differ greatly with their grade. Therefore, several grades of PLLA were optimized to follow the special demands of process and end-use performance. However, intrinsically PLLA has relatively poor melt strength, and the melt viscosity of PLLA is not very shear-sensitive. Branching of the polymer backbone commonly enhances these weaknesses. Branched PLLAs are more appropriate for extrusion coating, because of their improved shear thinning and melt strength [16,17]. In the last decades, polylactide polymers gained enormous attention as a replacement for synthetic polymers. As an example, general information about PLLA processing was summarized by Lim et al. [18], and the role of PLLAs in packaging materials was reviewed by Auras et al.[19]. Barrier properties preserve the product against gases, aroma, grease, and moisture. This ability is one of the main characteristics of a packaging material, and in PLLA the barrier properties are effected by crystallinity and molecular weight [20,21]. The water vapor transmission rate of PLLA decreases monotonically from 0 to 20% crystallinity, due to higher moisture resistance of crystalline structures compared to free amorphous regions, according to Tsuji et al [21]. Papers and paperboards have minimum barrier properties compared to polymer films [22], therefore PLLA-coated paperboards for corrugated box liners were studied [23]. Barrier properties of extrusion-coated paperboards are completely controlled by the polymer coat. During the extrusion coating, usually the PLLA film is quenched, and the polymer solidifies inhibiting further crystallization and packing. Said quenching leads the polymer to an amorphous state, and the PLLA loses its potential crystalline structure [24]. Heat sealability is another important property when considering PLLA as an extrusion-coated paperboard material. An amorphous PLLA film starts to seal at 80–85°C, and the best sealing temperature is around 110°C, under pressure for 1 to 5 seconds. Generally, the sealing at higher temperatures requires less time according to Auras et al. The sealing pressure is an important factor for the sealing quality, although a higher pressure does not improve the sealing strength [19].

1.3.   Objectives

The main purpose of this study was to produce various PLLA-based branched structures, and evaluate their potential as blends (with commercial PLLA) at extrusion coating of products of paperboards for food packaging purposes. Special emphasis was placed on the improvement of

the process runability (by increasing melt elasticity and strength) and the heat-seal performance (by reducing the heat sealing temperature). Furthermore, the materials and blends were studied for their thermal properties and crystallization behavior (using differential scanning calorimetry) as well as their rheological properties such as zero shear viscosity, shear thinning, loss modulus G', storage modulus G'' and tan delta which serve as indicators for the runability and miscibility of the materials in the extrusion coating process. The structure and chemical composition of blends were confirmed by ^{1}H-NMR analysis. To obtain the molecular weight of the copolymers, GPC technique was used. The gel content of peroxide-modified PLLA was measured using Soxhlet extraction. Finally, larger batches of several in-house made modified polymers were prepared and tested as blends at the pilot line at Tampere University of Technology (TUT).

More specifically, the objectives were:

- **Preparation of branched PLLA**

    This stage consists of two parts:
    a) Preparation of the branched/ cross-linked PLLA using various peroxides and reactive extrusion as a fast and convenient method. [I]
    b) Synthesis and characterization of series of the controlled branched four-arm star-shaped PLLA. [III]

- **Preparation of the tri-block copolymers PEGLA**

    Synthesis of several tri-block PLLA-PEG-PLLA copolymers using PEG_{600} and PEG_{6000} as initiators while varying the PLLA arm lengths and blending linear PLLA 3051D with the obtained modified PLLA structures. [IV]

- **Blending linear PLLA 3051D with modified PLLA structures**

    Two different blending methods are used:
    a) Blending by extrusion in order to determine thermal and film properties of the final material. [II, IV]
    b) Blending by solvent mixing in order to avoid premature degradation and to establish the rheological characterization comparable with the blend's properties while a real extrusion process. [II, III and IV]

- **Extrusion coating in pilot line in TUT**

    In all three cases, the most potential and promising materials are prepared and tested in the extrusion coating pilot line at Tampere University of Technology. [II, IV]

1.4.   Thesis Outline

Poly-L-lactide (PLLA) is a widely used sustainable and biodegradable alternative to replace synthetic plastic materials in the packaging industry. However, its processing properties are not always optimal, due to its low melt strength at higher temperatures. To use the PLLA in extrusion coating processes, which needs high temperatures, its properties needs to be modified to satisfy, and extend, end-use applications in food packaging. Chapter one focuses on a brief overview, background and objectives. Chapter two is a literature survey pertaining to biodegradable polymers, polylactic acid grades, synthesis methods, star polymers, branching and blending of PLA, PLA and PEG compositions, and reactive extrusion. Moreover, a brief explanation of packaging will be described in this chapter. Chapter three describes the materials, tests, preparation of the branched PLA based polymers and blending of them via extrusion, and copolymerization of PLA-PEG. Chapter four focuses on results and the discussions of the obtained tests from the synthesized copolymers and blends. Finally, chapter five contains the overall conclusions, which compares the results, and suggests the optimum compositions suitable for food packaging applications.

2. LITERATURE REVIEW

2.1. Biodegradable polymers

Biomaterials and biodegradable materials are two areas of great interest in material science. Medical, chemical, and environmental scientists contribute to human health care, boosting quality of life, preserving the environment from white pollution, and decreasing dependence on fossil fuels. Numerous polymers have been elaborated as potential biomaterials and biodegradable packaging materials due to their various compositions, special structures, and excellent properties that cover a wide range of applications [25]. Biodegradable polymers are widely used in the medical and packaging fields, and aliphatic polyesters might be the favorable alternatives as they consist of flexible ester bonds, and can degrade into nontoxic materials in different soils and pH solutions. Polylactones such as polylactic acid (PLA), polyglycolic acid (PGA), and polycaprolactone (PCL), as well as their copolymers are the most common synthetic biodegradable polymers, due to their prominent properties such as biodegradation, transparency, excellent film-forming properties via casting for coatings, and permselectivity. They have good thermo-mechanical and processing properties [25,26]. At present, most materials used for food packaging consist of a variety of petrochemical-based polymers, metals, glass, paper, and board, or combinations of the previous mentioned materials. The durability and degradability of packaging materials are two contradictory subjects; the first factor is desirable for packaging stability and protection of its contents during shelf life, while the second factor for its rapid degradation in the environment. In some polymers, degradation occurs in biological environments when they come into contact with living cells or microorganisms. Such environments include terrestrial soils, seas, rivers, and lakes, as well as the human body and animals [11]. Biodegradation is defined as the enzymatic degradation of a polymer in natural environments. This process entails changes in chemical structure, loss of mechanical and structural properties, then finally changing into other compounds [27]. Traditional polymer degradation happens mostly through scission of the main chains, or side-chains, of the polymer molecules, inspired by thermal activation, oxidation, photolysis, radiolysis, or hydrolysis.

2.2. Lactic acid and different lactide monomer types

Lactic acid is an organic acid, which can be found in many natural based products. It can be produced by animals and microorganisms, or derived from plants like corn, starch, and sugarcane bagasse. It also can be derived from renewable intermediary products such as ethanol and acetaldehyde, or from chemical derivatives, such as acetylene from coal, or ethylene extracted from oil. Lactic acid was first discovered by Scheele in 1780 as a component in sour milk. Lavoisier named this component ''acide lactique'' in 1789, which became the possible origin of the current terminology for lactic acid. Lactic acid is a widely produced carboxylic acid in nature, and the main industrial method of its preparation is based on the microbial fermentation of carbohydrates using bacteria, fungi and yeasts [28]. Afterwards, Carothers et. al. synthesized from lactic acid the lactide monomer, and thereof a polymer using the ring opening

polymerization. The polylactic acid polymer is unstable, and will begin hydrolysis in wet environments. In 1960 however, this degradation was found to be useful in medical applications [28]. Lactic acid also known as 2-hydroxypropanoic acid is a chiral molecule, and one of the smallest optically active molecules, with two stereoisomers, L(+) and D(-) enatiomers. Racemic lactic acid is an optical inactive form which is the 1:1 mixture of D(-) and L(+) isomers [29]. Lactic acid is a useful monomer in chemical reactions due to its carboxyl and hydroxyl functional groups [30]. Lactic acid is a multipurpose material in food, pharmaceutical, textile, chemical, medical industries, [31] and as a polymer, PLA, is a great choice for biodegradable polymer and composites, thus there is a large demand for lactic acid production [32]. Lactide (LA) monomer is obtained from lactic acid, and has different stereoisomers similar to lactic acid due to its chirality. L-Lactide (S-Lactide) and D-Lactide (R-Lactide) are the optically active isomers, while meso-lactide and rac-lactide are the optically non-active isomers. The optical purity of lactide is very influential during production of high molecular weight PLA, since a small amount of enantiomeric impurities during synthesis can intensely change its final properties, such as the crystallinity and biodegradation rate [33]. The biological activity is strongly dependent on the L-lactic acid units. For good biodegradability, D-lactic acid content or the average block length of D-LA units in the polymer should be reduced [34].

2.3. Poly-L-Lactide

Polylactic acid or polylactide (PLA) is a poly α-hydroxyester, and a versatile biodegradable polymer produced in several grades for different applications. Similar to lactic acid, polylactic acid is a chiral polymer containing a main chain with asymmetric carbon atoms and helical conformation, and comes in different grades such as poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and poly-D,L-lactic acid (PDLLA) [35]. PLLA has the highest percentage of production, since the majority of lactic acid from the biological sources exists in the L-isomer form. Depending on the composition of the optically active L- and D-enantiomers, PLA can crystallize in three forms (α, β, and γ). The α structure is more stable and has a melting temperature (T_m) of 185ºC compared to the β-structure with T_m of 175ºC [18]. Today, PLA is approved by the US Food and Drug Administration (FDA) and the European regulatory authorities to be used in food and medical applications [36]. Due to the existence of asymmetric carbon atoms in PLA, it has stereogenic centers in the main unit, which can show isotactic and syndiotactic structures. Isotactic polymers contain sequential stereogenic centers with the same configuration, while syndiotactic polymers contain sequential stereogenic centers of opposite configuration [37]. Poly-L-lactide (PLLA) is a multipurpose and useful plastic material for the packaging industry, and which has acquired much attention as a substitute for conventional packaging material. It has environmental advantages of being produced from renewable sources, its inherent biodegradability along with good grease resistance and an aroma barrier [38]. PLLA can be transformed into useful products by a variety of conventional melt processes, amongst others extrusion coating in combination with e.g. paperboard as a protecting film. Compostable products such as plastic containers, cups and plates can also be produce from PLLA [39–41]. High molecular weight PLA can be obtained using three different polymerization methods

including: polycondensation (direct, solid state (melt) and chain extension), ring opening polymerization and direct polymerization (azeotropic dehydrative condensation and enzymatic) [28]. Potentially higher molecular weight polymers are achieved with ROP. Fast polymerization was seen in the preparation of PLA by reactive extrusion, where activators such as triphenyl phosphine have been used to increase the polymerization rate [42–45]. PLA can be hydrolyzed and deteriorated by microbes, which is then transformed into carbon dioxide and water. Moreover, PLLA will not produce toxic gases when is burned in waste furnaces, and due to its low combustion heat, the furnace is not damaged. Therefore, due to PLLA`s biodegradation, biocompatibility, and sustainability, it has been subject of numerous studies for packaging purposes during the last few decades. PLA has been commercialized, and its synthesis and properties have been studied for more than a half of century from various perspectives. The currently dominant market leader for PLA polymers is Nature Works LLC, which is owned by Cargill, and produces PLA for packaging applications, fibers, and specialty textiles under the Ingeo™ trade mark.

2.4. Polymer blends and nanocomposites

A polymer blend is a macroscopically homogeneous mixture of two or more different species of polymer to obtain final products with new and special combinations of properties. Reduction of the cost by diluting high-cost engineering resin with low-cost polymers, developing property range of the final product, adjust composition to suit customers and recycling industrial/municipal plastics scrap are some common reasons for polymer blending. Polymer blends can be broadly divided into three categories; immiscible blends (phase separated blends) if the blend is made of two polymers, and two glass transition temperatures will be observed. Compatible blends are immiscible polymer blends that exhibit macroscopically uniform physical properties. Miscible blends (homogeneous polymer blend to the molecular level) is a polymer blend that is a single-phase structure. In this case, only one glass transition temperature will be observed [46]. In order to improve the properties of the plastics, many blends, composites and nanocomposites have been prepared using different additives, polymers and inorganic or natural fillers. Thermal stability, strength, low melt viscosity, barrier properties, good physical properties, and flammability are among the properties that can be accomplished using multiphase system. Therefore, preparation of biodegradable polymers-based nanocomposites would also potentially enhance the properties and biodegradability of these polymers. On the other hand, nano-reinforcement of the pristine biodegradable polymers to obtain nanocomposites will also improve some of the properties of the biodegradable polymers such as reduce gas permeability and heat distortion, brittleness, enhance processability, and lower the cost that restrict their uses in wide range of applications [12].

2.5. Reactive extrusion (REX)

Over the past decades the growing demands for specialty polymers has led to increasing scientific and industrial interest in chemical modification and melt blending of polymers.
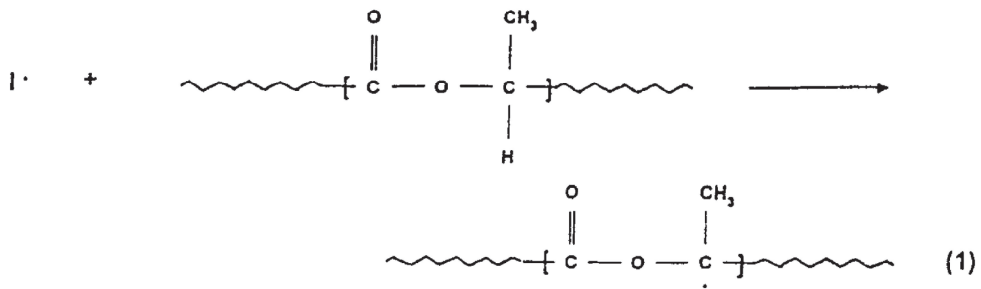
Reactive extrusion (REX), which means using the extruder as a chemical reactor is an efficient means for continuous polymerization of monomers and chemical modification of existing polymers. REX can be used for controlled degradation [47,48], chain extension [49], branching, grafting and modification of functional groups [50,51]. This tool can handle chemical reactions of high-viscosity polymers in the absence of solvents with a large operational flexibility. Reactive extrusion of PLLA as well as other polymeric materials is well known in the literature. The reported effects of treatment ranges from degradation, melt stability, and crosslinking to increase molecular weight and polydispersity depending on the reaction conditions and the e.g. used peroxide [2,47,48,52]. In reported studies peroxides are generally used in very low concentrations (< 0.1%) and in case of extrusion coating, the compounding/modification takes place during the actual coating process [39,41].
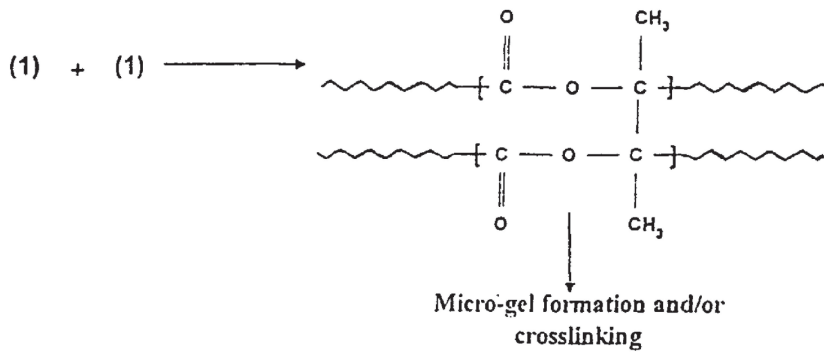
2.6. Branching of polymers and PLLA

Although PLLA has several advantages such as eco-friendly, biocompatibility, processability and cost effectiveness, it has few disadvantages, such as poor toughness, slow degradation rate, relative hydrophobicity, and lack of reactive side-chain groups. Due to PLLAs low melt viscosity compared to commercial packaging plastics like LDPE, it has poor runability, and this effect will be accentuated at low molecular weights [53]. In order to overcome this drawback, one solution would be to increase the degree of branching, and at the same time, increase the molecular weight, broadening the molecular weight distribution [54]. Branching in polymers is a useful structural variable that can be used to modify the processing characteristics and properties of polymers. Branching affects the crystallinity, crystalline melting point, glass transition temperature, physical properties, viscoelastic properties and melt viscosities of polymers. A branched polymer comprises molecules with more than one backbone chain; it is a nonlinear polymer. Different techniques have been used to synthesize branched polymers, including free radical, condensation, and ionic polymerization techniques. These techniques lead to various different types of branched polymers such as (I) hyper-branched, (II) comb or graft, (III) star and (IV) network polymers [55]. Enhanced melt strength and elasticity of linear polymers with low melt strength will improve their runability and applicability on commercial extrusion coating lines. For example, due to the higher degree of branching, higher molecular weight and broader distribution, LDPE shows higher melt elasticity/strength comparing to HDPE. There are several ways to increase molecular weight distribution (MWD) and/or branching of PLLA, such as polymer design, and polymerization conditions to change the molecular weight distribution, using multifuntional co-monomers or initiators for branching during the polymerization process, using free radical promoters like peroxides after polymerization to increase the branching and combination of the mentioned methods [41]. The treatment can be used depending of number of factors, which cost, efficiency and safety are the main factors which needs to be considered. The chemical modification of polymers can be economically achieved by using an extruder as an effective reactor (reactive extrusion)[56]. Due to the existence of active hydrogen in PLLA, by using peroxide, free radicals can be created alongside the backbone, and by bonding of these free radical sites together a branch in the polymer chain can be formed. This process usually takes

place in a short period inside an extruder [2,47,52,57–66]. In an extrusion-coating process "neck-in" and "draw-down-ratio" are two critical parameters, which express how well and fast the coat can be performed on the substrate. Comprehensive studies on polyethylene and polypropylene show that neck-in is related to the elasticity, and draw-down ability is mostly dependent on the viscosity of the polymer [67–69]. PLLA is a linear polymer with quite low melt elasticity, showing high neck-in and low draw-down-ratio comparing to branched LDPE. Branching or cross-linking of PLLA has been attained by multifunctional initiators [50,51], chain extension [49] and peroxide treatment [2,47,48]. The effect of peroxide-induced branching on melt flow properties has been reported in few studies [70–72], and also a few studies show the use of these materials in the extrusion coating process [39,41]. Improved melt processability can be achieved through use of linear polymers in combination with branched polymers for blends to enhance melt strength and stabilization [49,73–76]. Several studies have been focused on the property modification of different polymers by adding various branched structures to different resins such as polyethylene [77,78], polypropylene [79,80], polycaprolactone [81] as well as polylactide [76]. Long chain branching (LCB) has been verified to be useful for improving the melt flow properties (melt elasticity and strain hardening) of polymers for extrusion coating purposes [82]. It is well understood that these desirable properties merely originate from increased amount of chain entanglements in branched materials. Several groups have studied reactive extrusion and branching of PLLA with peroxides, but the available rheological information is rather limited.

In the current thesis, the peroxides were chosen due to their different decomposition rates at a reactive extrusion temperature of 190°C. During the reactive extrusion peroxide induces free radical sites on the PLLA backbone by abstracting α-hydrogens from PLLA, which further may undergo different reaction paths (cross linking and chain scission) as shown in Scheme 1. This leads either to chain scission and/or formation of branched/cross linked structures depending on the overall reaction conditions and the nature of peroxide, Scheme 2 [47,83]. The peroxides are further chosen according to their potential food contact clearance and earlier demonstrated effect on branching, increasing the molecular weight and polydispersity of PLLA, thus possibly enhancing the melt elasticity [54].

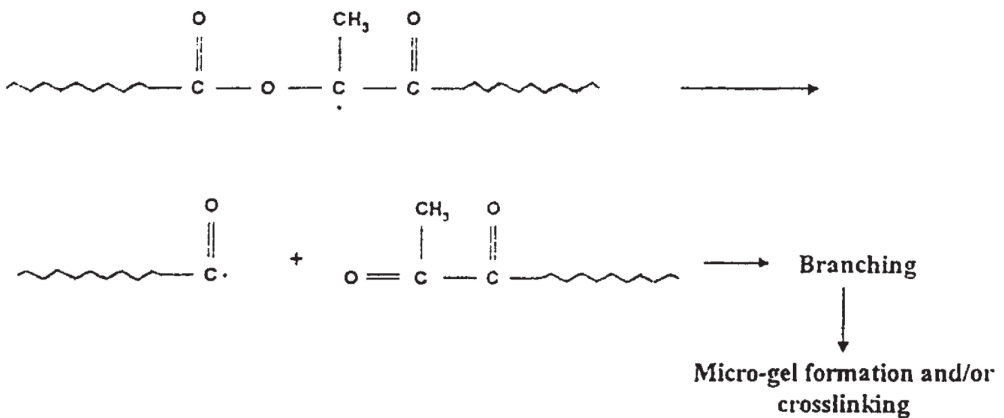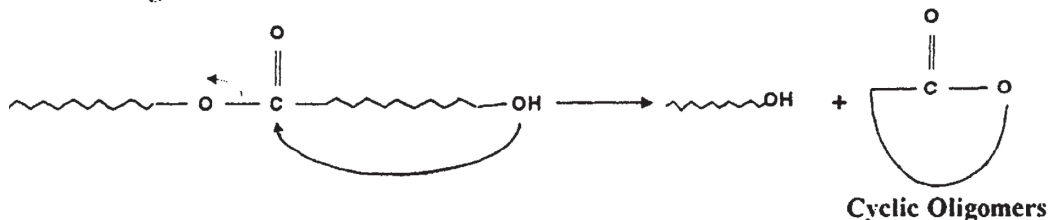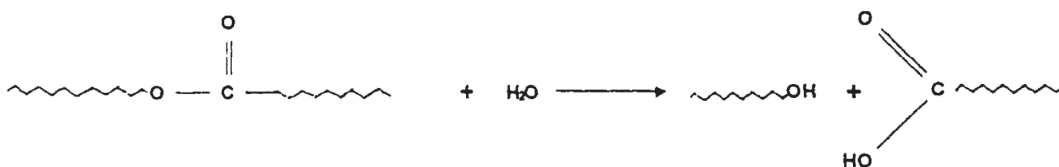**Hydrogen radical abstraction**

(1)

Radical coupling

Micro-gel formation and/or crosslinking

Chain Scission

Branching

Micro-gel formation and/or crosslinking

Scheme1. Proposed reaction mechanism for the branching of PLA [47]
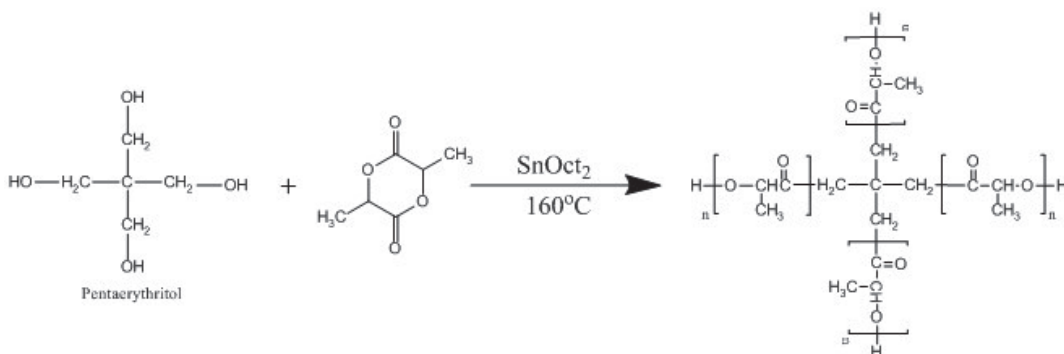
Back-biting

Cyclic Oligomers

Thermohydrolysis

Scheme2. Polylactide chain scissions [47]

2.7. Star-shaped polymers

A star-shaped polymer is a branched polymer, where a single branch point provides the ability for rising of multiple linear chains or arms. If the arms are identical, the star polymer is regular. If vicinal arms are created from different repeating subunits, the star polymer is variegated. Star-shaped polymers are the simplest class of branched polymers, generally modified form of the usual linear polymers, which have unique shape and associated properties, such as their compact structure, high arm density, efficient synthetic routes, and unique rheological properties, mainly their viscoelasticity, make them promising substances for use in different applications such as drug delivery, biomedical applications and nanoelectronics [84]. Pentaerythritol, dipentaerythritol or sorbitol and multifunctional PEO has been used in preparation of 4-arm, 6-arm and 9-arm polymers respectively [85–90]. Star-shaped polymers act somehow like grafted polymers, and can be obtained using star modifiers in reactive extrusion in very short time, while graft polymers need longer time and more accurate design.

2.7.1. Star-shaped PLA

Korhonen et al. prepared linear and star-shaped polylactides using alcohols with different numbers of hydroxyl groups [51]. They used polyglycerine, which has higher hydroxyl group content comparing to dipentaerythritol or sorbitol, and obtained star-shaped PLA with large number of arms as shown in scheme 3 [51]. In the preparation of high molecular weight polymers, an increasing number of hydroxyl groups in the initiator led to faster polymerization and higher molecular weight, while increase in hydroxyl content didn't cause drop in polymerization conversion or enhanced backbiting during extended polymerization time. Odelius

et. al. prepared block copolymer of hydroxyl-terminated four-armed PCL and PLA by condensation polymerization with Sn(Oct)$_2$ or Fe(OAc)$_2$ as an initiator. In a study star-shaped copolymers of ε-caprolactone, L-LA, and DXO were synthesized using spirocyclic tin, Sn(Oct)$_2$ and pentaerythritol ethoxylate as initiator, cocatalyst and coinitiator respectively [91]. Star-shaped four arm oligomers of PDLLA having methacrylate end groups with controlled and narrow molar mass distribution were synthesized via ethoxylated pentaerythritol initiator [92]. Photo-cross-linking of these functional oligomers yielded networks with high gel contents, and a glass transition temperature (T$_g$) completely dependent on the prepolymer molar mass [93]. High molecular weight star-shaped PLA have been synthesized using pentaerythritol as co-initiator [94]. McKee et. al. have studied various combinations of multi and mono-functional groups to achieve different PLA branch structures, and studied the branch length, number of branches, and branching architecture on rheological performance. Star-shaped PLAs have been widely studied in drug delivery applications [72]. The star-shaped four-arm block copolymer of PLLA and PEG was studied for the release of anticancer drugs 5-FU and paclitaxel [95]. Adeli et. al. synthesized seven armed copolymers with a core consisting of tosylated β-cyclodextrin (β -CD) and lactide 2-ethyl-2-oxazoline copolymer branches. The -OH group of (tosyl)7- β –CD was used as the initiator of lactide ROP [96]. The star-shaped PEG–PLA copolymers have faster degradation and superior amphiphilic properties, and may be excellent candidates for drug release [97]. The star-shaped PLA was attached to poly amidoamine (PAMAM) dendrimer by bulk polymerization. PAMAM-g-PLA has a high hydrophilicity and a faster degradation rate comparing to linear PLA with same molecular weight. The highly branched structure significantly accelerated the release of water-soluble bovine serum albumin from these graft copolymers, whereas a time lag was observed in linear PLLA of similar molecular weight [98]. According to rheological studies, shear thinning in branched PLA is much stronger than for linear form. The increase of zero shear viscosity and shear thinning behavior with the increase in branching is also reported by other studies on PLA polymers with star-shaped architectures [61,90,99].

Scheme 3. Reaction scheme of the polymerization of star shaped PLA using pentaerythritol [51].

2.8. Copolymerization and blending of PEG and PLA

PEG also referred to as polyethylene oxide (PEO) or polyoxyethylene (POE) has special properties. It can be solved in water and polar organic solvents, and it is completely insoluble in nonpolar solvents, including diethyl, ether, and heptane. PEG has FDA approval for food packaging and medical device usage in the human body [100], showing no signs of toxicity due to its high mobility and rapid clearance from the human body. The mentioned characteristics make it a suitable material and monomer in the preparation of copolymers with α-ester based monomers such as lactide (LA). The copolymerization of hydrophobic L-LA with hydrophilic poly(ethylene oxide) has been used to prepare diblock and triblock copolymers [101–103]. Several triblock copolymers of L-LA, D,L-lactide (DLLA), and PEG, in which PEG forms the central block have been reported in the literature [104–109]. The obtained copolymers show higher elasticity, faster biodegradation and more hydrophilic behavior comparing to PLLA as the hydrophilic PEG acts as a surface modifier to PLA, and enhance the stability of water-soluble molecules. The biodegradability and biocompatibility of these copolymers make them suitable candidates for controlled drug delivery systems [110]. The diblock and triblock copolymers have been prepared by bulk or solution polymerization using stannous chloride [110] or $[Sn(Oct)_2]$ at high temperatures (100–150°C) for several hours [111–113], potassium tert-butoxide [114], sodium hydride [107], calcium hydride/Zn [115], zinc metal [116] or even in the absence of catalysts [117]. The molecular weight of PLLA block during the polymerization can be decreased in high temperatures[113]. By changing the molecular weight of PEG and composition of lactide monomer in the initial feed, the T_g of copolymer will be affected [107] and significantly decreased by using high molecular weight or high amount of PEG [118]. However by the mentioned changes different products for various applications can be produced. With the help of ring opening polymerization thiol-functionalized PEG-b-PLA has been synthesized. PEG disulfide acts as a macro-initiator, and the disulfide bond was separated using tributyl phosphine to prepare a block copolymer having a thiol unit at the PEG end [119]. PEG can be added to PLLA as a plasticizer, since the addition of plasticizer decreases the T_g, improves the polymer ductility and draw-ability, but also increase the rate of crystallization, as shown by Kulinski and Piorkowska [120,121]. Low molecular weight PEG reduces the elastic modulus of a pure PLLA from an initial value of 2050 to 1488 MPa at a concentration of 10% and to 976 MPa at 20%, while the elongation at break increases from the initial level of 9% to 26% and 160%, respectively. Plasticization of PLA remarkably affects the mechanical properties and the concentration of PEG needs consideration in order to avoid losing physical and chemical characteristics, such as heat of fusion and, consequently, thermo-mechanical properties. The incorporation of PEG may also decrease material cohesion by creating intermolecular spaces [122]. Blending is one of the most common ways to use PEG and PLA together. PEG in PEG/PLA blends is used to enhance the hydrophilicity of PLA and to increase its degradation rate and the rate of drug release for medical applications, and act as a plasticizer [123]. According to previous studies, solution blends in different solvents such as acetonitrile, chloroform, THF, dichloromethane containing more than 20 wt% of either compound can crystallize, and the resulting blends are semi-miscible [101,124]. By adding PEG more than 30% no T_g was observed [125,126]. Thermal studies have shown that PEG is miscible with PLA with

a single T_g, but it is not stable in the PLA matrix, as the PEG reaches its solubility limit in the polymer [121]. When PEG content is between 0-30 wt%, the weight loss occurred mainly due to the enzymatic degradation of PLA. However at PEG content higher than 30 wt%, the weight loss mainly occurred due to the dissolution of PEG [127]. To control the blend properties and phase separation it's better to copolymerize PLA and PEG, and then use the copolymer as a miscible additive to neat PLLA. By producing PLLA-PEG copolymer (PEGLA) and blending the PEGLA and PLLA, the effective amount of PEG can be easily controlled. In this case the PEG content, being a petroleum-based material, will be very low in the final product, and the obtained blend will be nearly 100% from renewable resources.

2.9. Packaging industry

Packaging is the technology of confining or protecting products for distribution, storage, sale and use, considering the mentioned objects designing, evaluation, and production of packages is also of importance. Nowadays, packaging is extensive and fundamental. It encloses, improves and protects the goods, from processing and producing, through handling and storage, to the final consumer. Without packaging, materials handling would be an unorganized, inefficient and expensive exercise, and modern consumer marketing would be practically impossible. The packaging sector represents about 2% of the gross national product (GNP) in developed countries, and about half of all packaging is used to package food [128]. Despite the fact that large a number of barrier solutions are available on the market, they all have their disadvantages, such as cost, water-sensitivity, opacity, or limited mechanical resistance. At the same time the need for replacements of metal and glass containers forces industries to provide more efficient barrier alternatives. Over the last decades, plastic bags in packaging applications have developed, and at the current moment, the largest application for plastics is packaging. It has to be mentioned that the food packaging has the highest plastics demand due to tremendous advantages, such as thermoweld-ability, flexibility in thermal and mechanical properties, lightness and low price [129]. The majority of packaging food films and coatings contain at least one component that is a high molecular weight polymer, especially when a self-supporting film is required. Long-chain polymeric structures are demanded to have a high cohesive strength as a film matrix, when casted from a suitable solvent. Increased structural cohesion generally results in reduced film flexibility, porosity and permeability to gases, vapors and solutes. As length and polarity of polymer chains increase, cohesion will be elevated. A consistent distribution of polar groups along the polymer chain increases cohesion by increasing the inter-chain hydrogen bonding as well as ionic interactions. A variety of polysaccharides and their derivatives such as starch, cellulose, hemicellulose, chitosan and gums like alginates have been evaluated for potential use in food packaging. Lipids, proteins and bio-based polymers like PLA can also come to heavy use. The mentioned materials are abundant, low cost and easy to handle, as well as possessing good film forming properties [128]. Bio-based packaging materials are by definition made from renewable raw materials, and can be classified according to their origin and method of production. The packaging materials can be classified in four categories, polymers directly extracted from biomass (e.g. polysaccharides), classical polymers synthesized from bio-derived

monomers (e.g. PLA), polymers produced directly by natural or genetically modified organisms (e.g. PHBV) and the composites, nanocomposites or blends containing the mentioned materials with non-degradable polymers. Polymers such as LDPE, PP, and PET are widely used packaging materials because of their strength, inertness and ease of production, but these polymers are not readily biodegradable [130]. The use of mentioned packaging materials, PET and polyolefins and their processing has been approved by the U.S. Food and Drug Administration (FDA) for use with food containers and packaging [131,132]. Currently different standards such as: ASTM D6400, ASTMD6954, European standard EN13432 and British Standard BS8472, are used to determine biodegradability, oxo-degradability and exo-toxicity of packaging materials [128].

2.10. Extrusion Coating

There are two types of coating processes. In the first, an excess coating is applied to the web, and the extra amount will be removed after complete wetting (dispersion coating). In the second method, a predetermined amount is applied to the web using rollers, or other equipment (extrusion coating) [128]. Extrusion coating is an economic multi-purpose coating method of a synthetic polymer melt onto a substrate, which could be a plastic such as polyethylene, or paperboard, corrugated fiberboard, paper, aluminium foils, cellulose, or non-wovens [133]. In extrusion coating, a polymer melt is extruded onto a substrate, cooled, and wound into a roll. Extrusion coating was first practiced on a commercial scale in the production of LDPE-coated paperboard for milk cartons in the mid-1950's, as a replacement for wax-coated board [128]. Nowadays, nearly all wax-coated paperboard has been replaced by polyolefin-coated paper and board. According to the theoretical studies, almost all thermoplastics can be used as a coat onto a paper or other substrates. However, an acceptable level of melt elasticity, extensional viscosity and melt strength are required, and practically most extrusion coatings are from LDPE, PP, polyamides (PA) and polyethylene terephthalate (PET). An extrusion lamination is a specific use of extrusion coating, where the polymer melt is extruded between two substrates, which are stuck together, the polymer quenched, and finally the lamination is furled into roll form [134]. In the case of extrusion coating, is the process applicable to any thermoplastic material, but the technology has been highly developed mainly for polyethylene and associated copolymers, including ionomers [128]. Products from extrusion coating/laminating lines have six main market classifications: liquid packaging, flexible packaging, board packaging, industrial wraps, industrial products, and sacks. Multilayer coextrusion of thermoplastic films and sheets is one of the main applications of this method in plastic industry, as the product can compete with the traditional metal, glass, paper and textiles both economically and technically [135]. Co-extrusion is a single step process of two or more plastics, which are continuously extruded and shaped into a single die, to form a multilayer sheet or film. Consequently, this method reduces the cost and problems of conventional multistep lamination and coating processes. Thinner layers can be produced by coextrusion, therefore, only the necessary thickness of a high-performance polymer is used to meet a particular specification of the product. In other words, coextrusion is a commercial method to produce unique multilayer films with thicknesses less than 100 nm, which is difficult to manufacture with other methods. Layers may be used to place colors, bury recycle,

and screen UV radiation, and provide barrier properties. For example, additives such as antiblock, antislip, and antistatic agents can be added in specific layer positions. High-melt-strength layers can carry low-melt-strength materials during fabrication [134,136]. The largest market for coextruded films and sheets is in packaging applications. Trash bags and flexible and semi-rigid packages are consists of 2-3 layer or 5-9 layer films respectively. Different polymers may be used to obtain various properties, such as heat sealability, barrier, chemical resistance, toughness, formability, and aesthetics. Food packaging is a growing application. As mentioned earlier, the layers of a coextruded film are generally composed of different plastic resins, blends of resins, or plastic additives. The difference between a coextruded film and a resin blend lies in the existence of distinct layers in the coextruded film as opposed to the blend. A film requiring aroma barrier and easy sealability would be very difficult to make as a blend. The properties can be obtained in multilayers, however blending the materials of these layers may degrade some of them, i.e. a multilayer coextruded sample consisting of EVA and nylon, in case of blending these two materials the EVA would degrade at the temperature required to melt the nylon, and the nylon would lose much of its aroma barrier because it would be contaminated by the EVA [134]. The polymers used in coextrusion usually have low viscosity, and are extruded at high temperatures, therefore they flow very easily. To control this easy flow-ability, they need dies that are usually smaller in bulk and rigidity when compared to cast-film or other melting method dies. The higher temperatures are required to achieve good adhesion to the various substrates [136].
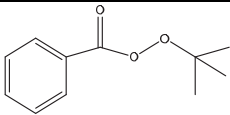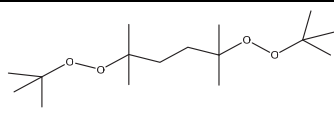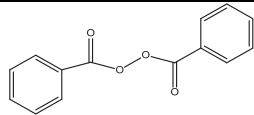
3. EXPERIMENTAL PART

3.1. Material

Polylactide (Nature works LLC) was provided by Cargill Central Research (commercial grade 3051D. The materials were received as granular pellets. L-Lactide (Purac Biomaterials, Netherlands) was dried in the vacuum oven (133 Pa) over night at 32.5°C before use.

Tert-Butyl peroxybenzoate, 98 % (The List of "Indirect" Additives Used in Food Contact Substances [38]), 2, 5-dimethyl-2, 5-di (tert-butylperoxy) hexane, 92 % (Lupersol 101) which are safe to use as antioxidants/stabilizers in polymers for indirect food contact and benzoyl peroxide, and which all were purchased from Acros. The physical and chemical properties of the peroxides used in this study are seen in Table 3.1. Pentaerythritol (PERYT) and poly(ethylene glycol) with number-average molecular weight 600 and 6000 g mol^{-1} were used as co-initiator and Sn(II) 2-ethylhexanoate as a catalyst (all from Sigma Aldrich, USA) without further treatment. Chromatography grade tetrahydrofuran (THF), CDCl$_3$, toluene, ethanol and chloroform were purchased from Sigma-Aldrich USA; all chemicals were used as received.

Table 3.1. The physical and chemical properties of the used peroxides (**MSDS**)

	Tert-Butyl peroxybenzoate	**Lupersol 101**	**Benzoyl peroxide**
Molecular Formula	C$_{11}$H$_{14}$O$_3$	C$_{16}$H$_{34}$O$_4$	C$_{14}$H$_{10}$O$_4$
Mw	194.23	290.44	242.23
Melting Point	8 °C	6 °C	104.5 °C
Boiling Point	75 - 76 °C at 0.2mmHg	55 - 57 °C @ 7 mmHg	N/A
Half time at 190°C	108 s	40 s	5 s
Structure			

3.2. Blend preparation and reactive extrusion

Two hundred grams of PLLA (Nature works LLC) were used in every experiment in order to obtain enough material for the second extrusion and preparation of the blends. PLLA was first dried in open polyethylene bags, placed in a vacuum oven (133 Pa) over night at 32.5°C, and then transferred to a desiccator where they were stored prior to use. The PLLA samples were manually mixed with the peroxide in plastic bags just before charged into the extruder. The first extrusion experiment with a die temperature at 190°C was used to minimize possible degradation, and the second extrusion experiment was performed at a die temperature of 235°C in order to obtain eligible results comparable to real extrusion coating processes. An Axon BX18, 18 mm single screw fitted with an 18 L/D ratio screw and 1.0 mm die-gap (25 mm width)

was used for both the first and second extrusion. The used temperature profiles for the extrusions are shown in Table 3.2.

Table 3.2. Temperature profiles of extruder (ºC)

Extruder zone	T Zone 1	T Zone 2	T Zone 3	T Zone 4	T Zone 5
First extrusion	140 ºC	180 ºC	190 ºC	200 ºC	190ºC
Second extrusion	165 ºC	190 ºC	215 ºC	240 ºC	235ºC

Obtained blends from extrusion were granulated using a Retch SM 300 cutting mill. The granulated materials for the second extrusion were dried in a vacuum oven (133 Pa) at 32.5ºC over night and then filled into the extruder hopper without adding any additives or PLLA. For a better comparison, pure poly-L-Lactide (called reference PLLA in all Tables and Figures) was extruded and re-extruded at the same reaction conditions as the peroxide-treated PLLA.

3.3.   Synthesis of star-PLLA, PEGLA and Preparation of Blends

The polymerization of star-shaped poly-L-lactide (sPLLA) and PEG-co-L-lactide (PEGLA) was performed in a flame-dried and nitrogen-purged 250ml flask reactor with magnetic stirring. First, the L-lactide monomer was fed to the reactor with an appropriate amount of PERYT or PEG. The amount of the co-initiator (PERYT/PEG) was calculated based on aimed number-average molecular weight, which varied between 2000-100 000 for star-shaped, and 12000- 80 000 for PEGLAs using Eq.1 [51].

Amounts of Co-initiator = (L-lactide * Efficiency * 74) / (Total aimed M_n)   Eq. (1)

After repeated evacuations and purges with nitrogen, the reactor was immersed into an oil bath at 160°C in a nitrogen atmosphere [51]. The polymerization was initialized by injecting 0.05 mol% $Sn(Oct)_2$ from a $Sn(Oct)_2$/toluene solution (10 wt%). The reaction time was from 60 to 75 minutes. The reaction was terminated by cooling the reactor to room temperature. The polymers were dissolved in chloroform and precipitated into a 10-fold excess of cold ethanol, isolated by filtration, and dried under vacuum (133 kPa) at 32.4 °C overnight. All blends were prepared in solution using chloroform and mixed overnight then evaporated and dried under vacuum (133 KPa) for 24 h. sPLLAs and PEGLAs were mixed with linear PLLA (3051D) separately at mass ratios of 10 and 30 wt%. Prior to blending, sPLLAs, PEGLAs and 3051D were dried in vacuum (133 kPa) over night at 32.4 °C.

3.4. Material analysis

3.4.1. Size exclusion chromatography (SEC)

Molecular weight and its distribution was measured by size exclusion chromatography (SEC). Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) is a type of chromatography that analyzes polymers according to separation by their size, rather than by chemical properties of the molecules. Although, absolute molecular weight cannot be obtained by using SEC independently, and the results must be calibrated against polystyrene standards (polymer samples having a very narrow polydispersity and whose molecular weight has been determined by techniques giving an absolute molecular weight). SEC is a high-performance liquid chromatography (HPLC) technique where the polymer chains, in solution, are separated based on differences in their sizes (basically hydrodynamic volume). This separation is usually achieved by use of a special packing material in a column. The column consists of a hollow tube, tightly packed with extremely small porous polymer spheres, which are often composed of polystyrene, crosslinked by addition of varying amounts of divinylbenzene, and are designed to have pores of different sizes. The hydrodynamic volume of the polymer molecules is the space that a particular polymer molecule takes up when it is in solution. However, by using SEC, the approximate molecular weight can be obtained due to the exact relationship of molecular weight and hydrodynamic volume of polystyrene that is used as the standard for the calibration of the SEC. Unfortunately, this relationship between the molecular weight and hydrodynamic volume of polystyrene is not the same for all the other polymer molecules, and therefore, only an approximate measurement can be achieved by this system.

In this study, the solutions were pumped through the pre-column (AN Gel Guard Column) and linear column (AM GPC Gel) with porosity linear 10um L/D 30/0.7 from American Polymer Corporation, by a computer controlled device, and analyzed by an evaporative light scattering detector (ELS). The experiments were performed in chromatography grade tetrahydrofuran (THF), and operation conditions in the system were as follows; the flow rate at 1.0 ml/min and the temperature at 40°C. The samples were dissolved in dried chromatography grade tetrahydrofuran (THF) with the concentration of 1 mg/ml and filtered through a PTFE 0.2 µm filter before injection to remove undissolved contaminants to prohibit possible blocking of the system. Polystyrene standards (PSS Company) were used for calibration. The sample volume was 50 µl, introduced by auto injector system.

3.4.2. Differential Scanning Calorimeter (DSC)

The glass transition (T_g), cold crystallization (T_{cc}), and melting temperatures (T_m) as well as the cold crystallization heat (ΔH_{cc}) and melting heat (ΔH_m) of the measured samples were obtained with the TA instruments Q1000 Differential Scanning Calorimeter in standard aluminum pans. All samples were cooled to -60°C, then heated at a rate of 10°C/min to 200°C to erase previous thermal history (the first heating scan), and then cooled to -60°C at a cooling rate of 10°C/min and heated again with 10°C to 200°C (the second heating scan). The runs were performed under nitrogen atmosphere, with a flow rate of 50 mL/min. T_g (glass transition temperature), T_{cc}

(temperature of cold crystallization), T_m (melting temperature), T_i (the initiation of degradation temperature for samples obtained by DSC in a separate run from -60 to 250), ΔH_{cc} and ΔH_m values were calibrated using benzophenone, indium and tin as standards. The percentage of crystallinity (X_c) of the PLLA samples was evaluated according to equation 2 using 93.1 J/g as the constant value of ΔH_m for 100% crystalline PLLA [2].

$$X_c\,(\%) = 100(\Delta H_{cc} + \Delta H_m)/93.1 \qquad (2)$$

3.4.3. Gel content

Gel content was measured using Soxhlet extraction with chloroform as solvent. Approximately 2 grams of the each sample were placed in a porous cellulose thimble, after drying in the vacuum oven (133 Pa) overnight, and weighted inside a glove box in order to prohibit moisture interference, then placed in the reflux chamber. At the end of the extraction process (24 hrs), the thimble containing the residue was first dried in the open air then under vacuum (133 Pa) and finally weighted inside the glove box. The gel content was calculated using the following formula:

$$\text{Cross-linked portion (\%)} = 100(W3 - W2)/W1 \qquad (3)$$

Where, W1 was the weight of the original specimen in grams, W2 was the weight of the thimble and W3 was the weight of the dried thimble and residue.

3.4.4. NMR analysis

^{1}H NMR spectra were recorded on a Bruker AV 600 MHz in CDCl3 at 25 °C and the peak positions are reported with respect to tetramethylsilane (TMS).

3.4.5. Rheological analysis

All materials were characterized in terms of their rheological behavior, with a TA Instruments AR2000 rotational rheometer using parallel-plate geometry. Isothermal frequency sweeps were performed from high to low frequencies (100 to 0.5 Hz), and started when the temperature had stabilized after loading the sample into the rheometer; typical stabilization times were three minutes. The measurements were performed at 240°C. The gap and diameter of the geometry was 1.0 and 25 mm respectively, and the applied strain was 0.125 %. The adopted strain was within the LVR checked by strain ramp experiments. The steady state flow step was also measured using the same parallel-plate geometry at both temperatures, using shear rates ($\dot{\gamma}$) from 0.005 s^{-1} to 175 s^{-1}. In order to minimize possible degradation of PLLA at high temperatures, all samples were kept in a nitrogen atmosphere during the measurement.

3.5. Extrusion coating of blends

In figure 3.1 the pilot co-extrusion coating line at Tampere University of Technology is shown (TUT). The line consists of the pretreatment station (e.g. corona and flame treater), followed by the laminator, which conveys the co-extrusion die and extruder productsas the coating process is started.
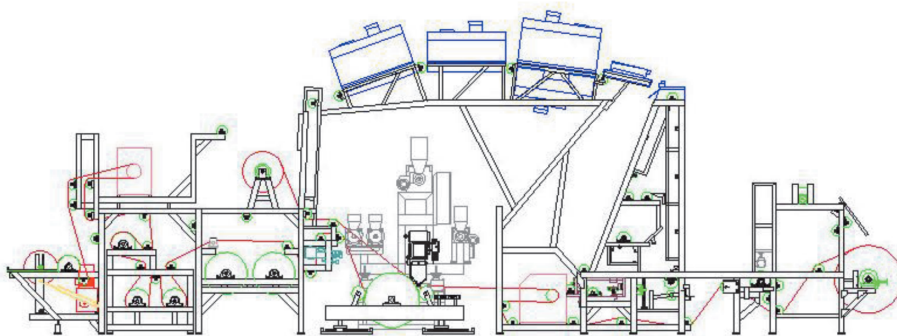

Figure 3.1: Co-extrusion coating pilot-line at TUT.

The TUT pilot co-extrusion coating line can reach a speed of up to 400 m min^{-1}. The maximum line speed of each polymer blend and the coating weight in g m^{-2} at each line speed were recorded. Above the maximum line speed, the polymer film was torn (so called draw down speed). The co-extrusion unit consists of the four extruders A, B, C and D, with the respective screw diameters being 60, 40, 30 and 30mm. The polymer melt temperature and pressure were recorded in the adapter pipe located between A-extruder and the feedblock. The co-extrusion layer structure can be changed via so-called selector plugs (Cloeren VG™ 5-Layer Dual Plane feedblock). Selector plugs used in these experiments were D/BBBBB/D. The used die to produce the film was Cloeren EBR™ III, a T-type die with edge encapsulation. The D-screw fed only the encapsulation edges and both, the material (LDPE CA9150, Borealis Polymers) and the screw speed (20 rpm) were fixed during the trials. The die/film width was adjusted to 570 mm. AAAAA and BBAAA layer combinations describe the film structure and feeding extruder for each layer - the first layer from the left is against the web. The coated web material was Stora Enso's 210 g m^{-2} CupForma paperboard. Co-extruded film and paperboard were laminated together in the nip between rubber covered pressure rolls (5.5 bar pressure), and matte finished chill roll (15 ºC). The air gap (die height) between die lips and laminator was adjusted to 175-215 mm in the trials. Prior to coating, the paperboard was pretreated with Vetaphone corona treatment at the power of 3.4 kW - the intention was to oxidize the paperboard surface to maximize the degree of adhesion to the polymer film. As the wound extrusion coating roll opened, the samples were cut and the coating weight was measured. At least 5 parallel samples were weighed at each test point.

Extrusion coated paperboard samples were then heat-sealed using the laboratory sealer SGPE 20 impulse (Kopp). It consists of two 3 mm wide heated bars, which were then pressed together while the sample was placed between them. In this study, paperboard coating was sealed against

its backside – thus polymer coating against paperboard. The dwell time was 0.5 s and the press force was 300 N. The heat seal ability was rated as follows:

Table 3.3: Evaluation criteria for heat sealing [137,138]

Value	Criteria of evaluation
1	No seal at all
2	Slight seal, crackly sound when tearing
3	Slight seal, fiber tear of under 50% of the area
4	Fiber tear of over 50% of the area
5	Total fiber tear

Adhesion between the coating and the paperboard was tested with a hand test according to the criteria presented in table 3.3. A 2 cm wide strip was cut from the sample in the machine direction. Ethanol was used at one end of the strip to separate the polymer coating from the paperboard. Then the coating was peeled at an approximate 90° angle to the forward direction of the coating. Adhesion was usually tested the day after the trial run.

Table 3.4: Evaluation criteria for adhesion in hand test [137,138]

Value	Criteria of evaluation
0	Layers do not adhere
1	Layers peel off each other
2	Layers peel off each other, some fibers are removed
3	Fiber tear of under 50% of the area
4	Fiber tear of over 50% of the area
5	Total fiber tear

Water vapor transmission rate (WVTR) was tested gravimetrically with a cup test. The coated substrate was sealed into a test cup. The weight of the cup increased because the humidity in the air diffuses into the cup. The cup contained $CaCl_2$ to absorb the water vapor. The test was done according to the ASTM E96 – 80 standards.

4.   RESULTS AND DISCUSSION

4.1.   Blends of linear PLLA 3051D and peroxide-modified PLLA [I; II]

4.1.1.   Reactive extrusion of linear PLLA 3051D using different peroxide [I]

In this part of the study, the intention was to prepare a branched PLLA and to blend them in different ratios with the linear 3051D during the extrusion coating process.

Three different peroxides [tert-butyl-peroxybenzoate (TBPB), 2,5-dimethyl-2,5-di-tert-butylperoxy-hexane (LOL1) and benzoyl peroxide (BPO)] were used during the first reactive extrusion, favorably performed at low temperature (190ºC) promoting peroxy-radical formation and branching while minimizing polymer degradation and cross linking. The peroxides were chosen according to their potential food contact clearance, and earlier demonstrated effect on branching, evaluated by the increase of the molecular weight and the polydispersity of PLLA, thus they possibly enhance the melt elasticity [54]. Applied peroxide concentrations were between 0 and 0.5 wt%. The effect of the extruder screw speed (40 and 70 rpm) was considered in this study. A simple observation of the results showed that, at a screw speed of 40 rpm reduced the molecular weight and increased the polydispersity especially for samples with a lower amount of added peroxide, and the PLLA reference compared to the screw speed of 70 rpm. This was attributed to the onset of polymer degradation at lower rpm, due to longer residence time in the extruder. Thus the corresponding materials were not further used, and the results are not included in the following sections. In addition, the effect of a second extrusion on the peroxide-modified PLLA at 240ºC was studied in order to simulate a second melting, mimicking the final blend processing step in industrial production. The best materials were blended with PLLA, analyzed and tested for their extrusion coating applicability. The thermal properties and molecular weight after the first and second extrusion are presented in table 4.1. and table 4.2., respectively.

Table 4.1: First reactive extrusion at 190ºC

Peroxide Added	Amount wt%	Amount mole ratio	DSC [a]				HPLC		MFI	Gel Content%
			T_g (ºC)	T_c (ºC)	T_m (ºC)	X_c (%)	MW $*10^3$	PD		
PLLA ref.	–	–	61	–	–	–	115	2.0	4.7	–
TBPB	0.1	0.6	61.5	–	–	–	125	2.3	–	3.3
TBPB	0.3	1.7	62.4	109.4	145.9	5.6	275	3.7	–	6.1
TBPB	0.5	2.8	62.2	109.9	145.4	6.8	290	4.7	0.1	35
LOL1	0.1	0.4	61.2	–	151.5	0.5	135	2.5	–	–
LOL1	0.3	1.1	61.9	–	149.4	0.3	285	3.0	–	5.5
LOL1	0.5	1.9	62.0	121.2	147.3	0.8	395	5.2	0.2	7
BPO	0.1	0.5	61.2	–	151.6	0.7	135	2.2	–	–
BPO	0.3	1.4	60.9	128.5	151.4	0.6	170	3.4	–	0.7
BPO	0.5	2.3	61.2	113.9	147.0	0.9	204	3.5	3.3	1.2

[a] Determined from second heating run.

Table 4.2: Second reactive extrusion at 240°C

Peroxide Added	Amount	DSC [a]				HPLC	
		T_g	T_c	T_m	X_c	MW	
	wt%	(°C)	(°C)	(°C)	(%)	*10^3	PD
PLLA ref.	–	60.9	–	152.4	0.3	96	2.1
TBPB	0.1	61.2	–	151.9	0.4	110	2.6
TBPB	0.3	61.7	110.3	144.9	2.9	210	4.2
TBPB	0.5	61.6	108.1	144.3	5.6	315	6.4
LOL1	0.1	61.0	–	151.9	0.4	105	2.2
LOL1	0.3	61.1	128.8	151.3	0.6	110	2.6
LOL1	0.5	61.2	114.6	145.4	1.2	220	5.4
BPO	0.1	60.1	–	151.6	0.8	102	2.3
BPO	0.3	60.7	126.6	150.6	0.5	115	2.2
BPO	0.5	61.1	112.8	146.6	3.1	160	2.9

[a] Determined from second heating run.

The weight-average molecular weight (Mw) of native PLLA was reduced by 25-30% (from 160 000 to 115 000 g mol^{-1}) after the first extrusion at 190°C, and after the second extrusion at 240°C it was reduced by another 15-20% (to 96 000 g mol^{-1}), which was expected, and obviously declines the melt strength of PLLA. Peroxides were studied and reported to stabilize and retard the degradation of PLLA melts [2,52]. During reactive extrusion, peroxides induce free radical sites on the PLLA backbone by abstracting α-hydrogens from PLLA which lead either to chain scission and/or formation of branched/cross-linked structures, depending on the reaction conditions, and the nature of the peroxide [139]. All peroxides used in this work showed similar influence on the Mw and the polydispersity (PD) when applied in low concentrations (0.1 wt%). In the extrusion process, the Mw was reduced less than using pure PLLA, and a minor increase in PD was observed. At high peroxide concentrations (0.5 wt%), LOL1 caused a 3.4-fold rise of Mw (to 395 000 g mol^{-1} compared to the reference PLLA) followed by TBPB (up to 2.5-fold). BPO showed a less pronounced impact on the Mw, though with 0.5 wt% BPO almost doubled the molar mass of comparable once extruded PLLA (204 000 vs 115 000 g mol^{-1}). These results are to some extent, in line with previously reported data. Carlson et al. studied the effect of 2,5-dimethyl-2,5-tert-butylperoxy-hexane (LOL1) on PLLA at various conditions (temperature and peroxide concentration) [47]. They concluded that at T >190°C branching starts to be counter-balanced with other thermal events, leading to decreased molar mass. Takamura et al. has comprehensively investigated the effect of different peroxides on PLLA taking into account their hydrogen abstraction ability, decomposition rates, molar ratio of peroxide-derived radicals to PLLA-chain and the effective number of radicals per PLLA chain [139,140]. He states that peroxides with shorter lifetime at given conditions caused more gelation/cross-linking due to higher local radical concentrations, resulting from faster peroxide decomposition and thus poorer distribution/diffusion in the polymer. Surprisingly, we observed least gelation in the BPO samples despite BPO has the shortest half lifetime (5s at 190°C) of all tested peroxides. While Tert-butyl-peroxybenzoate (TBPB) has the longest reported lifetime (108s at 190°C) and

afforded the most cross-linked material (35% gel content with 0.5 wt%), but has a lower molecular weight than LOL1. The gel formation was beside gel content measurements, also concluded tentatively from the macroscopic view of the extrudates, and measured MFI (table 4.1.).

The re-extrusion was performed at a higher temperature (240°C) to mimic industrial extrusion coating conditions for PLLA. All materials were re-extruded, despite their relatively high gel content. The appearance of the products was smooth and homogeneous after the re-extrusion, likely due to the higher extrusion temperature. Overall, their weight-average molecular weights slightly dropped after the re-extrusion (table 4.2.), but the TBPB-treated PLLAs showed the smallest change. The weight-average molecular weight of all re-extruded materials was higher than comparable neat PLLA. The presence of higher molecular weight species was detected by the SEC-chromatograph for the blends containing 0.3 and 0.5 wt% TBPB or 0.5 wt% LOL1 or BPO.

The thermal properties of PLLA (table 4.1.) changed with the peroxide treatment as seen from the DSC runs (figure 4.1.). The commercial grade PLLA showed neither crystallization, nor cold crystallization during the second heating ramp. The temperature and degree of cold crystallization depend on the peroxide type and concentration (table 4.1.). Evidently, the crystallinity formed during cooling, although very low, mitigates the cold crystallization during heating.

Several studies report that branched PLLA showed improved crystallization because the branching points act as nucleating sites [72,141]. Though, the chemistry and branch architecture seem to play a crucial role because all branched PLLA structures tested in this work do not show enhanced crystallinity or crystallization [142]. Interestingly, the blends with 0.3 wt% of TBPB or LOL1 show similar physical properties and gel content, but only the 0.3 wt% TBPB (cold) crystallizes the PLLA. This clearly substantiates the formation of different branched/cross-linked structures.
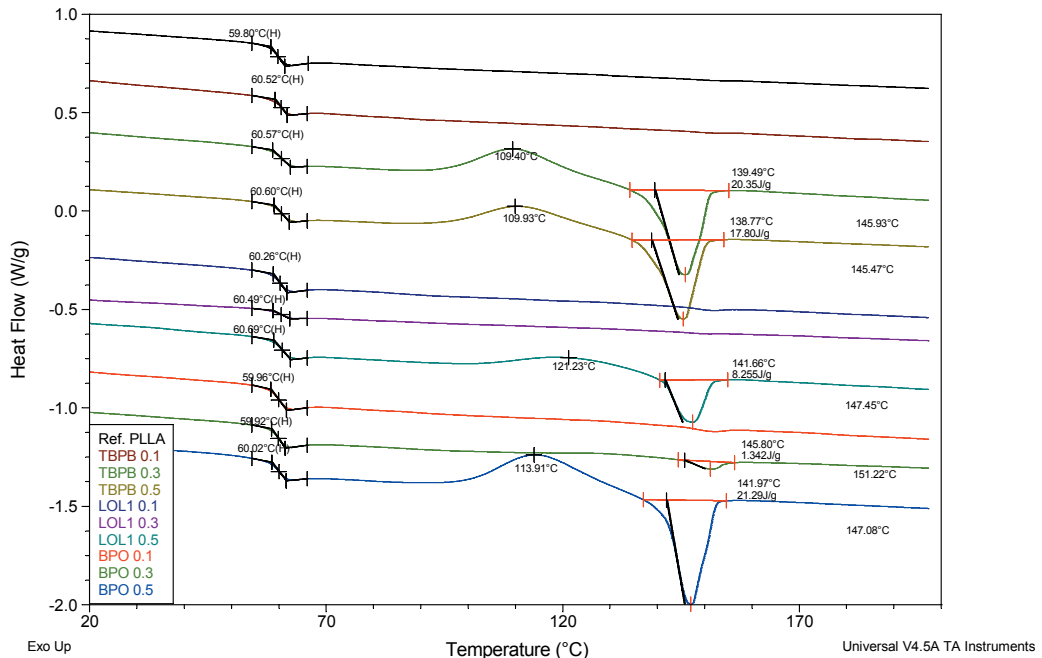
Figure 4.1: DSC curves of the first reactive extrusion at 190ºC (second heating scan).

The rheological behavior of modified PLLA at 240℃ was studied, providing realistic extrusion coating conditions at industrial processes. The existence of long chain branching (LCB) can be studied by means of a rotational rheometer in both, steady state, and oscillation modes. The introduction of LCB increase the relaxation time of the system, and this especially affects the shear viscosity at low shear rates, complex viscosity (η^*), the value of loss (G''), and the storage modulus (G') as well as their slopes in the terminal region. Of course, also other constitutional parameter like molar mass and polydispersity affect the melt flow properties. Except branching, the peroxide treatment is possibly connected with cross linking. From the extrusion coating point of view, cross-linking is problematic, because at some level of cross-linking, the polymer chain mobility is severely depressed, and the samples are not processable and impossible to melt-blend with other polymers. Figure 4.2 shows the shear viscosity curves (at 240°C) of all samples once extruded at 190°C. The peroxide treatment does in all cases increase the shear viscosity when approaching the lower shear rate region ($<0.01s^{-1}$). The shear viscosity increases with the peroxide concentration, and is in rather good agreement with measured Mw and gel content (taking into account the accuracy of these measurements). TBPB does increase the shear viscosity most, followed by LOL1. Furthermore, a more pronounced shear thinning is observed for those samples with high molecular weight. A change in the flow profile is detected at a shear rate of roughly 1 s^{-1}. At higher shear rates ($<100s^{-1}$) the differences in shear viscosity are less pronounced, which implies that the observed cross-linking does not necessarily inhibit traditional melt converting processes. The results above 60s^{-1} may strongly be affected by artifacts related to material removal from the geometry during shearing. The results for the complex viscosity are

27

shown in figure 4.3. An obvious increase in complex viscosity is observed with the reactive extrusion of PLLA with the peroxides. The trend is identical with the one observed in shear mode. Especially samples treated with 0.5 wt% peroxide show high complex viscosity, with linear increasing slopes at lower frequencies ($\omega \to 0$), and they do not yet level out into a typical Newtonian flow. This can be related to a cross-linked nature, as visible in the work of Ramos et al. [82]. Figure 4.4 shows the viscoelastic spectra (storage modulus G') of all samples. Compared to the pure PLLA, all modified samples show increased G', but differences among the modified materials is observed. The G'-curves are clearly divided into two categories (A and B) with LOL1 0.3 wt% as an intermediate. Group A contains samples treated with low concentration of peroxide (0.1 wt% and for BPO also 0.3 wt%), and they have a lower and more frequency-dependent storage modulus, having a similar progression as the pure PLLA sample though slightly upshifted. The slope of the storage modulus curve versus frequency (in the terminal region) for a melt mirrors changes in branching and molecular weight distribution [49,71,143]. One can observe an obvious deflection in the slope profile of treated samples in group A at around $\omega = 3$ rad s^{-1} and for LOL1 0.3 wt% at 0.6 rad s^{-1}, where the slope of 1.5 changes to a value below 1. This deflection could possibly be an indication of a relaxation process reflecting changes in polymer architecture and relaxation time, as compared with the neat PLLA. The group B materials show only a linear decrease in G' with curve slopes between 0.75-1. Either the relaxation is not yet observable at studied frequencies, or the material is that cross linked, and the relaxation will be the most difficult to detect.

Rheological plots such as Cole-Cole [143,144] and van Gurp-Palmen (vGP) [145] have been shown to adopt features indicating changes in the relaxation time of the polymeric system e.g. as a consequence of restricted mobility [144]. The characteristic transitions seen in the vGP plot related to LCB [145] was not observed for the materials in the present study (data not shown), but the Cole-Cole plot gave at hand indications of longer relaxation times among the samples from group B. For group-A materials and PLLA 3051D we do not observe the typical smooth semi-circle profiles, where a larger radius implies a higher molecular weight, but rather a directly descending arc profile implying faster relaxations.

All rheological analysis values of the second extrudates dropped dramatically almost to the same level for the pure re-extruded PLLA. This would be detrimental for the idea of achieving improved melt elasticity with the modified materials. We soon realized that the modified material was extremely sensitive towards thermal degradation (detected from MFI and molar mass analysis; not shown). Thus, while performing the rheological analysis on the re-extruded material, it actually underwent a third melting, and degraded heavily despite careful drying of the material even while running the experiments in nitrogen. Only the material treated with 0.5 wt% TBPB showed retained rheological properties after the second extrusion. Consequently, the rheological studies performed at 240°C on the once-extruded materials, describe better the material behavior of the modified samples intended for a second dry melt-blending.
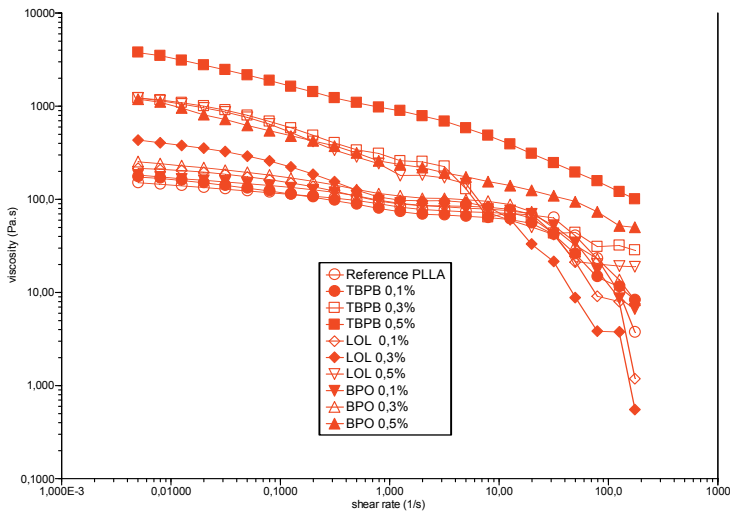
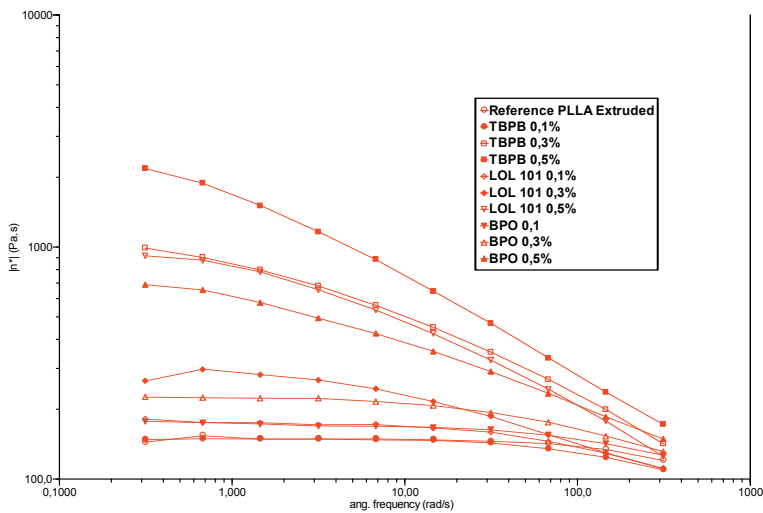**Figure 4.2.** Steady state flow step of all peroxide-modified samples after the first extrusion at 190ºC

Figure 4.3. Complex viscosity of all peroxide-modified samples after the first extrusion at 190ºC
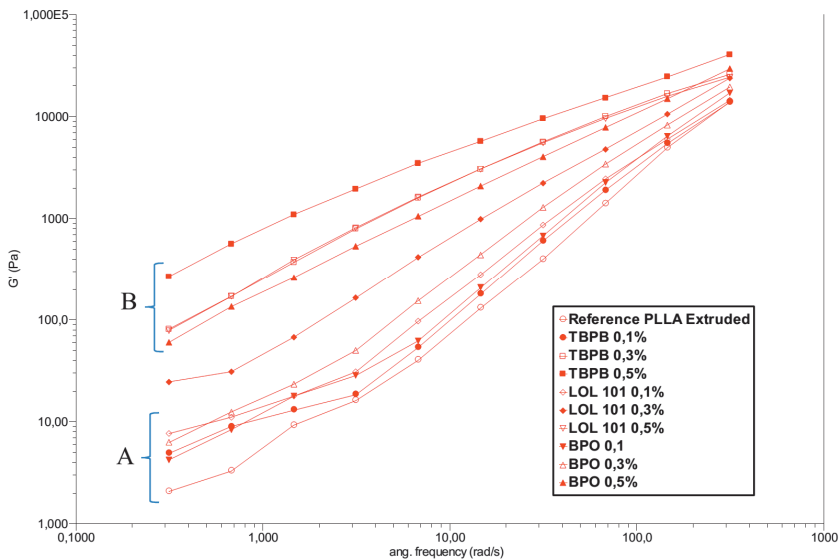
Figure 4.4. Storage modulus G´ of all peroxide-modified samples after the first extrusion at 190ºC

4.1.2. Blends of linear and branched peroxide-modified PLLA 3051D [II]

Peroxide-modified branched PLLAs were prepared and studied for their rheological properties. The impact of the peroxides on molecular weight, branching, gel content and rheological properties of PLLA were different. Comparing molecular weight and zero shear viscosity the effects were decreasing in the following order TBPB > LOL1 > BPO. Overall, 0.5 wt% peroxide was too much, causing gelation and strong die-swelling, producing very thick uneven films, especially for TBPB and LOL1. Applying 0.3 wt% peroxide afforded obvious changes in melt rheology but resulted in rather smooth, good quality films, therefore these materials were used for the blends with a linear PLLA (3051D).

Originally, peroxide-modified branched PLLA, made with 0.3 wt% peroxide [(TBPB; LOL1; BPO, 0.5wt%)] were melt-compounded in a single screw extruder with linear PLLA in the following weight ratios 5:95, 15:85 and 30:70. However, when conducting rheological analysis on the blends, the linear PLLA component underwent a second, and the peroxide-modified PLLA, a third melting, which strongly reduced the viscosity and provided misleading rheology data. Thus, rheological measurements were performed on solution mixed blends. Based on the rheological studies extrusion coating trials were performed with 90:10 blends of linear and branched material. In Table 4.3 is presented the thermal/ physical properties and molecular weight of the melt-compounded blends of peroxide-modified PLLA and linear PLLA. The increase in molecular weight follows rather well the rule of mixing, especially for TPBP and LOL1 taking into account the accuracy of the measurement. One can increase the overall molecular weight by 30-40% with a 10 wt% addition of TBPB-treated PLLA, going from extruded PLLA (96 000 g mol^{-1}) to 140 000 g mol^{-1} of the blend. This is observed in the SEC chromatograph as shift of M$_{peak\ max}$ towards

shorter elution times and one can further observe a small shoulder (broadening) at the high molecular weight region (data not shown).

Table 4.3. Material properties of linear PLLA, peroxide-treated PLLA and their blends

PLLA blends	DSC[a]			HPLC[a]		shear viscos.[b] [Pa s]; 240°C
	T_g (°C)	T_{cc} (°C)	T_m (°C)	M_w *10^3	PD	at 0.01 s^{-1}
PLLA ref.	61	127	152	96	2.1	147
TBPB 0.3%	62	110	145	275	3.7	533
5% TBPB 0.3%	60	122	150	117	2.9	316
15% TBPB 0.3%	60	124	151	146	3	340
30% TBPB 0.3%	60	119	150	175	3.7	307
LOL1 0.3%	61	129	151	285	3	347
5% LOL1 0.3%	60	118	149	135	3.2	365
15% LOL1 0.3%	60	119	150	142	2.7	315
30% LOL1 0.3%	61	122	150	145	4.5	223
BPO 0.3%	61	127	151	170	3.4	307
5% BPO 0.3%	60	119	150	130	3	303
15% BPO 0.3%	60	119	150	141	2.5	386
30% BPO 0.3%	61	120	150	138	2.4	307

a. Melt blended b. Solution mixed

The slightly improved crystallization and annealing ability of modified PLLA containing 0.5 wt% peroxide was not seen in the data obtained from the produced modified PLLA containing 0.3 wt% peroxide [54]. Furthermore, no significant differences were observed in the thermal properties comparing linear PLLA with blends of linear PLLA containing 0.3 wt% peroxide-treated PLLA. In DSC all blends remain amorphous during the cooling cycle, and showed similar annealing capacity (though reduced T_{cc}) heat of melting and melting temperatures during the second heating. The differences in glass transition temperature of the blend components are so small, that unambiguous conclusions regarding the miscibility in the blends cannot be drawn.

PLLA melt properties are not always appropriate for successful high speed extrusion coating processes, due to low melt strength and strain hardening. In addition, PLLA has rather poor thermal stability and can undergo chain-scission during high temperature melt processing [146]. Changing the chain architecture of e.g. PLLA from linear to branched increases zero-shear viscosity and elasticity, accentuating shear-thinning behavior, and relaxation time is prolonged which should favor extrusion coating [147,148]. Thus, blending branched peroxide-modified PLLA with linear PLLA seems to be a reasonable solution to overcome the aforementioned shortcomings.

Branched entities increase the relaxation time of the system, and this especially affects the zero viscosity (η_0), complex viscosity (η^*), the value of the loss (G'') and storage modulus (G') and their slopes in the terminal region. The steady state shear flow (at 240°C) of the linear PLLA and the peroxide-modified (0.3 wt%) PLLA are shown in figure 4.4.
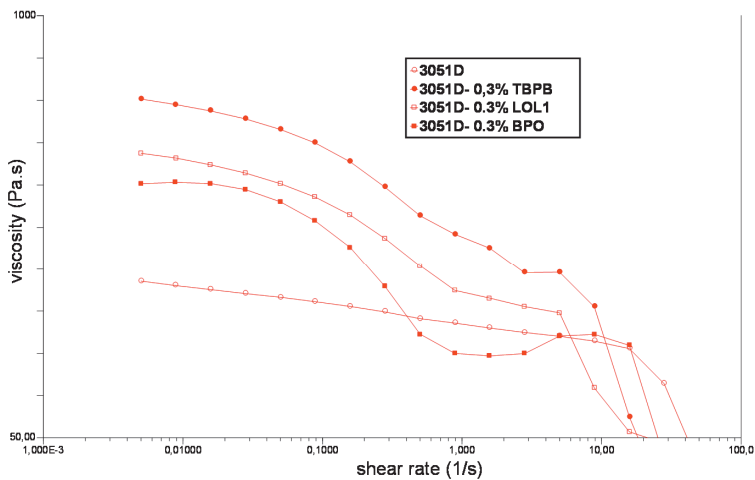
Figure 4.4. Steady state flow step of the linear PLLA (3051D) and different 0.3 wt% peroxide-modified 3051D at 240ºC
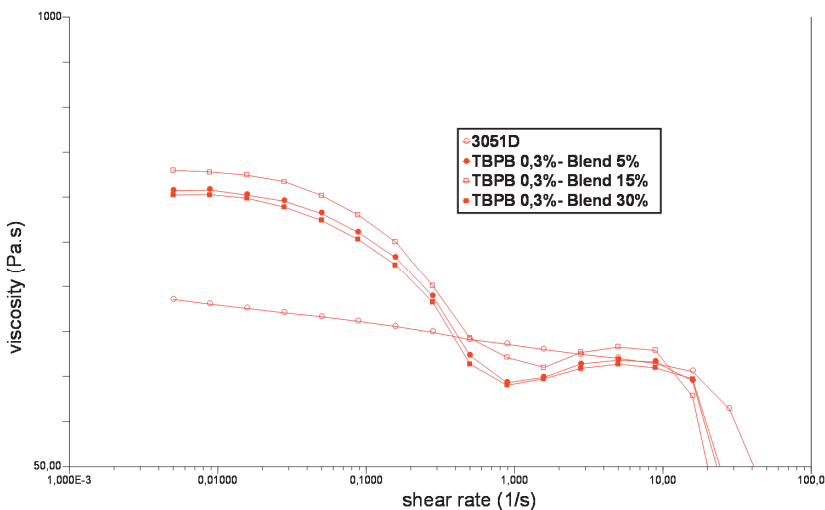

Figure 4.5. Steady state flow step of linear PLLA (3051D) and its blends with different ratios of the peroxide-modified PLLA (0.3 wt% TBPB) at 240ºC

It is recognized for branched polymers that well entangled arms results in higher viscosity, due to the suppression of longitudinal motions. The increase of the zero shear viscosity follows the anticipated branching and measured molecular weight (TBPB > LOL1 > BPO > neat PLLA; table 4.3). In addition, the branched PLLA exhibits a more prominent shear thinning behavior than the linear one, which originates from a greater compressibility of the branched polymers. The zero shear viscosities, and the shear thinning of the blends, are rationally increased in accordance to the flow properties of the added peroxide-treated PLLA. However, the blend ratio does not have a marked impact as shown for the blends with TBPB (figure 4.5).

The dynamic rheological response (complex viscosity and storage modulus) of the neat material and the blends, as a function of the angular frequency ω is shown in figures 4.6 and 4.7. The complex viscosity of the base material follows the same trend as the steady shear viscosity and a strong angular frequency dependency among the peroxide-treated PLLA is detectable (figure 4.6). Similarly, the blends complex viscosity (figure 4.7) were slightly ratio-dependent, showing strong frequency dependency and shear thinning, reaching the viscosity level of linear PLLA at rather low angular frequencies (0.5-10 rad s⁻¹).

Figure 4.6. Complex viscosity η* vs. angular frequency ω of the linear PLLA (3051D) and different peroxide-modified PLLA with 0.3 wt% peroxide at 240ºC
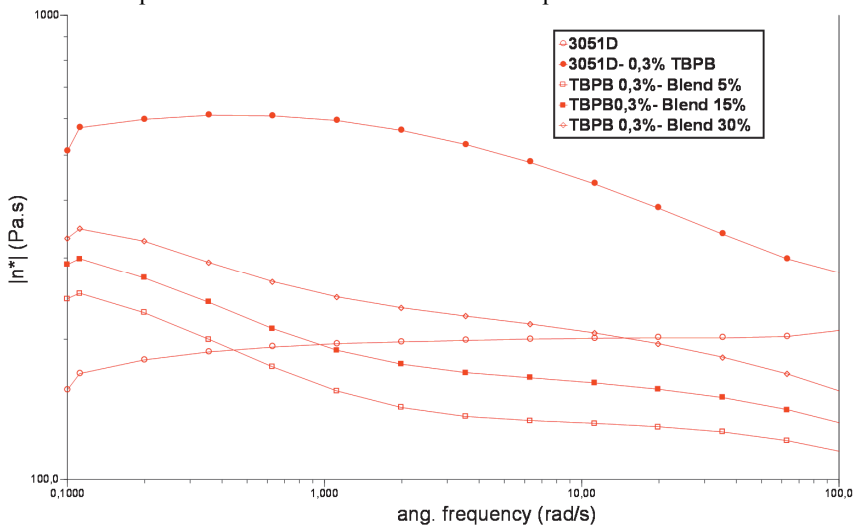

Figure 4.7. Complex viscosity vs. angular frequency of linear PLLA (3051D), PLLA with 0.3 wt% TBPB and their blends at different ratios at 240ºC

Evidence of increased elastic nature in the base material and the blends is clearly visible from the logarithmic plots of storage modulus (G') versus the angular frequency (ω) (figures 4.8 and 4.9). As seen in figure 4.8 only the neat linear PLLA (slope = 1.9) exhibits terminal viscoelastic relaxation, characterized by the power-law of its storage modulus data (G'∝ω²). All three peroxide-treated PLLA show a curve slope of 1.1 and the upshift in the G' (TBPB > LOL1 > BPO) demonstrate a more elastic nature with longer relaxation times, due to higher M_w and branched architecture not yet showing signs of reaching viscous flow at the lowest measured angular frequency. The various peroxide-treated PLLAs have comparable effect on the blend behavior. For all blends (only TBPB is shown), one can observe a deflection in the slope at ~7 rad s^{-1}, which is more pronounced with decreasing blend ratio. This can be interpreted as the mean relaxation of the two material phases, while the slope after the plateau (ω < 0.1 rad s^{-1}), is not yet approaching G'∝ω² [149]. Consequently, one can expect an additional relaxation process at even lower frequencies, deriving from the interfacial tension between the matrix and the dispersed phase.

Mixing polymers can lead to a range of phase behaviors, depending on the temperature and the composition [150]. Several rheological models and responses have been suggested as tools for resolving the blend morphology, whether the blend exists in a homogeneous or heterogeneous state [151,152]. Additionally, the heterogeneous blend can be categorized by a droplet-matrix or co-continuous morphology.
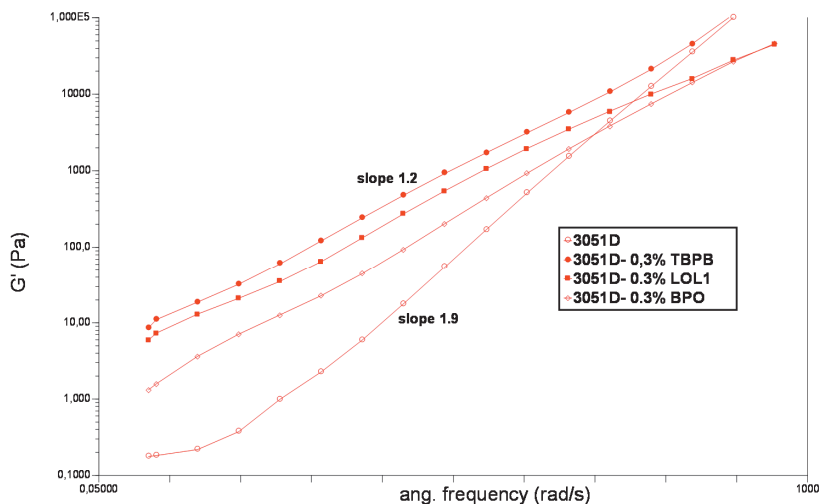

Figure 4.8. Storage modulus vs. angular frequency for the linear PLLA (3051D) and its blend with different ratios of 0.3 wt% peroxide-modified PLLA at 240°C
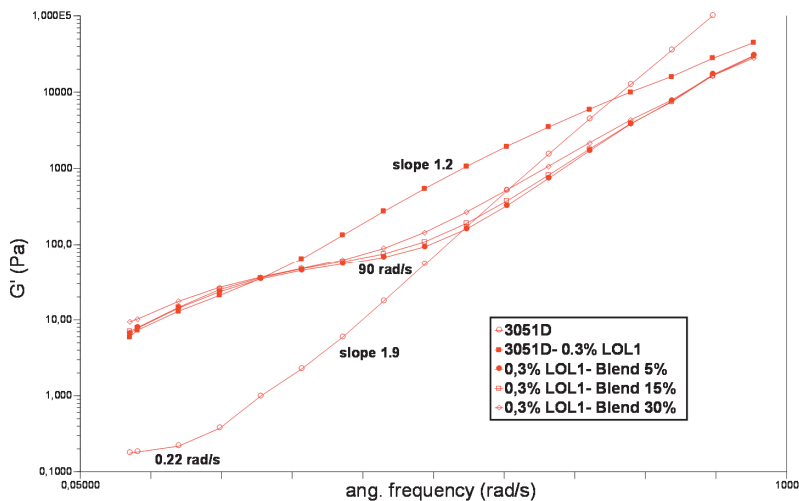
Figure 4.9. Storage modulus vs. angular frequency for linear PLLA (3051D), PLLA with 0.3 wt% LOL1 and their blends at different ratios at 240ºC

Cole-Cole plot (log imaginary part of viscosity-log real part of viscosity) is a well-known method to investigate the rheological behavior of two phase systems like polymer blends and filled polymer. A single circular arc-profile is interpreted as homogeneous blend [153]. The appearance of a second circular arc or tail implies a second phase with a second relaxation mechanism [152]. A Cole-Cole plot of peroxide-treated PLLA (0.3 wt% LOL1) and its blends with linear PLLA at different ratios is shown in figure 4.10. The existence of two phase morphology in the blends with two distinct relaxation mechanisms becomes evident from the two well resolved semi-arcs. With the applied blend ratios in the present study, and the large viscosity difference between the components, it is reasonable to expect that the peroxide-treated PLLA/linear PLLA blends exists in a droplet/matrix phase morphology [154]. The very distinct separation between the arcs can be explained by a low interfacial tension between the two phases. For the blends this is actually expected, as both phases consist of PLLA. The detectable vertical shift of the double arc profile stems from the blend ratio and is in accordance with results forward by Xu et. al. [155].
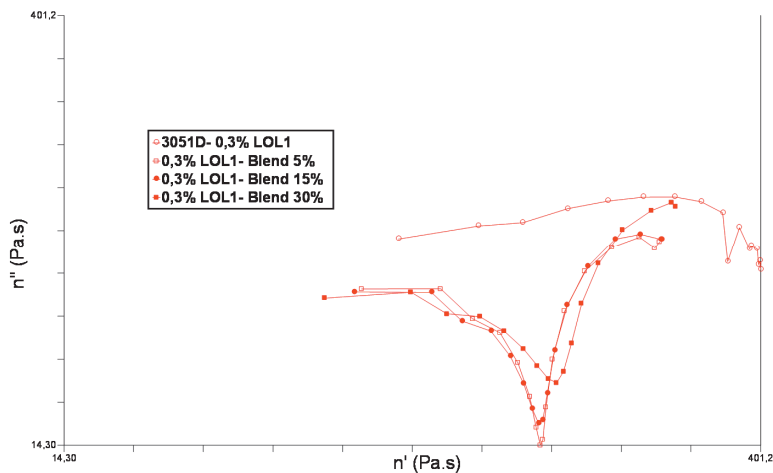
Figure 4.10. Cole-Cole plot of PLLA with 0.3 wt% of LOL1 and their blends with different ratios at 240°C

A log-log plot of storage modulus (G') against loss modulus (G") (Han plot) of different samples at a constant temperature (240°C) is shown in figure 4.11. The Han plot is sensitive for determining blend miscibility [156]. In general, Han plots have a slope of 2 in the terminal region if a blend is regarded as being truly homogeneous [157]. It is proposed that a binary blend which is compatible on a molecular level give rise to a composition-independent correlation in a G' vs G'' (Han) plot [157]. The peroxide-treated PLLAs and the blends deviate from a slope value of 2 over the whole studied frequency range. Thus, the deviation from the slope 2 may be applied in judging the heterogeneity of polymer systems, because the slope is decreased as the heterogeneity is increased [137]. All blends do show similar and composition-independent slope values deviating from 2 at higher frequencies. However, at G' ~900 Pa, one can detect an obvious inflection point, and a subtle composition-dependency in the curves is detected, which apparently mark that the polymers melt homogeneity changes with the shear frequency [158].
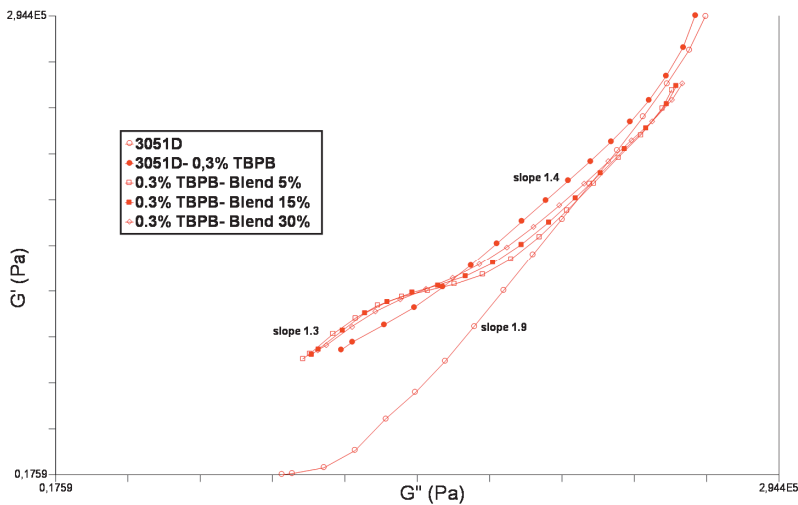
Figure 4.11. A log-log plot of storage modulus (G') vs. loss modulus (G") (Han plot) of linear PLLA (3051D), PLLA with 0.3 wt% of TBPB and its blends with linear PLLA at 240°C

Plotting the phase angle (δ) as a function of the absolute value of the complex modulus (|G*|) (van Gurpen-Palmen; vPG plot) has been established as a sensitive tool to detect the response of long chain branching [157] and phase separation [152] in the terminal region. From figure 4.12 one can observe that all blend ratios produce similar curve profiles. For the blends, the curves pass a maximum, and then begin to decrease, and finally create a valley when approaching lower frequencies (and |G*| values), which evidently substantiate a phase-separated droplet-matrix morphology. A small discrepancy is observable for the 30 wt% blend curve with a less pronounced formed valley which might reflect a tendency towards a co-continuous structure.
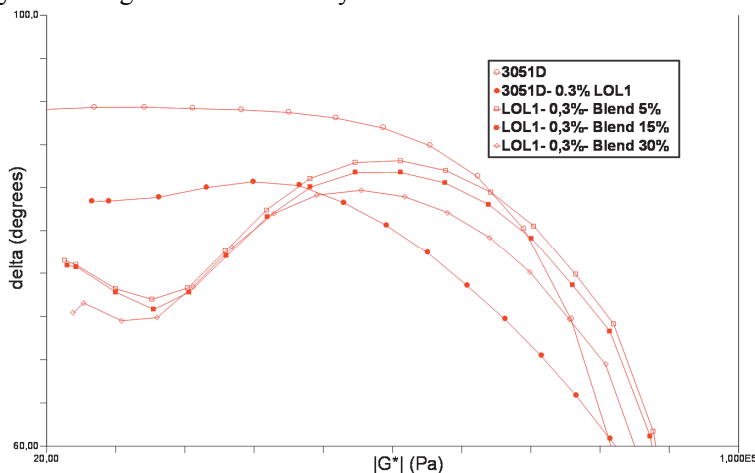

Figure 4.12. Van Gurpen-Palmen for linear PLLA (3051D), PLLA with 0.3 wt% of LOL1 and its blends with linear PLLA at 240°C

4.2. Synthesis and characterization of star-shaped PLLA and their blends with linear PLLA 3051D [III]

4.2.1. Synthesis and molecular characterization of sPLLA

The ring opening polymerization of L-LA was carried out using pentaerythritol (PERYT) as a tetra-functional initiator, and $Sn(Oct)_2$ as catalyst at 160°C for 60-75 minutes [51].

Molecular characterization of sPLLA samples, determined by SEC and ^{1}H-NMR are listed in table 4.4. Based on ^{1}H-NMR it is obvious that star-shaped poly-L-lactide (sPLLA) has been attained [51,159]. The results show that the number-average-molecular weight of the polymers obtained from SEC was in good agreement with the number-average-molecular weight, based on ^{1}H-NMR data. Though, in the case of the higher molecular-weight samples, the obtained molecular weight was slightly lower than expected based on feeding ([M] [I] $^{-1}$).

The DSC curves of all sPLLA during the first cooling scan, and the subsequent heating scan are shown in figure 4.13.

Three sets of crystallinity data for the sPLLAs are presented in table 4.4: Crystallinity formed during cooling X_c (%), crystallinity at cold-crystallization, X_{cc} (%) during the second heating, and total crystallinity at melting, X_m (%), which is a combination of the two other crystallization processes.

Concerning pristine sPLLA, only small, hardly detectable, exothermic crystallization peaks in the cooling ramp, X_c (%) were observed, except for two sPLLA samples, S4 and S5, revealing clear crystallization peaks centered at around 95°C (figure 4.13A).

The second heating scan showed a glass transition, T_g, centered at 34°C for S1 and the T_g increased gradually, with increasing molecular weight of the sPLLA to 57°C for S5. The S1 remained amorphous, while a broad endothermic (melting) peak centered at 136°C was displayed for S2 (ΔH_m= 5 J g^{-1}) increasing to 45 J g^{-1} for S5. A significant increase in the melting temperature (T_m) of 30°C was detected with increasing molecular weights from S2 to S5.

Initial degradation temperature T_i shown in the second heating scan figure 4.13B, started at 215°C for S1 and the T_i increased gradually with increasing molecular weight of the sPLLA to 240°C for S5. Notably, 3051D showed T_i, at 210°C which is lower than all sPLLAs.

From these results, one can conclude that sPLLA can be appropriate and helpful for faster crystallization during cooling, because the branch points can act as nucleating centers to accelerate crystallization. Nevertheless, the perfection of the crystals might be disturbed as a result, because branched PLAs are less capable of increasing the lamellar thickness due to their restricted mobility in comparison with linear PLLA [160].

In a study by Sakamoto et. al. they showed that the T_g (indicator of chain mobility), T_{cc} (indicator of ability to crystallize during heating), T_m (indicator of crystalline thickness), and ΔH_m (indicator of final degree of crystallinity during heating) of four-arm PLLA, increased with increasing M_w [159]. Similar trends can be observed in our work except for S1 with the lowest molecular weight, in which neither a cold crystallization nor a melting peak was observed, found in figure 4.13.

It has been found that the shear viscosity of low M_w star-shaped polymers is lower than for its corresponding linear polymer with similar molecular weight, due to higher segment density and reduced hydrodynamic volume [52]. However, the viscosity of the star-shaped polymer increases faster with the molecular weight, and surpasses that of the linear analog at some specific molecular weight, as the star-shaped polymer possesses restricted chain mobility due chain entanglements, and to motional constraints as one end of the arm is anchored to the star core [76].

The rheological properties of the low molecular weight samples S1 and S2 were not measureable at 190°C (Bohlin Vor Rheometer; rotational rheometer), because of their very low shear viscosity; therefore they had to be analyzed at 150°C. The flow curves of the neat star-shaped polymers (not included) showed an obvious influence of the molecular weight on the viscosity. A higher M_w yielded a slightly higher zero shear viscosity (η_0), also with a more pronounced shear thinning behavior. All our star-shaped polymers had lower shear viscosities compared to linear 3051D (M_w = 121 000 and *MWD* = 2.59), due to substantially lower molecular weights (M_w 2500-35 000 g mol^{-1}).

4.2.2. Blends of sPLLA and linear PLLA

Star-shaped PLLAs with increasing arm lengths (molecular weights) were synthesized, and their blends were prepared via solution blending with the content of 70 and 90 wt% of commercial 3051D PLLA (NatureWorks LLC). Three sPLLA, low, medium and high molecular weight (2500, 12500 and 35000 g mol^{-1}), were chosen for further rheological analysis as blends with the linear PLLA at 240°C.

To obtain more identical conditions with materials going through a dry-blending process during an extrusion coating, the sPLLA has been mixed in solution with 3051D PLLA, so that they are melted ("dry-blended") for the first time in the rheometer (same conditions as in an anticipated extruder dry-blending with 3051D pellets).

Thermal properties: The glass transition temperatures of neat star-shaped polymers S1-S5 were 34.4, 43.2, 53.1, 57.4 and 57°C, respectively, while the T_g of pure 3051D is 60°C (fable 4.4 and 4.5). Qiu et al. studied the crystallization and miscibility of different biopolymer blends [161]. They study the miscibility by the composition-dependency on T_g, change of T_m and cold crystallization temperature. Some degree of compatibility may be interpreted when the two separately observed T_gs are shifted towards each other or just one T_g appears in a binary polymer blend [116]. The T_g values of the present PLLA blends with S1-3 are slightly dependent on the blend composition, proving that the binary blends are partially miscible [161,162]. This suggests that the sPLLA acts as a plasticizer in linear PLLA. It has to be mentioned that T_g of neat PLLA, S4 and S5 are so close that it is ambiguous to conclude if any depression of T_g have appeared in the blends.

Table 4.4. Characterizations of synthesized sPLLAs

Star-PLAs	DSC							SEC			^{1}H-NMR
	T_c(ºC)/ X_c[a]	T_g (ºC) [b]	T_{cc}(ºC) [b]	T_m(ºC) [b]	X_{cc}[b]	X_m[b]	T_i (ºC) [b]	~M_n	~M_w	~PD	~M_n
S1	NA	34		Amorphous			215	2400	2700	1.1	2500
S2	NA	43	113	136	5	5	225	5400	8300	1.6	5500
S3	NA	53	110	147-156	39	39	228	11500	19000	1.7	12000
S4	94.3/ 3	57	104	167	40	45	230	14600	38000	2.6	15000
S5	95.4/ 25	57	97	168	25	49	240	33400	55000	1.7	35000

[a] Determined from first cooling run. [b] Determined from second heating run.

X_c (%) = $\Delta H_c/\Delta H_{m0} \times 100$

X_{cc} (%) = $\Delta H_{cc}/\Delta H_{m0} \times 100$

X_m (%) = $\Delta H_m/\Delta H_{m0} \times 100$

Table 4.5. Thermal properties of 3051D/ Star-PLA Blends

Samples	DSC				
	T_g(ºC)	T_m(ºC)	T_c(ºC)/ X_{cc}	X_m	T_i (ºC)
3051D/ 10%-S1	57		Amorphous		210.4
3051D/ 10%-S2	59		Amorphous		211.4
3051D/ 10%-S3	60		Amorphous		211.7
3051D/ 10%-S4	61		Amorphous		212.2
3051D/ 10%-S5	60		Amorphous		213.5
3051D/ 30%-S1	53		Amorphous		212.6
3051D/ 30%-S2	56	147	123/ 1.6	1.6	215.1
3051D/ 30%-S3	57	147	121/ 5	5	216.3
3051D/ 30%-S4	60	148	124/ 10	10	218.6
3051D/ 30%-S5	60	148-152	120/ 30	30	222.2
3051D Ref.	60		Amorphous		210

All data determined from second heating run

Xcc (%) = $\Delta H_{cc}/\Delta H_{m0} \times 100$

Xm (%) = $\Delta H_m/\Delta H_{m0} \times 100$

No crystallization was detected during the cooling ramp, which was followed by an amorphous plateau during heating, showing that sPLLA in the used concentrations could not crystallize nor improve the crystallization of pure PLLA (figure 4.14). The initial degradation temperature (T_i) of the PLLA 3051D, and corresponding blends with sPLLA are shown in table 4.5. PLLA 3051D showed a T_i at 210ºC, and an addition of 10 wt% S1-S5 increased the T_i slightly from 210 to 214ºC respectively. Remarkably, blends with 30 wt% of sPLLAs displayed increment from 215ºC for S1 to 222ºC for 30 wt% S5. Initial degradation temperature is a sign of thermal stability of polymers. Notably, 3051D showed a T_i at 210°C, which is lower than all sPLLA and their blends emphasizing an improvement of thermal stability by using the star-shaped structure. No significant influence on the crystallization of the neat PLLA was observed on the second heating ramp, since the amounts of total crystallinity equalizes to the proportion of crystalline

sPLLA in the blend. However, the crystallization on heating (annealing) of the blend of S5-30 wt% was nearly doubled, as estimated based on the content of S5, and a sharp melting peak appeared which would be sign of melting of linear PLLA, figure 4.14. Therefore, one could conclude that S5 increased ability of 3051D to crystallize on the heating ramp. This would be due to the reorganization of amorphous segments into crystalline ones, as a result of increased macromolecular freedom upon increasing temperature [163].

Comparing the thermal behavior of the pure PLLA and sPLLA with the corresponding blends, the T_g value was attributed to the combined sPLLA/3051D amorphous domains. The exothermic peaks owe to the crystallization of sPLLA blocks, and the broad endothermic peak due to the overlapping of the melting temperature of the crystallites with different crystalline size [159].
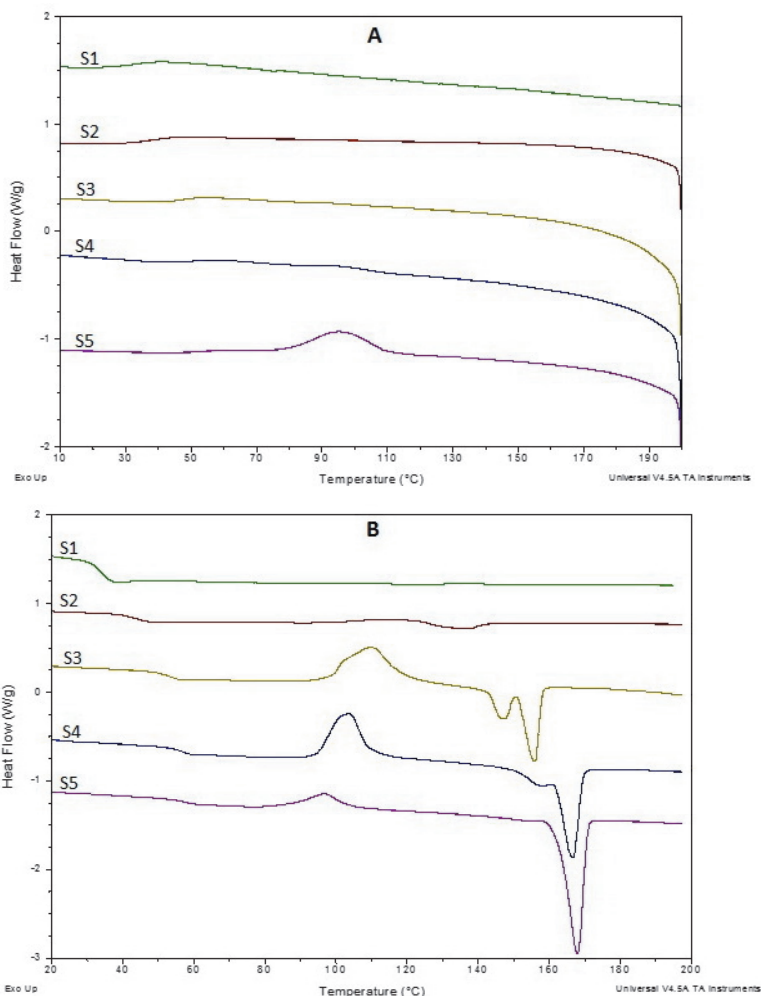

Figure 4.13. DSC curves of all sPLLA: (A) the first cooling scan and (B) the second heating scan
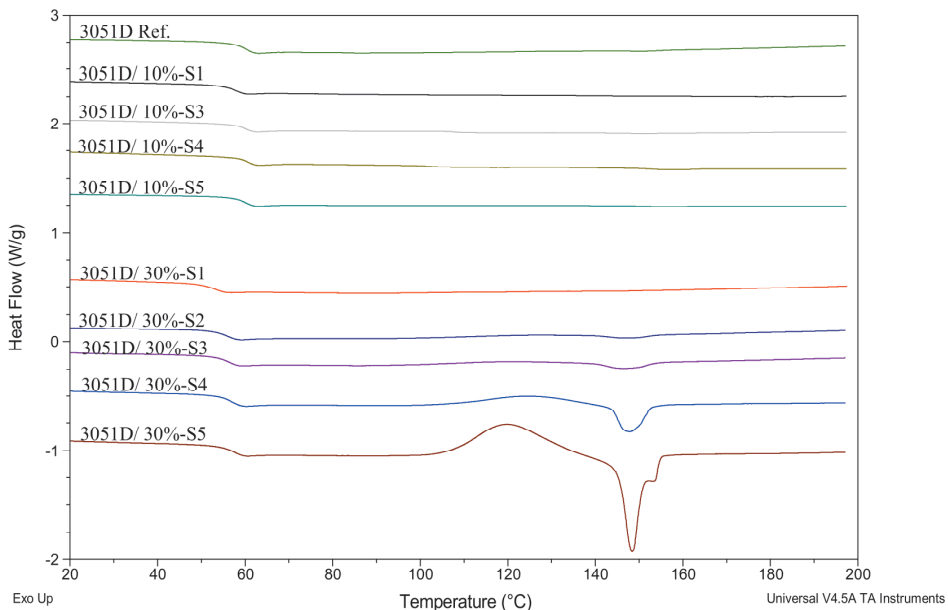
Figure 4.14. DSC curves of PLLA/sPLLA blends from the second heating scan

Rheological properties: A detailed investigation of the rheological behavior of these blends with varying sPLLA concentration was done, performing the rheological measurements at 240°C. All blends were mixed in solution (chloroform) and dried to obtain the "true" material behavior during its first melting (as it would be in the case of a dry-mix during extrusion). The main focus has been on the rheological properties, such as storage modulus (G′), loss modulus (G″), complex viscosity (η*), and shear viscosity (η). The storage modulus G′ reflects the elastic part, and loss modulus G″ the viscous part of polymer melts. Branching is often introduced to polymeric material to modify the flow properties for specific melt-forming operations. It is well understood that when the branch length exceeds some critical value, it leads to an increase in the viscosity compared to the linear molecule with the same molecular weight due to entanglements by the branches [164].

Complex viscosity, storage modulus of PLLA 3051D and blends are shown in figure 4.15. The PLLA 3051D exhibit terminal flow behavior at low frequency in the dynamic storage modulus (G′) and loss modulus (G″), i.e. scales to G′αω^2 and G″αω respectively, which are characteristics for a viscoelastic liquid. For all blends containing 10 wt% of sPLLA and 30% of S5, a shoulder (deflection in curve slope) on the G′ curve is seen (frequency ~2Hz) which indicates that the storage modulus exhibit weak frequency dependency at moderately low frequencies. This non-terminal behavior indicates the presence of a longer relaxation process not detected in the linear PLLA. It should correspond to the ''additional'' elastic response originating from the surface interaction between the droplets (sPLLA) in the discrete phase and the continuous matrix (linear PLLA), and has been reported for many blends with lower level of miscibility or immiscible blends [149]. Similar results were reported by Lee et al. [165] with experimental values of the G′ obtained from either phase separated or degraded polymer blends.

This result could be examined together with complex viscosity frequency dependence of the same blends (figure 4.16).
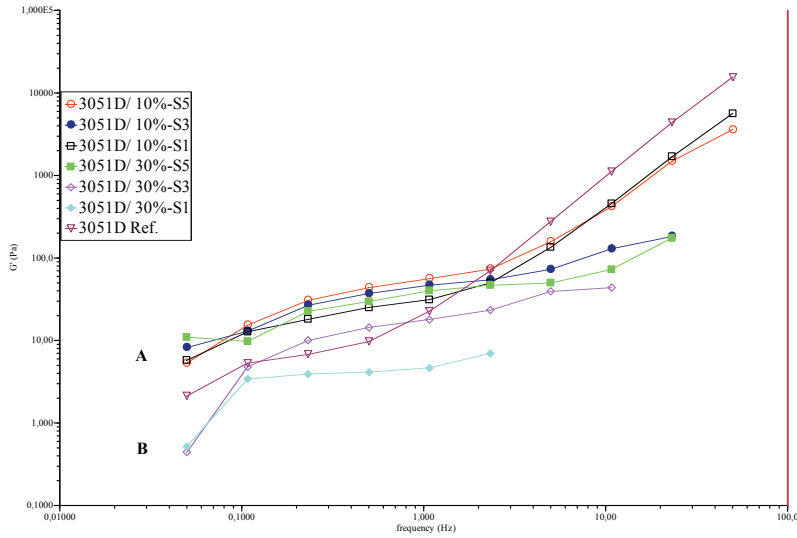

Figure 4.15. Storage modulus vs. frequency for linear PLA 3051D and sPLLA blends with different molecular weight and concentrations.
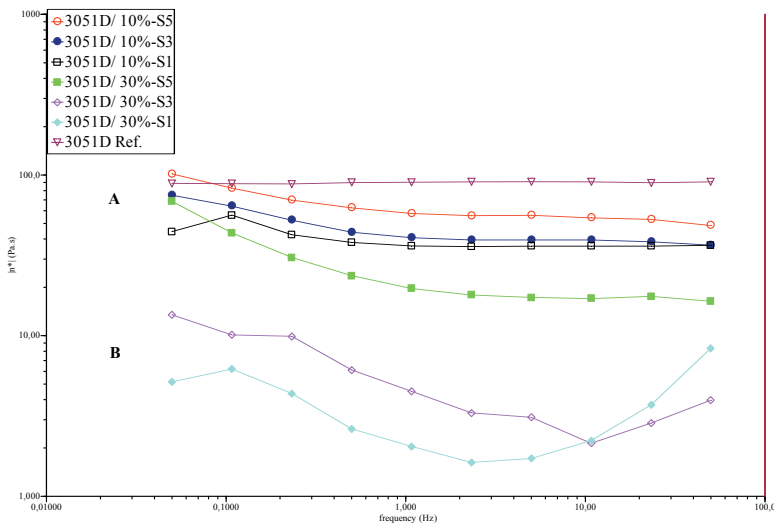

Figure 4.16. Complex viscosity vs. frequency for linear PLA 3051D and sPLLA blends with different molecular weight and concentrations.

The complex viscosity increases as the frequency decrease, as is typical for yield stress fluids. The shear viscosity of a molten polymer typically displays a constant value at very low shear rates, (zero shear viscosity η_0), and which begins to deviate from η_0 at some characteristic shear rate (non-Newtonian).
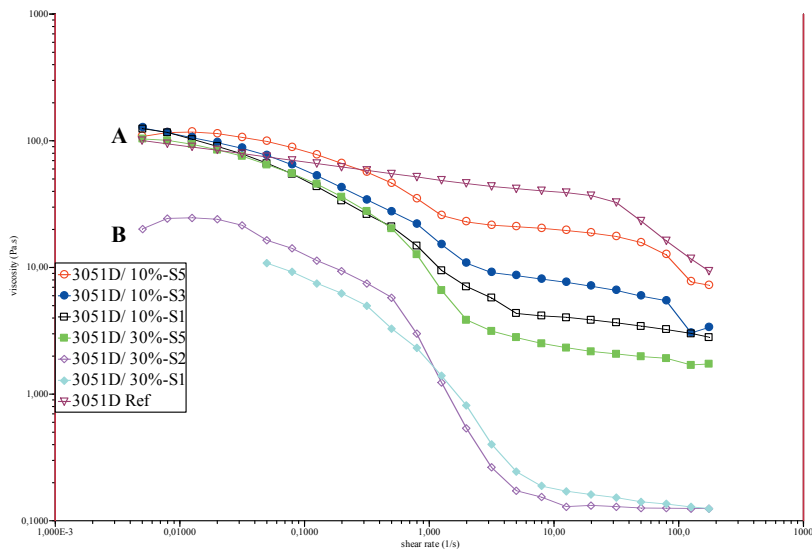
Figure 4.17. Shear viscosity vs. shear rate for linear PLLA 3051D and blends with sPLLA of different molecular weight and concentrations.

Figure 4.17 summarizes the shear viscosity (η) of linear PLLA and its blends with sPLLAs at 240°C. Linear PLLA has a zero shear viscosity η_0 of about 100 Pas, and approaches power law behavior at higher shear rates. Blends containing 10% of all sPLLAs and 30% of S5 show zero shear viscosity (η_0) similar to linear PLLA (3051D) as well as shear thinning starting almost immediately (shear rate of ~0.1s[1]), and finally leveling to different, rather constant viscosities, 2Pas at 30% of S1 to 30Pas for 10% of S5. This point out that total molecular weight of these blends remained rather unaffected, while their polydispersity have increased. In case of blends with 30% of S1 and S3, the zero shear viscosity decreased one order of magnitude which indicates declined total molecular weight. These blends also showed shear thinning, beginning at shear rates of ~0.1 s[1], and finally the viscosity decreased to a very low level of about 0.1 Pas. These latter blends showed a larger range of viscosity values, due to stronger shear thinning which is attributed to plasticizing effects of low molecular weighted sPLLAs at this concentration.

4.3. Synthesis and characterization of tri-block PLLA-PEG-PLLA copolymers (PEGLA) and their blends with linear PLLA 3051D [IV]

4.3.1. Synthesis and properties of tri-block copolymers PEGLA

Four series of tri-block copolymers with different lengths of PLLA segments (degree of polymerization, *DP*= 34 to 480) were obtained by ring opening polymerization. For structure characterization, and to estimate the LA:EO molar ratio in the copolymers, ^{1}H-NMR spectra

were recorded at 600 MHz [166]. The results show that the number-average-molecular weights of the tri-block PLLA-PEG-PLLA copolymers (PEGLAs) obtained from ^{1}H-NMR was in good agreement with the theoretical number-average-molecular weights based on feeding ([M]/ [I]).

Table 4.6. Characterization of synthesized triblock PLLA-PEG-PLLA.

Copolymers	DSC[a]				^{1}HNMR	Shear viscosity
	T_g (°C)[a]	T_{cc}(°C)[a]	T_m(°C) [a]	X_c(%)[a]	$\sim M_n$[b]	1 s^{-1}
PEGLA1	1	44 and 91	75 and 118	1	11000	1
PEGLA2	9	97	132	10	17000	3
PEGLA3	33	98	144 and 153	33	30000	30
PEGLA4	40	110	153 and 161	37	76000	200

[a] Determined from second heating run. [b] M_n of PLA block

X_c (%) = $\Delta H_c/\Delta H_{m0} \times 100$

X_m (%) = $\Delta H_m/\Delta H_{m0} \times 100$

Thermal properties: Differential scanning calorimetry (DSC) data of all tri-block copolymers are listed in table 4.6, and their DSC curves at the second heating scan are shown in figure 4.18. In this part, PEG$_{6000}$ with melting point of 62°C was used for the synthesis of PLLA-PEG-PLLA. Concerning pristine PEGLA, no detectable exothermic crystallization peaks in the cooling ramp, X_c (%) were observed. The second heating scan showed a glass transition, T_g, centered at 1°C for PEGLA1, and the T_g increased gradually with increasing molecular weight of the PLLA block to 40°C for PEGLA4, indicating the variable composition in the amorphous phases due to higher molecular weight of PLA segments [166].
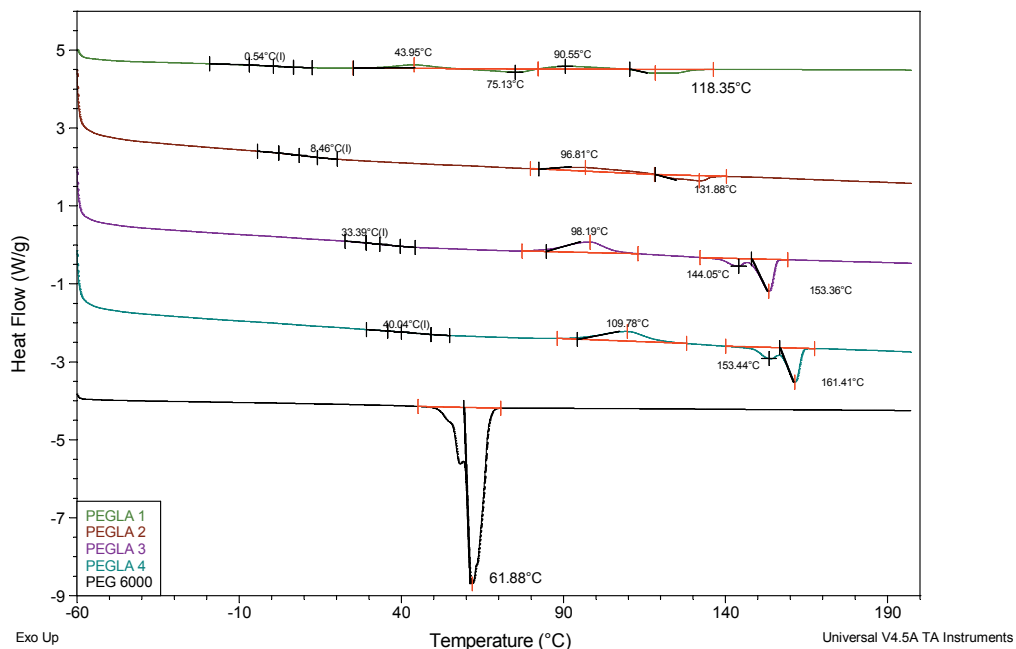

Figure 4.18. DSC curves of PEGLAs and PEG$_{6000}$ at the second heating scan

45

PEGLA1 displayed two broad exothermic (cold crystallization) peaks centered at 44 and 91°C (T_{cc}), and two melting peaks (T_m) at 75°C and 118°C, as shown at figure 4.18. However, this exothermic peak around 44°C, and its corresponding melting endotherm at 75°C, should be associated with crystallization of PLLA, rather than that of PEG. Zhang et. al. has studied this behavior with IR and melt-quenched PLLA-PEG-PLLA, and concluded that the PLLA constituent exists in crystalline mesophase, which is not a normal amorphous, or crystalline phase (mesophase is an intermediate state between crystal and amorphous states when a polymer with fast crystallization rate is rapidly quenched). [167]. However, the copolymers with larger PLLA size showed just one melting peak ranging from 131-161°C which was due to higher proportion of PLLA in the structure.

Rheological properties of PEGLA at 190°C**:** As can be seen in table 4.6 and figure 4.19 with increased molecular weight, the zero shear viscosity (η_0) is increased. All samples show a Newtonian-like behavior, and the narrow polydispersity, which was expected because of the linear structure.
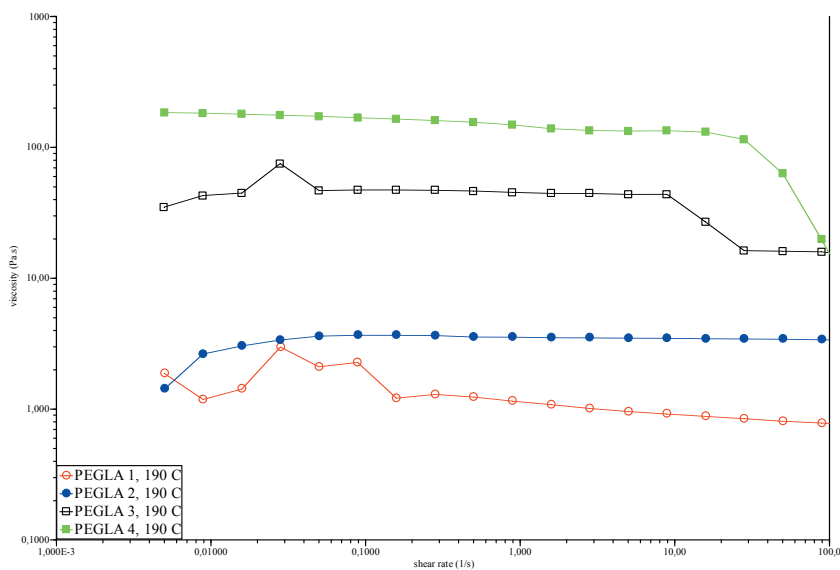

Figure 4.19. Shear viscosity vs. shear rates for PEGLAs with different molecular weight at 190°C

4.3.2. Blends of PEGLA and linear PLLA.

A series of tri-block PLLA-PEG-PLLA copolymers using PEG_{6000} with increasing PLLA segment lengths were synthesized, and their blends were prepared via solution mixing with 70 and 90 wt% of commercial 3051D PLLA (NatureWorks LLC) in the same manner as it have been done for sPLLA in previous section 4.2.

Table 4.7. Thermal properties of 3051D/ PEGLA blends

Samples	DSC			
	T_g(ºC)	T_m (ºC)	T_c (ºC)/ X_{cc}	X_m
3051D/ 10%-PEGLA1	55		Amorphous	
3051D/ 10%-PEGLA2	55		Amorphous	
3051D/ 10%-PEGLA3	56		Amorphous	
3051D/ 10%-PEGLA4	60		Amorphous	
3051D/ 30%-PEGLA1	55		Amorphous	
3051D/ 30%-PEGLA2	59		Amorphous	
3051D/ 30%-PEGLA3	59		Amorphous	
3051D/ 30%-PEGLA4	57		Amorphous	
3051D Ref.	60		Amorphous	

All data determined from second heating run
Xcc (%) = $\Delta H_{cc}/\Delta H_{m0} \times 100$
Xm (%) = $\Delta H_m/\Delta H_{m0} \times 100$

The basic information on the pure PEGLA is listed in table 4.6. Three PEGLAs, i.e. low, medium, and high molecular weight PEGLA1, 3 and 4 respectively, were chosen for further rheological analysis as blends with the linear PLLA at 240ºC.

Thermal properties: The effect of PEGLA addition on the thermal behavior of commercial PLLA NatureWorks 3051D was investigated. The glass transition temperatures of the neat copolymers PEGLA1- 4 were 1, 9, 33 and 40°C, respectively, while the T_g of pure 3051D is 60ºC (table 4.6 and 4.7). The T_g values of the present PLLA was not affected significantly by adding different proportion of PEGLAs in the blend. However, appearance of one T_g proves that the binary blends are partially miscible [161,162]. PEGLA consist of three blocks, two of which are PLLA, and the middle block is PEG with molecular weight of 6000 g mol^{-1}. Each PLLA in PEGLA1 has a molecular weight of 2500, giving an overall molecular weight of 11000 g mol^{-1} and in PEGLA4, each PLLA has a molecular weight of 35000 g mol^{-1}, therefore the overall molecular weight will be 76000 g mol^{-1}. Thus, due to the higher content of PLLA in all PEGLAs (except PEGLA1), the T_g will be nearer to the PLLA value based on law of mixture [44]. The first heating scan of pristine linear PLLA pellets showed an endothermic peak (melting, T = 149ºC, not shown), but no detectable melting in the second heating scan. The curves of the second heating scan of all blends containing 10 and 30% of PEGLA displayed; one glass transition temperature (T_g) centered at 55–60ºC, implying compatibility of these blends. Though, no crystallization was detected during the cooling ramp, followed by an amorphous plateau during second heating show that PEGLAs used in the present concentrations could not crystallize by themselves, neither improve the crystallization of pure PLLA (figure 4.20).
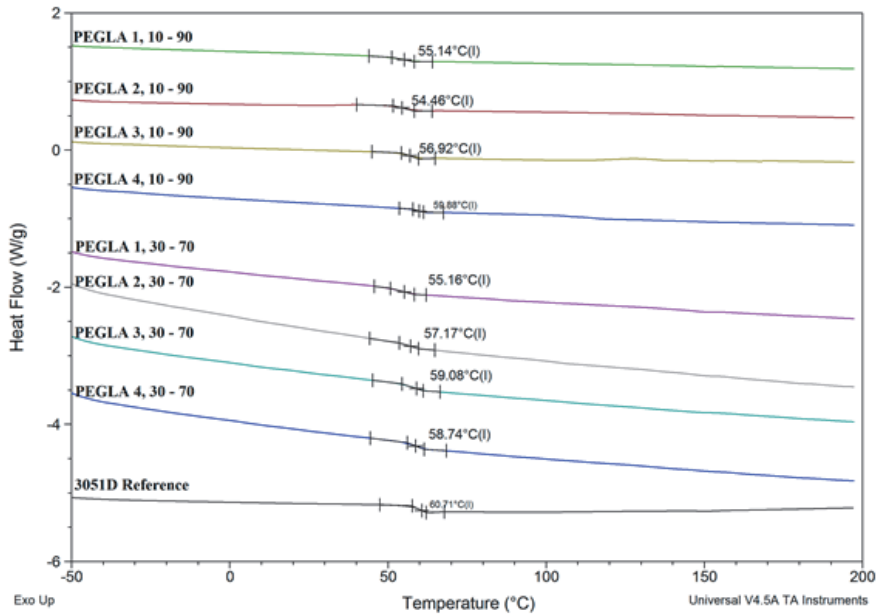
Figure 4.20. DSC curves of all blends containing 10 and 30% of PEGLAs at the second heating scan

Rheological properties: To elucidate and find the most beneficial melt flow properties of the PLLA-PEGLA blends, with respect to the extrusion coating process, a detailed dynamic rheological study on these blends with varying PEGLA concentration was performed at 240°C. Loss modulus, storage modulus and complex viscosity as a function of angular frequency of neat PLLA and all blends are shown in figure 4.21- 4.23.
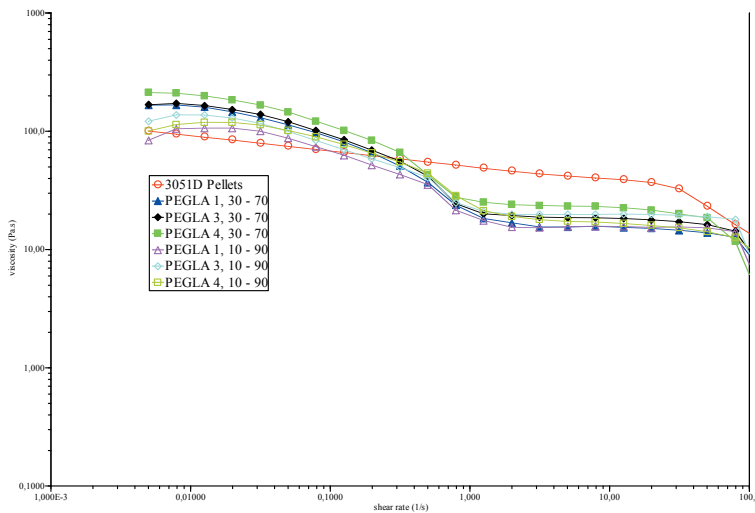

Figure 4.21. Shear viscosity vs. shear rate for all blends containing 10 and 30% of PEGLAs at 240°C
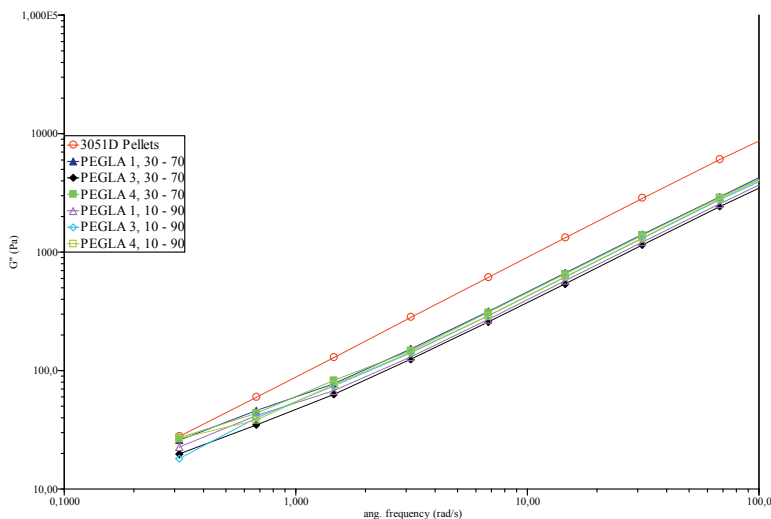
Figure 4.22. Loss modulus vs. angular frequency for all blends containing 10 and 30% of PEGLAs at 240ºC
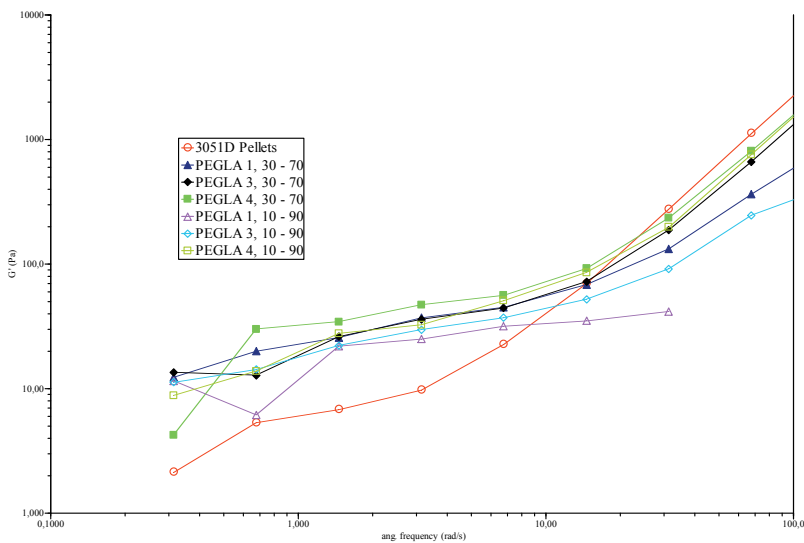

Figure 4.23. Storage modulus vs. angular frequency for all blends containing 10 and 30% of PEGLAs at 240ºC

Neat PLLA exhibits terminal flow behavior at low frequency in the dynamic storage modulus (G′), and loss modulus (G″), i.e. scales to G′αω² and G″αω respectively, which are characteristics for a viscoelastic liquid. For all blends containing 10 and 30 wt% of PEGLA, a shoulder (deflection in curve slope) on the G′ curve is seen (frequency ~15 rad s⁻¹ for 10% and frequency ~30 rad s⁻¹ for 30 wt% blends), which indicates that the storage modulus exhibit weak frequency dependency at moderately low frequencies. This non-terminal behavior indicates the presence of a longer relaxation process not detected in the linear PLLA. It should correspond to the ''additional'' elastic response originating from the surface interaction between the PEGLA in the

49

discrete phase, and the continuous matrix (linear PLLA), and has been reported for many blends with lower level of miscibility, or immiscible blends [149]. Lee et al. reported similar experimental values of the G′ obtained from either phase separated, or degraded polymer blends [165].

4.4. Extrusion coating results from TUT for PLLA based modified material and their blends with 3051D[II, III, IV]

The most potential and promising peroxide modified, star-shaped and PEGLAs were prepared and tested in the extrusion coating pilot line at Tampere University of Technology. All extrusion coating experiments were conducted with dry-mixed commercial PLLA 3051D pellets and in-house grinded materials (particle size 3-5 mm).

Extrusion coating experiments on paperboard were conducted with a blend ratio of 90:10 of PLLA and peroxide-modified PLLA. In case of TBPB and LOL1 modified-PLLA, the 0.3wt% based product was tested. However, as BPO had a less obvious impact on the molecular weight [54], the 0.5 wt% BPO based product was chosen for the coating experiments. Despite lower molecular weight of the 0.5wt% BPO treated PLLA (204 000 g mol^{-1}), compared with those treated with 0.3wt% TBPB and LOL, 275 000 and 285 000 g mol^{-1}, respectively, it showed a distinct higher shear viscosity (not shown) [54]. The 90:10 blend ratio was chosen, while the difference in rheological properties was marginal, between blend ratio of 5:95 to 20:80. Figure 4.24 presents the coating weight as a function of line speed. In other words, the coat thickness is plotted against the drawing (elongation) rate. Because all of the materials were extruded at same screw speed (80 rpm), it is clear that there is a remarkable difference in the output rates between the polymers at lower line speeds. The minor differences between the die height and neck-in values (at lower line speeds) do not explain the output differences. The blends with peroxide-modified PLLA increased the output, which is a consequence from higher viscosity (which is substantiated in the rheological analysis). This is further supported by the observed higher power need, and the increased melt pressures in extrusion (not shown). Another finding in figure 4.24 is that at the highest line speed (200 m s^{-1}) the blend of 0.5wt% BPO afforded an unexpected low coating thickness, while for neat PLLA (3051D), and the 0.3wt% LOL1 and TBPB blends the thickness follows the Power law trend (not shown). It is likely that at a higher line speed (higher elongation rate) the 0.5wt% BPO blend show reduced neck-in (wider coating) which results in a thinner coating. This was actually visually confirmed, for BPO blend, unfortunately the neck-in values were not recorded from these samples. The observed reduced neck-in for the BPO blend and the coating weight reduction at high line speeds is not surprising, considering the BPO blend also shows by far the highest shear viscosity and storage modulus [54]. The PLLA output at maximum line speed (80rpm) was rather low compared to literature values [138,169]. The obvious reason for this was too low output at higher line speeds (above 200 m min^{-1}).
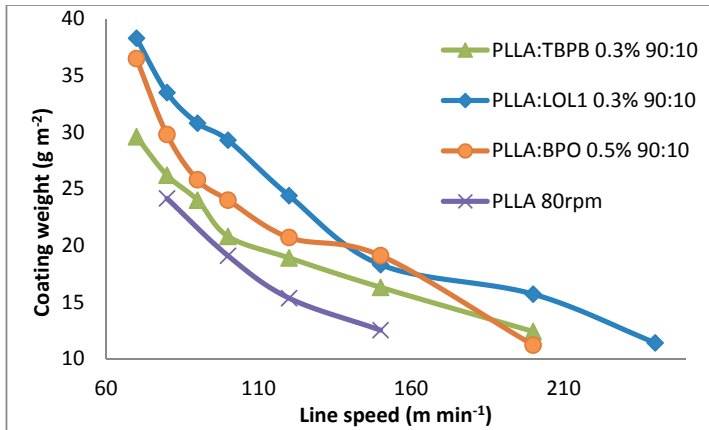
Figure 4.24. Extrusion coating weight vs. line speed.

Figure 4.25 and figure 4.26 show the obtained adhesion of the used polymers. It is useful to discuss the impacts of line speed and coating weight together on the adhesion.
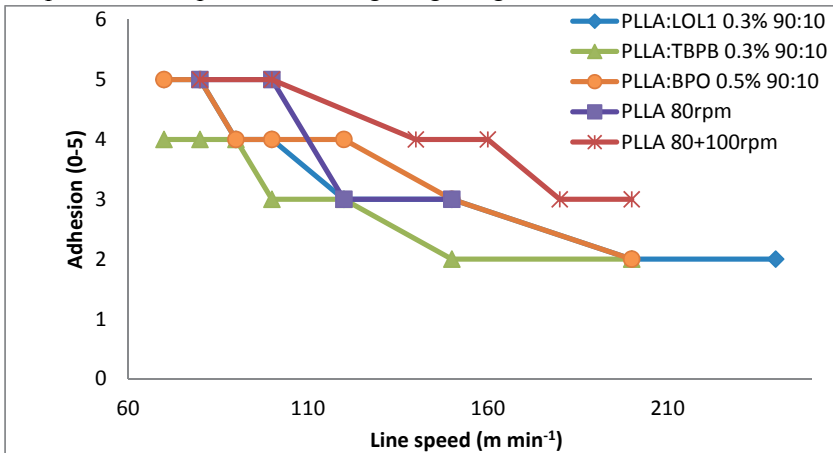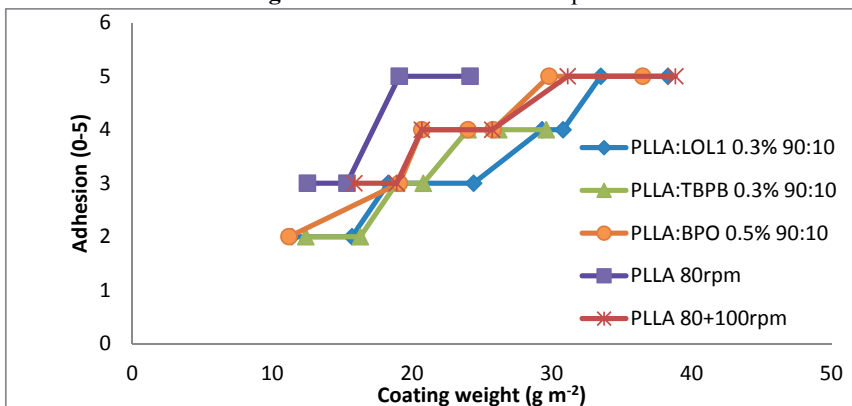

Figure 4.25. Adhesion vs. line speed.

Figure 4.26. Adhesion vs. line speed.

Because PLLA extruded at 80 rpm had a much lower output compared to peroxide blends, the PLLA results of (80+100rpm, A+B extruders) were included into the results to equal outputs vs. peroxide blends. Regarding various line speeds, the thickest PLA samples (80+100rpm) exhibited best adhesion. The thinner PLLA (80rpm) samples showed also good adhesion, but the difference against blends was not as significant. The results are supported by Hartman's findings [138]: in his studies, viscosity of PLLA is substantially increased with line speed due to heat loss, which in turn weakens the adhesion. On the other hand, as adhesion is plotted against thickness (coating weight) the thinner PLLA (80rpm) samples showed the best adhesion performance, and the adhesion results of the higher output PLLA samples fell among the blends. Here, similar thickness of PLLA (80rpm) samples was produced at lower line speed compared to blend samples. Hence, it is obvious that both the thickness and line speed greatly affect the polymer/board adhesion in the PLLA extrusion coating. However, pure PLLA exhibits slightly better adhesion than the blend qualities, probably due to lower viscosity which enables improved penetration into the fiber porosity in paperboard surface. The differences of adhesion results between the blends were negligible.

Figure 4.27. Heat sealability vs. sealing bar temperature (criteria of evaluation in Table 3).

Figure 4.27 indicates that the hot bar sealing results did not show any major difference between pure PLLA and blend samples. Heat sealing of extrusion coated substrates is very case sensitive, due to multiple affecting parameters such as coating, paper or paperboard thickness. Nevertheless the results are well in line with literature values [16,138].
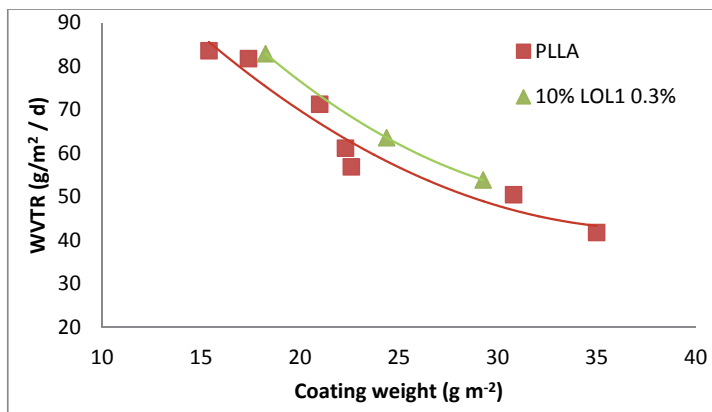
Figure 4.28. Water vapor transmission rates (WVTR, 23°C 50% R.H.) of PLLA and of LOL1 modified PLLA – PLLA blend.

Figure 4.28 shows that water vapor transmission rates were slightly lower with PLLA than peroxide modified PLLA (LOL1 0.3%) samples. This might derive from poorer coating quality, due to the presence of crosslinked fractions and micro gelation in the peroxide treated PLLA, though the difference in WVTR was rather small. The water vapour transmission rate (WVTR) results of pure PLLA are at similar levels as found in literature [169,170].

PEGLA4 and PEGLA2 were tested with PLLA in 15:85; 10:90; 5:95 and 2.5:97.5 ratios, respectively. The amount of PEGLA was chosen to keep the polyethylene glycol content below 5 wt%. The 90% 3051D + 10% PEGLA4 was tested with line speeds up to 120 m min^{-1} (10.8 g m^{-2} minimum coat weight) (figure 4.29). The coating procedure was smooth, but at 120 m min^{-1} edge weaving began, and prohibited higher line speeds. This was a common problem with all tested PEGLA materials. The neck-in appeared to be smaller than with pure 3051D (figure 4.30). The blend with 85% 3051D + 15% PEGLA4 was tested with poorer runability results (line speeds up to 80 m min^{-1}, 19.7 g m^{-2} minimum coat weight) whereas the lower amounts of PEGLA4 maximum speed was at least 200 m min^{-1}. The adhesion level was the same with these concentrations, and comparable to 3051D. WVTR was at the same level, or maybe a little better than of 3051D.

The lower molar mass PEGLA2 afforded poorer runability of the blends. A blend with 5% of PEGLA2 was the highest concentration that could be used for coating (10.4 g m^{-2} minimum coat weight), while 10 % PEGLA2 was tried in extrusion coating, but the encapsulation was detached. A higher amount of vapour (VOC) than normally could be seen in the air gap. Furthermore 2.5 % PEGLA2 was used for coating (9.8 g m^{-2} minimum coat weight) and blends with both 2.5 and 5% PEGLA2 concentrations achieved line speeds up to 120 m min^{-1}. However, the adhesion and output were poorer than with the higher molar mass PEGLA4, and the neck-in was not improved. The adhesion was better on the outsides of the board than in the middle parts, due to clearly higher coat weight. The uneven thickness derives from flow issues at the die.

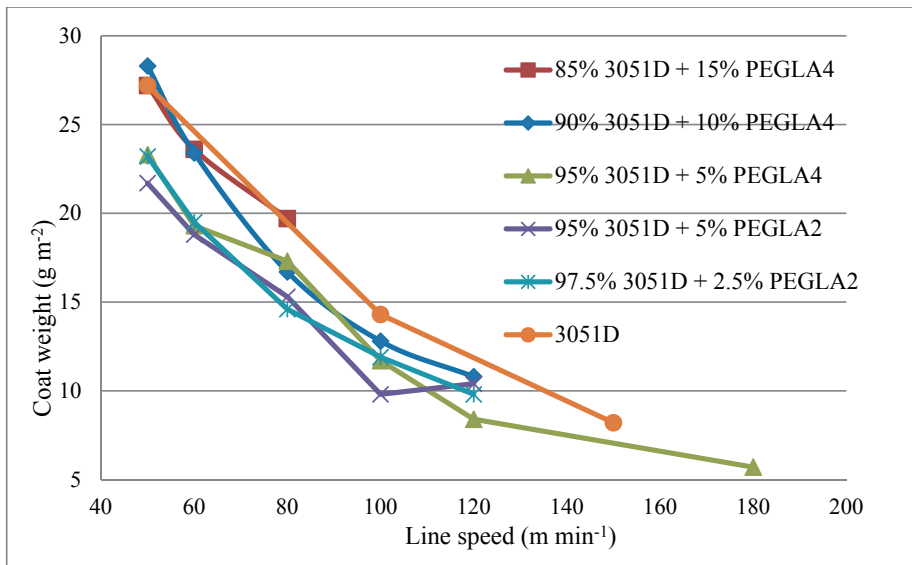**Figure 4.29.** Line speed vs. coat weight of the studied materials in extrusion coating
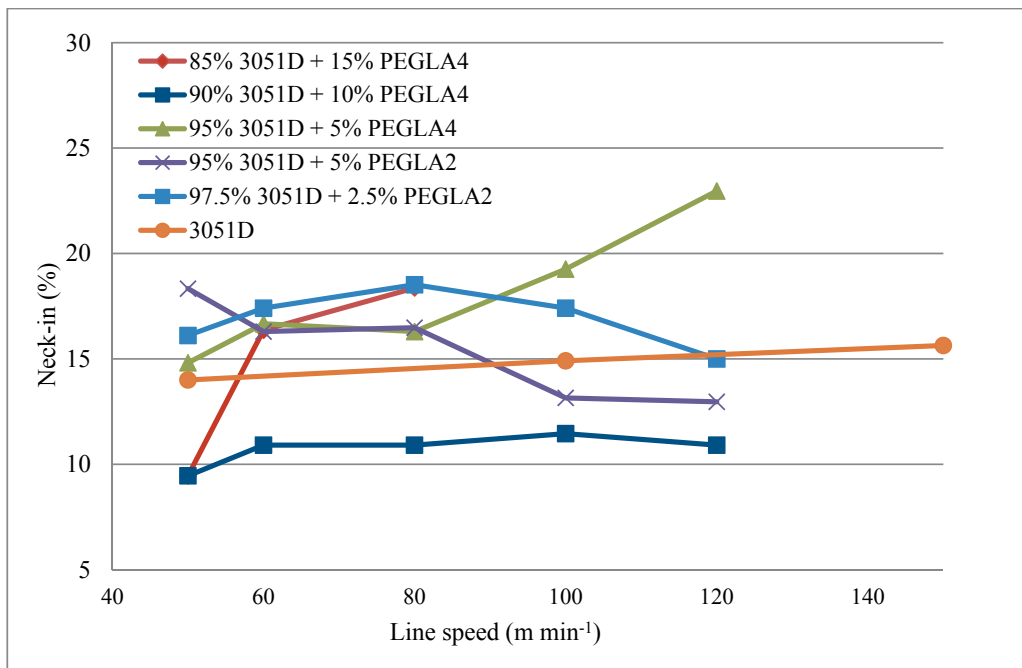

Figure 4.30. Neck-in vs. line speed

The hot air sealability of all blends showed a slight improvement (table 4.8). However, the 2.5% PEGLA2 addition did not visibly affect the heat sealability. Overall, the water vapour transmission rate (WVTR) was not altered by the addition or used amount of PEGLA.

Table 4.8. Analysis results of extrusion coated samples.

Sample	Coat weight g m^{-2} [a]	Adh.	Heat sealing [b]	WVTR 23 °C/50 % g m^{-2} 24 h	WVTR 38 °C/90 % g m^{-2} 24h	WVTR 23°C/50 %[c] /25 g m^{-2}	WVTR 38 °C/90 %[c] /25 g m^{-2}	Neck-in %[d]
3051D +15% PEGLA4	27.2/23.6	3.5	420	67.2	289.7	63.4	273.5	9.5
3051D +10% PEGLA4	25.8/21.3	3	420	52.0	227.8	53.7	235.1	9.5
3051D + 5% PEGLA4	23.3/19.3	3	420	63.0	262.1	58.7	244.3	
3051D + 5% PEGLA 2	21.7	2	420	83.3	356.4	72.3	309.4	14.8
3051D+2.5% PEGLA2	23.2	2	430	62.4	255.7	57.9	237.3	15.4
3051D	25	3-4	430	-	-	58-80	-	14.0

[a] Adhesion, heat sealing/WVTR. [b] Hot air temperature °C against CF 210 board 5/5 seam. [c] WVTR normalized to 25 gm^{-2}. [d] At 50 m min^{-1} line speed. 3051D results from previous tests.

5. CONCLUSIONS

In order to improve the processability of the linear PLLA, 3051D NatureWorks different branched structure, and tri-block copolymers have been produced. Branched PLLA have been produced by reactive extrusion using different peroxides, and by ring opening polymerization using pentaerythritol as the initiator. Triblock co-polymers PLLA-PEG-PLLA have also been synthesized as plasticizers. All materials have been melt-blended using an extruder, or solution mixed with chloroform. Miscibility of the blends has been investigated by studying thermal and rheological properties.

- Reactive extrusion of poly-L-lactide and three different peroxides with rather varying life times at fairly high concentrations (0.1-0.5 wt%) have been examined. A qualitative rheological analysis clearly indicates structural changes in the modified materials. Increasing the peroxide concentration strongly affect the molecular weights, especially with tert-butyl-peroxybenzoate (TBPB), and 2,5-dimethyl-2,5-di-tert-butylperoxy-hexane (LOL1). Also, the rheological studies indicate the formation of branched structures. However, surprisingly BPO, expected to cause the strongest gelation due to shortest life span, showed the lowest gel content (1.2%), as compared with TBPB (7-35%). The combined effect from higher gel content and more branching is likely to cause the unusually high viscosities measured using 0.5 wt% TPBP. In brief, branched and partially cross linked structures were obtained depending on peroxide and peroxide concentration. Preliminary oxygen and water vapor barrier tests were performed with hot pressed films after a second extrusion, and no collapse of barrier properties were observed (results not included). Accordingly, all studied materials remained re-meltable, and were applicable in a forthcoming melt blending step with neat PLLA and further testing for extrusion coating of paperboard.

- Blends of linear PLLA and various peroxide-treated PLLA with a branched structure have been prepared and studied for their thermal and rheological properties. The thermal properties of the blends with 0.3 wt% peroxide-treated PLLA were virtually not changed, as compared with the linear PLLA. All blends remained amorphous during the cooling cycle, and showed similar annealing capacity, heat of melting, and melting temperatures during the second heating. The rheological analysis revealed improved melt elasticity for the blends. Among peroxides, tert-butyl-peroxybenzoate had the strongest impact on the flow behavior of both the modified PLLA and the blends. The effect of blend ratio (5, 15, 30 wt%) on the rheology was marginal, and similar for all studied blends. Blends of 10% peroxide-modified PLLA and 3051D were extrusion coated as a monolayer on paperboard. Generally, all blends were runnable, the LOL1 based blend worked best, and the melt flow was smooth. Compared to PLLA 3051D, it was possible to increase the line speed by 50% with LOL1 blend. The adhesion levels with all peroxides were marginally weaker than for pure 3051D, and also the heat sealing on the heat bar sealer was slightly

worse than for pure 3051D. The water vapor barrier (WVTR) was more or less the same for LOL1 blend and neat PLLA.

- Star-shaped (4-arm) PLLAs, with various total molecular weights were synthesized using pentaerythritol. The sPLLAs were further blended with commercial PLLA by solvent-mixing. Star-shaped PLLA showed higher thermal stability, and the initial degradation temperature of linear PLLA was increased by blending with sPLLA, which proves that blending improved the thermal stability of linear PLLA 3051D. All blends appear to have some level of compatibility, since only one T_g have been observed. The interface between two polymers plays an important role in the viscoelastic response of molten sPLLA/ linear PLLA blends. It could be concluded that, miscibility, phase behavior, and crystallization of the blends were influenced significantly by amounts and type of the added sPLLA, i.e. as we postulate, sPLLA can act as a nucleating agent due to its branched structure. Blending of 3051D with 5 and 10 % of S5 was tested on an extrusion coating pilot line. Star-shaped polymer seems to enhance heat sealability, but did not reduce neck-in or improve adhesion. Water vapor transmission rate (WVTR) was similar to pure 3051D, but in the lower concentration, WVTR was increased.

- PLLA–PEG–PLLA triblock copolymers (PEGLA), with various total molecular weights were synthesized using PEG_{6000} as initiator and further blended with commercial PLLA (3051D Nature Works) by solvent-mixing. All blends appear have some level of compatibility, since only one T_g have been observed. However, rheological data suggest a low level of miscibility and immiscibility in all blend compositions. Highest molar mass PEGLA had good extrusion coating runability, and lower neck-in but lower molar mass ones, and star shaped PLA had too low viscosity. PEGLA improved heat sealability. WVTR and adhesion remained on the same level with 3051D with all samples. PEGLA blends had about the same hot air heat sealability as 3051D.

6. RECOMMENDATIONS AND SUGGESTIONS FOR FUTURE WORK

The following recommendations for future work are proposed:

- ✓ Only one grade of PLA (3051D) was investigated in this work. However, other available grades of PLA could be examined (especially higher viscosity grades) to determine the effects of the different grades on the rheological characteristics and properties of the films.

- ✓ Study of different peroxides with higher decomposition temperatures to produce a more homogenous product during reactive extrusion.

- ✓ Apply appropriate impregnation of the peroxide into the polymer pellets before reactive extrusion for more homogenous materials.

- ✓ Examine PEG core- molecules with higher molecular weights.

- ✓ Study the degradation behavior of these films/coated paperboards in various environments. This could include experiments of monitoring the crystallinity, and weight loss of the materials during the degradation trials.

REFERENCES

[1] S. Pilla, Processing and Characterization of Novel Biobased and Biodegradable Materials, ProQuest, 2009.

[2] A. Soedergaard, M. Niemi, J.-F. Selin, J.H. Naesman, Changes in peroxide melt-modified poly (L-lactide), Ind. Eng. Chem. Res. 34 (1995) 1203–1207.

[3] J.-W. Rhim, P.K. Ng, Natural biopolymer-based nanocomposite films for packaging applications, Crit. Rev. Food Sci. Nutr. 47 (2007) 411–433.

[4] K. Marsh, B. Bugusu, Food packaging—roles, materials, and environmental issues, J. Food Sci. 72 (2007) R39–R55.

[5] C.S. Cleveland, T.S. Reighard, J.I. Marchman, Biodegradable paper-based laminate with oxygen and moisture barrier properties and method for making biodegradable paper-based laminate, US8637126 B2, 2014.

[6] D.F. Massouda, Multiple layer paperboard laminate, US4950510 A, 1990.

[7] V. Siracusa, P. Rocculi, S. Romani, M.D. Rosa, Biodegradable polymers for food packaging: a review, Trends Food Sci. Technol. 19 (2008) 634–643.

[8] Y.-W. Mai, Z.-Z. Yu, Polymer Nanocomposites, Woodhead Publishing, 2006.

[9] R.A. Gross, B. Kalra, Biodegradable Polymers for the Environment, Science. 297 (2002) 803–807.

[10] M. Gill, Bioplastic: A Better Alternative to Plastics, Int. J. Res. Appl. Nat. Soc. Sci. 2 (2014) 115–120.

[11] Y. Ikada, H. Tsuji, Biodegradable polyesters for medical and ecological applications, Macromol. Rapid Commun. 21 (2000) 117–132.

[12] S. Sinha Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, Prog. Polym. Sci. 28 (2003) 1539–1641.

[13] L. Avérous, E. Pollet, Environmental Silicate Nano-Biocomposites, London, 2012.

[14] R.P. Babu, K. O'Connor, R. Seeram, Current progress on bio-based polymers and their future trends, Prog Biomater. 2 (2013) 1–16.

[15] L.Z. Wang, L. Liu, J. Holmes, J.F. Kerry, J.P. Kerry, Assessment of film-forming potential and properties of protein and polysaccharide-based biopolymer films, Int. J. Food Sci. Technol. 42 (2007) 1128–1138.

[16] K. Lahtinen, S. Kotkamo, T. Koskinen, S. Auvinen, J. Kuusipalo, Characterization for water vapour barrier and heat sealability properties of heat-treated paperboard/ polylactide structure, Packag. Technol. Sci. 22 (2009) 451–460.

[17] R.E. Drumright, P.R. Gruber, D.E. Henton, Polylactic acid technology, Adv. Mater. 12 (2000) 1841–1846.

[18] L.-T. Lim, R. Auras, M. Rubino, Processing technologies for poly (lactic acid), Prog. Polym. Sci. 33 (2008) 820–852.

[19] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, Macromol. Biosci. 4 (2004) 835–864.

[20] T. Komatsuka, A. Kusakabe, K. Nagai, Characterization and gas transport properties of poly (lactic acid) blend membranes, Desalination. 234 (2008) 212–220.

[21] H. Tsuji, R. Okino, H. Daimon, K. Fujie, Water vapor permeability of poly (lactide) s: effects of molecular characteristics and crystallinity, J. Appl. Polym. Sci. 99 (2006) 2245–2252.

[22] V. Stannett, M. Szwarc, R.L. Bhargava, J.A. Meyer, A.W. Myers, C.E. Rogers, Permeability of Plastic Films and Coated Paper to Gases and Vapors, Tappi Monogr. Ser. No 23. (1962) 18.

[23] J.-W. Rhim, J.-H. Lee, S.-I. Hong, Increase in water resistance of paperboard by coating with poly (lactide), Packag. Technol. Sci. 20 (2007) 393–402.

[24] J. Kuusipalo, PHB/V in extrusion coating of paper and paperboard, Tampere University of Technology, 1997.

[25] Y. Cheng, S. Deng, P. Chen, R. Ruan, Polylactic acid (PLA) synthesis and modifications: a review, Front. Chem. China. 4 (2009) 259–264.

[26] D. Cava, E. Giménez, R. Gavara, J.M. Lagaron, Comparative performance and barrier properties of biodegradable thermoplastics and nanobiocomposites versus PET for food packaging applications, J. Plast. Film Sheeting. 22 (2006) 265–274.

[27] M. Jamshidian, E.A. Tehrany, M. Imran, M. Jacquot, S. Desobry, Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies, Compr. Rev. Food Sci. Food Saf. 9 (2010) 552–571.

[28] S.M. Davachi, B. Kaffashi, Poly Lactic Acid in Medicine, Polym.-Plast. Technol. Eng. 54 (2015) 944–967.

[29] B. Gupta, N. Revagade, J. Hilborn, Poly(lactic acid) fiber: An overview, Prog. Polym. Sci. 32 (2007) 455–482.

[30] S. Varadarajan, D.J. Miller, Catalytic Upgrading of Fermentation-Derived Organic Acids, Biotechnol. Prog. 15 (1999) 845–854.

[31] R.P. John, G.S. Anisha, K.M. Nampoothiri, Ashok Pandey, Direct lactic acid fermentation: focus on simultaneous saccharification and lactic acid production., Biotechnol. Adv. 27 (2009) 145–152.

[32] M.G. Adsul, A.J. Varma, D.V. Gokhale, Lactic acid production from waste sugarcane bagasse derived cellulose, Green Chem. 9 (2007) 58–62.

[33] S. Sinha Ray, Polylactide-based bionano-composites: A promising class of hybrid materials, Acc. Chem. Res. 45 (2012) 1710–1720.

[34] K. Seavey, Y.A. Liu, Step-Growth Polymerization Process Modeling and Product Design, John Wiley & Sons, 2009.

[35] L.G. Griffith, Polymeric biomaterials, Acta Mater. 48 (2000) 263–277.

[36] K.J. Lampe, R.M. Namba, T.R. Silverman, K.B. Bjugstad, M.J. Mahoney, Impact of lactic acid on cell proliferation and free radical-induced cell death in monolayer cultures of neural precursor cells, Biotechnol. Bioeng. 103 (2009) 1214–1223.

[37] T.M. Ovitt, G.W. Coates, Stereochemistry of lactide polymerization with chiral catalysts: new opportunities for stereocontrol using polymer exchange mechanisms., J. Am. Chem. Soc. 124 (2002) 1316–1326.

[38] J.-W. Rhim, P.K. Ng, Natural biopolymer-based nanocomposite films for packaging applications, Crit. Rev. Food Sci. Nutr. 47 (2007) 411–433.

[39] N.F. Whiteman, M. Hartmann, Polylactide, A New Thermoplastic For Extrusion Coating, in: Polym. LAMINATIONS Coat. Conf., 2000: pp. 467–474.

[40] K. Lahtinen, P. Maydannik, P. Johansson, T. Kääriäinen, D.C. Cameron, J. Kuusipalo, Utilisation of continuous atomic layer deposition process for barrier enhancement of extrusion-coated paper, Surf. Coat. Technol. 205 (2011) 3916–3922.

[41] C.M. Ryan, M.H. Hartmann, J.F. Nangeroni, Branching of poly (lactic acid) to increase melt strength for extrusion coating, in: Polym. Laminations Coat. Conf., Tappi Press, 1997: pp. 139–144.

[42] P. Degee, P. Dubois, R. Jerome, S. Jacobsen, H.-G. Fritz, Synthesis of Degradable Polymers, Ring-opening Polymerization and Stepwise Polymerization-24. New catalysis for fast bulk ring-opening polymerization of lactide monomers, in: Macromol. Symp., Basel; Oxford, CT: Huthig & Wepf, 1994-, 1999: pp. 289–302.

[43] P. Degée, P. Dubois, S. Jacobsen, H.-G. Fritz, R. Jérôme, Beneficial effect of triphenylphosphine on the bulk polymerization of L, L-lactide promoted by 2-ethylhexanoic acid tin (II) salt, J. Polym. Sci. Part Polym. Chem. 37 (1999) 2413–2420.

[44] S. Jacobsen, H.G. Fritz, P. Degée, P. Dubois, R. Jérôme, Single-step reactive extrusion of PLLA in a corotating twin-screw extruder promoted by 2-ethylhexanoic acid tin (II) salt and triphenylphosphine, Polymer. 41 (2000) 3395–3403.

[45] S.M. Davachi, B. Kaffashi, Preparation and Characterization of Poly L-Lactide/Triclosan Nanoparticles for Specific Antibacterial and Medical Applications, Int. J. Polym. Mater. 64 (2015) 497 – 508.

[46] R. Fayt, P. Hadjiandreou, P. Teyssie, Molecular design of multicomponent polymer systems. VII. Emulsifying effect of poly (ethylene–b–styrene) copolymer in high-density polyethylene/ polystyrene blends, J. Polym. Sci. Polym. Chem. Ed. 23 (1985) 337–342.

[47] D. Carlson, P. Dubois, L. Nie, R. Narayan, Free radical branching of polylactide by reactive extrusion, Polym. Eng. Sci. 38 (1998) 311–321.

[48] M. Takamura, T. Nakamura, T. Takahashi, K. Koyama, Effect of type of peroxide on cross-linking of poly (l-lactide), Polym. Degrad. Stab. 93 (2008) 1909–1916.

[49] J. Liu, L. Lou, W. Yu, R. Liao, R. Li, C. Zhou, Long chain branching polylactide: Structures and properties, Polymer. 51 (2010) 5186–5197.

[50] T. Ouchi, S. Ichimura, Y. Ohya, Synthesis of branched poly (lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film, Polymer. 47 (2006) 429–434.

[51] H. Korhonen, A. Helminen, J.V. Seppälä, Synthesis of polylactides in the presence of co-

initiators with different numbers of hydroxyl groups, Polymer. 42 (2001) 7541–7549.

[52] A. Södergård, J.H. Näsman, Stabilization of poly (L-lactide) in the melt, Polym. Degrad. Stab. 46 (1994) 25–30.

[53] R.M. Rasal, A.V. Janorkar, D.E. Hirt, Poly(lactic acid) modifications, Prog. Polym. Sci. 35 (2010) 338–356.

[54] M.B. Khajeheian, A. Rosling, Rheological and Thermal Properties of Peroxide-Modified Poly (l-lactide) s for Blending Purposes, J. Polym. Environ. (n.d.) 1–10.

[55] W. Elhrari, Synthesis and characterization of comb-polymers with controlled structure, Stellenbosch: University of Stellenbosch, 2006.

[56] A.V. Machado, J.A. Covas, M. Van Duin, Monitoring polyolefin modification along the axis of a twin screw extruder. I. Effect of peroxide concentration, J. Appl. Polym. Sci. 81 (2001) 58–68.

[57] C.M. Ryan, M.H. Hartmann, J.F. Nangeroni, Branching of poly (lactic acid) to increase melt strength for extrusion coating, in: Tappi Press, 1997: pp. 139–144.

[58] A. Södergård, J.-F. Selin, M. Pantke, Environmental degradation of peroxide modified poly (L-lactide), Int. Biodeterior. Biodegrad. 38 (1996) 101–106.

[59] H.J. Lehermeier, J.R. Dorgan, Melt rheology of poly (lactic acid): Consequences of blending chain architectures, Polym. Eng. Sci. 41 (2001) 2172–2184.

[60] J. Burlet, M.-C. Heuzey, C. Dubois, P. Wood-Adams, J. Brisson, Thermal stabilization of high molecular weight l-polylactide, Ecole Polytech. Montr. Concordia Univ. Univ. Laval ANTEC. (2005) 1133–1137.

[61] J.R. Dorgan, H. Lehermeier, M. Mang, Thermal and rheological properties of commercial-grade poly (lactic acid) s, J. Polym. Environ. 8 (2000) 1–9.

[62] N. Ogata, H. Sasayama, K. Nakane, T. Ogihara, Preparation of poly (L-lactide) film having high elastic recovery, J. Appl. Polym. Sci. 89 (2003) 474–480.

[63] M.G. Lachtermacher, A. Rudin, Reactive processing of LLDPEs in counterrotating nonintermeshing twin-screw extruder. III. Methods of peroxide addition, J. Appl. Polym. Sci. 59 (1996) 1775–1785.

[64] M.G. Lachtermacher, A. Rudin, Reactive processing of LLDPEs with peroxides in counter-rotating nonintermeshing twin-screw extruder. IV. Effects of molecular structure of LLDPEs, J. Appl. Polym. Sci. 59 (1996) 1213–1221.

[65] B.K. Kim, C.H. Choi, Reactive extrusion of polyolefin ternary blends, J. Appl. Polym. Sci. 60 (1996) 2199–2206.

[66] D.V. Plackett, V.K. Holm, P. Johansen, S. Ndoni, P.V. Nielsen, T. Sipilainen-Malm, et al., Characterization of l-polylactide and l-polylactide–polycaprolactone co-polymer films for use in cheese-packaging applications, Packag. Technol. Sci. 19 (2006) 1–24.

[67] G.B. Kang, M.H. Kim, Y. Son, O.O. Park, Extrusion coating performances of iPP/LDPE blends, J. Appl. Polym. Sci. 111 (2009) 3121–3127.

[68] N. Toft, M. Rigdahl, Extrusion coating with metallocene-catalysed polyethylenes, Int. Polym. Process. 17 (2002) 244–253.

[69] M.G. Lachtermacher, A. Rudin, Reactive processing of LLDPEs in corotating intermeshing twin-screw extruder. I. Effect of peroxide treatment on polymer molecular structure, J. Appl. Polym. Sci. 58 (1995) 2077–2094.

[70] K.M. Dean, E. Petinakis, S. Meure, L. Yu, A. Chryss, Melt strength and rheological properties of biodegradable poly (lactic aacid) modified via alkyl radical-based reactive extrusion processes, J. Polym. Environ. 20 (2012) 741–747.

[71] K. Sungsanit, N. Kao, S.N. Bhattacharya, S. Pivsaart, Physical and rheological properties of plasticized linear and branched PLA, Korea-Aust. Rheol. J. 22 (2010) 187–195.

[72] J.R. Dorgan, H. Lehermeier, M. Mang, Thermal and rheological properties of commercial-grade poly (lactic acid) s, J. Polym. Environ. 8 (2000) 1–9.

[73] J. You, L. Lou, W. Yu, C. Zhou, The preparation and crystallization of long chain branching polylactide made by melt radicals reaction, J. Appl. Polym. Sci. 129 (2013) 1959–1970.

[74] Y. Wang, L. Yang, Y. Niu, Z. Wang, J. Zhang, F. Yu, et al., Rheological and topological characterizations of electron beam irradiation prepared long-chain branched polylactic acid, J. Appl. Polym. Sci. 122 (2011) 1857–1865.

[75] L. Wang, X. Jing, H. Cheng, X. Hu, L. Yang, Y. Huang, Rheology and crystallization of long-chain branched poly (l-lactide) s with controlled

branch length, Ind. Eng. Chem. Res. 51 (2012) 10731–10741.

[76] M.G. McKee, S. Unal, G.L. Wilkes, T.E. Long, Branched polyesters: recent advances in synthesis and performance, Prog. Polym. Sci. 30 (2005) 507–539.

[77] D.J. Groves, T.C. McLeish, R.K. Chohan, P.D. Coates, Predicting the rheology of linear with branched polyethylene blends, Rheol. Acta. 35 (1996) 481–491.

[78] J. Kim, D.H. Kim, Y. Son, Rheological properties of long chain branched polyethylene melts at high shear rate, Polymer. 50 (2009) 4998–5001.

[79] S.H. Tabatabaei, P.J. Carreau, A. Ajji, Rheological and thermal properties of blends of a long-chain branched polypropylene and different linear polypropylenes, Chem. Eng. Sci. 64 (2009) 4719–4731.

[80] T.J. McCallum, M. Kontopoulou, C.B. Park, E.B. Muliawan, S.G. Hatzikiriakos, The rheological and physical properties of linear and branched polypropylene blends, Polym. Eng. Sci. 47 (2007) 1133–1140.

[81] L. Wang, W. Ma, R.A. Gross, S.P. McCarthy, Reactive compatibilization of biodegradable blends of poly (lactic acid) and poly (ε-caprolactone), Polym. Degrad. Stab. 59 (1998) 161–168.

[82] V.D. Ramos, H.M. da Costa, A.O. Pereira, M.C. Rocha, A. de S Gomes, Study of low concentrations of dicumyl peroxide on the molecular structure modification of LLDPE by reactive extrusion, Polym. Test. 23 (2004) 949–955.

[83] D. Carlson, L. Nie, R. Narayan, P. Dubois, Maleation of polylactide (PLA) by reactive extrusion, J. Appl. Polym. Sci. 72 (1999) 477–485.

[84] N. Hadjichristidis, M. Pitsikalis, H. Iatrou, P. Driva, G. Sakellariou, M. Chatzichristidi, 6.03 - Polymers with Star-Related Structures: Synthesis, Properties, and Applications, in: K.M. Möller (Ed.), Polym. Sci. Compr. Ref., Elsevier, Amsterdam, 2012: pp. 29–111.

[85] A. Schindler, Y.M. Hibionada, C.G. Pitt, Aliphatic polyesters. III. Molecular weight and molecular weight distribution in alcohol-initiated polymerizations of ε-caprolactone, J. Polym. Sci. Polym. Chem. Ed. 20 (1982) 319–326.

[86] S.H. Kim, Y.-K. Han, Y.H. Kim, S.I. Hong, Multifunctional initiation of lactide polymerization by stannous octoate/pentaerythritol, Makromol. Chem. 193 (1992) 1623–1631.

[87] S.H. Kim, Y.-K. Han, K.-D. Ahn, Y.H. Kim, T. Chang, Preparation of star-shaped polylactide with pentaerythritol and stannous octoate, Makromol. Chem. 194 (1993) 3229–3236.

[88] S.H. Kim, Y.H. Kim, Direct condensation polymerization of lactic acid, in: Wiley Online Library, 1999: pp. 277–287.

[89] Y.K. Choi, Y.H. Bae, S.W. Kim, Star-shaped poly (ether-ester) block copolymers: synthesis, characterization, and their physical properties, Macromolecules. 31 (1998) 8766–8774.

[90] J.R. Dorgan, J.S. Williams, D.N. Lewis, Melt rheology of poly (lactic acid): Entanglement and chain architecture effects, J. Rheol. 1978-Present. 43 (1999) 1141–1155.

[91] K. Odelius, A.-C. Albertsson, Precision synthesis of microstructures in star-shaped copolymers of ε-caprolactone, L-lactide, and 1, 5-dioxepan-2-one, J. Polym. Sci. Part Polym. Chem. 46 (2008) 1249–1264.

[92] M. Stolt, M. Viljanmaa, A. Södergård, P. Törmälä, Blends of poly (ε-caprolactone-b-lactic acid) and poly (lactic acid) for hot-melt applications, J. Appl. Polym. Sci. 91 (2004) 196–204.

[93] A.S. Karikari, W.F. Edwards, J.B. Mecham, T.E. Long, Influence of peripheral hydrogen bonding on the mechanical properties of photo-cross-linked star-shaped poly (D, L-lactide) networks, Biomacromolecules. 6 (2005) 2866–2874.

[94] S.H. Kim, Y.-K. Han, K.-D. Ahn, Y.H. Kim, T. Chang, Preparation of star-shaped polylactide with pentaerythritol and stannous octoate, Makromol. Chem. 194 (1993) 3229–3236.

[95] L.E. Salaam, D. Dean, T.L. Bray, In vitro degradation behavior of biodegradable 4-star micelles, Polymer. 47 (2006) 310–318.

[96] M. Adeli, Z. Zarnegar, R. Kabiri, Amphiphilic star copolymers containing cyclodextrin core and their application as nanocarrier, Eur. Polym. J. 44 (2008) 1921–1930.

[97] L.M. Pitet, S.B. Hait, T.J. Lanyk, D.M. Knauss, Linear and branched architectures from the polymerization of lactide with glycidol, Macromolecules. 40 (2007) 2327–2334.

[98] Q. Cai, Y. Zhao, J. Bei, F. Xi, S. Wang, Synthesis and properties of star-shaped polylactide attached to poly (amidoamine) dendrimer, Biomacromolecules. 4 (2003) 828–834.

[99] J.R. Dorgan, J. Janzen, D.M. Knauss, S.B. Hait, B.R. Limoges, M.H. Hutchinson, Fundamental solution and single-chain properties of polylactides, J. Polym. Sci. Part B Polym. Phys. 43 (2005) 3100–3111.

[100] FDA, Food Additives & Ingredients - Food Additive Status List, (n.d.).

[101] H. Younes, D. Cohn, Phase separation in poly(ethylene glycol)/poly(lactic acid) blends, Eur. Polym. J. 24 (1988) 765–773.

[102] Y. Kimura, Y. Matsuzaki, H. Yamane, T. Kitao, Preparation of block copoly (ester-ether) comprising poly (l-lactide) and poly (oxypropylene) and degradation of its fibre *in vitro* and *in vivo*, Polymer. 30 (1989) 1342–1349.

[103] T. Yamaoka, Y. Takahashi, T. Ohta, M. Miyamoto, A. Murakami, Y. Kimura, Synthesis and properties of multiblock copolymers consisting of poly (L-lactic acid) and poly (oxypropylene-co-oxyethylene) prepared by direct polycondensation, J. Polym. Sci. Part Polym. Chem. 37 (1999) 1513–1521.

[104] D. Cohn, H. Younes, G. Marom, Amorphous and crystalline morphologies in glycolic acid and lactic acid polymers, Polymer. 28 (1987) 2018–2022.

[105] H. Younes, D. Cohn, Morphological study of biodegradable PEO/PLA block copolymers, J. Biomed. Mater. Res. 21 (1987) 1301–1316.

[106] X.M. Deng, C.D. Xiong, L.M. Cheng, R.P. Xu, Synthesis and characterization of block copolymers from D, L-lactide and poly (ethylene glycol) with stannous chloride, J. Polym. Sci. Part C Polym. Lett. 28 (1990) 411–416.

[107] Z. Jedliński, P. Kurcok, W. Walach, H. Janeczek, I. Radecka, Polymerization of lactones, 17. Synthesis of ethylene glycol-L-lactide block copolymers, Makromol. Chem. 194 (1993) 1681–1689.

[108] K.J. Zhu, L. Xiangzhou, Y. Shilin, Preparation, characterization, and properties of polylactide (PLA)–poly (ethylene glycol)(PEG) copolymers: a potential drug carrier, J. Appl. Polym. Sci. 39 (1990) 1–9.

[109] H.R. Kricheldorf, C. Boettcher, Polylactones 27. Anionic polymerization of L-lactide. Variation of endgroups and synthesis of block copolymers with poly (ethylene oxide), in: Makromol. Chem. Macromol. Symp., Wiley Online Library, 1993: pp. 47–64.

[110] X. Deng, Y. Liu, M. Yuan, X. Li, L. Liu, W.X. Jia, Preparation and characterization of poly-DL-lactide–poly (ethylene glycol) microspheres containing λDNA, J. Appl. Polym. Sci. 86 (2002) 2557–2566.

[111] H.R. Kricheldorf, J. Meier-Haack, Polylactones, 22 ABA triblock copolymers of L-lactide and poly (ethylene glycol), Makromol. Chem. 194 (1993) 715–725.

[112] J. Mohammadi-Rovshandeh, S.M.F. Farnia, M.N. Sarbolouki, Synthesis and characterization of novel ABA triblock copolymers from l-lactide, glycolide, and PEG, J. Appl. Polym. Sci. 74 (1999) 2004–2009.

[113] J.M. Onyari, S.J. Huang, Triblock copolymers of lactide with poly (ethylene glycol) and influence of stereochemical composition, in: Macromol. Symp., Wiley Online Library, 2003: pp. 143–158.

[114] H.R. Kricheldorf, C. Boettcher, Polylactones, 24. Polymerizations of racemic and meso-D, L-lactide with Al O initiators. Analyses of stereosequences, Makromol. Chem. 194 (1993) 1653–1664.

[115] S. Li, S. Anjard, I. Rashkov, M. Vert, Hydrolytic degradation of PLA/PEO/PLA triblock copolymers prepared in the presence of Zn metal or CaH_2, Polymer. 39 (1998) 5421–5430.

[116] S. Li, M. Vert, Synthesis, characterization, and stereocomplex-induced gelation of block copolymers prepared by ring-opening polymerization of L (D)-lactide in the presence of poly (ethylene glycol), Macromolecules. 36 (2003) 8008–8014.

[117] P. Cerrai, M. Tricoli, Block copolymers from L-lactide and poly (ethylene glycol) through a non-catalyzed route, Makromol. Chem. Rapid Commun. 14 (1993) 529–538.

[118] B. Buntner, M. Nowak, J. Kasperczyk, M. Ryba, P. Grieb, M. Walski, et al., The application of microspheres from the copolymers of lactide and ϵ-caprolactone to the controlled release of steroids, J. Controlled Release. 56 (1998) 159–167.

[119] N.C. Kalarickal, S. Rimmer, P. Sarker, J.-C. Leroux, Thiol-Functionalized Poly(ethylene glycol)-b-polyesters: Synthesis and Characterization, Macromolecules. 40 (2007) 1874–1880.

[120] Z. Kulinski, E. Piorkowska, Crystallization, structure and properties of plasticized poly (L-lactide), Polymer. 46 (2005) 10290–10300.

[121] M. Baiardo, G. Frisoni, M. Scandola, M. Rimelen, D. Lips, K. Ruffieux, et al., Thermal and mechanical properties of plasticized poly (L-lactic acid), J. Appl. Polym. Sci. 90 (2003) 1731–1738.

[122] O. Martin, L. Averous, Poly (lactic acid): plasticization and properties of biodegradable multiphase systems, Polymer. 42 (2001) 6209–6219.

[123] Q. Cai, J. Bei, S. Wang, In vitro study on the drug release behavior from Polylactide-based blend matrices, Polym. Adv. Technol. 13 (2002) 534–540.

[124] W. Jiang, S.P. Schwendeman, Stabilization and controlled release of bovine serum albumin encapsulated in poly (D, L-lactide) and poly (ethylene glycol) microsphere blends, Pharm. Res. 18 (2001) 878–885.

[125] Y. Hu, M. Rogunova, V. Topolkaraev, A. Hiltner, E. Baer, Aging of poly (lactide)/poly (ethylene glycol) blends. Part 1. Poly (lactide) with low stereoregularity, Polymer. 44 (2003) 5701–5710.

[126] Y. Hu, Y.S. Hu, V. Topolkaraev, A. Hiltner, E. Baer, Aging of poly (lactide)/poly (ethylene glycol) blends. Part 2. Poly (lactide) with high stereoregularity, Polymer. 44 (2003) 5711–5720.

[127] M. Sheth, R.A. Kumar, V. Davé, R.A. Gross, S.P. McCarthy, Biodegradable polymer blends of poly (lactic acid) and poly (ethylene glycol), J. Appl. Polym. Sci. 66 (1997) 1495–1505.

[128] G.L. Robertson, Food packaging: principles and practice, CRC press, London, 2012.

[129] J. Lange, Y. Wyser, Recent innovations in barrier technologies for plastic packaging—a review, Packag. Technol. Sci. 16 (2003) 149–158.

[130] I. Vroman, L. Tighzert, Biodegradable polymers, Materials. 2 (2009) 307–344.

[131] FDA, CFR - Code of Federal Regulations Title 21, (n.d.).

[132] FDA, MHG Biopolymers - FDA Approved for Food Contact, MHG Meredian - 100 Biodegrad. Bioplastics. (n.d.).

[133] B.H. Gregory, Extrusion Coating: A Process Manual, Trafford Publishing, 2008.

[134] K.L. Yam, The Wiley Encyclopedia of Packaging Technology, John Wiley & Sons, 2010.

[135] J. Dooley, H. Tung, Coextrusion, encyclopedia of polymer science and technology, New York: John Wiley & Sons, Inc, 2002.

[136] J. Fowle, M.J. Kirwan, Paper-based flexible packaging, Handb. Pap. Paperboard Packag. Technol. Second Ed. (2013) 91–123.

[137] E.S. Kim, B.C. Kim, S.H. Kim, Structural effect of linear and star-shaped poly (L-lactic acid) on physical properties, J. Polym. Sci. Part B Polym. Phys. 42 (2004) 939–946.

[138] M. Hartmann, N. Whiteman, Polylactide, a New Thermoplastic for Extrusion Coating (1024), in: Tech. Pap. Annu. Tech. Conf.-Soc. Plast. Eng. Inc., 2001: pp. 2–6.

[139] M. Takamura, T. Nakamura, T. Takahashi, K. Koyama, Effect of type of peroxide on cross-linking of poly (l-lactide), Polym. Degrad. Stab. 93 (2008) 1909–1916.

[140] M. Takamura, M. Sugimoto, S. Kawaguchi, T. Takahashi, K. Koyama, Influence of extrusion temperature on molecular architecture and crystallization behavior of peroxide-induced slightly crosslinked poly (L-lactide) by reactive extrusion, J. Appl. Polym. Sci. 123 (2012) 1468–1478.

[141] M. Takamura, T. Nakamura, S. Kawaguchi, T. Takahashi, K. Koyama, Molecular characterization and crystallization behavior of peroxide-induced slightly crosslinked poly (L-lactide) during extrusion, Polym. J. 42 (2010) 600–608.

[142] T. Ouchi, S. Ichimura, Y. Ohya, Synthesis of branched poly (lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film, Polymer. 47 (2006) 429–434.

[143] F. Zulli, L. Andreozzi, E. Passaglia, S. Augier, M. Giordano, Rheology of long-chain branched polypropylene copolymers, J. Appl. Polym. Sci. 127 (2013) 1423–1432.

[144] D. Wu, L. Wu, M. Zhang, Y. Zhao, Viscoelasticity and thermal stability of polylactide composites with various

functionalized carbon nanotubes, Polym. Degrad. Stab. 93 (2008) 1577–1584.

[145] D. Schulze, T. Roths, C. Friedrich, Classification of model topologies using the δ versus G* plot, Rheol. Acta. 44 (2005) 485–494.

[146] M. Niaounakis, Biopolymers: Processing and Products, William Andrew, 2014.

[147] M. Mihai, M.A. Huneault, B.D. Favis, Rheology and extrusion foaming of chain-branched poly (lactic acid), Polym. Eng. Sci. 50 (2010) 629–642.

[148] C. Liu, J. Wang, J. He, Rheological and thermal properties of m-LLDPE blends with m-HDPE and LDPE, Polymer. 43 (2002) 3811–3818.

[149] D. Graebling, R. Muller, J.F. Palierne, Linear viscoelastic behavior of some incompatible polymer blends in the melt. Interpretation of data with a model of emulsion of viscoelastic liquids, Macromolecules. 26 (1993) 320–329.

[150] R. Li, W. Yu, C. Zhou, Phase behavior and its viscoelastic responses of poly (methyl methacrylate) and poly (styrene-co-maleic anhydride) blend systems, Polym. Bull. 56 (2006) 455–466.

[151] C. Weis, J. Leukel, K. Borkenstein, D. Maier, W. Gronski, C. Friedrich, et al., Morphological and rheological detection of the phase inversion of PMMA/PS polymer blends, Polym. Bull. 40 (1998) 235–241.

[152] R. Li, W. Yu, C. Zhou, Rheological Characterization of Droplet-Matrix versus Co-Continuous Morphology, J. Macromol. Sci. Part B. 45 (2006) 889–898.

[153] W. Li, A.B. Spoelstra, J.G.P. Goossens, Morphology and rheological properties of silica-filled poly(carbonate)/poly(methyl methacrylate) blends, Polym. Eng. Sci. (2014) Early View 10.1002/pen.24036.

[154] J.K. Lee, C.D. Han, Evolution of polymer blend morphology during compounding in a twin-screw extruder, Polymer. 41 (2000) 1799–1815.

[155] L.-Q. Xu, H.-X. Huang, Z.-K. Chen, X.-J. Wu, Effects of emulsion parameters on relaxation behaviors for immiscible polymer blends, J. Appl. Polym. Sci. 131 (2014) 39690/1–39690/9.

[156] G. Ding, K. Cui, J. Liu, Miscibility and rheology behaviors of poly (3-hydroxybutyrate)/poly (p-vinylphenol) blends with homogeneous amorphous compositions, J. Appl. Polym. Sci. 122 (2011) 617–623.

[157] B. Patham, K. Jayaraman, Creep recovery of random ethylene-octene copolymer melts with varying comonomer content, J. Rheol. 1978-Present. 49 (2005) 989–999.

[158] S.-I. Han, S.S. Im, D.K. Kim, Dynamic mechanical and melt rheological properties of sulfonated poly (butylene succinate) ionomers, Polymer. 44 (2003) 7165–7173.

[159] Y. Sakamoto, H. Tsuji, Crystallization behavior and physical properties of linear 2-arm and branched 4-arm poly (L-lactide) s: Effects of branching, Polymer. 54 (2013) 2422–2434.

[160] Y. He, Z. Fan, Y. Hu, T. Wu, J. Wei, S. Li, DSC analysis of isothermal melt-crystallization, glass transition and melting behavior of poly (l-lactide) with different molecular weights, Eur. Polym. J. 43 (2007) 4431–4439.

[161] Z. Qiu, S. Fujinami, M. Komura, K. Nakajima, T. Ikehara, T. Nishi, Structure and Properties of Biodegradable Polymer-Based Blends, in: Macromol. Symp., Wiley Online Library, 2004: pp. 255–264.

[162] M. Zuideveld, C. Gottschalk, H. Kropfinger, R. Thomann, M. Rusu, H. Frey, Miscibility and properties of linear poly (l-lactide)/branched poly (l-lactide) copolyester blends, Polymer. 47 (2006) 3740–3746.

[163] F. Signori, M.-B. Coltelli, S. Bronco, Thermal degradation of poly (lactic acid)(PLA) and poly (butylene adipate-co-terephthalate)(PBAT) and their blends upon melt processing, Polym. Degrad. Stab. 94 (2009) 74–82.

[164] B. Blottiere, T.C.B. McLeish, A. Hakiki, R.N. Young, S.T. Milner, Rheology and tube model theory of bimodal blends of star polymer melts, Macromolecules. 31 (1998) 9295–9304.

[165] J.H. Lee, M.L. Ruegg, N.P. Balsara, Y. Zhu, S.P. Gido, R. Krishnamoorti, et al., Phase behavior of highly immiscible polymer blends stabilized by a balanced block copolymer surfactant, Macromolecules. 36 (2003) 6537–6548.

[166] W.S. Drumond, C.G. Mothé, S.H. Wang, Quantitative analysis of biodegradable amphiphilic poly (L-lactide)-block-poly (ethyleneglycol)-blockpoly (L-lactide) by using TG, FTIR and NMR, J. Therm. Anal. Calorim. 85 (2006) 173–177.

[167] J. Zhang, Y. Duan, A.J. Domb, Y. Ozaki, PLLA Mesophase and Its Phase Transition Behavior in the PLLA− PEG− PLLA Copolymer As Revealed by Infrared Spectroscopy, Macromolecules. 43 (2010) 4240–4246.

[168] S.M. Davachi, B. Kaffashi, J.M. Roushandeh, Synthesis and characterization of a novel terpolymer based on L-lactide, glycolide, and trimethylene carbonate for specific medical applications, Polym. Adv. Technol. 23 (2012) 565–573.

[169] J. Kuusipalo, S. Auvinen, J. Avellan, K. Hartikainen, I. Hatanpää, R. Joukio, et al., Papermaking Science and Technology, 2nd ed., Tappi Paperi ja Puu Oy, 2008.

[170] T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, J. Marles, V. Miikkulainen, M. Karppinen, Effect of corona pre-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer-coated paperboard, Appl. Surf. Sci. 257 (2010) 736–740.