

THESIS ON CHEMISTRY AND CHEMICAL ENGINEERING G34

Composites of Low-Density Polyethylene and Poly(Lactic Acid) with Cellulose and its Derivatives

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Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

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/töö autori nimi ja allkiri/



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KEEMIA JA KEEMIASTEHNKA G34

**Madaltiheda polüetüleenini ja
polü(piimhappe) komposiidid tselluloosi
ning selle derivaatidega**

DMITRI ŠUMIGIN

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LIST OF PUBLICATIONS

They key results of the thesis have been published in four cited papers:

- I** Shumigin, D.; Tarasova, E.; Krumme, A.; Meier, P. (2011). Rheological and Mechanical Properties of Poly(lactic) Acid/Cellulose and LDPE/Cellulose Composites. *Materials Science (Medžiagotyra)*, 17(1), 32 - 37.
- II** Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2012). Influence of cellulose content on thermal properties of poly(lactic acid)/cellulose and low-density polyethylene/cellulose composites. *Proceedings of the Estonian Academy of Sciences*, 61(3), 237 - 244.
- III** Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2013). Influence of Cellulose Stearate (CS) Content on Thermal and Rheological Properties of Poly(lactic acid)/CS Composites. *J. Zicans, R. M. Meri (Toim.)*. *Key Engineering Materials* 559 (2013) 99–104. Trans Tech Publications Ltd
- IV** Tarasova, E.; Šumigin, D.; Kudrjašova, M.; Krumme, A. (2013). Preparation of Cellulose Stearate and Cellulose Acetate Stearate in 1-Butyl-3-Methylimidazolium Chloride. *J. Zicans, R. M. Meri*. *Key Engineering Materials* 559 (2013) 105–111. Trans Tech Publications Ltd

In addition, results of this thesis have been presented at different scientific conferences:

Tarasova, E.; Šumigin, D.; Krumme, A.; Viikna, A. (2012). Cellulose esters: sythesis in ionic liquid and characterization. *Baltic Polymer Symposium, Liepaja, Latvia, Sept 19-22, 2012*, 107.

Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2012). Influence of Cellulose Content on Thermal Properties of Poly(lactic) acid/cellulose and Low-density Polyethylene/cellulose composites. *12th International Confernece on Biocomposites: Transition to Green Materials, May 6-8, 2012, Niagara Falls, Ontatio, Canada., 2012*, 54.

Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2012). Thermal and Rheological Properties of Composites Based on Poly(lactic acid) and Cellulose Derivatives. *Baltic Polymer Symposium, Liepaja, Latvia, Sept 19-22, 2012*, 229.

Šumigin, D.; Tarasova, E.; Krumme, A.; Meier, P. (2011). Influence of cellulose content on rheological and mechanical properties of poly(lactic) acid/cellulose and low-density polyethylene/cellulose composites. *11th International conference on Wood*

& Biofiber Plastic Composites & Nanotechnology in Wood Composites Symposium, May 16-18, Madison, USA., 2011, 51.

Šumigin, D.; Tarasova, E.; Krumme, A. (2011). Influence of Cellulose Content on Thermal Properties of Poly(lactic) Acid/Cellulose and Low-density Polyethylene/Cellulose Composites. Baltic Polymer Symposium, 21-24 sept, Tallinn, Estonia. Tallinn University of Technology, 2011, 98.

Šumigin, D.; Poltimäe, T.; Tarasova, E.; Krumme, A.; Meier, P. (2010). Influence of Cellulose Content on Rheological and Mechanical Properties of “Green” Poly(Lactic) Acid/Cellulose Composites. Baltic Polymer Symposium-2010, Sept. 08-11, Palanga, Lithuania, 2010, 122.

Šumigin, D.; Tarasova, E.; Meier, P. (2010). Influence of cellulose content on rheological and mechanical properties of poly(lactic) acid/cellulose and LDPE/cellulose composites. Proceedings of the 6th meeting of the Nordic-Baltic Network in Wood Material Science and Engineering (WSE), October 21-22, Tallinn, Estonia. Tallinn University of Technology Press, 2010, 187.

Šumigin, D.; Poltimäe, T.; Tarasova, E.; Krumme, A.; Meier, P. (2010). Rheological and Mechanical Properties of Poly(Lactic) Acid- and Polyethylene-Based Cellulosic Composites. In: BIOCAMP-2010, 10th Pacific Rim Bio-Based Composites Symposium, 5-8 October 2010, Alberta, Canada., 2010.

Author’s contribution to the publications

- I** The author completed rheological experiments, analysed the results and wrote the paper together with E. Tarasova.
- II** The author completed measurements of thermal properties and wrote the paper.
- III** The author fulfilled the experimental measurements of rheological and thermal properties and wrote the paper.
- IV** The author analysed the results and wrote the paper together with E. Tarasova.

INTRODUCTION

The growing environmental awareness and new rules and regulations are forcing modern packaging industries to seek more ecologically friendly materials for their products. Today, modern packaging industries rely on commodity plastics derived from the petrochemical industry, such as polyethylene and polypropylene as major polymeric materials currently in use. However, wastes of these and other polymers constitute a large ecological problem and have increased environmental pressure for reducing waste of non-degradable plastics (Madera-Santana *et al.* 2010). One of the alternatives to guarantee at least partial biodegradation of these plastics is blending them with biodegradable natural polymers (Madera-Santana *et al.* 2010), such as cellulose and its derivatives to produce so-called bio-based composites (matrix: low density polyethylene (LDPE), reinforcement/filler: cellulose (Cell)).

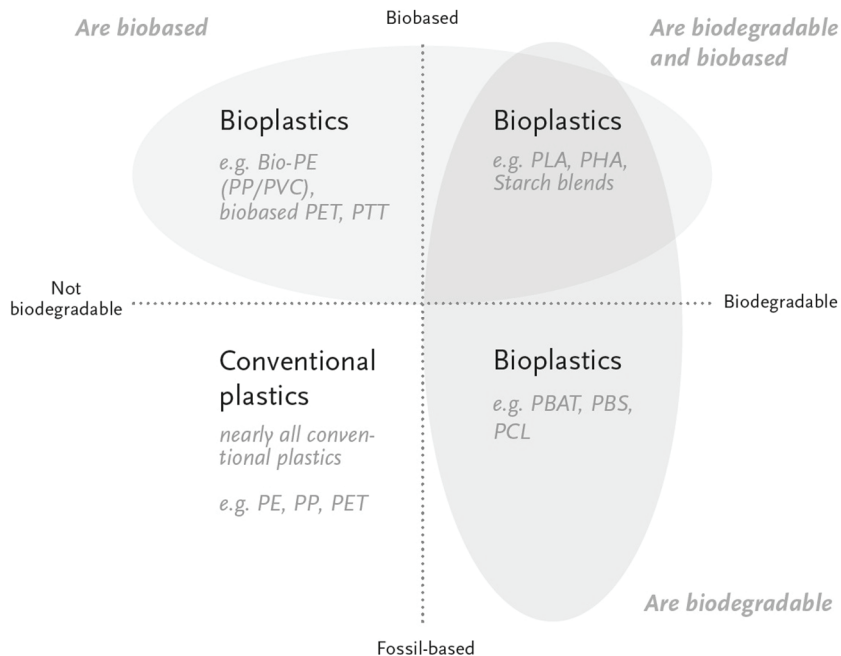


Figure 1. Different plastic materials (Bioplastics 2012).

Another alternative is to create a readily biodegradable composite fully based on renewable resources (see Figure 1), however, less work has been done to study composites with matrices originating from renewable raw materials. One of the most promising bio-based polymers that have attracted the interest of many researchers is poly(lactic acid) (PLA), which is made from carbohydrate sources, such as corn, sugarcane, or tapioca, and is readily biodegradable. The problems with PLA have been

brittleness and poor processability. Reinforcing with fillers, such as cellulose and its derivatives is one possibility of solving the above-mentioned problems (Oksman *et al.* 2003), (Wool and Sun 2005), (Ahmed *et al.* 2010).

Plastics are typically fabricated into useful articles in the molten state through melt flow, and therefore rheological properties of a polymer are considered to be of great importance (Dorgan 2010). The topic of PLA and LDPE composites with cellulose and aliphatic long-chain $-\text{CO}(\text{CH}_2)_n\text{CH}_3$ with $n \geq 6$ cellulose esters such as, for example, cellulose laurate (CL) and cellulose stearate (CS), is new and these materials would offer a great possibility of compatibility with PLA due to ester groups and LDPE due their longer aliphatic chain similar to polyolefins. Cellulose fibres have higher crystallinity and therefore superior mechanical properties relative to cellulose esters but incompatible surface with PLA and LDPE. However, cellulose esters would add flexibility and better flow properties compared to native cellulose which is highly crystalline and has a solid-like rheological behaviour in composites (Kim *et al.* 2013). Long carbohydrate chains in cellulose esters, which can act as lubricants and help cellulose esters to be distributed uniformly in LDPE or PLA matrix, would become compatibilizers (Jandura *et al.* 2001).

Composites of LDPE and PLA with cellulose and its esters are more sustainable than pure matrix polymers. Addition of cellulose and its esters improves biodegradability of LDPE and reduces usage of PLA, which is derived from edible resources that could be used for food applications. However, to replace pure LDPE and PLA in their current packaging applications, such as plastic bags for household bio waste, barriers for sanitary products and diapers, planting cups, disposable cups and plates (Oksman *et al.* 2003), the novel composites should have properties identical to the matrix polymers. For PLA to be able to compete with more flexible and ductile commodity polymers, such as polyethylene or polypropylene, there is a need to plasticize or compatibilize PLA matrix (Ahmed *et al.* 2010), and cellulose derivatives could be a promising direction in that respect.

Investigation of nonisothermal behaviour of polymers and especially their composites is of pronounced significance from the technological viewpoint, as most of the fabrication processes for polymeric materials such as injection and extrusion moulding are conducted under nonisothermal condition. In contrast to isothermal crystallization, nonisothermal crystallization is carried out over a broad temperature range, which allows understanding of the overall crystallization behaviour during solidification of polymers, which is crucial as various end properties of PLA and LDPE significantly depend on its crystallinity (Liang *et al.* 2012). Higher crystallinity results in a harder and more thermally stable, but also more brittle material, whereas the amorphous regions provide certain elasticity and impact resistance (Acton 2013). The degree of crystallinity and crystallite size as well as the melting temperature and crystallization temperature of polymers are considered to be influenced by the fillers, and these observations are important for the processing of the composites (Huang *et al.* 2007).

Hence, the addition of cellulose or cellulose esters could have a significant effect on thermal behaviour of PLA and LDPE.

Fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, injection moulding, fibre spinning, and film blowing etc. Therefore, novel composites should be first analysed by rheological measurements before using them in production and processing. To utilize and design materials successfully for industrial applications, it is first imperative to determine material properties that will affect performance at certain temperatures (Baillie 2004).

It is well known that the final morphology, which may occur during melt mixing, affects the composite properties and in turn the application is also highly affected by the melt rheological properties. Thus, understanding the melt rheological properties, thermal properties and morphology of a composite is not only important in gaining fundamental knowledge of the processability and composite properties, but is also helpful in understanding the morphology-rheology-property relationship for the final stage of the composite (Yu *et al.* 2011), (Shin *et al.* 2007).

Rheological and crystallization behaviour of LDPE and PLA composites with cellulose esters has been poorly studied in the literature. Only several studies of thermal properties of LDPE with short-chain cellulose acetate phthalate (Sailaja and Seetharamu 2009) and several long-chain cellulose esters $-\text{CO}(\text{CH}_2)_n\text{CH}_3$ ($n = 10, 16$ and 20) (Freire *et al.* 2008), (Pasquini *et al.* 2008) were performed. Addition of CL and CS to PLA matrix was not investigated at all.

Therefore, the novelty of this thesis lies in the creation and study of rheological and thermal behaviour of new almost unstudied composite materials.

Hence, the aim of this research is the following:

- To create new sustainable composites based on PLA and LDPE with cellulose and long-chain fatty acid cellulose esters that would replace pure PLA and LDPE in their current applications.
- Taking into account that CL and CS are not conventionally available materials, they were synthesized in this work by a novel homogeneous method. Rheological and thermal properties of novel composites were studied.

Such research, being more fundamental by its origin than applied, allows studying the effect of additives, their contents and structure on the rheological and thermal behaviour of polymers. This work would bring a new knowledge of creation and rheological and crystallization/melting behaviour of LDPE and PLA composed with native cellulose and its derivatives.

To reach the aim of the research, several tasks will be fulfilled: studying the effect of added filler content (from 2 up to 60 wt%) and its nature (Cell, CL, CS) on rheological and thermal properties of LDPE and PLA composites.

The following research activities will be conducted to analyse these properties: Melt rheology and Differential Scanning Calorimetry (DSC). Melt rheology is used for examining and understanding the interaction of the constituents of a multi-component mixture and their influence on the flow properties (storage modulus (G'), loss modulus (G''), complex viscosity (η^*)) of such materials. Differential scanning calorimetry (DSC) is used to study melting and crystallization behaviour of composites by obtaining thermal parameters such as crystallization temperature (T_c), melting temperature (T_m), degree of crystallinity (X_c) crystallization enthalpy (ΔH_c), melting enthalpy (ΔH_m) and lamellar thickness and its distribution.

LIST OF SYMBOLS AND ABBREVIATIONS

LDPE	low density polyethylene
PLA	poly(lactic acid)
Cell	cellulose
CL	cellulose laurate
CS	cellulose stearate
AGU	anhydroglucose unit
BmimCl	1-butyl-3-metylimidazolium chloride
DSC	differential scanning calorimetry
DS	degree of substitution
G'	storage modulus
G''	loss modulus
HDPE	high density polyethylene
LLDPE	linear low density polyethylene
LVE	linear viscoelastic range
η^*	complex viscosity
η'	dynamic viscosity
η''	imaginary viscosity
η_0^*	zero shear viscosity
PLM	polarized light microscopy
PDLA	Poly-D-lactic acid
PLLA	Poly-L-lactic acid
PDLLA	Poly-D-L-lactic acid
T_c	crystallization temperature
T_{cc}	cold crystallization temperature
T_{fm}	melting end temperature
T_g	glass transition temperature
T_{im}	melting onset temperature
T_{mc}	melting temperature of crystallites formed during the cold crystallization
$T_m = T_{pm}$	melt peak temperature
X_c	degree of crystallinity
ΔH_c	crystallization enthalpy
ΔH_{cc}	cold-crystallization enthalpy
ΔH_m	melting enthalpy
ΔH_{mc}	melting enthalpy of crystallites formed during the cold crystallization
ω	angular frequency

1. LITERATURE REVIEW

Composites are a special category of materials that consist of at least two or more materials. Mainly they consist of reinforcement (gives strength to a composite), matrix (occupies the space between reinforcement) and interface (holds matrix together with reinforcement on chemical (bond) or physical (interaction) level). Usually composites are made to get rid of weaknesses of the components. Cellulose as reinforcement is hygroscopic, therefore it is combined with plastic matrix and the result is cellulose plastic composite is not so sensitive to moisture. PLA as a matrix is very brittle and addition of natural fibres would make it more flexible. On the other hand, LDPE has excellent flexibility, but poor mechanical properties, which could be improved by addition of cellulose and other natural fillers (Baillie 2004).

Usually when the use of fillers is considered, a compromise has to be made between the improved mechanical properties in the solid state, the increased difficulty in melt processing, the problem of achieving uniform dispersion of the filler in the polymer matrix and the economics of the process due to the added step of compounding. It has been recognized that addition of filler to the polymer brings a change in processing behaviour. The presence of the filler increases the melt viscosity leading to increases in the pressure drop across the die but gives rise to less die swell due to decreased melt elasticity. The decrease in melt elasticity can raise the critical shear rate at which melt fracture during extrusion starts to occur and hence one could often consider increasing the throughput rate in the case of filled polymer melt processing (Shenoy 1999). On the other hand, addition of fillers can also alter melting and crystallization behaviour of the polymers that would lead to change of processing conditions. As an example, several fillers can act as nucleating agents that would facilitate melting and crystallization process of a composite during its manufacture. This is commonly used in industry to shorten the processing times and to govern the desired material properties (Huang *et al.* 2007).

This chapter presents properties of components of studied composites: matrices (PLA and LDPE) and fillers (Cell, CL and CS). It also gives a theoretical background of the studied methods and overview of rheological and thermal properties of composites presented in the literature.

1.1 Components of composites

1.1.1 PLA

PLA $-(\text{CH}(\text{CH}_3)\text{-CO-O})_n-$ is a thermoplastic aliphatic polyester obtained by condensation polymerization directly from its basic building block lactic acid or by conversion of lactide - the cyclic dimer of lactic acid - to PLA via ring-opening polymerization (Groot *et al.* 2010), which in turn are obtained from the fermentation of renewable resources such as corn, sugarcane, or tapioca (Biresaw and Carriere 2002).

Processing, crystallization, and degradation behaviour of PLA depend on the structure and composition of the polymer chains, in particular the ratio of the L- (or S-) to the D- (or R-) stereoisomer of lactic acid (see Figure 2). L-lactic acid has a slightly positive specific optical rotation and is frequently named L-(+)-lactic acid and therefore PLA made of this monomer is called Poly-L-lactic acid (PLLA). Alternatively, PLA manufactured of D-(–)-lactic acid is Poly-D-lactic acid (PDLA). The use of mix of optical D- and L-lactic acid monomers to prepare PLA results in formation of Poly-D-L-lactic acid (PDLLA) (Groot *et al.* 2010).

This stereochemical structure of PLA can be modified by copolymerization of mixtures of L-lactide and meso-, D-, or rac-lactide resulting in high molecular weight amorphous or semicrystalline polymers with a melting point in the range from 130 to 185°C. PLLA homopolymer comprising L-lactic acid only is a stereopure semicrystalline material with higher melting point compared to impure D-lactic acid which act much like co-monomers. Therefore, PLA copolymers with higher D-isomer content exhibit lower melting points and dramatically slower crystallization behaviour, until they finally become amorphous at D-contents higher than 12–15% (Groot *et al.* 2010), (Henton *et al.* 2005).

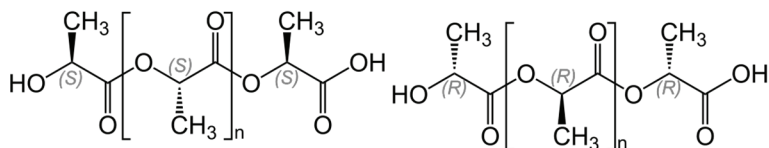


Figure 2. Stereochemical structure of PLA.

PLA has a number of promising properties (e.g., biocompatibility, thermal plasticity and mechanical properties), it is readily fabricated, thus being a promising polymer for blending with different fibres for various end-use applications (Lehermeier and Dorgan 2001). However, the major limitations of PLA are its inherent brittleness and low toughness. The flexibility and toughness of PLA can be enhanced by modifying its physical properties through several approaches including copolymerization, blending and incorporation of filler materials by compounding (Ahmed *et al.* 2010).

1.1.2 LDPE

Polyethylene $-(\text{CH}_2-\text{CH}_2)_n-$ is classified into three types according to its density and structure: high density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low density polyethylene (LLDPE). LDPE (see Figure 3) is a highly branched thermoplastic polymer manufactured only by free radical polymerization at very high pressure (100-300 MPa) and temperature ($> 200^\circ\text{C}$) (Malpass 2010).

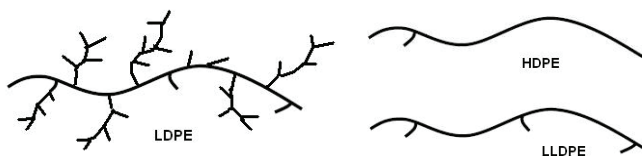


Figure 3. Structures of Polyethylene.

It can be melted and shaped into a form, which can then be subsequently re-melted and shaped (recycled) into other forms. Polyethylene does not typically have a sharp melting point (T_m), but rather a melting range owing to differences in molecular weight, crystallinity (or amorphous content), chain branching, etc.

Low-density polyethylene (LDPE) has excellent flexibility and elasticity, near-zero moisture absorption, excellent chemical inertness, low coefficient of friction, ease of processing. However, the mechanical properties of pure LDPE are not sufficient to meet the high requirements of certain applications (Blaszczak *et al.* 2010), (Huang *et al.* 2007).

1.1.3 Fillers

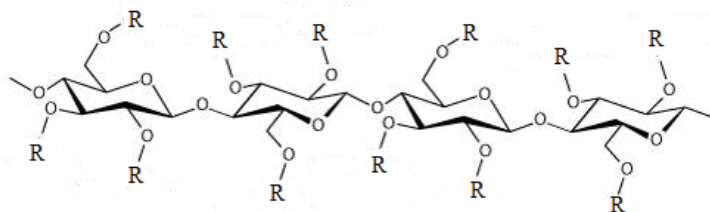
The addition of fillers is a common, easy and often inexpensive way to modify the properties of the base polymer matrix. The extensive use of fillers has allowed the development of composites for a wide range of applications owing to the fact that one can judiciously maintain the desirable traits of the component materials while improving or eliminating undesirable ones (Blaszczak, Brostow *et al.* 2010).

Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units with the formula $(C_6H_{10}O_5)_n$ (see Figure 4). It is one of the strongest and stiffest fibres available in its micro- and nanoforms due to high fibre length to diameter ratio and it has a high potential to act as a reinforcing agent in biopolymers. Cellulose-based polymer composites are characterized by low cost, desirable fibre aspect ratio, low density, high specific stiffness and strength, biodegradability, flexibility during processing with no harm to the equipment, and good mechanical properties (Huda *et al.* 2005).

However, cellulose has limitations in its processability. It is neither meltable nor soluble in most common solvents because of the large amount of inter- and intramolecular hydrogen bonding and its high degree of crystallinity in structure (Ratanakamnun *et al.* 2012).

Therefore, the modification or conversion of cellulose to its derivatives renders it processible into various useful forms such as fibre or film. The substitution group can be used to reduce interchain hydrogen bonding and force the chain apart. As a result, cellulose derivatives can be dissolved in common organic solvents and/or melt at

relatively low temperatures making them attractive materials in a wide range of applications (Ratanakamnun *et al.* 2012).



1. Native cellulose: $R = \text{H}$
2. Cellulose laurate: $R = \text{C}(=\text{O})\text{C}_{11}\text{H}_{23}$
3. Cellulose stearate: $R = \text{C}(=\text{O})\text{C}_{17}\text{H}_{35}$

Figure 4. Structure of cellulose (1), cellulose laurate (2) and cellulose stearate (3). If all groups in the anhydride unit are substituted by fatty acid groups, it means that the degree of substitution reaches its maximum value of 3.

One of the most interesting aspects of cellulose chemical modification is the production of cellulose fatty acid esters. Short-chain cellulose esters, such as cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate, have been applied in fields such as coatings, composites, and laminates. However, these short-chain cellulose esters have a narrow processing temperature window between melting temperature and decomposition; their applications have been limited (Huang 2012). To cover the shortages of short-chain cellulose esters, long-chain aliphatic acid esters of cellulose (see Figure 4) have been identified as potential biodegradable plastics in which OH-groups of cellulose are substituted by long-chain fatty acids $-\text{CO}(\text{CH}_2)_n\text{CH}_3$ with $n \geq 6$ (Sealey *et al.* 1996).

Several methods have been developed to prepare long-chain cellulose esters. These methods involved heterogeneous acylation by using acyl chloride, acyl chlorides under vacuum or aliphatic acids with trifluoroacetic acid, and homogeneous acylation in *N,N*-Dimethylacetamide/lithium chloride (DMAc/LiCl) (Huang 2012).

Recently, ionic liquids have been shown to be a perfect solvent for cellulose that can also be a reaction media for homogeneous modification of cellulose. In particular 1-butyl-3-methylimidazolium chloride (BmimCl) seems to be the most efficient ionic solvent for cellulose to manufacture cellulose derivatives with long-chain fatty acids. Cellulose is added to BmimCl and during constant stirring under vacuum cellulose gets dissolved. By employing a homogeneous reaction with acyl chloride under nitrogen atmosphere, the whole cellulose chain is accessible for modification and problems related to two-phase (industrial) reactions are avoided (Huang 2012), (Liebert and Heinze 2008).

1.2 Rheological properties of composites

1.2.1 Theoretical background

Rheology is the study of the flow and deformation of matter. It is a subfield of continuum mechanics that combines elements of both solid and fluid mechanics. Polymer rheology is a highly advanced science that reveals very important features of polymeric materials like PLA and LDPE. The melt rheology of polymeric materials reflects the relationship between molecular structure and dynamic properties. Of these properties, the viscosity and elasticity of the molten polymer are of primary importance in processing of plastics into useful articles (Dorgan 2010).

Melt rheology employs non-resonant forced vibration techniques for determining the complex viscosity and viscoelastic characteristics of thermoplastic materials as a function of frequency, strain amplitude, temperature and time. A wide range of frequencies can be used, typically from 0.01 to 100 Hz (Klyosov 2007).

For non-Newtonian fluids, the stress is out of phase with the rate of strain. In this situation a measured *complex viscosity* (η^*) contains both the shear viscosity, or dynamic viscosity (η'), related to the ordinary steady-state viscosity that measures the rate of energy dissipation, and an elastic component (the imaginary viscosity η'' that measures an elasticity or stored energy) (Klyosov 2007):

$$\eta^* = \eta' + i\eta'' \quad (1)$$

These two viscosities are calculated using the following equations (Klyosov 2007):

$$\eta' = \frac{G''}{\omega} \quad \text{and} \quad \eta'' = \frac{G'}{\omega} \quad , \quad (2), (3)$$

where ω is the fixed angular frequency of the oscillations in radians per second $\omega = 2\pi f$, f is the frequency in hertz, G' is the storage (elastic) modulus and G'' is the loss (viscous) modulus.

The storage modulus measures the elastic response of a polymer while the loss modulus measures the energy dissipated during flow deformation. The ratio of the loss modulus to the storage modulus, G''/G' , is known as $\tan \delta$ and is an important characteristics of viscoelastic materials. In perfectly elastic materials G'' is zero, and in perfectly viscous materials (Newtonian fluids) G' is zero. Typically, both G' and G'' are functions of frequency and temperature (Klyosov 2007).

As a matter of fact, the most reliable rheological data on filled polymer systems can be obtained through the use of dynamic oscillatory measurements. The dynamic

amplitude sweep and the dynamic frequency sweep would be most suitable for assessing the internal structure of the system.

During an amplitude sweep the amplitude of the deformation – or alternatively the amplitude of the shear stress – is varied while the frequency is kept constant. At low deformation G' and G'' are constant and the sample structure is undisturbed. This region is called linear-viscoelastic (LVE). As soon as the moduli start to decrease, the structure is disturbed, which means that the end of the LVE-region is reached: the plateau value of G' in the LVE-region describes the rigidity of the sample at rest; the plateau value G'' is a measure for the viscosity of the unsheared sample. The ratio of the two moduli gives information about the characteristic of the sample: if the storage modulus is larger than the loss modulus – like shown in figure 5 (WEE-Solve 2013) – the sample behaves more like a viscoelastic solid (solid-like behaviour). In the opposite case – $G'' > G'$ in the LVE-region – the sample has the properties of a viscoelastic fluid (fluid-like behaviour) (WEE-Solve 2013).

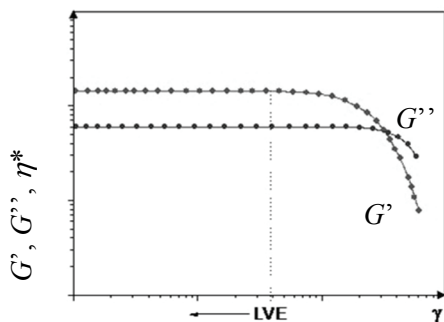


Figure 5. Example of amplitude sweep.

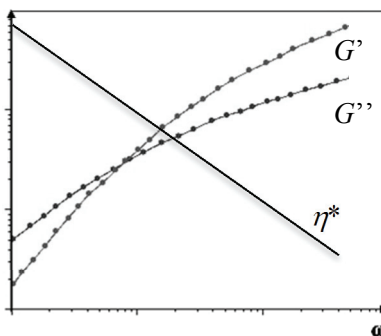


Figure 6. Example of frequency sweep.

Having determined the amplitude that keeps tests of a particular sample safely within the linear viscoelastic (LVE) region, one can then proceed with further tests using the frequency sweep to measure the sample's viscoelastic behaviour. During the frequency sweep the frequency is varied while the amplitude of the deformation – or alternatively the amplitude of the shear stress – is kept constant. For the analysis the storage and loss moduli as well as viscosity are plotted against the frequency ω (see Figure 6 – typical for a polymer melt or polymer solution (WEE-Solve 2013)). The data (G' , G'' and zero shear viscosity η_0^*) at low frequencies describe the behaviour of the samples at slow changes of stress. Oppositional behaviour at fast load is expressed at high frequencies (WEE-Solve 2013), (Schramm 2000). For filled systems, because of the sensitivity of the dynamic response to the level of strain, it is always important to determine the dynamic viscoelastic properties at a strain that is low enough not to affect the material response. As the filler loading increases, the level of strain below which the response is unaffected is reduced (Shenoy 1999).

1.2.2 Rheology of LDPE and PLA composites

Before going into details of composites rheological behaviour, it is essential to know and understand the basis of the rheology of pure PLA and LDPE.

PLA, like many thermoplastics, is a pseudoplastic, non-Newtonian fluid. Above the melting point, PLA behaves as a classic flexible-chain polymer across all optical compositions. PLA's zero shear viscosity and shear thinning behaviour have been measured by a variety of groups (Lehermeier and Dorgan 2001), (Palade *et al.* 2001), (Dorgan *et al.* 2000), (Gruber *et al.* 2008). However, complicated by the array of optical compositions studied, the difficulty associated with measuring the absolute molecular weight of PLA, and the issues of melt stability, the interpretation of PLA's rheology has not always been consistent (Gruber *et al.* 2008). LDPE like PLA is also a pseudoplastic, non-Newtonian fluid and has a strong shear thinning behaviour. LDPE rheology is typical for a polymer melt or polymer solution: at lower angular frequencies LDPE exhibits fluid-like behaviour (loss modulus is higher than storage modulus) and with increase of angular frequency the behaviour becomes solid-like (storage modulus becomes higher than loss modulus) (Sdrobis *et al.* 2012).

The rheological properties of composites provide important information on processing parameters, such as the viscosity and possible effects of deformation on the microstructure, including the extent to which the reinforcement has been distributed in the matrix (Satyanarayana *et al.* 2009).

The use of natural-organic fillers in replacement for traditional mineral inorganic ones allows a considerable reduction in the use of non-biodegradable polymers and non-renewable resources. Furthermore, these fillers are usually drawn from renewable sources, they are also much less abrasive than inorganic-mineral fillers to processing machinery, less dangerous for the production employers in case of inhalation, easy to be incinerated, they lead to final composites with lower specific weight (in comparison to mineral-filled counterparts), biodegradability, high specific stiffness and strength. The most widely known and used natural-organic fillers are based on cellulose (Sdrobis *et al.* 2012).

During last couple of decades a deliberate interest to look for systems of adding cellulose and its direct derivatives to PLA to improve its brittleness and thermal stability appeared (Kim *et al.* 2013). PLA/Cellulose composites have been studied by different methods, such as different scattering techniques, electron microscopy and thermo-gravimetric analysis (George *et al.* 1996, Mathew *et al.* 2005), (Oksman *et al.* 2003), (Huda *et al.* 2006). However, rheological properties of such composites are poorly studied. PLA/chemically modified plasticized starch composites with filler content up to 20% showed Newtonian flow behaviour, while the filler itself had strong pseudoplastic fluid shear thinning behaviour (Shin *et al.* 2007). Addition of triticale straw increased the complex viscosity of PLA biocomposites as the interactions

triticale-matrix and triticale particle-particle were increased (Mihai and Ton-That 2013). One study (Kim *et al.* 2013) indicated that addition of cellulose based fillers like microcrystalline cellulose and lignin tends to change the fluid-like behaviour of PLA to solid-like for PLA composites, where storage modulus is higher than loss modulus.

Melt rheological behaviour of composites based on LDPE and cellulosic materials has also been studied. Oscillatory rheological tests of LDPE/cellulose pulp fibres exhibited a strong shear thinning behaviour. Addition of short pineapple fibre brought an increase in the viscosity of LDPE composites (George *et al.* 1996). The same trend was seen in LDPE/hemp composites. Increase in shear rate, on the other hand, reduced the difference between the viscosities of different mixtures since all the compounds are shear thinning (Kakroodi *et al.* 2013).

The acylation of cellulose macromolecules with fatty acids represents an interesting way to prepare reinforcing elements for composites with common thermoplastic matrices (Freire *et al.* 2008), such as PLA and LDPE. This strategy is particularly relevant because of the renewable and biodegradable nature of fatty acids and, obviously, contrary to cellulose, they can melt and thus be formed using classical polymer processing methods (Besson and Budtova 2012). However, melt rheology of these composites is practically not studied. Several studies have only been carried out where cellulose acetate butyrate compositions with HDPE demonstrated slight viscosity increases in the calculated corresponding additive values and storage moduli were in good accordance with the additive model (Besson and Budtova 2012) and various cellulose esters lowered viscosity of LLDPE composites oppositely to cellulose fibres. Though, there have been studies carried out on melt rheology of cellulose based composites with various matrices: polyacrylamide (Zhou *et al.* 2011), acrylic copolymer (Mabrouk *et al.* 2011), cement (Hoyos *et al.* 2013), ethylene vinyl acetate (Mahi and Rodrigue 2012), polyamide 6 (Kiziltas *et al.* 2013). Therefore, there is a large scope in this work to study rheological properties of composites based on PLA and LDPE with cellulose and cellulose esters.

1.3 Thermal Properties of composites

1.3.1 Theoretical background

Unlike inorganic crystalline materials, semicrystalline polymers have a broad melting and crystallization range. Melting range of polymers consists of a series of overlapping melting points that correspond to the melting of lamellae of various thicknesses. If the material crystallizes in non-isothermal conditions, different molecular species tend to crystallize at different temperatures. The melting curve reflecting this non-uniform structure is shown in Figure 7. At the melting onset temperature T_{im} the thinner or less perfect crystallites begin to melt and at the melting end temperature T_{fm} thicker crystallites are melted and the crystalline order has been destroyed. Therefore the

melting curve indirectly characterizes the lamellar thickness distribution. The melting peak temperature T_{pm} is the temperature at which most of the crystallites melt (Peacock 2000).

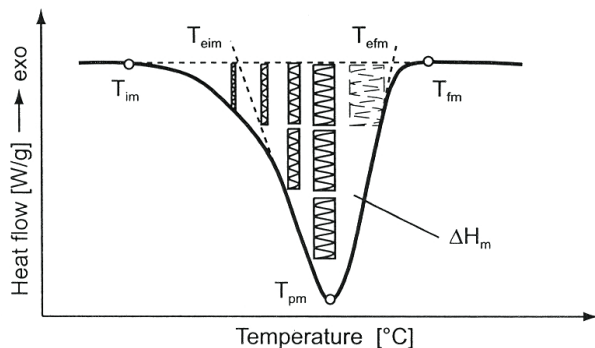


Figure 7. Melting curve and lamellar thickness distribution for a semicrystalline thermoplastic (Ehrenstein *et al.* 2004).

The processes, by which polymers crystallize, reflect the properties of the disordered state from which the ordered phase condenses. Thus levels of chain entanglements, molecular dimensions, and viscosity all play important roles. The factors affecting the structure of disordered state are molar mass average, MMD, and concentration, type, and distribution of branches.

When a semicrystalline polymer is cooled to a temperature that is below the melting temperature T_m but above the glass transition temperature T_g , the polymer undergoes crystallization. Processes that increase enthalpy, such as melting or evaporation are endothermic while those that reduce enthalpy, like crystallization, are called exothermic. The change in enthalpy is measured with calorimeter, by recording the displacement of enthalpy (ΔH) from a baseline. The baseline is a linear section of the curve that represents conditions in which no reaction or transition occurs.

Non-isothermally crystallized sample is melted at a constant heating rate and it is assumed that the rate of heat flow at a given melting temperature is proportional to the fraction of lamellae that have a certain thickness L . Thompson-Gibbs equation relates the melting temperature T_m to the lamella thickness L :

$$T_m = T_m^0 \left[1 - \frac{2\sigma}{\Delta H^0 \rho L} \right] \quad (4)$$

Other parameters in this equation are the equilibrium melting temperature T_m^0 , σ is the specific fold surface free energy, ΔH^0 is the enthalpy of fusion, ρ is the lamella phase density and L is the lamella thickness.

However, during melting, recrystallization or reorganization of lamellae into larger forms with higher melting points can also occur. This process disturbs analysis of the original lamellae thickness distribution. Recrystallization can be avoided by increasing the heating rate (Gedde 1995).

1.3.2 Thermal properties of LDPE and PLA composites

Significant efforts have been made to study crystallization of polymers in the presence of fillers, because fillers have great influence on the properties of composite materials. The effects of microfillers on polymer crystallization were extensively investigated in detail through a considerable number of calorimetric studies, according to which, the degree of crystallinity, crystallite size, melting temperature and crystallization temperatures of polymers are considered to be influenced by the fillers, and these observations are important for the processing of the composites (Huang *et al.* 2007).

The thermal behaviour of poly(lactic acid) has attracted much attention since differential scanning calorimetry (DSC) studies detected multi-phase transitions such as glass transition, excess enthalpy of chain relaxation, cold crystallization, melting and crystallization. Of these thermal phenomena, crystallization and melting are the most important from both a scientific and commercial viewpoint, because many mechanical properties of PLA significantly depend on its crystallinity (Yu *et al.* 2008).

Figure 8 shows a typical DSC analysis of thermal behaviour of two initially amorphous PLAs, that is, a PDLA ($M_w = 70$ kDa) sample that is intrinsically amorphous and PLLA ($M_w = 200$ kDa) that was quenched to the amorphous state by fast cooling at $100^\circ\text{C}/\text{min}$ after melting. It is a good example of thermal behaviour of different PLA compositions. In both cases, the T_g is evident and is located at about 65°C . PDLA does not have a melting temperature, nevertheless PLLA has it, however, cold crystallization and melting enthalpies are equal which makes PLLA sample also amorphous (Fambri and Migliaresi 2010).

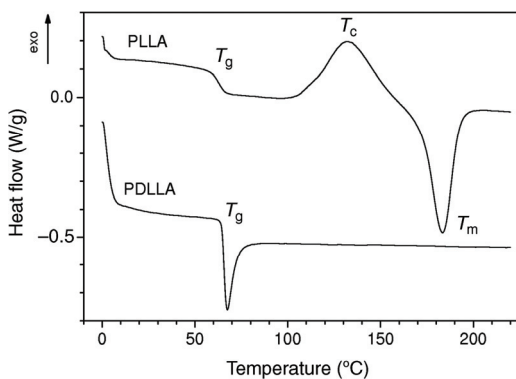


Figure 8. Differential scanning calorimetry thermograms of amorphous PLLA and PDLA (heating rate $10^\circ\text{C}/\text{min}$) (Fambri and Migliaresi 2010).

Various studies on thermal properties of PLA composites with natural fibres such as kenaf, bamboo fibre, and hemp have been carried out. The effect of kenaf fibre content on crystallization and melting behaviour of PLA (Anuar and Zuraida 2011) showed that the amorphous state of PLA remained unchanged with changing kenaf fibre content and it did not significantly make kenaf fibre to act as a nucleating agent for PLA. On the other hand, it was found that bamboo fibre acted as a nucleating agent in PLA/bamboo fibre composites. The DSC plots showed that bamboo fibre increased the overall crystallization rate of PLA (Qian *et al.* 2013). Analysis of thermal behaviour of hemp fibre composite with PLA revealed that hemp fibre promoted recrystallization in the melting temperature range (Mustapa *et al.* 2013), besides, soy flour and modified soy flour acted as nucleation agents and facilitated the crystallization behaviour of PLA by increasing the degree of crystallinity (Li *et al.* 2010).

Non-isothermal crystallization behaviour of composites based on some forms of cellulose and some of derivatives with pure PLA have been also investigated. It was found that addition of microcrystalline cellulose raises the cold crystallization temperature of PLA, such an increase is possible because the nano-sized microcrystalline cellulose acts as a nucleating agent (Kim *et al.* 2013). Addition of another cellulose fibre type – microfibrillated cellulose to PLA delivered faster crystallization times for composites (Suryanegara *et al.* 2010). On the other hand, cellulose fibres did not significantly affect the crystallization behaviour of the PLA matrix (Huda *et al.* 2005). Cellulose nanofibres were also introduced as fillers for PLA and the nucleating effect of them was confirmed (Frone *et al.* 2013). The addition of cellulose nanocrystals increased the degree of crystallinity of PLA in composites and significantly improved tensile modulus and strength of the nanocomposite (Pei *et al.* 2010).

The investigations on the thermal properties of the LDPE/natural fibre composites were generally conducted by comparing the degradation and changes in crystallization/melting behaviour of natural fibre, pure LDPE, and compared to their composites. Investigation of LDPE/kenaf cellulose composites revealed that kenaf delayed crystallization of LDPE (Tajeddin *et al.* 2009). On the other hand, Doum fibres promoted crystallization of LDPE, however, at higher concentration > 10%, the growth of crystallites was delayed due to restricted alignment of LDPE molecules network caused by natural fibres, this leads to a low mobility of polymer segments in the regions of lamellae surfaces during polymer melting process (Arrakhiz *et al.* 2013). Cellulosic sisal fibre also decreased melting temperature of LDPE/short sisal fibre composites substantially, at the same time, crystallinity of LDPE was lowered (Luyt and Malunka 2005). However, another study of LDPE/sisal fibres (Luyt and Ahmad 2012) resulted in the same T_m values of LDPE in all the unmodified samples regardless of the fibre content, and the same trend was seen for LDPE/henequen fibre composites (Herrera-Franco and Aguilar-Vega 1998). This indicates that the size of the crystalline domains, which is directly related to T_m , is retained in the matrix (Luyt and Ahmad 2012).

Several studies on composites of LDPE and short- and long-chain fatty acids of cellulose esters have been performed. Addition of cellulose acetate phthalate resulted in a decrease of melting temperature and a loss of crystallinity for the LDPE phase as cellulose acetate phthalate restricts the close packing of LDPE chains segments (Sailaja and Seetharamu 2009). In another study, low-density polyethylene was filled with unmodified cellulose and fatty acid (hexanoic, dodecanoic, octadecanoic and docosanoic acids) esterified cellulose fibres. Addition of fibre did not significantly affect the melting temperature, regardless of the fibre content and fatty acyl chain length. As expected, the melting enthalpy of composites decreased with the fibre loading due to the corresponding decrease in the amount of matrix. Moreover, the degree of crystallinity of the composite materials was not detectably affected by the fibre content and properties (Freire *et al.* 2008). On the contrary, the degree of crystallinity values of LDPE composites with CL and CS increased up to a filler content of 15% and then decreased for higher filler concentrations (Pasquini *et al.* 2008). To conclude, melting and crystallization behaviour of composites based on long-chain fatty acid cellulose esters with LDPE and PLA is insufficiently studied in the literature. Therefore, the topic of thermal properties of PLA and LDPE composites with long-chain cellulose esters is novel and one aim of this work is to investigate these properties.

2. EXPERIMENTAL METHODS

This chapter gives an overview of materials used in this work, processing and analysis methods applied to study properties of composites.

2.1 Materials

Two types of composites were investigated in this work: LDPE with 3 different fillers (Cell, CL, CS) and PLA with Cell and CS. LDPE powder was obtained from Borealis Polymers Co (product name: PE FA3220). NatureWorks LLC supplied Poly(lactic acid) granules (PLA Polymer 4042D). M_w of LDPE and PLA are 318 kg/mol and 120 kg/mol, respectively. The Cellulose used was acid-free α -cellulose purchased from Hahnemühle FINEART.

Materials and their contents in composites are shown in Table 1:

Table 1. LDPE and PLA composites

Type of composites	Content (wt%)
LDPE composites with	
Cellulose (Cell)	2, 5, 10, 20
Cellulose Laurate (CL)	10, 20, 50
Cellulose Stearate (CS)	10, 20, 50
PLA composites with	
Cellulose (Cell)	2, 5, 10, 20
Cellulose Stearate (CS)	10, 20, 50, 60

Cellulose laurate (CL) and cellulose stearate (CS) were prepared by esterification reaction of cellulose with lauroyl and stearyl chloride respectively in ionic liquid 1-Butyl-3-methyl-imidazolium Chloride (BmimCl). The synthesis of cellulose esters was done according to common procedure (Barthel and Heinze 2006): lauroyl chloride or stearyl chloride at 5 moles per anhydroglucose unit (AGU) were carefully added to the solution of cellulose in BmimCl. The temperature was kept at 80°C for 3 hours. All reactions were carried out under nitrogen atmosphere and with the use of reflux condenser. Isolation was carried out by precipitation into 200 ml of methanol, washing with large amount (2 litres) of methanol and drying under vacuum at 70°C for 12 hours. After that the samples were dissolved in chloroform and precipitated by adding of methanol. The precipitate was dried again and the same procedure was repeated twice to remove any intermediate products and unreacted materials. A series of cellulose laurates and stearates has been successfully produced by linking aliphatic acyl chlorides (C12) and (C18) onto cellulose backbone. The degree of substitution (DS) of cellulose laurate and cellulose stearate was analysed by titration method

(Whistler and Wolfrom 1967) and for both CS and CL degree of substitution was 0.4. Results of cellulose esters synthesis are presented in Paper IV from the list of publications.

Lauroyl and stearoyl chlorides of technical grade were purchased from Sigma-Aldrich Company. The molar mass of cellulose, obtained by viscometry in ethylenediamine-copper(II) using Mark-Houwink equation (Brandrup *et al.* 2005), was 100 kg/mol.

2.2 Processing methods

First, cellulose and polymer powders were prepared. Cellulose sheets were crushed into pieces and then ground to a powder using the cutting mill Retsch SM 100. PLA and LDPE granules were then pulverized in the Retsch cutting mill and then PLA powder was dried in an oven at 105°C for 24 h.

Matrix/filler mixtures of different compositions were mechanically mixed by rotating drum. Then PLA and LDPE composites with Cell, CL and CS were prepared by compounding in micro-conical twin-screw compounder (Thermo Scientific HAAKE MiniCTW). Pre-blended matrix/filler mixtures were melted and mixed in the extruder via the rotating screws to produce the final molten product that is extruded at the end as strands through hole in a die plate. Equal temperature could be set up in the 2 zones of the extruder from hopper to die. PLA/Cell, PLA/CS and LDPE/Cell, LDPE/CL LDPE/CS composites were compounded at 180°C. Both pure LDPE and PLA had undergone the same extrusion procedure as their composites. The molten strand was then air cooled by ventilators and chopped into pellets and further cooled for 1 h.

2.3 Analysis methods

2.3.1 Rheological analysis

The melt rheological properties of the samples were determined using a rheometer Anton Paar Physica MCR 501. The measurements were performed in the dynamic oscillatory mode with 25 mm cone-plate measuring geometry, the angle of the cone surface being 2 degrees and gap setting 0.051 mm. All measurements were carried out in a nitrogen atmosphere at 190°C. Amplitude sweep was performed with all the samples at 10 rad/s and 5% strain was kept in all composite samples frequency scans. Frequency scans were taken between 0.05...0.5 and 500 rad/s for PLA, LDPE and their composites.

In order to get samples for rheology measurements, compression moulding was used. LDPE- or PLA-cellulose powder granules were placed into a stainless steel round-shape mould (height=1.06 mm, diameter=26 mm) and heated for 5 min without pressure at 220°C, thereafter it was hot pressed at the same temperature for 1 min

under 50 MPa hydraulic pressure; then the composite was cooled with cold water to room temperature. Testing specimens in a disc shape were obtained.

2.3.2 Thermal analysis

The nonisothermal crystallization and melting behaviours of composites were analysed using a Perkin Elmer differential scanning calorimeter DSC-7 at scanning rates of 5, 20 and 100°C/min. The instrument was calibrated using indium and tin at all applied heating rates. Nitrogen was used as a furnace purge gas. DSC measurements had been calibrated for a sample mass of 3 mg. In all DSC experiments the sample mass was 3.00±0.03 mg. Flat samples were packed into aluminum sample pans to maximize thermal contact between the sample and calorimetric furnace. During the measurement, the sample was first held at 190°C for 5 min for deleting its thermal history. Then it was cooled to 0°C at a definite scanning rate to obtain an exotherm. After that the sample was held at 0°C for 5 min and then heated to 190°C at the same scanning rate to get an endotherm. Both melting and crystallization parameters were obtained from the exotherms and endotherms.

The degree of overall crystallinity of each sample is calculated using the relationship (Pasquini *et al.* 2008):

$$X_c(\% \text{ crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad , \quad (5)$$

where ΔH_m is the melting enthalpy, ΔH_m^0 is the melting enthalpy for a 100% crystalline PLA sample ($\Delta H_m^0 = 93$ J/g) (Fischer *et al.* 1973) or 100% crystalline LDPE sample ($\Delta H_m^0 = 293$ J/g) (Mathot 1994), and w is the weight fraction of PLA or LDPE in the composite.

No antioxidants were used because as it is known from (Bigg 2005) that for PLA no considerable oxidation occurs at temperatures lower than 200°C: thermal degradation mainly occurs due to the chain splitting and not hydrolysis (Migliaresi *et al.* 1991). LDPE itself is rather thermally stable at the used temperatures (Peacock 2000).

2.3.3 Polarized light microscopy with hot-stage

The polarized light microscopy (PLM) pictures of samples were obtained by the polarized light optical microscope Zeiss Axioskop-2 with total magnification of 100 × (10 × objective and 10 × eyepiece), equipped with a hot-stage Mettler FP 80. Test specimens for hot-stage microscopy were prepared by pressing the composite pellets between two cover glasses at 200°C, using a hot plate to produce a very thin composite film with an average thickness of 20 μm measured by the thickness meter Sony DZ521. Samples were first heated from 20 to 190°C at 20°C/min, held at this temperature during 5 min, and then cooled at the same rate to 25°C and heated again. Snapshots at different temperatures during the second heating were recorded.

3. RESULTS AND DISCUSSION

3.1 Rheological properties of composites

Rheological properties of LDPE/Cell and PLA/Cell composites are mostly presented in Paper I and rheological properties of PLA/CS composites in Paper III from the list of publications.

3.1.1 Composites based on LDPE matrix

This chapter studies the rheological behaviour of composites using dynamical amplitude and frequency sweep measurements.

First of all, the linear viscoelastic range characterized by the onset of the strain dependent behaviour for pure LDPE and its composites with cellulose, cellulose laurate and cellulose stearate was studied. As an example Figure 9 shows amplitude (strain) sweeps for pure LDPE and LDPE/Cell composites (published in Paper I). The dynamic modulus of the matrix polymer remains linear up to 10% of strain. Addition of the filler to LDPE slightly reduces the linear viscoelastic range. A decrease in storage modulus with percentage strain (Shenoy 1999) is an indicator of the occurrence of structural breakdown in the system. During a dynamic frequency sweep, it is best to maintain the strain as low as possible within the system constraints, in order to be in the linear viscoelastic region of the material (Shenoy 1999). Therefore, the strain of 5% was chosen as constant for the dynamic frequency sweeps of all composites samples. The same trend is observed for LDPE/CL and LDPE/CS composites.

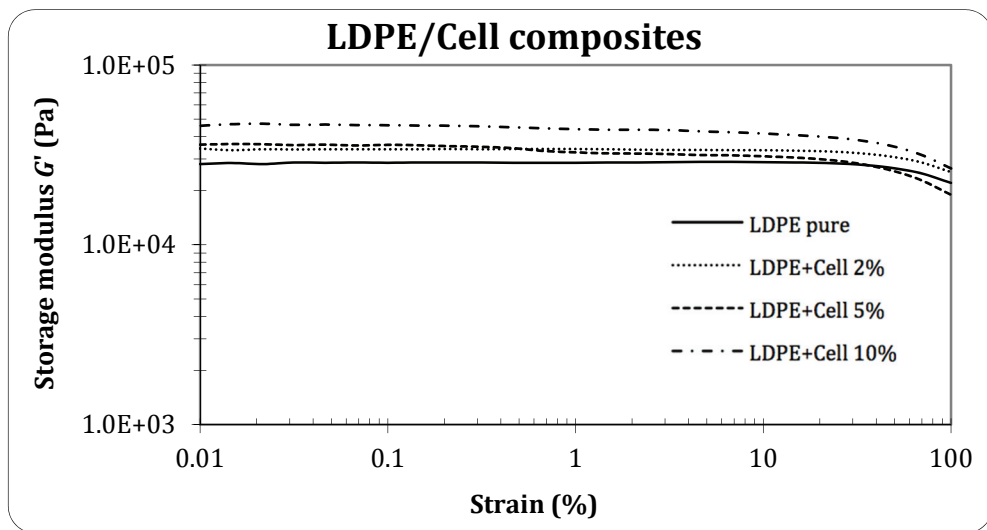


Figure 9. Determination of the LVE range for LDPE/Cellulose samples.

Angular frequency ω dependence of complex viscosity η^* , storage modulus G' and loss modulus G'' was measured in frequency sweeps in the range of $\omega = 0.05 \dots 500$ rad/s for LDPE composites.

Figures 10, 11, and 12 show complex viscosity curves for LDPE and its composites with Cell, CL and CS, respectively. As can be seen from the figures the Newtonian flow is hardly observed. All samples show shear thinning, which is a common feature of LDPE (Sdrobis *et al.* 2012).

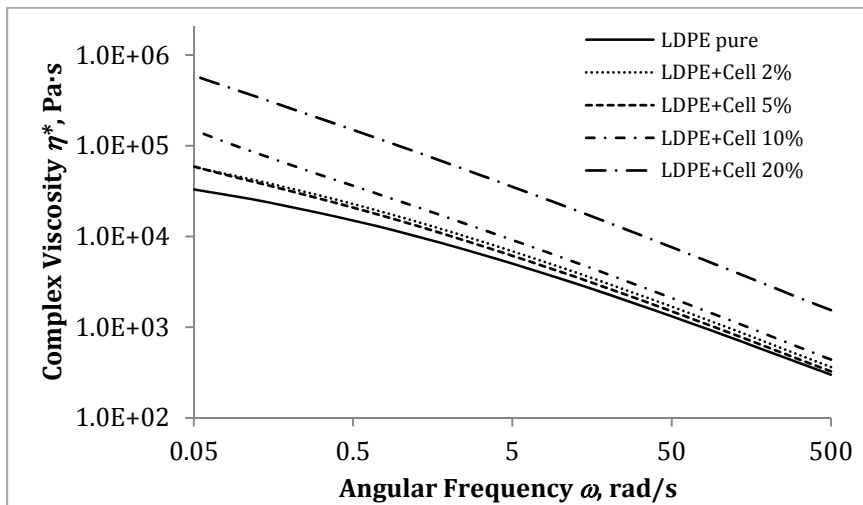


Figure 10. Complex viscosity η^* as a function of angular frequency ω for LDPE/Cellulose composites with different cellulosic content.

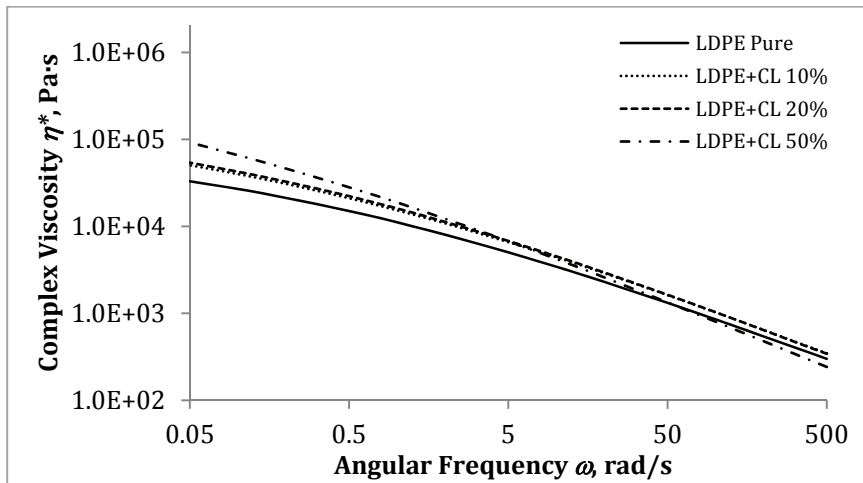


Figure 11. Complex viscosity η^* as a function of angular frequency ω for LDPE/Cellulose laurate composites with different CL content.

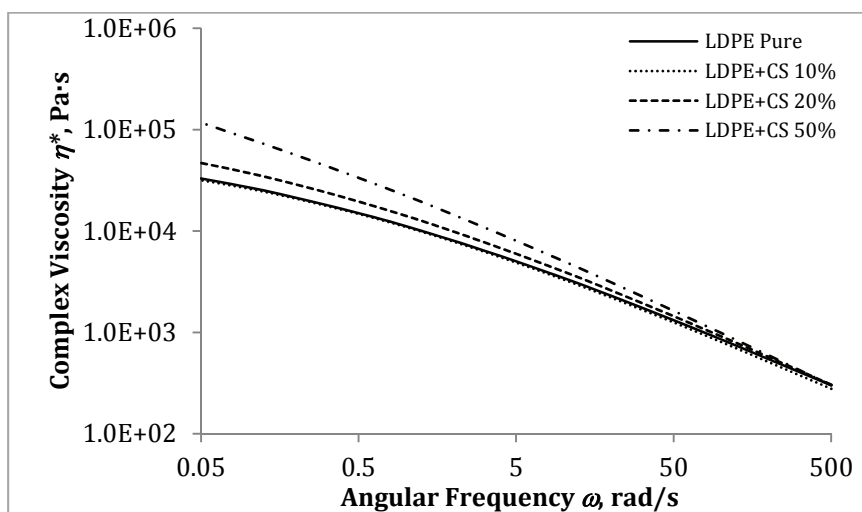


Figure 12. Complex viscosity η^* as a function of angular frequency ω for LDPE/Cellulose stearate composites with different CS content.

The complex viscosities of all LDPE composites compared to matrix LDPE at very low shear rates were significantly increased due to the presence of filler in the melt. The filler particles confine a part of the matrix material in their inter-particle voids and decrease the volume fraction of the matrix around, and that leads to a sharp increase in viscosity (Jahani 2010) at low ω . With ω increase, polymer and filler molecules will orient along the direction of flow and the viscosity values will decrease demonstrating shear thinning behaviour.

As it is known (Shenoy 1999), the increase of viscosity can depend on the filler content, particle size, particle size distribution and shape of the filler. The presence of filler particles perturbs normal polymer flow and hinders the mobility of chain segments. Therefore, as can be seen from Figures 10-12, the higher the amount of the filler, the higher is the viscosity of the filled polymer. Similar viscosity increases and shear thinning behaviour were obtained by other authors for LDPE composites with different inorganic fillers such as fly ash (Hashmi *et al.* 2007), glass beads (Liang and Li 1999), ceramics (Błaszczak *et al.* 2010), perlite (Sahraeian *et al.* 2012), ethylene-co-vinyl acetate/clay (Botta *et al.* 2009) and cellulosic fillers: spartium flour (Ikhlef *et al.* 2012), pineapple fibre (George *et al.* 1996) and hemp (Kakroodi *et al.* 2013).

One of the most important rheological parameters that can be obtained from viscosity curves is zero shear viscosity η_0^* . It is the value of the η_0^* of a liquid in the limit of zero shear rate (i.e., when the fluid is at rest). Zero shear viscosity represents the ability of the material to avoid sedimentation in storage. A high zero shear viscosity is interpreted as the potential homogeneity of the material during long storage.

The zero shear viscosity η_0^* , i.e. viscosity at $\omega=0$, cannot be directly calculated from the obtained curves in Figures 10, 11 and 12, therefore, η_0^* can be estimated by the value taken at the lowest ω , which is to be called apparent η_0^* . As an example, Figure 13 shows dependence of apparent zero shear viscosities of LDPE composites with different fillers. The general trend in η_0^* for all LDPE composites is an increase with the growth of filler content. However, this increase is strongly dependent on the filler type. For LDPE/Cell composites the increase of zero shear viscosity is higher than for LDPE cellulose ester composites that can be seen from the slope of the curve. It is known from literature (Shenoy 1999) that the increase in the level of complex viscosity would be more pronounced for rigid fillers than for flexible fillers because they resist deformation to a greater extent. As can be seen from Figure 13, at the same filler content of 10%, η_0^* of cellulose composites increases much strongly compared to cellulose esters composites: for cellulose the apparent η_0^* value is 76% higher than that of matrix LDPE, while for CL and CS it is around 10%.

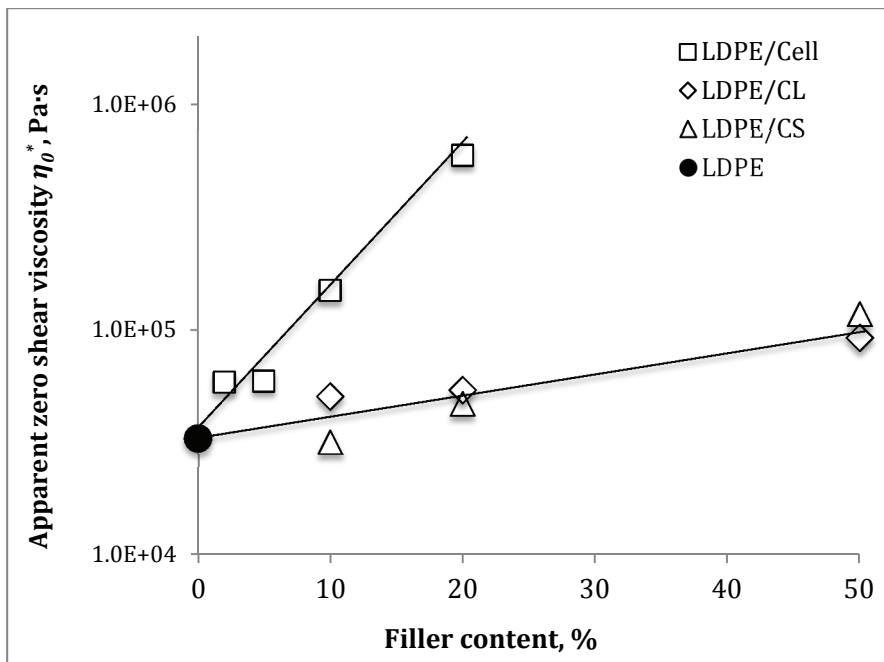


Figure 13. Dependence of apparent zero shear viscosities η_0^* of LDPE composites.

Figure 14 shows rheological behaviour of pure CL and CS. As can be seen, cellulose esters show viscoelastic behaviour in the measured ω range, but with a dominance of elastic modulus. CL has a more rigid structure than CS resulting in higher G' values. Therefore, flexibility and flowability of CS is higher compared to CL due to less rigid structure caused by longer fatty acid chains attached to cellulose. Dominance of elastic modulus over viscous modulus of cellulose esters can be attributed to the low degree

of substitution $DS=0.4$ for both fillers. Apparently, if DS were increased, cellulose esters would become more flexible, having better viscoelastic properties and composites with better flowability and viscoelastic properties identical to matrix LDPE could be obtained (Besson and Budtova 2012). Rheological behaviour of native cellulose was not studied because it was not possible to mould and form cellulose, probably due to its high stiffness and crystallinity. For the same reason, composites with 50-60% of native cellulose were not produced, in contrast to cellulose esters.

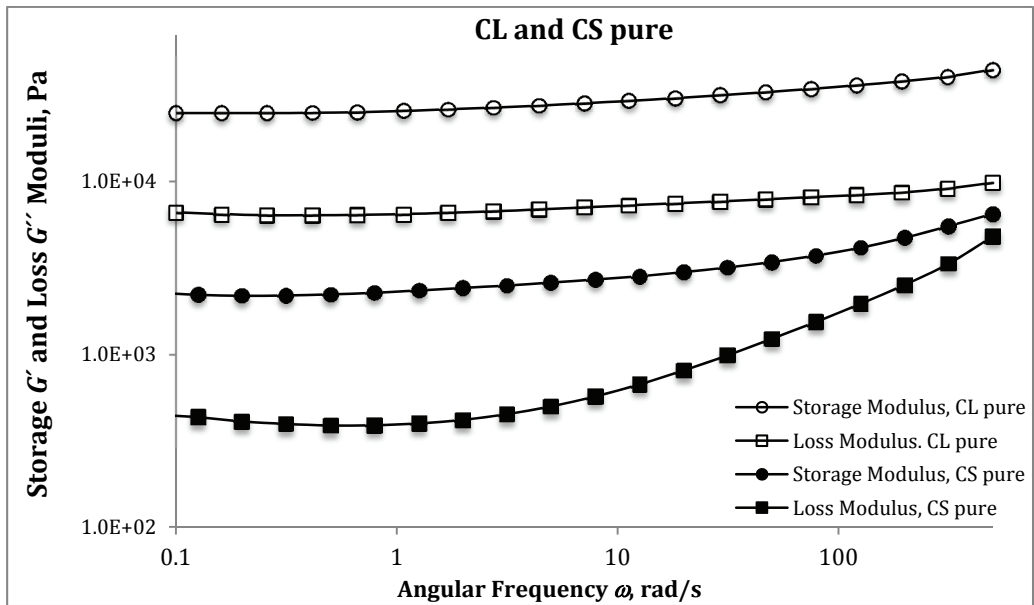


Figure 14. Frequency dependence of storage modulus G' and loss modulus G'' for pure CL and CS.

Consequently, as has been assumed, CL and CS are more flexible than native cellulose and show a less pronounced influence on viscosity of composites than rigid cellulose, which can be used in production of composites via improved processing conditions.

Dynamic frequency sweeps for LDPE/Cell (published in Paper I), LDPE/CL and LDPE/CS composites with 10% filler loading are shown, as an example, in Figure 15. Behaviour of LDPE composites with other filler contents is similar. At low angular frequencies ω composites show viscoelastic fluid behaviour where loss modulus is higher than the storage modulus ($G'' > G'$), however, with frequency increase storage modulus overrides loss modulus, indicating viscoelastic solid behaviour ($G' > G''$), which is a standard behaviour of LDPE (Sdrobis *et al.* 2012) and other thermoplastics. When comparing G' and G'' of LDPE/Cell with LDPE/cellulose esters, the highest values of dynamic moduli are observed for LDPE/Cell samples due to higher rigidity of cellulose.

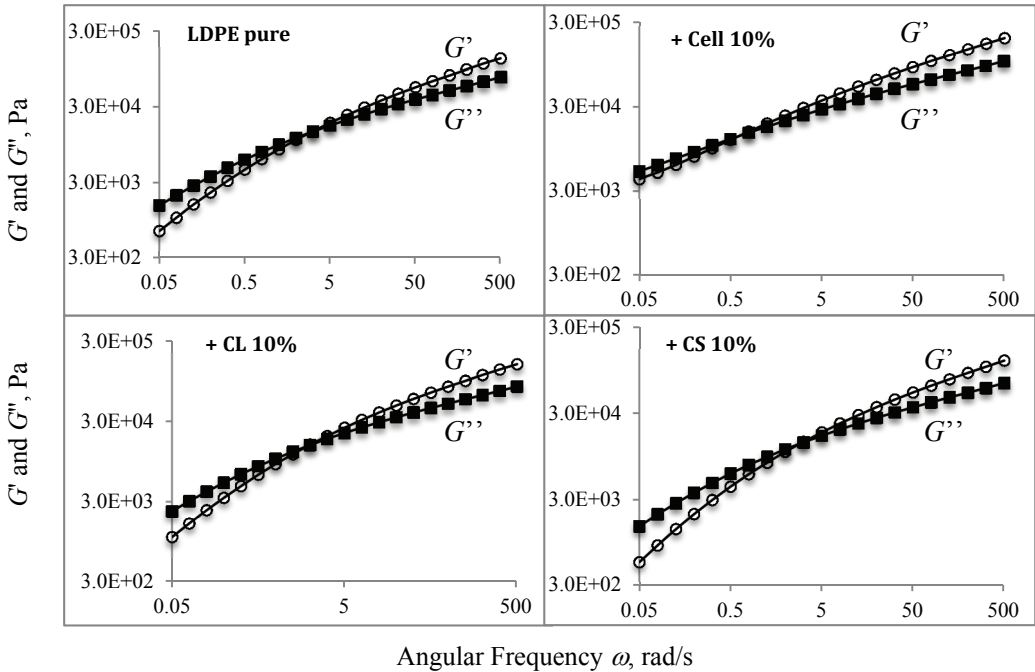


Figure 15. Frequency dependence of storage modulus G' and loss modulus G'' for pure LDPE, LDPE/Cell-10%, LDPE/CL-10% and LDPE/CS-10% composites.

It is known that the elastic properties of composites depend on energy storage mechanisms at the interphase and the relaxation time of the dispersed phase itself is often longer than the relaxation time of the polymer chains of the individual components (Han 2007). If taking a deeper look into the dynamic behaviour of LDPE composites, Figure 16, presenting storage moduli curves of LDPE composites, shows that addition of fillers increases storage moduli values. This can be attributed to the intrinsic rigidity of the fillers, as the storage moduli of composites are higher than pure matrix, especially for the highest filler content, indicating that stress transfers from the matrix to the fillers. This behaviour can be explained by the fact that filler particles restrict deformation of the LDPE matrix.

The enhancement observed in storage moduli is significantly higher at low ω than at high ω (see Figure 16A, B and C). The higher the filler content, the higher is the volume fraction and particle size of Cell and droplet size of CL and CS phase, and the higher is the G' at low ω . Consequently, the larger the filler content, the worse the dispersion of filler inside the matrix. At high ω the effect of filler decreases and the matrix contributions dominate.

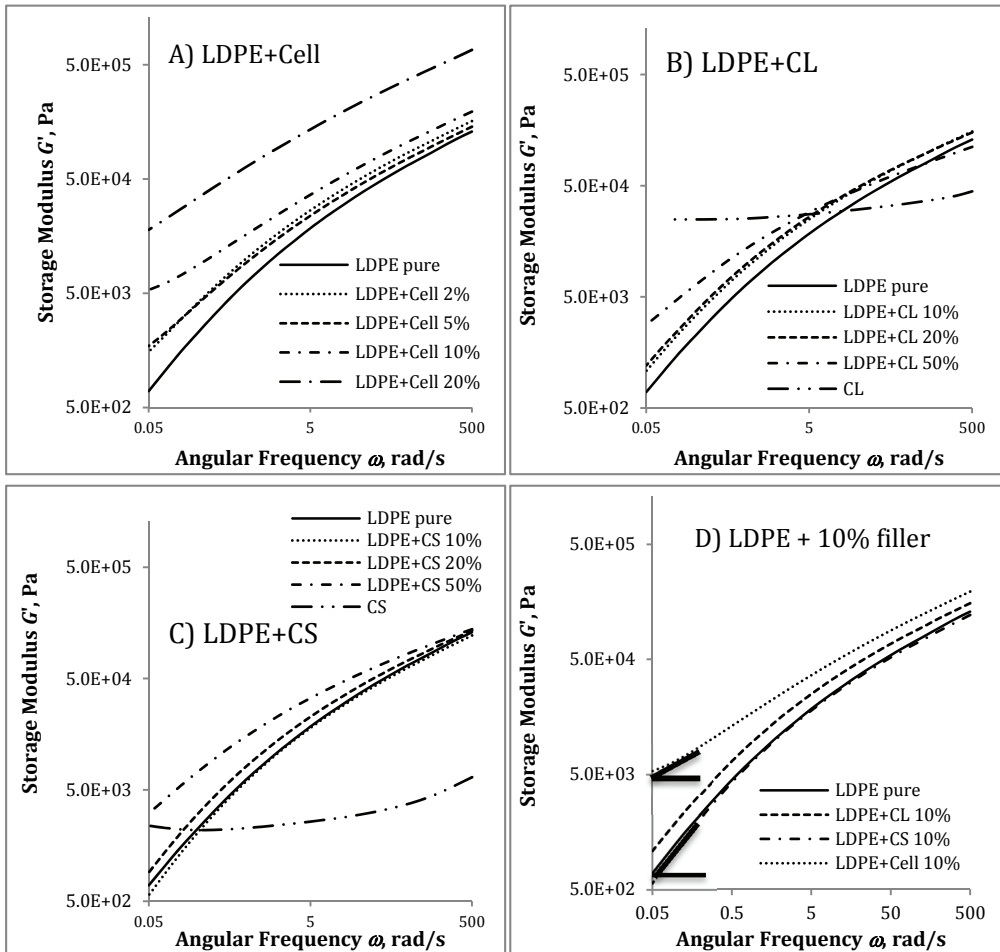


Figure 16. Frequency dependence of storage modulus G' for LDPE/Cellulose (A), LDPE/Cellulose laurate (B), LDPE/Cellulose stearate (C) and LDPE composites with 10% filler content (D).

Figure 16D shows the effect of filler nature on storage moduli curves for LDPE composites at fixed 10% filler content. The slope of LDPE/CL-10% and LDPE/CS-10% curves at low ω is approximately the same as for pure LDPE, indicating more or less good homogenization of CL and CS in LDPE matrix, probably due to better flexibility and flowability compared to native cellulose. The lower is the slope at low ω , the higher is the solid-like behaviour of the material (Han 2007). Furthermore, even at higher filler content of 20%, LDPE/CL and LDPE/CS composites still show the same slope as pure LDPE. On the other hand, LDPE/Cell-10% sample has significantly lower slope at low ω , which means that the dispersion of cellulose in the

composite material is not homogeneous, probably due to higher stiffness of cellulose structure compared to cellulose esters, and the filler not being aligned.

A similar effect can be seen in a PLM study that was used to investigate the morphology of the composites. As an example, PLM pictures of LDPE/Cell, LDPE/CL and LDPE/CS composites are presented in Figure 17.

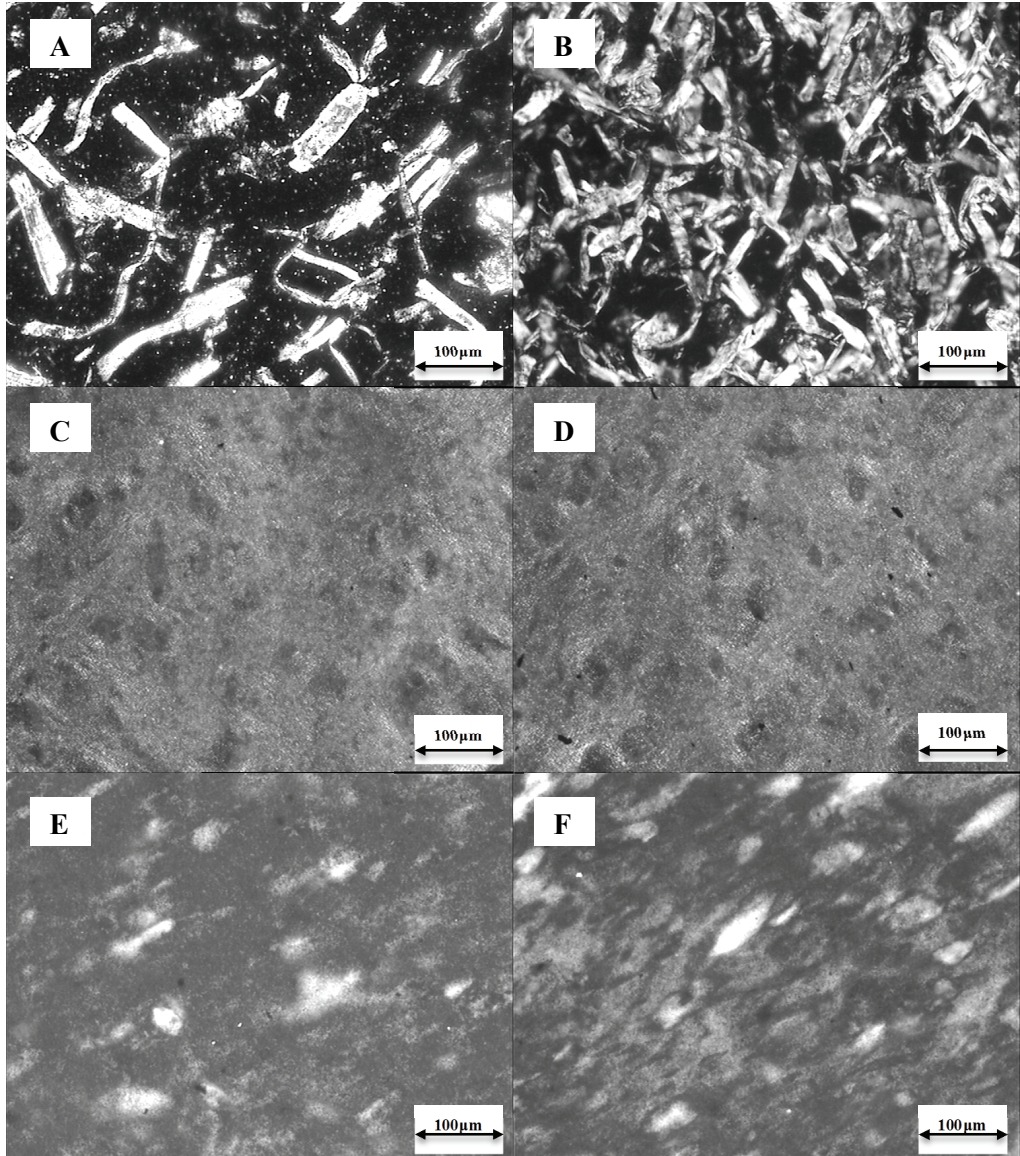


Figure 17. PLM pictures of LDPE composites taken at 25°C: A – LDPE/Cell-10%, B – LDPE/Cell-20%, C – LDPE/CL-10%, D – LDPE/CL-20%, E – LDPE/CS-10% and F – LDPE/CS-20%.

The dispersion of fillers in the composites is clearly noticeable from the obtained pictures. Even though two separate phases still exist in composites, there are large variations in cellulose particle size and its distribution, which are not observed for CL and CS. CL and CS are distributed as viscous droplets inside the matrix, while cellulose is spread as rigid particles.

One of the interesting parameters in rheology studies is frequency crossover point, where storage modulus G' is equal to loss modulus G'' , and it is associated with the inversion of the longest relaxation time. Figure 18 shows crossover points of angular frequency dependence on the filler content. By increasing the angular frequencies, the crossover point indicates a transition from a more fluid-like deformation to a solid-like elastic behaviour. The shift in crossover frequency represents the changes in molecular mobility and relaxation time behaviour (Liu *et al.* 2011). As seen in Figure 18, the crossover frequency of composites decreases at higher filler loadings. This is because the restriction in molecular mobility is more significant at higher filler content, which leads to lower crossover frequency and higher relaxation time (Jahani 2010). At the same filler content cellulose has lower crossover frequency compared to cellulose esters indicating earlier transition of the melt to solid-like behaviour. At the same time, the G' , G'' modulus of composites at crossover point (not presented in Figure 18) has shown a significant increase at higher filler content, which is attributed to increased elasticity of the melt. The higher the elasticity of the melt, the higher is the crossover modulus, which is evidenced by the melt solid-like behaviour (Jahani 2010).

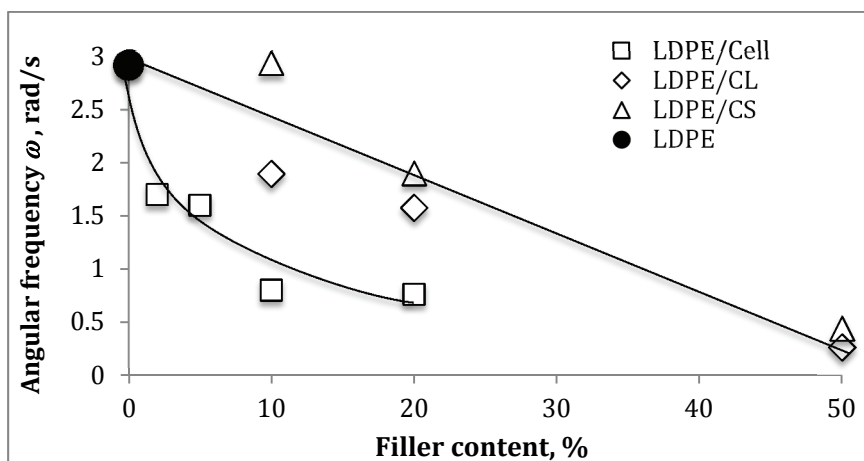


Figure 18. Crossover points angular frequency dependence on filler content.

3.1.2 Composites based on PLA matrix

In this work, PLA composites with rigid cellulose and flexible CS were studied. No studies on PLA/CL composites were performed, because based on LDPE/CL and LDPE/CS studies presented in Figures 13, 15, 16 and 18, LDPE composites with CL

and CS show similar behaviour. Therefore, it was decided to choose CS for the research with PLA matrix due to its being more flexible filler than CL according to Figure 14.

As well as for LDPE composites, the LVE range of PLA and its composites was determined (published in Paper I). As an example, figure 19 illustrates the LVE range of PLA/cellulose samples, which was obtained from amplitude sweep tests. The same tendency was observed with PLA/CS composites. The dynamic modulus of the matrix polymer remains linear up to 10% of strain. It is clear that with the addition of cellulose into the matrix, the non-linearity zone shifts to lower strain in comparison with the matrix polymer. Therefore, as with LDPE samples, the strain value of 5% was chosen for the dynamic frequency sweeps of all composites samples.

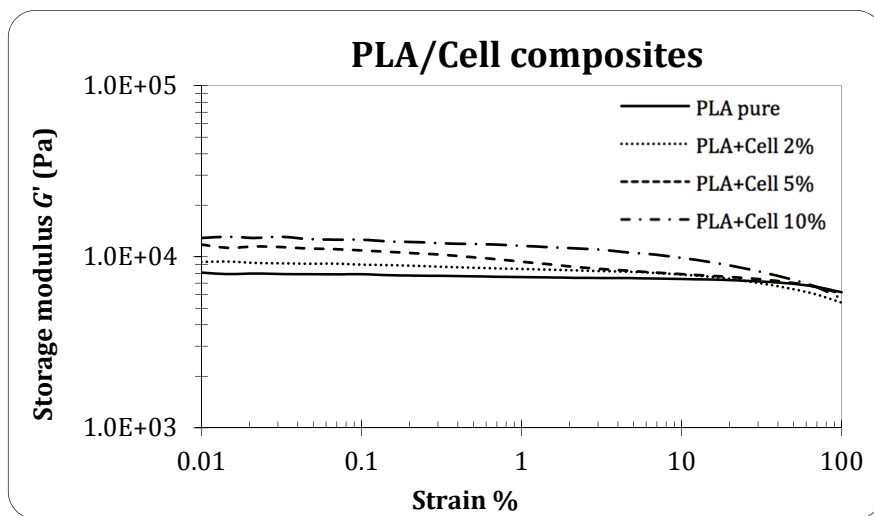


Figure 19. Determination of the LVE range for PLA/cellulose samples.

In order to determine the angular frequency dependence of the complex viscosity η^* , storage modulus G' and loss modulus G'' , dynamic frequency sweeps were performed in the range of $\omega = 0.5 \dots 500$ rad/s for PLA composites.

Figures 20 and 21 demonstrate viscosity dependences on angular frequency for PLA and its composites. All composites show shear thinning behaviour, which arises from the stretching of an “entangled” state of polymer chains to an “oriented” state when the applied shear rate is higher than a certain critical value (Gupta 2000).

Contrary to LDPE, matrix PLA shows a Newtonian flow at angular frequencies ω lower than 10 rad/s as can be seen in Figure 20. Addition of a small amount (2-10%) of native cellulose to the matrix polymer reduced the Newtonian flow region down to 5

rad/s. Behind these values dynamic viscosity decreases showing shear thinning behaviour.

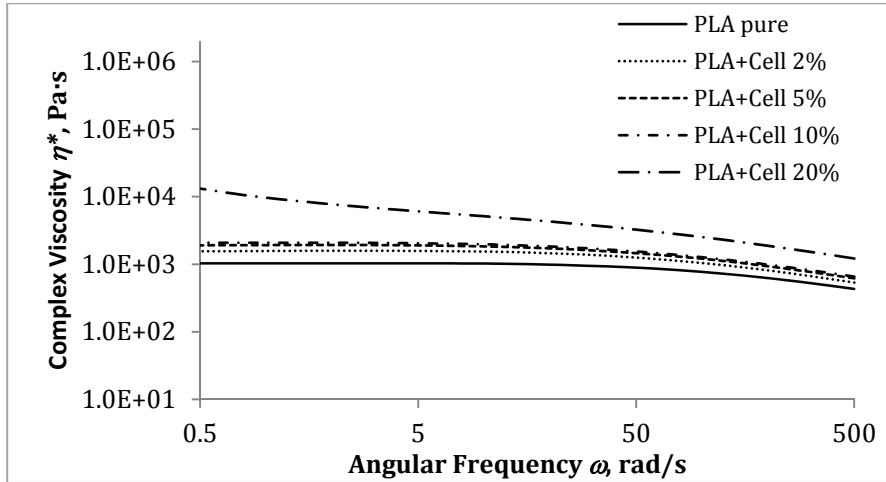


Figure 20. Dynamic viscosity η^* as a function of angular frequency ω for PLA/Cell composites with different content of cellulose.

Figure 21 shows viscosity curves for PLA and its composites with cellulose stearate (published in Paper III). Addition of CS exhibits Newtonian flow in the region of up to 20% filler content. The same behaviour was revealed for PLA composites with chemically modified plasticized starch with filler content up to 20%. Taking into account that plasticized starch and CS are flexible by their nature (Shin *et al.* 2007) while cellulose is rigid, it can be suggested that PLA composites with rigid and flexible fillers have similar frequency dependence of viscosity at filler contents less than 20%. However, at higher CS loadings no Newtonian flow is observed for PLA/CS composites and only shear thinning behaviour is present throughout the measured ω range.

In comparison with pure PLA, PLA/CS composites have higher melt viscosity η^* at low ω , where the contribution of CS phase becomes apparent. With growing CS loading, the behaviour of PLA/CS composites is becoming similar to pure CS. Behaviour of PLA/CS-20% sample is an intermediate between behaviours of pure PLA and pure CS. At higher CS contents of 50-60%, viscosity curves of PLA/CS-50% and PLA/CS-60% composites show identical behaviour to pure CS with viscosity approximately one order of magnitude higher than that of pure CS. At high ω , viscosity of PLA/CS composites equalizes with pure PLA.

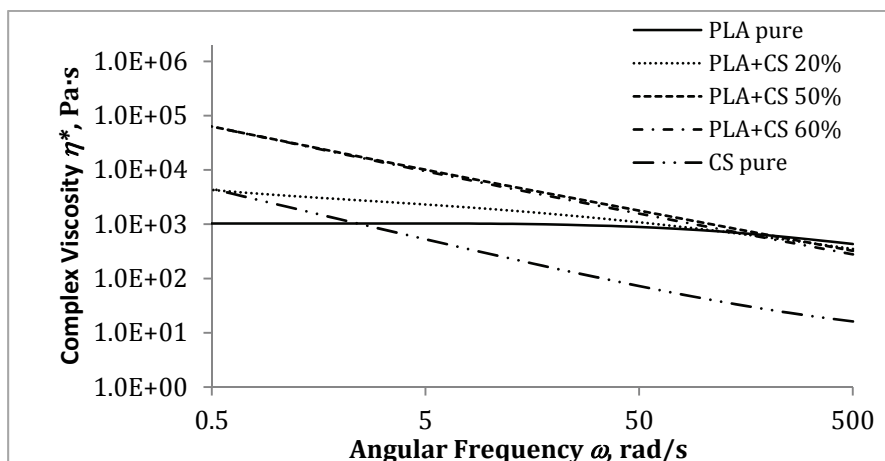


Figure 21. Dynamic viscosity η^* as a function of angular frequency ω for PLA/CS composites with different cellulose stearate contents.

Figure 22 shows dependence of apparent zero shear viscosities η_0^* of PLA composites. Viscosity dependence on the filler content follows LDPE trends: the higher the filler content in composites, the higher are the values of melt viscosity η^* , which can be attributed to perturbation of normal polymer flow as was explained for LDPE composites (see page 30). However, in contrast to LDPE composites, filler nature has no effect on viscosity and as can be seen from the figure 22, with increasing filler content rigid Cell and flexible CS show similar increase in apparent η_0^* . Similar increase in viscosity caused by filler nature was obtained for other PLA composites with flexible triticale straw (Mihai and Ton-That 2013) and rigid microcrystalline cellulose (Kim *et al.* 2013). Obviously, this behaviour is typical for PLA composites with rigid as well as with flexible fillers.

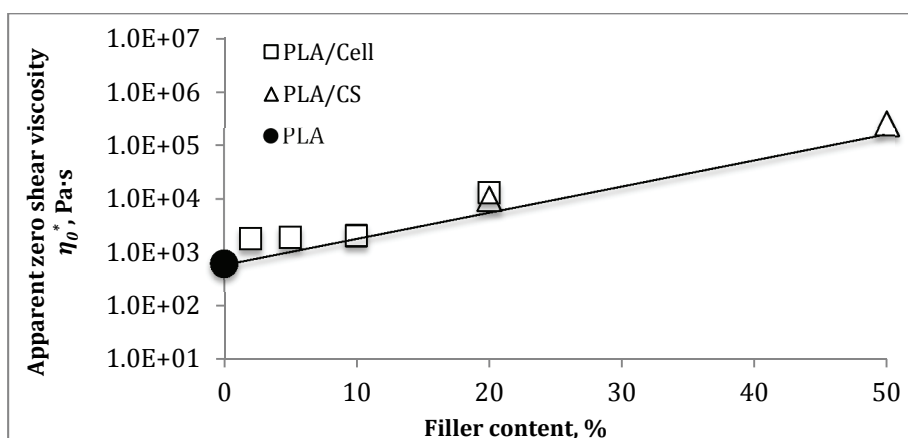
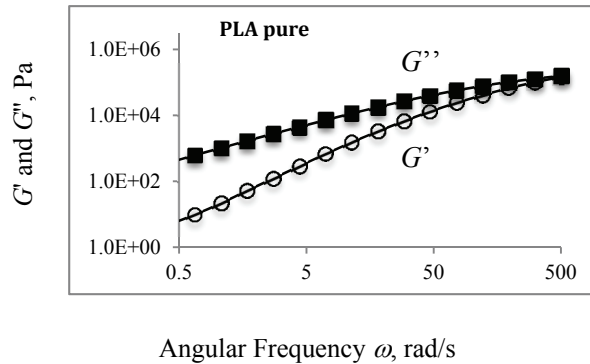


Figure 22. Dependence of apparent zero shear viscosities η_0^* of PLA composites.

Loss and storage moduli curves of PLA/Cell (published in Paper I) and PLA/CS composites (published in Paper III) can be seen in Figure 23. Matrix PLA shows viscoelastic behaviour and addition of cellulose has a minor effect on the shape of storage/loss moduli curves, as these are similar to pure PLA. PLA/CS composites at low filler content of 20% show similar behaviour to pure PLA and PLA/Cell-20% sample.

(A) Frequency dependence of storage modulus G' and loss modulus G'' for PLA



(B) Frequency dependence of storage modulus G' and loss modulus G'' for PLA/Cellulose composites

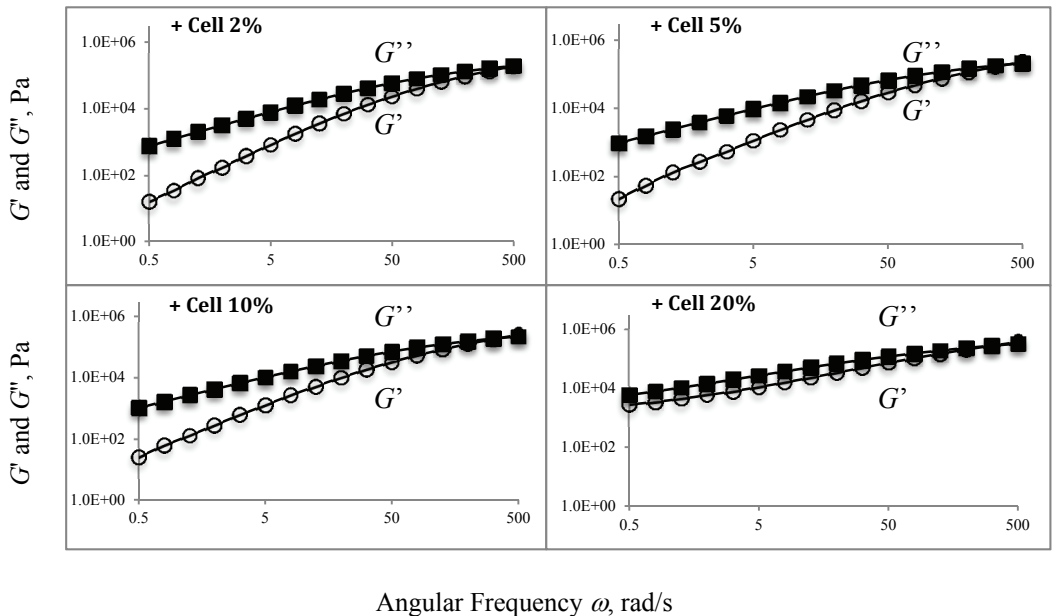


Figure 23 (A, B). Frequency dependence of storage modulus G' and loss modulus G'' for PLA (A), PLA/Cellulose (B) composites.

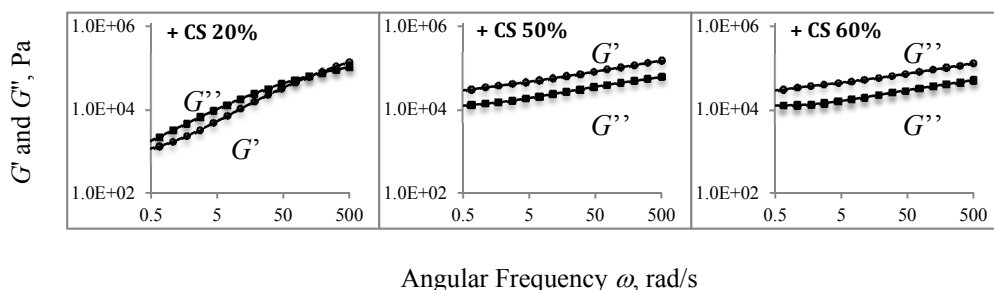


Figure 23 (C). Frequency dependence of storage modulus G' and loss modulus G'' PLA/Cellulose stearate (C) composites.

However, when CS content in PLA composites becomes higher than 20%, behaviour of dynamic moduli curves is becoming similar to pure CS, where elastic component dominates throughout the measured angular frequency range. Therefore, based on G' and G'' data serving as the measure of molecular rigidity, it can be concluded that when CS content is higher than 20% composites become much more rigid than matrix PLA.

Figures 24A and 24B show storage moduli curves of PLA composites with Cell and CS at various filler loadings. As it can be seen from figures the storage moduli of composites are higher than that of pure PLA, which has also been reported in the literature for PLA composites with clay (Ahmed *et al.* 2010), talc (Jain *et al.* 2012), layered silicate (Ray and Okamoto 2003), nanographite (Narimissa *et al.* 2014), lignin and microcrystalline cellulose (Kim *et al.* 2013). This behaviour can be explained by the fact that filler particles restrict deformation in the same manner as it was explained for LDPE (see page 33). As can be seen in Figure 24A, addition of cellulose up to 10% does not change the slope of the PLA curve indicating good homogenization with the matrix PLA. On the other hand, at 20% filler loading the slope of the modulus curve decreases as observed also for PLA/CS-20% sample (see Figure 24B) indicating worse dispersion of filler inside matrix. With further filler loading as can be seen for PLA/CS composites, dispersion deteriorates as the slope of G' for PLA/CS-50% and PLA/CS-60% curves follows pure CS trend. Filler content influences viscosity and storage modulus values in a similar manner resulting in an increase in these values. By comparing LDPE composites with PLA composites, similar trend in G' with growing filler loadings is observed.

The effect of nature of the added filler type can be clearly seen in Figure 24C, where PLA composites with 20% filler content are shown. Both PLA/Cell and PLA/CS samples are having a similar slope, which can be attributed to identical dispersion of fillers in PLA. However, the opposite trend was obtained from storage moduli curves of LDPE composites at the same filler content. By comparing the behaviour of LDPE and PLA composites, it can be concluded that CS is more compatible with the matrix LDPE than with PLA.

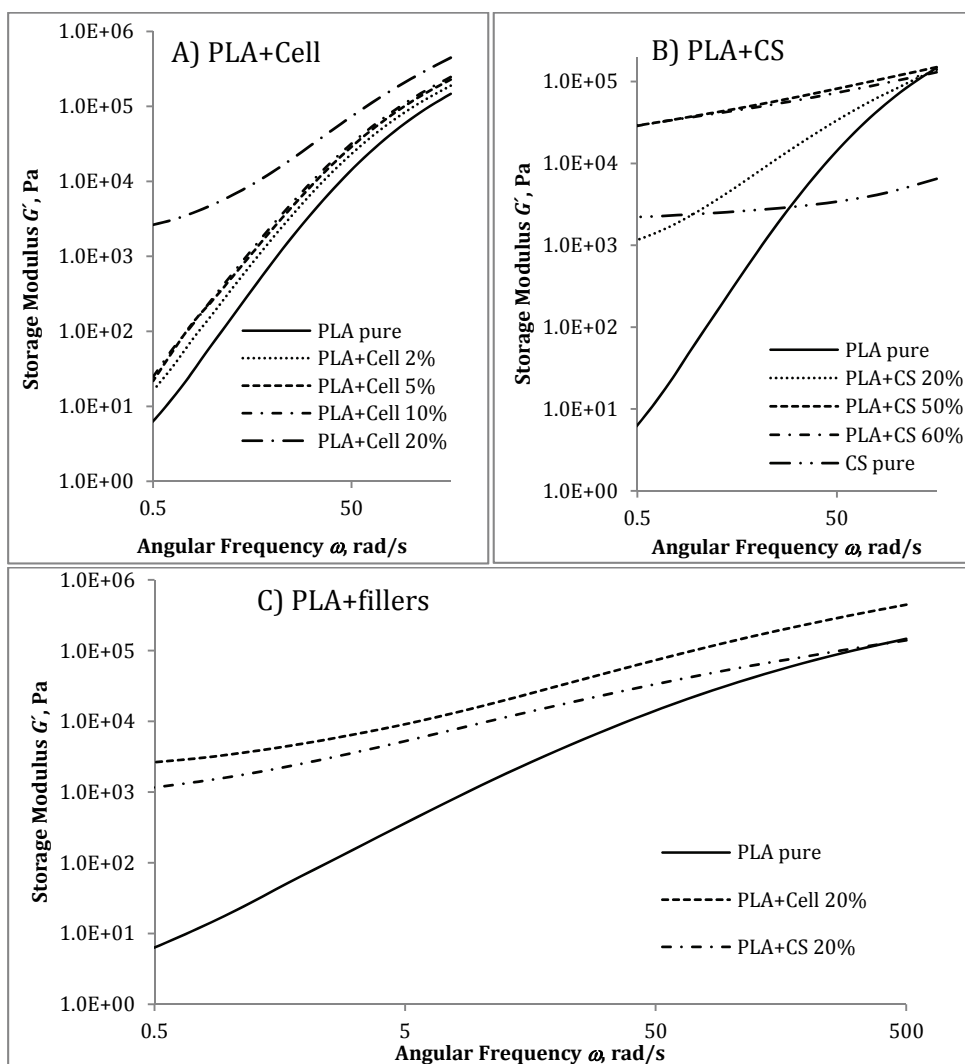


Figure 24. Frequency dependence of storage modulus G' for PLA/Cellulose (A), PLA/Cellulose stearate (B) and PLA composites with 20% filler content (C).

Frequency crossover points of PLA composites are presented in Table 2. Considering composites based on native cellulose, crossover frequency point of loss and storage modulus of PLA/Cell composites decreases with the filler content growth due to the restriction in molecular mobility, and crossover modulus increases at higher filler loadings attributed to the increased elasticity of the melt. By comparing crossover frequency and crossover modulus changes with increasing filler content in LDPE composites (see Figure 18 and details on page 36), identical trends in both properties can be seen.

It is difficult to analyse crossover frequency trends of PLA/CS composites due to a lack of a series of crossover points. Crossover frequency of PLA/CS-20% sample is lower than that of pure PLA, which indicates an earlier change from liquid-like to solid-like behaviour of the melt. Furthermore, at 50% or higher CS content – there is no crossover frequency for these composites due to elastic component domination at the measured angular frequency range. This confirms that CS is less compatible with the PLA matrix than with LDPE, where all LDPE/CS composites have shown similar viscoelastic behaviour to LDPE.

Table 2. Crossover points of Loss and Storage moduli for PLA/cellulose and PLA/CS composites.

Sample	Content, wt%	ω (rad/s)	$G'=G''$ (kPa)
PLA	0	428	174
PLA/Cell 2%	2	395	180
PLA/Cell 5%	5	374	192
PLA/Cell 10%	10	362	196
PLA/Cell 20%	20	308	275
PLA/CS 20%	20	230	72
PLA/CS 50%	50	-	-
PLA/CS 60%	60	-	-

3.2 Thermal properties of composites

Thermal properties of LDPE/Cell and PLA/Cell composites are mostly presented in Paper II and thermal properties of PLA/CS composites in Paper III from the list of publications.

3.2.1 Composites based on LDPE matrix

This chapter explains thermal behaviour of composites under non-isothermal crystallization and melting conditions using DSC technique.

Non-isothermal exo- and endotherms of LDPE and its composites with cellulose (published in Paper II) and cellulose esters (CL and CS) are demonstrated in Figures 25, 26 and 27. The most important values obtained from DSC curves are listed in Table 3. LDPE is characterized by the presence of two crystallization peaks at 61-62°C and 98°C (designated by C in Figure 25) whereas the endotherm has only one broad melting peak at 111°C (designated by M in Figure 25). However, such thermal behaviour is usual for LDPE materials (Mathot 1994).

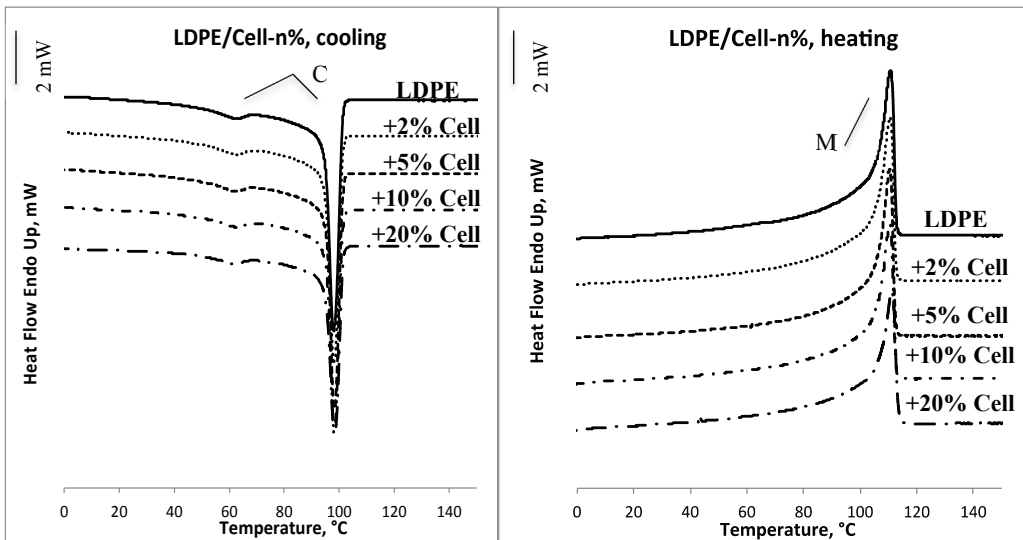


Figure 25. DSC exotherms (left) and endotherms (right) of LDPE and its composites with cellulose: 2nd heating, heating rate of 20°C/min.

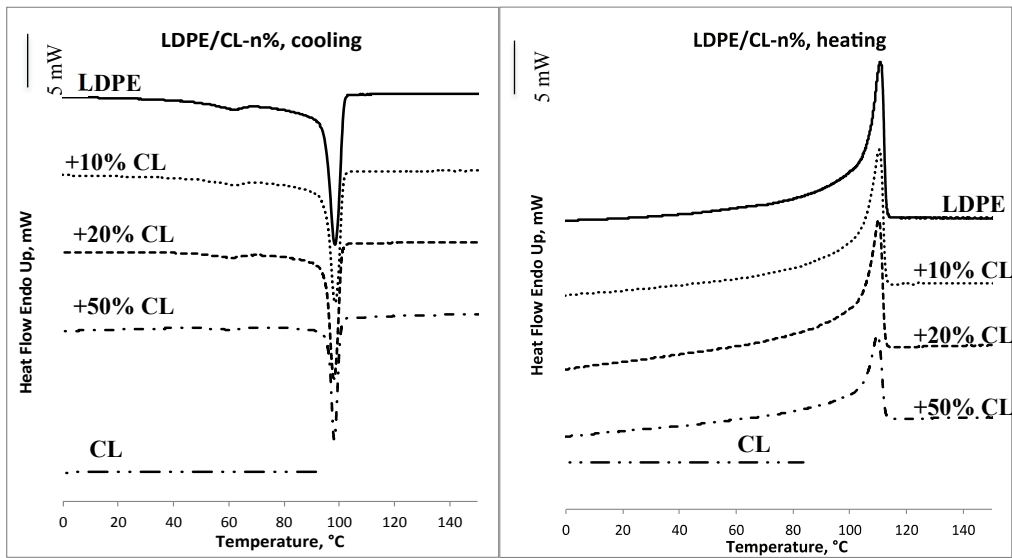


Figure 26. DSC exotherms (left) and endotherms (right) of LDPE and its composites with cellulose laurate: 2nd heating, heating rate of 20°C/min.

Considering the behaviour of LDPE composites with cellulose and cellulose laurate it was established, that addition of cellulose and CL does not affect any crystallization and melting temperatures regardless of filler contents, as has also been seen in the literature for LDPE composites with other fillers: boehmite alumina (Khumalo *et al.*

2010), sisal cellulosic fibres (Luyt and Ahmad 2012), henequen cellulosic fibres (Herrera-Franco and Aguilar-Vega 1998) and various cellulose esters (Freire *et al.* 2008). As it is known, the melting point of a semicrystalline polymer is determined by the size and perfection of its crystals, i.e. by the lamellar thickness (see eq. 4) (Mathot 1994). Taken into account that melting temperatures of LDPE and its composites with cellulose and CL do not change with increasing filler content it can be suggested that size of LDPE crystallites keeps the same value.

Melting enthalpies ΔH_m defined by the area under the melting peak and the degree of crystallinity X_c were studied for LDPE/Cell and LDPE/CL composites. It was found that both ΔH_m and X_c were affected by the presence of the filler. For all systems, ΔH_m decreases as the filler content in the composite increases, as expected, because of the decrease of the matrix material in the composites. However, degree of crystallinity, calculated by eq. (5) and accounted for the effective matrix amount in the composites (Pasquini *et al.* 2008), decreases with higher filler loading for LDPE/Cell composites from 42% for pure LDPE to lowest 35% for LDPE/Cell-20% and to lowest 29% for LDPE/CL-50% composite. Probably, cellulose and CL hinder the migration and diffusion of LDPE chains resulting in a weaker crystallization process compared to neat LDPE, which has been observed in composites with other fillers such as kenaf cellulose (Tajeddin *et al.* 2009), sisal fibre (Luyt and Malunka 2005) and cellulose acetate phthalate (Sailaja and Seetharamu 2009).

More pronounced and interesting thermal behaviour is observed when CS is added to the matrix polymer. CS itself crystallizes as presented in the Figure 27. Its crystallization can be attributed to the so-named side chain crystallization, when a fraction of the alkyl (long fatty acid) chains of CS is able to crystallize (Sealey *et al.* 1996). As the structure of CS side-chains is chemically identical to LDPE chains, co-crystallization of LDPE with CS can be expected. It is also possible that CL could show side chain crystallization, but due to shorter side chain lengths compared to CS, and relatively high scanning rate, such as 20°C/min, used in this work, crystallization and melting behaviour of CL is hardly observed. Pure CS has a melting peak at 40°C and crystallization peak at 34°C. For the composite with 10% of CS, the peak related to CS crystallites is hardly observed, probably due to the low content of CS in the composite and the much higher crystallization enthalpies of LDPE compared with CS. However, at CS content higher than 10%, namely 20% and 50%, the contribution of CS crystallites into the overall crystallization/melting process of the composites, becomes evident and crystallization/melting peaks of CS can be detected in the thermograms.

To find out whether the observed melting peaks correspond to completely separated crystallites of LDPE and CS, which formed independently, the melting enthalpies of LDPE and CS peaks were compared with the predicted value in the composites, as if both components had crystallized independently. For example, for 50% of added CS, the overall predicted melting enthalpy ($\Delta H_m = 80$ J/g) of both peaks is higher than the

measured melting enthalpy ($\Delta H_m = 70$ J/g) obtained from the LDPE/CS-50% sample melting curve. Lower measured melting enthalpy of the composites compared to the predicted value has been taken from other sources (Morgan *et al.* 1999), (Poltimäe *et al.* 2011) as an argument in favour of co-crystallization (Tashiro *et al.* 1995). The observed melting behaviour of the LDPE/CS-50% composite therefore suggests that co-crystallization to some limited extent is present in the LDPE/CS composites.

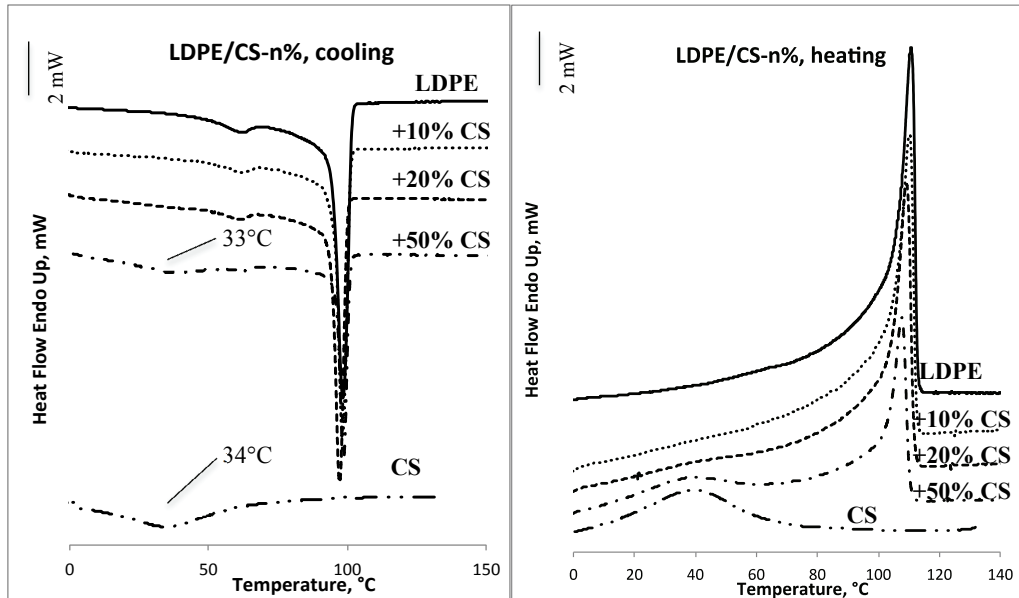


Figure 27. DSC exotherms (left) and endotherms (right) of LDPE and its composites with cellulose stearate: 2nd heating, heating rate of 20°C/min.

Degree of crystallinity of LDPE/CS composites increases with the growing filler content till the maximum value of 48% for LDPE/CS-50% composite. Visually, the height of the peak related to LDPE in the composites decreases with the growing CS content, however, overall crystallinity related to the area under the peak (see eq. 5) increases. This can be explained by the so-named “compensation effect”: reduction of LDPE crystallinity is compensated for the increase in CS crystallinity and co-crystallization of LDPE with CS.

The effect of the filler nature on melting of LDPE composites can be analysed from Table 3. At a fixed filler content, addition of Cell and CL reduces the degree of crystallinity of LDPE, however, CS increases these values. Therefore, it can be also concluded that Cell and CL do not facilitate crystallization of LDPE, unlike CS.

Table 3. Calorimetry data for LDPE composites

Sample	Content	T_m , °C	T_c , °C	X_c , %
LDPE	100	111	98 and 62	42
LDPE/Cell	2	111	98 and 62	41
	5	111	98 and 62	40
	10	111	98 and 62	38
	20	111	98 and 62	35
LDPE/CL	10	111	98 and 62	38
	20	111	98 and 62	33
	50	111	98 and 62	29
LDPE/CS	10	111	98 and 62	42
	20	41 (CS) 111	97, 62 and 33 (CS)	44
	50	41 (CS) 111	97, 62 and 33 (CS)	48
CS	100	40	34	-

3.2.2 Composites based on PLA matrix

The nonisothermal crystallization and melting behaviour of PLA and its composites were also investigated. The nonisothermal endothermic thermograms of the second heating scan at various scanning rates of pure PLA are shown in Figure 28. The inset of this figure presents exotherms of PLA at the same scanning rates.

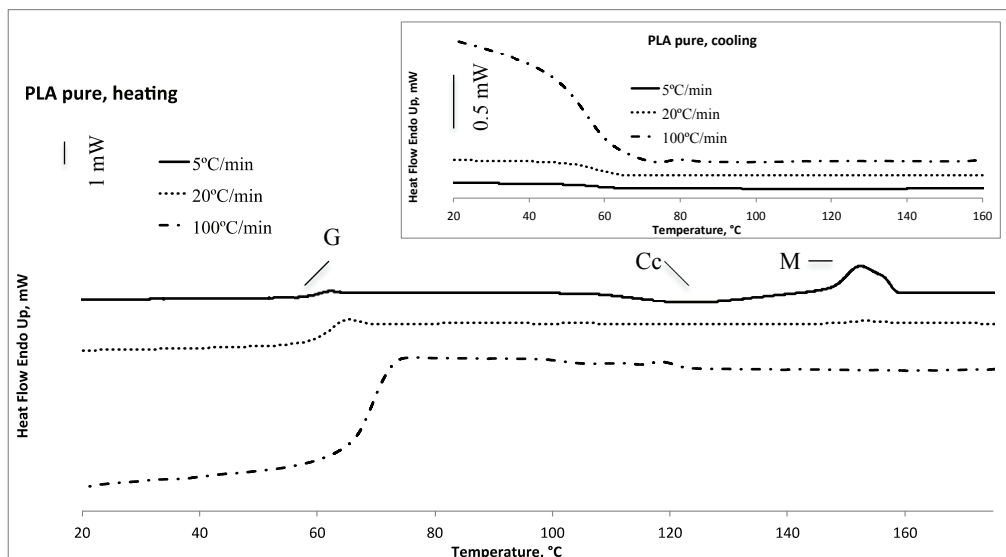


Figure 28. DSC melting/cooling curves of PLA at different scanning rates: 5, 20, 100°C/min.

Pure PLA is characterized by glass transition temperature T_g at 58.0°C, cold crystallization peak T_{cc} at 134°C and melting peak T_{mc} at 152°C. Cold crystallization T_{cc} of PLA (designated by Cc) is noticeable at low heating rate of 5°C/min and this effect is significantly diminished with increased heating rate. Under this fast heating conditions, the amorphous PLA chains do not have enough time to self-adjust well, resulting in reduced cold crystallization (Fortunati *et al.* 2012). In addition, with increasing the heating rate, the T_{cc} shifts gradually to higher temperatures due to the thermal activation while with heating rates above 5°C/min, both the cold crystallization and melting peaks (designated by M) weaken significantly and are hard to be observed as has been previously reported in the literature (Fortunati *et al.* 2012). As expected, with increased scanning rate the relaxation time becomes shorter and therefore the glass transition region (designated by G) is shifted to a higher temperature. On the cooling curves only glass transition temperatures (T_g) appeared.

Figure 29 shows the typical non-isothermal DSC thermograms of PLA composites with cellulose, recorded at cooling/heating rate 20°C/min (published in Paper II). Cold crystallization and melting peaks for pure PLA are hardly observed. As can be seen from the melting curves, all PLA/Cell composites cold crystallization peaks (T_{cc}), being located at 129-134°C (designated by Cc in Figure 29) and subsequent melting peaks (T_{mc}) at 152-153°C (designated by M in Figure 29), are clearly observed even at a scanning rate of 20°C/min. Detailed data of DSC studies is presented in Table 4. However, it should be noted here that matrix PLA and PLA/Cellulose composites are assumed to be amorphous since the cold crystallization enthalpy ΔH_{cc} and the following melting enthalpy ΔH_{mc} values are almost the same and no crystallization peaks are observed in cooling curves.

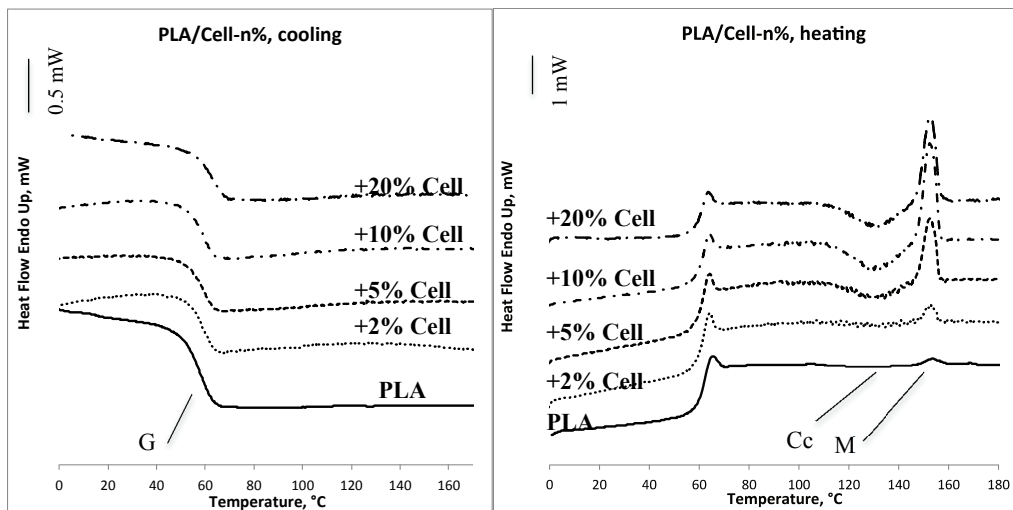


Figure 29. DSC exotherms (left) and endotherms (right) of PLA and PLA/Cell composite materials: 2nd heating, heating rate of 20°C/min.

Cold crystallization peaks indicate regions of realignment and transition from amorphous to crystalline phases. As an example, figure 30 shows an evolution of cold crystallinity in PLA/Cell-5% composite observed by PLM (published in Paper II). Temperatures of 25°C, 135°C and 155°C were chosen for snapshots. During a non-isothermal melting process it was observed that the amount of crystallites increased in the range of 130-140°C and a snapshot of this effect was taken at 135°C. Finally, the formed crystals melt at 155°C.

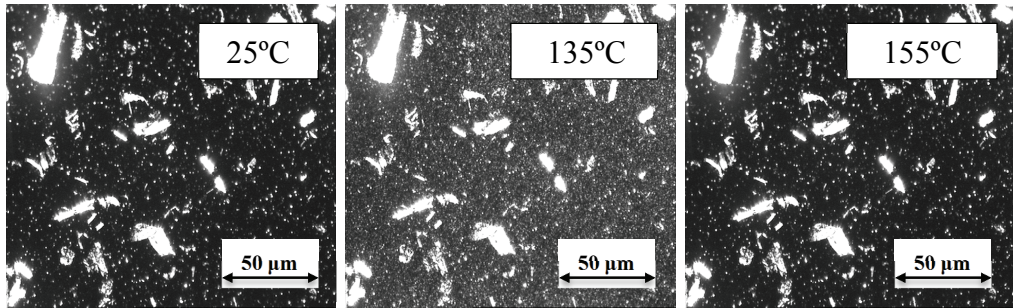


Figure 30. PLM pictures of PLA/Cellulose-5% snapped at temperatures 25°C, $T_{cc} \cong 135^\circ\text{C}$ and 155°C during heating at 20°C/min.

From DSC data of PLA/Cellulose composites it was found out that T_{cc} decreases with the cellulose content from 134°C for pure PLA down to 127°C for PLA/Cellulose-50%. At the same time, the values of ΔH_{mc} and ΔH_{cc} of PLA/CELL samples increased with cellulose content. This behaviour indicates cellulose inducing crystal nucleation of PLA (Liu *et al.* 2010). Cellulose appeared to facilitate nucleation and subsequent crystallization of PLA rather effectively in the amorphous composites (Anuar and Zuraida 2011).

Interesting and dissimilar to PLA/Cell composites behaviour was observed from DSC curves of PLA/CS composites shown in Figure 31 (published in Paper III). PLA/CS composites have cold crystallization peaks (T_{cc}) located at 124-134°C and subsequent melting peaks (T_{mc}) at 152-153°C, glass transition temperatures at 58°C, other DCS data is presented in Table 4.

Table 4. Calorimetry data for PLA composites

Sample	Content	T_{mc} , °C	T_{cc} , °C	T_m , °C	T_c , °C	T_g , °C
PLA	100	152	134	-	-	58
PLA/Cell	2	152	134	-	-	58
	5	152	132	-	-	58
	10	153	130	-	-	58
	20	153	129	-	-	58
PLA/CS	10	151	124	32	32	58
	20	152	128	35	33	58
	50	153	134	36	33	58
	60	153	134	38	34	58
CS	100	-	-	40	34	-

CS shows the highest crystallization ability at lowest loadings (PLA/CS-10%) due to better homogenization of the matrix and filler phases. Melting enthalpies of PLA in composites with increasing CS content decrease proportionally to the weight fraction of the added CS, and melting enthalpies of peaks related to CS, respectively, increase. As can be seen from Figure 31, the higher is CS content the higher are crystallization and melting enthalpies of CS in composites. CS crystallization peak grows gradually and already at equal PLA and CS contents in composite, the crystallization peak of CS crosses over the glass transition region of PLA and also cold crystallization of PLA is hardly observed.

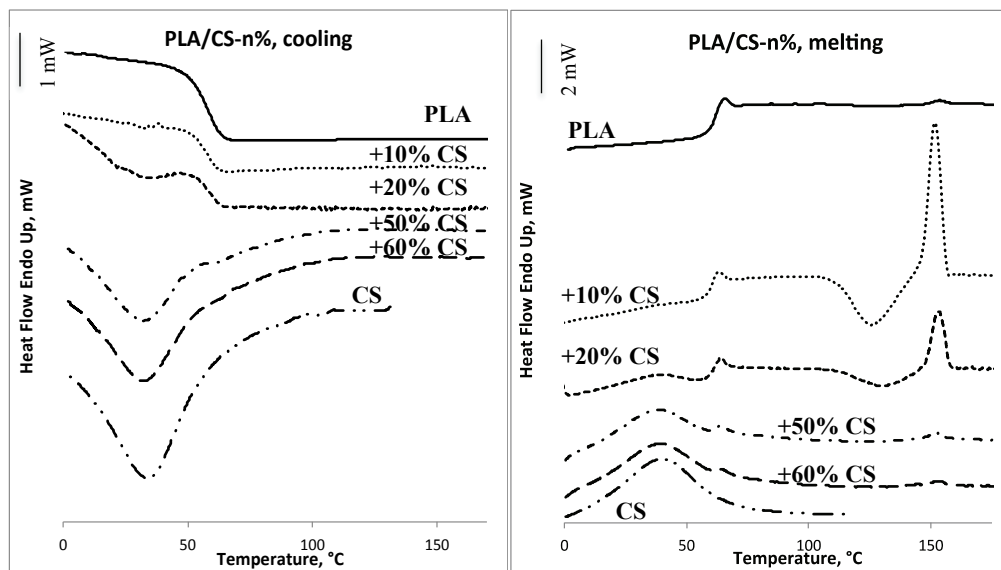


Figure 31. DSC exotherms (left) and endotherms (right) of PLA and its composites with cellulose stearate: 2nd heating, heating rate of 20°C/min.

All these facts point out that PLA and CS crystallize independently in composites and no co-crystallization can be seen as has been observed in LDPE/CS composites. Therefore, it can be suggested that PLA and CS surfaces are not fully compatible, in spite of both polymers having similar ester groups.

The effect of filler nature on the thermal behaviour of composites can be analysed from Figure 32 that shows melting curves of PLA composites at 10% filler loading. Pure PLA has the lowest ΔH_{cc} and ΔH_{mc} . Addition of fillers increases cold crystallization and melting enthalpies of PLA due to nucleation abilities of fillers. It can be concluded that CS promotes cold crystallization of PLA to almost four times higher levels than cellulose, probably due to the existence of side chain crystallites in CS that act as nucleation centres for PLA and gives an incentive to cold crystallization.

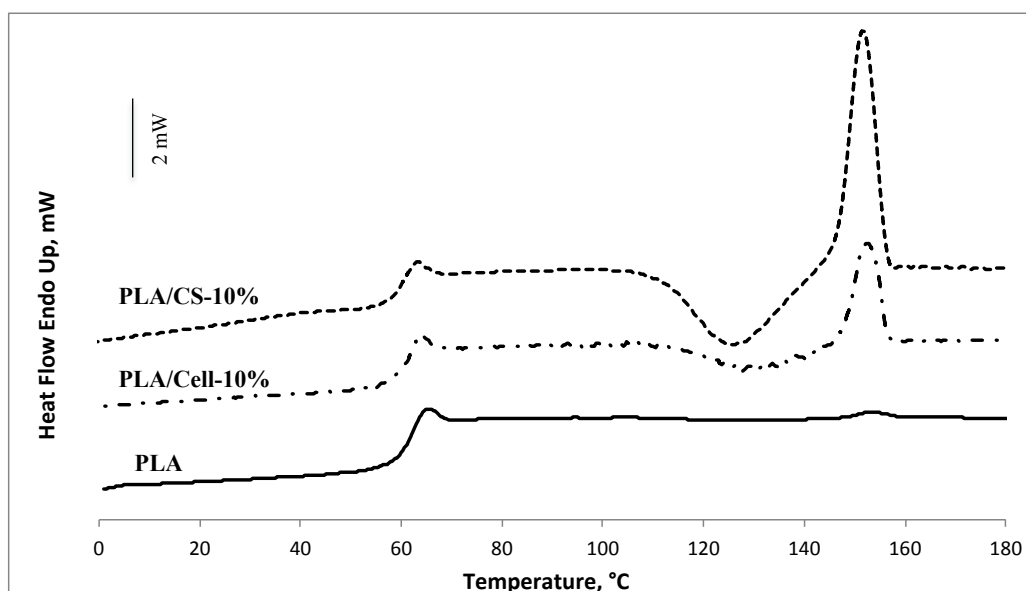


Figure 32. Melting curves for PLA composites with 10% filler content.

CONCLUSIONS

In this work cellulose esters (CL and CS) in ionic liquid BmimCl have been synthesized, which is the latest technology in the synthesis of cellulose esters. Novel composites based on CL and CS have been created.

Based on rheological measurements the following conclusions can be made:

1) Effect of filler content on η , G' , ω

- The complex viscosities of all LDPE and PLA composites compared to matrix polymers at very low shear rates were significantly increased due to the presence of filler in the melt.
- Due to the intrinsic rigidity of fillers, storage moduli values for all LDPE and PLA composites increase with growing filler content, indicating hardening of the composites.
- Crossover frequencies of all composites compared to matrix polymers decrease with the increase of filler loadings, indicating earlier transition of the melts to solid-like behaviour. It was found that filler content $\leq 20\%$ in a composite is the optimum amount for composites to reserve their plasticity, since at higher filler loadings behaviour of the composites becomes identical to pure filler behaviour.

2) Effect of filler nature on η , G' , ω

- For PLA composites the cellulose and cellulose esters influence η in a similar manner. However, in LDPE composites CL and CS show less pronounced influence on viscosity than cellulose, probably due to better flexibility and compatibility of cellulose esters with LDPE.
- The slopes of storage moduli curves of LDPE/CL and LDPE/CS composites with filler content up to 20% are approximately the same as for pure LDPE, indicating good homogenization of CL and CS with LDPE matrix.
- LDPE/Cell composites have lower crossover frequencies compared to LDPE/cellulose esters, indicating more solid-like behaviour.

Based on DSC measurements the following conclusions can be made:

1) Effect of filler content on LDPE and PLA composites

- Addition of cellulose and CL does not change the melting and crystallization temperatures of LDPE/Cell and LDPE/CL composites. Therefore, it can be suggested that the size of LDPE crystallites keeps the same value. Addition of CS affects the crystallization temperatures of LDPE caused by partial co-crystallization of LDPE and CS.

- Incorporation of cellulose and CL to LDPE reduces the overall crystallinity X_c of LDPE composites. On the contrary, X_c of LDPE/CS composites increases with growing CS content due to added crystallinity of CS and co-crystallization of LDPE and CS.
- Both Cell and CS induce nucleation of cold crystallization of PLA. However, all PLA/Cell composites are assumed to be amorphous since cold crystallization enthalpy ΔH_{cc} and melting enthalpy ΔH_{mc} values are almost the same and no crystallization peaks are observed in cooling curves. However, PLA/CS composites have crystallites due to crystallization of CS, and cannot be considered as amorphous.

2) Effect of filler nature on LDPE and PLA composites

- Comparing three different fillers it is seen that Cell and CL do not facilitate nucleation and crystallization of LDPE, while CS promotes crystallization of LDPE.
- CS promotes cold crystallization of PLA to almost four times higher levels than cellulose. This can be attributed to the existence of side chain crystallization of CS that promotes cold crystallization development.

Based on the results of this thesis, it was found that both cellulose esters CL and CS have good compatibility with LDPE. On the contrary, native cellulose, due to its rigidity and non-flowability, is a much worse candidate for LDPE composites. For PLA composites, rigid cellulose and flexible CS influence properties of composites in a similar manner.

Rheological and thermal characteristics of composites with cellulose esters are similar compared to pure matrices for up to 20% of filler loading. However, rigid cellulose can only be added at contents not exceeding 10% in order not to cause deterioration of composite properties. Therefore, these novel composites could replace pure LDPE and PLA in their current packaging applications.

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ABSTRACT

Landfills around the world are full of plastics and packaging materials, some of which may take decades or longer to completely break down. Therefore, in recent years, a deliberate interest to look for composites that are environmentally friendly and biodegradable appeared. One of the most promising bio-based polymers is poly(lactic acid) (PLA), which is made from plants and is readily biodegradable. Conventional plastics like low density polyethylene (LDPE) are widely used in various applications and can be biodegradable in composites with natural fillers.

Therefore, the aim of this research was to create new sustainable composites based on PLA and LDPE with cellulose (Cell), cellulose laurate (CL) and cellulose stearate (CS) that could replace pure LDPE and PLA in their current applications. For this work, cellulose esters (CL and CS) were prepared by a novel synthesis method - esterification reaction of cellulose in ionic liquid 1-Butyl-3-methyl-imidazolium Chloride (BmimCl). LDPE and PLA composites with fillers were manufactured by compounding on twin-screw extruder.

The influence of added cellulose and its novel derivatives on rheological and thermal behaviour of LDPE and PLA was investigated in this work. Two key methods were used to analyse these properties: Differential scanning calorimetry (DSC) and melt rheology. Melt rheology has been used for examining and understanding the interaction of the constituents of a multi-component mixture and their influence on the flow and other properties of such materials. DSC was the main technique used to study melting and crystallization behaviour.

The following results in rheology were obtained: Complex viscosities and storage moduli of all LDPE and PLA composites compared to matrix polymers at low shear rates were increased. No difference in influence of Cell and cellulose esters on viscosity of PLA was observed. However, in LDPE composites CL and CS show less pronounced influence on viscosity than cellulose, probably due to better flexibility and compatibility of cellulose esters with LDPE. The slopes of storage moduli curves of LDPE/CL and LDPE/CS composites with filler content up to 20% are approximately the same as for pure LDPE indicating good homogenization of CL and CS with LDPE matrix. Identical results were observed for cellulose in matrix PLA at maximum content of 10%.

The following results in DSC were obtained: Cell and CL decrease crystallinity of LDPE. However, degree of crystallinity of LDPE/CS composites increases with growing CS content due to added crystallinity of CS and co-crystallization of LDPE with CS. Addition of Cell and CS raises cold crystallization and melting enthalpies of PLA due to nucleation abilities of fillers. It was found that CS facilitates cold crystallization of PLA almost to four times higher levels than cellulose. However, all PLA/Cellulose composites are assumed as amorphous since cold crystallization

enthalpy and following melting enthalpy values are almost the same and no crystallization peaks are observed in cooling curves, while overall crystallinity of PLA/CS composites is determined by crystallinity of CS as PLA itself is amorphous.

Based on results of this thesis, it was found that both cellulose esters CL and CS do not deteriorate rheological and thermal properties of matrix polymers at filler contents not exceeding 20%. However, rigid cellulose is applicable only at maximum content of 10%. These composites have similar properties to matrix polymers and it can be suggested that novel composites could replace pure LDPE and PLA in their current packaging applications.

KOKKUVÕTE

Viimastel aastatel on süvenenud vajadus keskkonnasõbralike ja biolagunevate polümeerkomposiitide uurimise ja arendamise järele, et vähendada taastumatutel loodusvaradel põhinevate polümeermaterjalide ökoloogilist jalajälge.

Seetõttu oli antud töö eesmärk luua uusi ja jätkusuutlikke komposiite madaltiheda polüetüleen (LDPE) ja polü(piimhappe) (PLA) baasil tselluloosi, tsellulooslauraadi (CL) ja tselluloosstearaadiga (CS), mis võiksid asendada puhtaid LDPE ja PLA materjale nende praegustes rakendustes. Töös kasutati kaubanduslikke LDPE ja PLA materjale ning tselluloosi. Tselluloosi estrid CL ja CS valmistati ionvedelikus (1-butüül-3-metüülimidiasookloriid ehk BmimCl) lahustatud tselluloosi esterdamisel vastavalt laurüül- või stearyülkloriidiga. LDPE ja PLA komposiidid vastava täiteainetega valmistati kompaundimise teel kaheteelises ekstruuderis.

Antud töö raames selgitati tselluloosi ja selle derivaatide mõju LDPE ja PLA reoloogilistele ja termilistele omadustele. Komposiitide komponentide vastastikuse toime uurimiseks ja antud materjalide viskoossuse, jääk- ja kaomooduli selgitamiseks kasutati sulandi reoloogia analüüsi. Diferentsiaalne skaneeriv kalorimeetria (DSC) oli põhiline meetod komposiitide sulamis- ja kristallisatsioonikäitumise analüüsil.

Sulandi reoloogia uuringute olulisemad tulemused olid järgnevad. Kõikide LDPE ja PLA komposiitide kompleksviskoossused ja jääkmoodulid suurenesid madalatel nihkesagedustel. Tselluloos ja tselluloosi estrid avaldasid sarnast mõju PLA viskoossusele. LDPE komposiitides mõjutasid CL ja CS viskoossust tselluloosiga võrreldes vähese kasvu suunas, tõenäoliselt tänu paremale paindlikkusele ja tselluloosi estrite kokkusobivusele LDPEga. LDPE/CL ja LDPE/CS komposiitide jääkmooduli kõverate kaldenurgad täiteainete sisaldusel kuni 20% on samad, mis puhta LDPE korral, mis osutab CL ja CS heale homogeniseeritusele LDPE maatriksis. Sarnane tulemus saadi tselluloosi puhul PLA maatriksis täiteaine maksimaalsel sisaldusel 10%.

Termilise analüüsi olulisemad tulemused olid järgnevad. Tselluloos ja CL vähendavad LDPE kristallisatsiooniastet. Samas CS lisamine LDPE maatriksisse suurendas komposiitide kristallisatsiooniastet tänu CS enda kristalliseerumisele ning LDPE ja CS kooskristalliseerumisele. Tselluloos ja CS suurendavad PLA külmkristalliseerumis- ja sulamisentalpiaid tänu nende täiteainete nukleatsioonivõimele. Seejuures CS soodustab PLA külmkristalliseerumist neli korda rohkem kui tselluloos. Kõik PLA/tselluloosi komposiidid olid toatemperatuuril amorfseid, kuivõrd külmkristalliseerumis- ja sulamisentalpiad olid peaaegu võrdsed ja eksotermidelt ei leitud kristalliseerumisele iseloomulikke piike. Samas kogu kristallisatsiooniaste PLA/CS komposiitides oli määratud ainult CS kristalliseerumisega, kuna PLA ise on antud tingimustel amorfne.

Antud töö tulemustest saab järeldada, et mõlemad tselluloosi estrid (CL ja CS) ei halvenda maatrikspolümeeride reoloogilisi ja termilisi omadusi nende sisaldusel mitte üle 20%. Kuigi, jäik tselluloos on kohaldatav ainult maksimaalsel sisaldusel 10%. Antud komposiitidel on sarnased omadused oma maatrikspolümeeridega ja seetõttu võiksid nad asendada puhtaid LDPE ja PLA materjale nende tänapäevastes rakendustes pakenditööstuses.

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Bachelor thesis supervision: Inga Gromõko, Sliced veneer and its production, 2012.

PAPER I

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Rheological and Mechanical Properties of Poly(lactic) Acid/Cellulose and LDPE/Cellulose Composites

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In our work we studied composites of poly(lactic) acid (PLA) and low density polyethylene filled with cellulose fibres. The studied composite materials were manufactured with a twin-screw extruder. The extruded compound was processed in to samples using compression moulding. The content of cellulose in polymer/cellulose composites was varied. Effect of low amounts of cellulose on the rheological and tensile properties was studied. Tensile tests showed that the incorporation of cellulose into PLA matrix lead to stiffer but slightly more brittle and weaker materials, since Young's modulus increases and tensile strength and elongation at break slightly decrease. Mechanical results are in agreement with rheological behaviour: the composites exhibit the improvement in the storage and loss moduli of composites compared with that of matrix polymers. The composite dynamic viscosity increases with cellulose content in the same manner as loss and storage moduli. The processing and material properties of PLA/cellulose composites were compared to the more commonly used low-density-polyethylene/cellulose composites.

Keywords: poly(lactic) acid, low-density-polyethylene, cellulose, biodegradable composite, rheology, mechanical properties.

1. INTRODUCTION

Polyolefins are very important and useful synthetic polymers because they possess good properties, well-known technology of production and low cost. A representative polyolefin is low-density-polyethylene (LDPE), which has been extensively studied for many years. Even though the mechanism of photochemical and thermal degradation of LDPE is well understood, the knowledge of the behaviour of this polymer in blends with other synthetic or natural materials is not sufficient.

The wide use of non-renewable raw polymers in many industrial and domestic fields causes ecological problems connected with their utilization. Some synthetic plastics including polyolefins are characterized by relatively high stabilities under both photochemical and environmental conditions. The use of natural or synthetic photo- and biodegradable polymers is promising, but still problematic, for packaging materials [1].

As a result, the use of natural/bio-fibre reinforced composites has been rapidly expanded due to the availability of natural/bio-fibres derived from annually renewable resources, for use as reinforcing fibres in both thermoplastic and thermosetting matrix composites as well as for the positive environmental benefits gained by such materials [2].

Recently, a deliberate interest to look for systems that are even more eco-friendly and biodegradable appears. Therefore materials based on raw materials derived from natural resources of plant are being studied. One of the most promising bio-based polymers that have attracted the interest of many researchers is poly(lactic) acid (PLA), which is made from plants and is readily biodegradable [3]. The problems with PLA have been poor commercial

availability, poor processability, low moisture and thermal stability. The long-term properties of renewable materials are also very important especially if the products are not single use application. Reinforcing with fibres is one possibility to solve such problems [2].

Cellulose is one of the strongest and stiffest fibres available and it has a high potential to act as reinforcing agent in biopolymers. Cellulose-based polymer composites are characterized by low cost, desirable fibre aspect ratio, low density, high specific stiffness and strength, biodegradability, flexibility during processing with no harm to the equipment, and good mechanical properties [2].

PLA and LDPE based composites with different type of cellulose are widely studied by various methods such as different scattering techniques, electron microscopy, thermal analysis, etc., [4–9] but rheological characterization of such composites is seldom and diverged. However, the rheology is interested from the point of the view of flow behaviour which is involved in the processing and fabrication of such materials in order to make useful objects. Thus, fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, injection moulding, fibre spinning, and film blowing etc. Rheological measurements are often used for examining and understanding the interaction of the different constituents of a multi-component or multiphase mixture and their influence on the flow and other properties of such materials [10].

Mechanical properties are sufficient for end-use of polymers. Mechanical properties of cellulose-plastic composites, such as stiffness, strength, impact resistance etc., play an important role in determining the suitability of these products in various applications [11].

It is known that due to the cellulosic hydrophilic and polymer (LDPE and PLA) hydrophobic nature, such composites have poor surface adhesion between the components of composites. In numerous research studies

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the compatibility between composite components is chemical modification of components. At present in our work we did not use any compatibilizers, coupling agents or additives because the explanation of rheological data would be complicated by the fact that such hybrid composites contain several types of particles (cellulose, compatibilizers, etc.) with different mechanical, surface and rheological properties. Therefore, we decided to start the investigation of rheological and mechanical behaviour from the simple two-component system – polymer and filler. By the same reasons we added the low amount of the filler to the matrix polymer. Hence, the present work is the starting point for future research, which will help to understand and easily compare the various properties of initial (two-component) composites with derived composites composed with compatibilizers or other additives.

Therefore, the aim of this work was to prepare composites by extrusion and injection moulding to investigate the influence of added pure cellulose on rheological and mechanical behaviour of PLA and compare it with that of LDPE. We have manufactured and studied two-component composites to have a comparison reference for future research of multi-component composite materials.

2. EXPERIMENTAL PART

2.1. Materials

Two types of composites were investigated. First, composites compounded of PLA and cellulose fibres, which were abbreviated as PLA/CELL-n%, where $n = 0, 2, 5$ and 10 means the cellulosic content in composites. Content of cellulose is expressed in weight percent to the weight of matrix polymer. The second type contained LDPE and cellulose, abbreviated as PE/CELL-n%, where $n = 0, 2, 5$ and 10 . Low density polyethylene powder was obtained from Borealis A/S (product name: PE FA3220). NatureWorks LLC supplied Poly(lactic) acid granules (PLA Polymer 4042D). Molecular weights (Mw) were estimated by rheology at $T = 180^\circ\text{C} - 210^\circ\text{C}$ for LDPE and $T = 150^\circ\text{C} - 190^\circ\text{C}$ for PLA using single exponential model for MWD (Molecular Weight Distribution) determination. Apparent Mw of LDPE and PLA are 400 kg/mol and 77 kg/mol respectively. Acid-free α -cellulose (chemically clean, no lignin) with length $60\ \mu\text{m} \pm 10\ \mu\text{m}$ and width $5 \pm 2\ \mu\text{m}$) were supplied by Hahnemühle FINEART.

2.2. Composite processing

At first cellulose powder was prepared. Cellulose sheets were crushed into pieces and then ground to a powder using the cutting mill Retsch SM 100. Composites of LDPE and PLA with cellulose were prepared by addition of cellulosic powder to matrix polymer.

Matrix polymer and cellulose were mechanically mixed for 10 min at 60 rpm in a mixer. Then polymer/cellulose samples with different compositions were prepared by compounding on twin-screw extruder: LDPE and PLA powders pre-blended with cellulose are fed to the extruder at controlled feed-rates. After this the powders

were mixed and melted in the extruder via the rotating screws to produce the final molten product that is extruded at the end as strands through hole in a die plate. There are 4 temperature zones in extruder from hopper to die; melting begins from the second zone. The following temperatures were set at respective zones: 150°C near the feeder, 175°C and 190°C in the middle zones, and 210°C at the die for LDPE. For PLA different temperatures in 4 zones were used 160°C , 170°C , 180°C , 180°C . The molten strand is then cooled by ventilators and chopped into pellets and then left cooling for 1 h.

In order to get samples for rheology measurements compression moulding was used. LDPE- or PLA-cellulose powder granules were placed into stainless steel round-shape mould (height = 1.06 mm , diameter = 26 mm) and left heating for 5 min without pressure, after it was hot pressed at 220°C for 1 min under pressure 50 MPa; the composite was cooled with cold water at room temperature. Testing specimens in a disc shape were obtained. PLA samples were dried in an oven at 105°C for 24 h.

Test specimens for measuring mechanical properties of composites were injection moulded at 160°C , 170°C and 180°C temperatures in the barrel zones of injection moulding machine.

We did not use any antioxidants because as it is known from [12] that for PLA the strong oxidation at temperatures lower than 200°C does not occur: thermal degradation mainly occurs due to the chain splitting and not hydrolysis [13]. LDPE itself is rather thermally stable at the used temperatures.

2.3. Measurements

2.3.1. Rheological Measurements

The melt rheological properties of the samples were determined using a rheometer Anton Paar Physica MCR 501. The measurements were performed in the dynamic oscillatory mode and 25 mm parallel cone-plate measuring geometry with gap setting of about 0.051 mm . All measurements were carried out in a nitrogen atmosphere at 190°C . Amplitude sweep was performed with all the samples at 10 rad/s and was kept at 5 % in all composite samples frequency scans. Frequency scans were taken between 0.01 rad/s and 500 rad/s for PE/CELL composites, and between 1 rad/s and 500 rad/s for PLA/CELL composites.

2.3.2. Tensile Testing

The uni-axial tensile properties (modulus, tensile strength, elongation-at-break) were measured at room temperature ($\sim 23^\circ\text{C}$) with a 10 kN load cell on an Instron Model 5866 tensile tester. The cross-head speed was set at 50 mm/min . All samples were tested after having been subjected to room temperature and atmospheric conditions for a week. Twenty specimens of each sample were tested and the average results were reported. The dumb-bell-shaped specimens used in this method were prepared according to ISO 527-2 standard. For the most precise measurements each specimen sizes were measured separately. Average specimen parameters are: thickness of 2.06 mm , width of 2.1 mm and length of 12 mm .

3. RESULTS AND DISCUSSION

3.1. Rheological properties

First of all, the linear viscoelastic range characterized by the onset of the strain dependent behaviour for all composites was detected. As an example, Figure 1 shows the selected amplitude (strain) sweeps for two extreme cases – pure matrix polymers and composites with the maximum amount of added cellulose (10 wt%). The dynamic modulus of matrix polymer remains linear up to 10 % of strain. Addition of the filler to LDPE and PLA polymers slightly reduces the linear viscoelastic range. Therefore, the strain of 5 % was chosen as constant for the dynamic frequency sweeps of all composites samples.

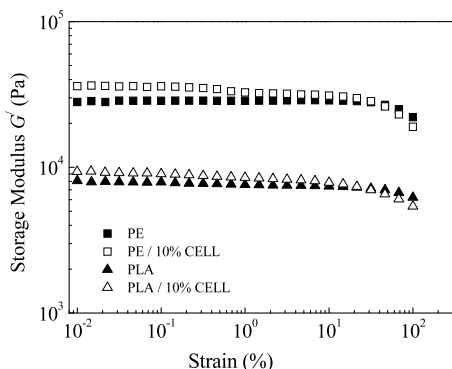


Fig. 1. Amplitude sweep (190 °C, $\omega = 10$ rad/s) for matrix polymers PLA and PE and their composites with 10 wt% of cellulose

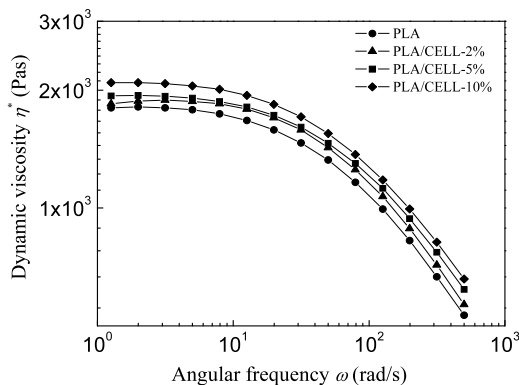


Fig. 2. Dynamic viscosity η^* as a function of angular frequency ω for PLA/CELL composites with different content of cellulose

Figs. 2 and 3 demonstrate the dynamic frequency sweeps for matrix polymers and their composites with cellulose. All the PLA composites as well as the matrix polymer show a Newtonian flow at angular frequencies ω lower than 5 rad/s. Behind these values dynamic viscosity decreases showing shear thinning behaviour as previously observed in other filler melts [14–16]. This behaviour can be attributed to the higher degree of polymer-filler

interaction, which requires higher shear stress and longer relaxation times for the composites to flow. For PE/CELL composite the Newtonian flow is hardly observed and yielding may occur in this case.

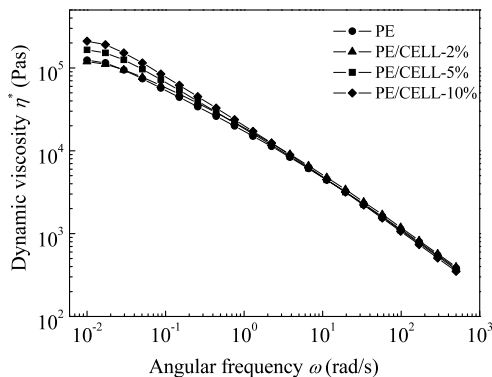


Fig. 3. Dynamic viscosity η^* as a function of angular frequency ω for PE/CELL composites with different cellulosic content

As can be seen from the figures presented data the processability of composites is affected by the addition of fibres to the polymer melts. In comparison with matrix polymers the cellulosic filled polymers have higher melt viscosity, especially, at low ω , where contribution of cellulosic phase becomes apparent. As an example, the zero shear viscosities η_0^* obtained by extrapolation of η^* to zero ω for PLA/CELL-10% are on 16 % higher than that of the matrix PLA. For PE/CELL composites the η_0^* can not be directly calculated from the obtained curves. However, we can estimate η_0^* by the value taken at the lowest ω . The estimated apparent zero shear viscosity of PE/CELL – 10 % composite are on 76 % higher than that of the matrix LDPE.

The increase of the viscosity depends on the concentration, particle size, particle size distribution and shape of the filler. The presence of cellulose particles perturbs normal polymer flow and hinders the mobility of chain segments. Therefore, the higher the amount of the cellulose, the worse is the dispersion of the minor phase in the melt and the higher is the viscosity of the filled polymer.

Comparing the dynamic viscosities of PLA- and PE-based composites it is seen that the η^* of PLA/CELL are two orders of magnitude lower than that of PE/CELL. It can be caused both by difference in molecular weight and different viscous nature of used matrix polymers.

The elastic properties of composites depend on energy storage mechanisms at the interphase. The relaxation of the dispersed phase itself is often longer than the relaxation of the polymer chains of the individual components [17]. As example, Fig. 4 shows the dynamic spectrum of PE/CELL composites with different content of minor cellulosic phase. The same but less pronounced frequency dependence of storage G' and loss modulus G'' was observed for PLA/CELL composites. As it can be seen from this figure, due to the intrinsic rigidity of cellulose

powder, the storage modulus of composites are higher than pure matrix, especially for the highest cellulose content, indicating that stress transfers from the matrix to the cellulose fibres. This behaviour can be explained by the fact that filler particles restrict deformation in the same manner as it was explained for viscosity.

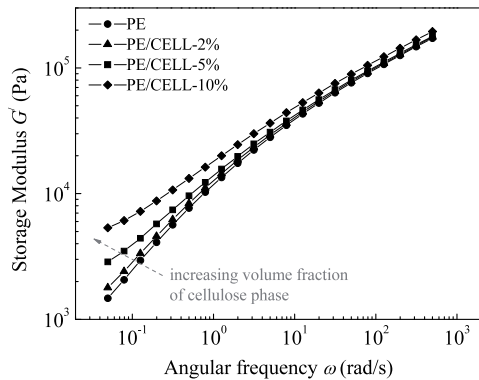


Fig. 4. Frequency dependence of storage modulus G' for PE/CELL composites with different content of cellulose. Arrow shows the increasing volume fraction of cellulosic phase in the matrix melt

The enhancement observed in dynamic modulus is significantly higher at low ω than at high ω . For storage moduli the slope of the modulus curves diminish with increasing amounts of filler. The additional low frequency contributions in G' (shown by an arrow in Fig. 4) can be due to the relaxations of the large dispersed domains of the minor phase. It means that the dispersion of cellulose fibres in composite material is not homogeneous and fibres are not aligned that additionally confirmed by viscosity results. The higher the cellulose content, the higher is the volume fraction and droplet size of cellulose phase, and the higher is the G' at low ω . At high ω the effect of filler decreases and the matrix contributions dominate.

Finally based on G' data serving as the measure of molecular rigidity we can conclude that with addition of the cellulose filler the samples become more rigid: for comparison, at $\omega = 10$ rad/s the G' of PLA/CELL and PE/CELL are up to 13 % and 30 % higher, respectively, than G' of the matrix polymers. As we will see later this agrees with the tensile test results.

3.2. Tensile properties

The tensile properties of the cellulose-polymer composites are presented in Table 1. As seen, the addition of 5 wt% of cellulose to matrix material determines the increase of the Young's modulus E that overcomes the corresponding standard deviations. At lower content of cellulose no significant effect is observed. It is detected that with increasing cellulose content the modulus E becomes up to 12 % and 30 % higher for PLA/CELL and PE/CELL, respectively, compared to matrix polymers indicating the reinforcing action of the filler. These results are in accordance with the rheological data on storage modulus G' . Such behaviour is expected because it is well

known that the modulus of a filled system depends on the properties of the two components, the filler and the matrix [18, 19]. Thus, the E of the filler (cellulose), being higher than the E of the matrix materials, causes the increase in E of composites. Increasing modulus of elasticity of composites compared with matrix polymer can also be associated with the restrictions of macromolecules mobility and deformability imposed by the presence of cellulose particles, and this is in agreement with obtained rheological data. Since the Young's modulus is a measure of the material stiffness, we can say that with increasing cellulose content the materials become stiffer. At the same time the PLA and their composites having much higher E are much stiffer than LDPE and its composites.

Table 1. Tensile properties of matrix polymers (LDPE, PLA) and their composites with cellulose

Polymer/Filler, wt%	Young's modulus E , MPa ($\pm 7\%$)	Elongation at break ϵ_b , % ($\pm 7\%$)	Tensile strength σ_b , MPa ($\pm 10\%$)
PLA	1975	9.3	55
PLA/CELL-2 %	2017	7.1	53
PLA/CELL-5 %	2020	6.5	54
PLA/CELL-10 %	2187	6.5	54
PE	152	78	18
PE/CELL-2 %	153	69	16
PE/CELL-5 %	159	63	15
PE/CELL-10 %	197	54	14

In comparison with matrix polymer, a dramatic loss in elongation at break ϵ_b was observed for all composite samples. Fig. 5 illustrates typical tensile stress-strain curves for pure matrix polymers and their composites. The data clearly show that both elongation at break and toughness, obtained from the area under the curve, are up to 30 % lower for the composites with 10 wt% of cellulose compared to matrix polymers. Increased filler content in the LDPE and PLA matrix results in the stiffening and hardening of the composite materials and, as a consequence, the decay in resilience and toughness are observed.

The addition of cellulose into the matrix melts causes slight decrease in tensile strength σ_b of composite in comparison with pure polymer. As the experimental error of strength values are within the limits of differences, we can conclude that for all the composites the strength remains almost constant for all composites. The decrease in elongation and strength of composite compared to pure polymers can be associated with inadequate wetting of the fibre with the matrix [20], uneven aligning of the cellulose fibres [6] and most probable poor adhesion between the filler and matrix [21]. The poor adhesion between matrix and fibre initiates numerous voids at the fibre matrix interface, and the stress transfer to the fibres, which are the load bearing entities, becomes inefficient leading to lower strength and elongation values.

To obtain materials with improved mechanical properties, the good dispersion of the one phase in the

other and strong interfacial adhesion is required. Compatibilizers, coupling agents addition or chemical modification of surfaces, can improve the rheological and mechanical properties. This is the purpose of our future research.

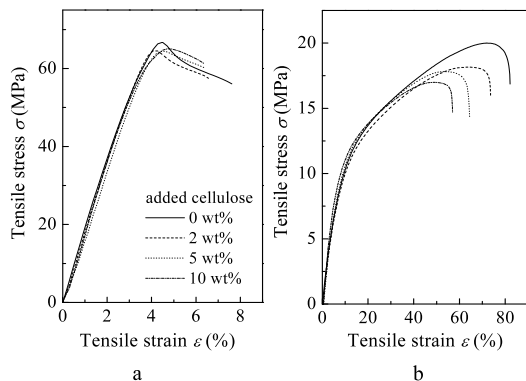


Fig. 5. Stress-strain curves for composites containing various content of cellulose: a – PLA/CELL, b – PE/CELL

The tensile modulus and strength of PLA/CELL composites are in 13 and 3 times higher, respectively, compared to the PE/CELL composites. As a result, the elongation and toughness are higher for PE composites than for PLA. The same is true for pure PLA and LDPE. It means that LDPE is more elastic and tough whereas PLA is stiffer and more brittle. However, the trend of mechanical and rheological behaviour with the addition of cellulose into the matrix materials is similar for PE and PLA.

4. CONCLUSIONS

The preliminary results show that PLA can be processed similarly to LDPE and both of them work well as matrix material for natural fibre composites.

Increasing content of cellulose in composites causes the sufficient increase in their dynamic viscosities η^* (up to 16 % and 76 % for PLA/CELL and PE/CELL, respectively, compared to the matrix polymer) and elastic moduli G' (13 % and 30 % for PLA and PE based composites, respectively), especially at low shear rates and high cellulose content. This can be explained by both inhomogeneous dispersion and aligning of cellulose phase in composites and/or perturbation of normal polymer flow and breaking the mobility of chain segments due to the presence of cellulose particles. As a result, the viscosity and moduli of filled polymer increases with the amount of filler. The most significant changes in the rheological properties occurs when the filler content is increased up to 10 wt%.

The mechanical properties of PLA/CELL and PE/CELL composites are promising. The reinforcing effect of cellulose in PLA/CELL and PE/CELL composites is pointed out by the pronounced increase of tensile modulus up to respectively 12 % and 30 % higher than unfilled polymers. However, the increase in cellulose content negatively influences the elongation at break and

toughness of such composites, while tensile strength approximately the same value.

Acknowledgements

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PAPER II

Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2012). Influence of cellulose content on thermal properties of poly(lactic acid)/cellulose and low-density polyethylene/cellulose composites. *Proceedings of the Estonian Academy of Sciences*, 61(3), 237–244.



Influence of cellulose content on thermal properties of poly(lactic) acid/cellulose and low-density polyethylene/cellulose composites

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Abstract. Crystallization behaviour of polylactic acid/cellulose (PLA/CELL) and linear low-density polyethylene/cellulose (LDPE/CELL) composites was studied by differential scanning calorimetry (DSC) and polarized light microscopy equipped with hot-stage. The effect of addition of cellulose on thermal properties of PLA/CELL and LDPE/CELL composites was considered. The DSC experiments were performed at different scanning rates.

For pure PLA the crystallization peak at $T = 98.8^\circ\text{C}$ was observed in DSC scans at $20^\circ\text{C}/\text{min}$ with the corresponding melting peak at 110.1°C . With addition of cellulose no crystallization peaks and melting peaks related to them were found. For all samples cold crystallization peaks at around 130°C and corresponding melting peaks at $152\text{--}153^\circ\text{C}$ were observed in endotherms. Cold crystallinity is strongly affected by cellulose content: the higher the cellulose content, the higher is the cold crystallinity of the samples. At the same time overall crystallinity for all PLA/cellulose composites is negligible contrary to pure PLA, which is slightly crystalline.

Unlike PLA, LDPE and its composites have no cold crystallization, which is a usual behaviour for LDPE materials. A general crystallization/melting behaviour of LDPE/cellulose composites is identical to that of pure LDPE. However, the crystallinity of LDPE/composites decreases with increasing cellulose content.

Key words: calorimetry, light microscopy, composites, cellulose, polylactide, low-density polyethylene.

INTRODUCTION

Over the past decade, much attention has been focused on biodegradable and biocompatible polymers. Natural polymers, biopolymers, and synthetic polymers based on annually renewable resources are the basis for the twenty-first-century portfolio of sustainable, eco-efficient plastics. In this direction, polylactide (PLA) is one of the most promising candidates. Polylactide has good mechanical properties, thermal plasticity, and is readily fabricated, thus being a promising polymer for various end-use applications. Along with other bio-sourced materials, PLA will gradually replace the currently existing family of oil-based polyolefin polymers (polyethylene, polypropylene, polyethylene terephthalate) as they become cost- and performance-wise competitive [1,2]. Polyolefins are hardly biodegradable, therefore addition of cellulose as filler can improve that property [3].

Most sustainable plastics cannot compete economically with conventional petroleum-derived plastics in their present state. Economically favourable composites, therefore, are expected to be made from costly sustainable plastics in combination with inexpensive natural reinforcement fibres.

Cellulosic materials are the most abundant form of biomass and the form most likely to be used as reinforcement fibres, not only for ecological and economic reasons, but also because of their high mechanical and thermal performance. To utilize and design materials successfully for industrial applications, it is imperative to determine first the material properties that will affect performance [4].

The thermal behaviour of PLA and low-density polyethylene (LDPE) cellulose-based composites has attracted much attention and has been well studied by dynamic mechanical thermal analysis and thermogravimetric analysis [2,5–13]. However, differential scanning calorimetry (DSC) studies of PLA and LDPE composites have been poorly presented in literature. The

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most part of these studies has been performed in the isothermal mode [2,6–9]. Nevertheless, non-isothermal crystallization is also important from both the scientific and commercial viewpoints, because polymer processing is mainly conducted under non-isothermal conditions and this, in turn, affects mechanical properties of the end-product [6].

The non-isothermal behaviour of two-component composites of cellulose with pure PLA or LDPE has not been well investigated [7,14,15]. Therefore, the aim of this work was to study the influence of added pure cellulose on the non-isothermal behaviour of PLA and LDPE by DSC. We have manufactured and studied two-component composites to have a comparison reference for future research of multi-component composite materials containing compatibilizer/coupling agents.

EXPERIMENTAL PART

Materials

Two types of composites were investigated. First, composites compounded of PLA and cellulose fibres, which were abbreviated as PLA/CELL- n %, where $n = 0, 2, 5$, and 10 means the cellulosic weight content in composites. The content of cellulose is expressed in weight per cent to the weight of composite. The second type contained LDPE and cellulose, abbreviated as LDPE/CELL- n %, where $n = 0, 2, 5$, and 10. The LDPE powder was obtained from Borealis Polymers Co (product name: PE FA3220). NatureWorks LLC supplied poly(lactic) acid granules (PLA Polymer 4042D). It has been found in work [1] that this polymer consists of L-isomer 92% and D-isomer 8%. PLA 4042D has an overall degree of crystallinity 2.0%, which can be explained by a high D-isomer content of 8%. Molar masses (weight-averaged M_w) were estimated by rheology using a single exponential model for molecular weight distribution determination with the rheometer Anton Paar Physica MCR 501. Apparent M_w of LDPE and PLA are 400 kg/mol and 77 kg/mol, respectively. Acid-free α -cellulose (chemically clean, no lignin) with a maximum length of 60 ± 10 μm and width 5 ± 2 μm were supplied by Hahnemühle FINEART. Cellulose dimensions were measured by the polarized light optical microscope Zeiss Axioskop-2.

Composite processing

First, cellulose and polymer powders were prepared. Cellulose sheets were crushed into pieces and then ground to a powder using the cutting mill Retsch SM 100. Polylactide and LDPE granules were then pulverized in the Retsch cutting mill and then PLA powder was dried in an oven at 105°C for 24 h. Composites of LDPE and PLA with cellulose were prepared by addition of cellulosic powder to matrix polymer.

Polymer/cellulose mixture of different compositions was mechanically stirred for 10 min at 60 rpm in a Labor mechanical mixer. Then polymer/cellulose samples were prepared by compounding on a twin-screw extruder (Brabender Plasti-Corder PLE 651 with a twin-screw compounder DSK 42/7): LDPE and PLA powders pre-blended with cellulose are fed to the extruder at controlled feed-rates. After this the powders were mixed and melted in the extruder via the rotating screws to produce the final molten product that is extruded in the end as strands through a hole in a die plate. There are four temperature zones in the extruder from hopper to die; melting begins from the second zone. The following temperatures were set at respective zones: 150°C near the feeder, 175 and 190°C in the middle zones, and 210°C at the die for LDPE composites. For PLA composites different temperatures in four zones were used: 160, 170, 180, and 180°C. Both pure LDPE and PLA have undergone the same extrusion procedure as their composites. The molten strand is then cooled by ventilators and chopped into pellets, and then left to cool for 1 h.

We did not use any antioxidants because, as it is known from [16], for PLA strong oxidation at temperatures lower than 200°C does not occur: thermal degradation mainly occurs due to the chain splitting and not hydrolysis [17]. Low-density polyethylene itself is thermally rather stable at the used temperatures.

Measurements

Differential scanning calorimetry

The Perkin Elmer differential scanning calorimeter DSC-7 was used for thermal analysis at scanning rates of 5, 20, 50, and 100°C/min. The instruments were calibrated using indium and tin at all applied heating rates. Nitrogen was used as furnace purge gas. Differential scanning calorimetry (DSC) measurements were calibrated for a sample mass of 3 mg. In all DSC experiments the sample mass of 3.00 ± 0.03 mg was held constant. Flat samples were packed into aluminium foil to maximize the thermal contact between the sample and the calorimetric furnace. During the measurement, the sample was first held at 190°C for 5 min to delete its thermal history. Then it was cooled to 0°C at a definite scanning rate and an exotherm was obtained. After that the sample was held at zero temperature for 5 min and then heated to 190°C at the same rate to get an endotherm. Both melting and crystallization parameters were obtained from the exotherms and endotherms.

The degree of overall and cold crystallinity of each sample was calculated using the relationship [7]

$$X_c (\% \text{ crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w}, \quad (1)$$

where ΔH_m is the enthalpy of melting, ΔH_m^0 is the enthalpy of melting for a 100% crystalline PLA sample ($\Delta H_m^0 = 93 \text{ J/g}$) [18] or 100% crystalline LDPE sample ($\Delta H_m^0 = 293 \text{ J/g}$) [19], and w is the weight fraction of PLA and LDPE in the composite.

Polarized light microscopy with hot-stage

The polarized light microscopy (PLM) pictures of all samples were obtained by the polarized light optical microscope Zeiss Axioskop-2 with total magnification of $100\times$ ($10\times$ objective and $10\times$ eyepiece), equipped with a hot stage Mettler FP 80. Test specimens for hot-stage microscopy were prepared by pressing the composite pellets between two cover glasses at 200°C , using a hot plate to produce a very thin composite film with an average thickness of $20 \mu\text{m}$ measured by the thickness meter Sony DZ521. Samples were first heated from 20 to 190°C at $20^\circ\text{C}/\text{min}$, held at this temperature during 5 min, and then cooled at the same speed to 25°C and heated again. Snapshots at different temperatures during the second heating were recorded.

RESULTS AND DISCUSSION

Figure 1 shows the typical non-isothermal DSC thermograms of pure PLA and PLA/cellulose composites,

recorded at $20^\circ\text{C}/\text{min}$. The pure PLA is characterized by glass transition temperature T_g (marked in Fig. 1 as G) at 58.0°C , which agrees with literature data [7], the crystallization peak at $T_c = 98.8^\circ\text{C}$ (Fig. 1a, marked with C), and the corresponding melting peak T_m at 110.1°C (see Fig. 1b, marked with M). In-depth analysis of these thermograms revealed a small endothermic peak around 60°C , typically attributed to stress relaxation on heating [20]; after fast cooling to a temperature below T_g , the material goes into the glassy state and tends to decrease its excess enthalpy moving towards the equilibrium glassy state. This excess enthalpy is recovered at the glass transition region during the subsequent heating process.

Addition of cellulose results in diminishing the crystallization peak on the cooling curves and as a consequence no corresponding melting peak on the heating curves has been found. The degree of crystallinity of pure PLA was only about 2% and addition of cellulose makes composites fully amorphous. This implies that addition of cellulose produces a negative effect into the overall crystallinity of composites. A similar behaviour was observed in work [7] for PLA composites: the degree of crystallinity of composites with different cellulose reinforcements decreased compared to pure PLA.

As can be seen from the melting curves in Fig. 1, all PLA composites, including the pure polymer, have cold crystallization peaks (T_{cc}) located at $130\text{--}134^\circ\text{C}$ (marked with Cc in Fig. 1b) and subsequent melting peaks (T_{mc})

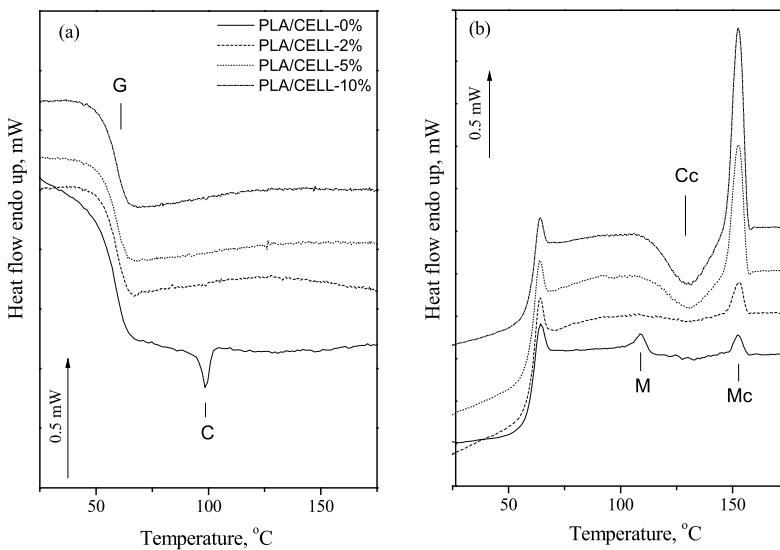


Fig. 1. DSC exotherms (a) and endotherms (b) of PLA and PLA/CELL composite materials: 2nd heating, heating rate $20^\circ\text{C}/\text{min}$. The arrows indicate the glass transition (G), the cold crystallization (Cc), and the melting related to the cold crystallization peak (Mc). There is an additional melting peak (M), related to the crystallization peak C of pure PLA.

at 152–153 °C (marked with M_c in Fig. 1b). However, it should be noted here that the PLA/CELL composites are assumed to be amorphous since cold crystallization enthalpy ΔH_{cc} and melting enthalpy ΔH_{mc} values are almost the same. Cold crystallization peaks indicate regions of realignment and transition from amorphous to crystalline phases. Figure 2 shows an evolution of cold crystallinity in PLA/CELL composites observed by PLM. Temperatures of 25, 135, and 155 °C were chosen for snapshots. It is clearly seen that the amount of crystallites increases gradually in the range of 130–140 °C during the non-isothermal process and, finally, the formed crystals melt at 155 °C.

From DSC data of PLA/CELL composites it was found that T_{cc} decreases with cellulose content downwards from 134 °C for pure PLA to 130 °C for PLA/CELL-10%. At the same time, the values of ΔH_{mc} and ΔH_{cc} of PLA/CELL samples increased with cellulose content. This behaviour indicates that cellulose induces crystal nucleation of the PLA polymer [21]. Cellulose appeared to facilitate nucleation and subsequent crystallization of PLA rather effectively in amorphous composites. Similar results were obtained by different authors in the case of PLA/talc and PLA/kenaf composites [22,23]. The enhancement in melting and cold crystallization enthalpies are opposed to several studies reported on PLA composites reinforced in the presence of a coupling agent [23,24].

Further, values of ΔH_{mc} and ΔH_{cc} are dependent on cooling/heating rates. Figure 3 shows DSC curves for PLA/CELL-10% at different heating rates. The heating rate dependence on glass transition temperature T_g is an experimentally observed fact [25,26]: if the heating or cooling rate is increased in magnitude, then the relaxation time becomes smaller and the transition region is shifted to a higher temperature. In the present study, too, T_g increases with increasing heating rate.

It is more interesting that peaks related to cold crystallization are dependent on the heating rate. With

increasing heating rate, T_{cc} shifts gradually to a higher temperature owing to the thermal delay [27]. It is notable that as the heating rate rises above 20 °C/min, both ΔH_{mc} and ΔH_{cc} decrease significantly and peaks are hardly observed. When scanned at 5 °C/min, two endothermic peaks appeared. Apparently, the amorphous PLA chain does not have enough time to well self-adjust with increasing heating rate. This results in the decrease in cold crystallization, and the multi-melting behaviour, which can be attributed to the simultaneous occurrence of melting of thinner lamellae and recrystallization. Such a behaviour is very common for most of the composites based on PLA, for example PLA/flax [21], PLA/nucleating agent $\text{SiO}_2(\text{TiO}_2)$ [2], PLA/clay [27], etc., and is probably attributed to the PLA nature. However, the filler can affect the cold crystallization process of PLA in one way or another. Remarkably, the cold crystallization process is dependent only on the heating rate and independent of the cooling rate during the cooling process prior to the 2nd heating. Indeed, as can be seen from the inset to Fig. 3, T_{cc} , ΔH_{mc} , and ΔH_{cc} are identical for all used cooling rates if the heating rate is the same.

The thermal behaviour of LDPE-based composites differs strongly from that of PLA/CELL composites. First of all, LDPE has no cold crystallization regions on the heating curves, which is usual for LDPE materials [19].

Figure 4 shows a non-isothermal cooling and heating process of LDPE and their cellulose composites. Exotherms are characterized by the presence of two crystallization peaks at 61–62 °C and 98 °C, whereas the endotherm has only one broad melting peak at 110–111 °C. However, such a thermal behaviour is expected for LDPE material [19].

Addition of cellulose does not affect any crystallization and melting temperatures. As is known, the melting point of a semicrystalline polymer is determined by the size and perfection of its crystals (i.e. by the lamellar

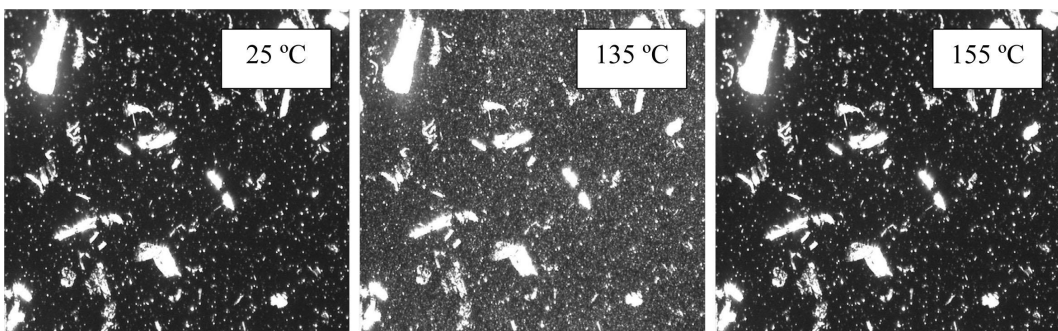


Fig. 2. PLM pictures of PLA/CELL-5% snapped at temperatures 25 °C, $T_{cc} \cong 135$ °C, and 155 °C during heating at 20 °C/min.

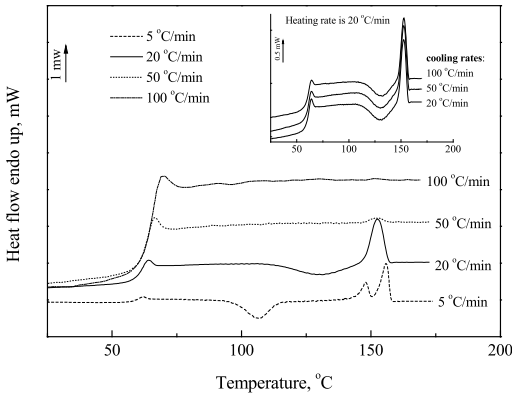


Fig. 3. DSC melting curves of PLA/CELL-10% at different heating rates. The inset shows endotherms for the same sample at different cooling rates, but at the same heating rate of 20 °C/min.

thickness) [19]. Taking into account that the crystallization and melting temperatures of the LDPE and LDPE/CELL samples do not change with cellulose content, it can be concluded that the size of LDPE crystallites keeps the same value.

On the contrary, both ΔH_m and the degree of crystallinity were affected by the presence of the filler. For all systems, ΔH_m decreases monotonously as the filler content in the composite increases, as expected,

because of the decrease in the matrix material in composites. However, the degree of crystallinity, calculated by eq. (1) and accounted for the effective matrix amount in the composites, also decreases with cellulose content from 42% for pure LDPE to 38% for LDPE/CELL-10%. Decrease in crystallinity is clearly observed in PLM pictures presented in Fig. 5. The filler seems to hinder the crystallization of the surrounding polymeric matrix and formation of crystalline domains.

CONCLUSIONS

The non-isothermal crystallization and melting behaviour of PLA/CELL and LDPE/CELL composites prepared by compounding in a twin-screw extruder was studied using DSC and polarized light microscopy with a hot-stage.

Thermal analysis showed an increase in cold-crystallization enthalpy in PLA composites, indicating that cellulose enhances nucleation and crystal growth.

Addition of cellulose has no effect on glass transition temperature T_g of PLA/CELL composites. However, the heating rate has an impact on T_g and T_{cc} , showing increasing values with a higher heating rate. At the same time, the heating rate affects ΔH_{mc} and ΔH_{cc} , resulting in the disappearance of the cold-crystallization process under applied high heating rates above 50 °C/min. Obviously a high heating rate does not allow enough time for PLA chains to rearrange, resulting in the decrease in cold crystallization.

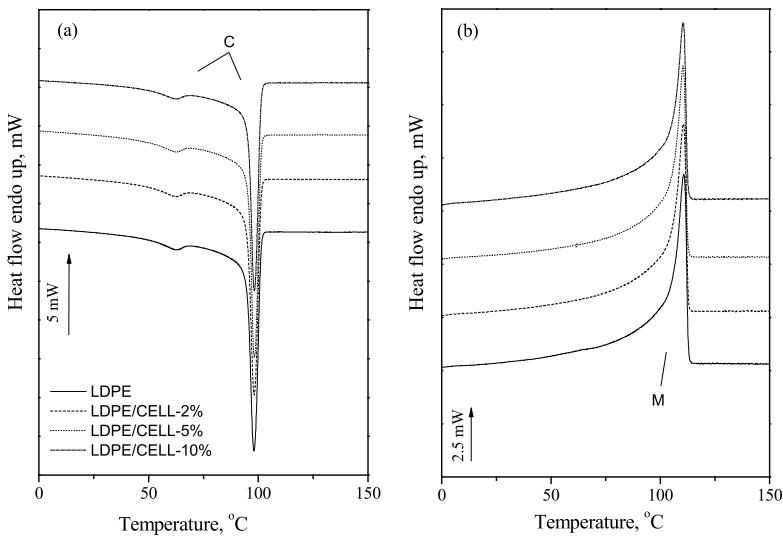


Fig. 4. DSC exotherms (a) and endotherms (b) of LDPE and its composites with cellulose: 2nd heating, heating rate 20 °C/min. The arrows indicate the crystallization (C) and the melting (M) related to crystallization peaks.

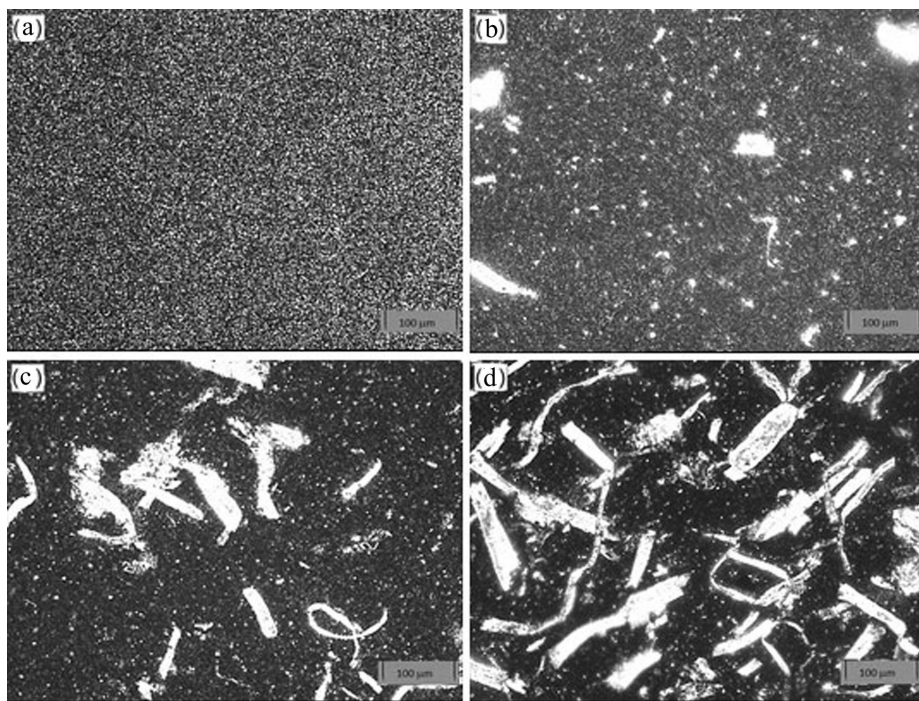


Fig. 5. PLM pictures of LDPE and its composites taken at 25 °C: (a) pure LDPE, (b) LDPE/CELL-2%, (c) LDPE/CELL-5%, (d) LDPE/CELL-10%.

The thermal behaviour of LDPE/CELL composites in general is similar to that of pure LDPE. Crystallization and melting temperatures of composites and LDPE are the same and do not change with an increasing cellulose content. Incorporation of cellulose to LDPE reduces only the overall crystallinity of composites. Probably, cellulose hinders the migration and diffusion of LDPE chains resulting in a weaker crystallization process compared to neat LDPE.

ACKNOWLEDGEMENT

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Tselluloosi sisalduse mõju polülaktiidi/tselluloosi ja madaltiheda polüetüleenit/tselluloosi komposiitide termiliste omadustele

Dmitri Šumigin, Elvira Tarasova, Andres Krumme ja Anti Viikna

Käesolevas töös uuriti polülaktiidi/tselluloosi (PLA/CELL) ja madaltiheda polüetüleenit/tselluloosi (LDPE/CELL) komposiitide termilisi omadusi, kasutades diferentsiaalset skaneerivat kalorimeetriat (DSC) ning kuumaluse valgusmikroskoopiati. Komposiidid valmistati kompaundimise teel, kasutades kaheteelist ekstruderit. DSC ja kuumaluse valgusmikroskoopia uuringud viidi läbi mitteisotermilises režiimis kuumutus- või jahutuskiirusega 20 °C/min.

Tselluloosi lisamine muudab PLA/CELL-i komposiidid amorfseteks. Siiski on PLA ja selle komposiidide iseloomulikuks omaduseks külmkristalliseerumine kuumutusprotsessis. Kõikidel PLA/CELL-i komposiidide DSC endotermidel esinesid külmkristalliseerumise haripunktid vahemikus 130–134 °C ja nendele vastavad sulamisharipunktid temperatuuril 152–153 °C. Summaarselt on PLA/CELL-i komposiidid siiski amorfset, sest külmkristalliseerumise entalpia ΔH_{cc} ja sulamise entalpia ΔH_{mc} on peaaegu võrdsed. Lisaks vähenevad ΔH_{mc} ja ΔH_{cc} oluliselt kuumutuskiiruse suurenemisega üle 20 °C/min ning seetõttu on haripunkte raske tuvastada. Ilmselt ei ole amorfsetel PLA ahelatel kuumutuskiiruse suurenemisega ümberkordistamiseks piisavalt aega ja selle tulemusena väheneb külmkristalliseerumise aste. PLA/CELL-i (tselluloosi sisaldus 10%) sulamisprotsessi mikroskoopilisel vaatlusel tuvastati kristalliliste superstruktuuride moodustumine temperatuurivahemikus 130–140 °C ja nende täielik sulamine temperatuuril 155 °C.

DSC uuringute põhjal määrati kindlaks, et tselluloosi lisamine ei mõjuta PLA klaasistumistemperatuuri, kuigi kuumutuskiiruse kasv põhjustab selle tõusu.

LDPE ja selle komposiitide käitumine erineb tugevalt PLA/CELL-i komposiitidest. LDPE-l puudub külm-kristalliseerumine. LDPE/CELL-i komposiitide DSC eksotermidel esineb kaks haripunkti: 61–62 °C ja 98 °C. Nendele vastab üks lai LDPE-le iseloomulik sulamisharipunkt temperatuuril 110–111 °C. Tulemused näitavad, et lisatud tselluloos ei mõjuta komposiitide kristalliseerumis- ja sulamistemperatuure. Samas alandab tselluloosi lisamine komposiitide kristallisatsiooniaset: 42 protsendilt puhta LDPE puhul kuni 38 protsendini LDPE/CELL-10% komposiidi puhul. Mikroskoopiapiltidel on selgelt näha tselluloosikoguse kasvust tingitud kristalliliste superstruktuuride arvu vähenemine komposiitides. Võib oletada, et tselluloos takistab LDPE makromolekulide migratsiooni ja difusiooni kristallisatsioonifronti. Seda saab ka tõlgendada kui nõrka segunevust LDPE/CELL-i segudes.

Kokkuvõtteks võib järeldada, et kuigi PLA ja LDPE leiavad kasutust sarnastes rakendustes, on termilistest omadustest lähtuvalt tegu väga erinevate materjalidega.

PAPER III

Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2013). Influence of Cellulose Stearate (CS) Content on Thermal and Rheological Properties of Poly(lactic acid)/CS Composites. J. Zicans, R. M. Meri (Toim.). Key Engineering Materials 559 (2013) 99–104. Trans Tech Publications Ltd

Influence of Cellulose Stearate (CS) Content on Thermal and Rheological Properties of poly(lactic acid)/CS composites

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Keywords: calorimetry, rheology, composites, cellulose stearate, polylactide, low-density polyethylene.

ABSTRACT

Recently, a deliberate interest to look for composites that are eco-friendly and biodegradable appears. Therefore materials based on raw materials derived from natural resources of plant are being studied. One of the most promising bio-based polymers that have attracted the interest of many researchers is poly(lactic acid), which is made from plants and is readily biodegradable. Cellulose is one of the strongest and stiffest fibres available and it has a high potential to act as reinforcing agent in biopolymers. In our work we esterified cellulose using stearyl chloride in ionic liquid and studied the effect of cellulose stearate addition to matrix polymers on thermal and rheological properties.

INTRODUCTION

Over the past decade, much attention has been focused on biodegradable and biocompatible polymers. Natural polymers, biopolymers, and synthetic polymers based on annually renewable resources are the basis for the twenty-first-century portfolio of sustainable, eco-efficient plastics. In this direction, polylactide (PLA) is one of the most promising candidates, having a good mechanical properties [1,2].

Most sustainable plastics cannot compete economically with conventional petroleum-derived plastics in their present state. Economically favorable composites, therefore, are expected to be made from costly sustainable plastics in combination with inexpensive natural reinforcement fibers. Cellulosic materials are the most abundant form of biomass and the form most likely to be used as reinforcement fibers, not only for ecological and economic reasons, but also because of their high mechanical and thermal performance. To utilize and design materials successfully for industrial applications, it is first imperative to determine material properties that will affect performance [3].

The thermal and rheological behavior of PLA composites based on native cellulose or cellulose acetates has been well studied by different thermal analysis [2,4-10]. However, to our knowledge, studies of thermal and especially rheological properties of PLA composites based on cellulose esterified with high fatty acids (C18) have not been presented in literature. Nevertheless, thermal and rheological behaviour is important from both a scientific and industrial viewpoint, because polymer processing is mainly affected by thermal parameters and flow behaviour of polymers [5]. Thus, fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, injection moulding, film blowing etc. Rheological measurements are often used for examining and understanding the interaction of the different constituents of a multi-component or multiphase mixture and their influence on the flow and other properties of such materials [11].

EXPERIMENTAL PART

Materials

The used Cellulose was acid-free α -cellulose with length 60 ± 10 μm and width 5 ± 2 μm purchased from Hahnemühle FINEART. Cellulose stearate (CS) was prepared by esterification reaction of cellulose with stearoyl chloride in ionic liquid 1-Butyl-3-methyl-imidazolium Chloride (BmimCl) [12]. Stearoyl chloride of technical grade was purchased from Sigma-Aldrich Company. NatureWorks LLC supplied Poly(lactic acid) granules (PLA Polymer 4042D). Composites of PLA with cellulose stearate were abbreviated as PLA/CS-n%, where n = 0, 20, 50 and 60 means the cellulose stearate weight content in composites. Content of cellulose stearate is expressed in weight percent to the total weight of composite. Molar masses (weight-averaged M_w) of PLA were estimated by rheology using single exponential model for Molecular Weight Distribution determination using rheometer Anton Paar Physica MCR 501. M_w distribution of CS was obtained by GPC at 160°C in trichlorobenzene. Apparent M_w of PLA and CS are 77 kg/mol and 300 kg/mol respectively.

Composite processing

The synthesis of cellulose stearate was done using the following procedure: stearoyl chloride (5 mole per anhydride glucose unit, AGU) was carefully added to the solution of cellulose in BmimCl. The temperature was kept at 80°C for 3 h. Reaction was carried out under nitrogen atmosphere and with the use of reflux condenser. Isolation was carried out by precipitation into 200 ml of methanol, washing with large amount (2 liters) of methanol and drying under vacuum at 70°C for 12 h. After that the sample was dissolved in chloroform and precipitated by adding of methanol. Again it was dried, and the same procedure was repeated twice to remove any intermediate products and unreacted materials. The degree of substitution (DS) of cellulose stearate was analyzed by titration method which gave $\text{DS}=0,4$. Composites of PLA with CS were prepared by addition of cellulose stearate powder to matrix polymer. PLA/CS mixture of different compositions was mechanically mixed for 10 min at 60 rpm in a Labor mechanical mixer. Then PLA/CS samples were prepared by compounding on micro-conical twin screw compounder (Thermo Scientific HAAKE MiniCTW Micro compounder). For PLA/CS composites temperature of 180°C was held constant in all sections during compounding.

Differential scanning calorimetry

Perkin Elmer differential scanning calorimeter DSC-7 was used for non-isothermal measurements at scanning rate of $20^\circ\text{C}/\text{min}$. The instruments were calibrated using indium and tin at all applied heating rates. Nitrogen was used as furnace purge gas. In all DSC experiments sample mass of 3.00 ± 0.03 mg was held constant.

Rheology

The melt rheological properties of the samples were determined using a rheometer Anton Paar Physica MCR 501. All measurements were carried out in a nitrogen atmosphere at 190°C . Amplitude sweep was performed with all the samples and was kept at 5% in all composite samples frequency scans.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Fig. 1 shows the typical non-isothermal DSC endotherms of pure PLA and PLA/CS composites, recorded at 20°C/min. The pure PLA is characterized by glass transition temperature (marked in Fig. 1 as G) at 58.0 °C that agrees with literature data [6] and melting temperature of 151 °C.

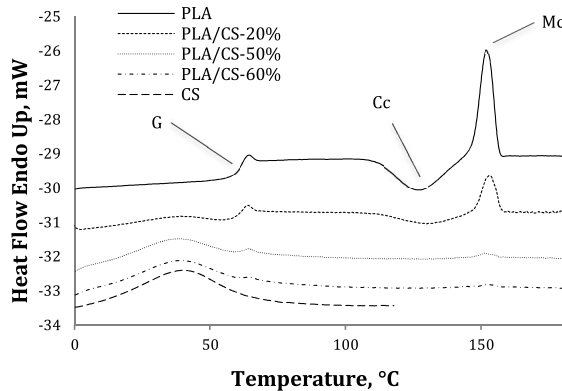


Figure 1. DSC endotherms of PLA, CS and PLA/CS composite materials: 2nd heating, heating rate of 20°C/min.

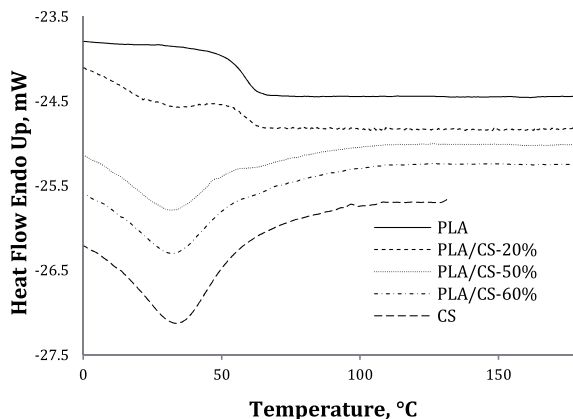


Figure 2. DSC exotherms of PLA, CS and PLA/CS composite materials: 2nd heating, heating rate of 20°C/min.

As can be seen from the melting curves all PLA composites including the pure polymer have cold crystallization peaks located at 124-127°C (marked with Cc in Fig. 1) and subsequent melting peaks at 151-153 °C (marked with Mc in Fig. 1). However it should be noted here that the PLA/CS composite are assumed as amorphous since cold crystallization enthalpy and melting enthalpy values are almost the same. Cold crystallization peaks indicate regions of realignment and transition from amorphous to crystalline phases.

It was established by us that when the fatty chain length (attached to the cellulose) exceeds 12 carbon atoms, a fraction of the alkyl chains is able to crystallize (so-named side chain crystallization) and crystallization and melting peaks are observed in DSC thermograms for CS at 34°C and 40°C, respectively.

Addition of CS to matrix PLA has no impact on PLA glass transition and melting temperatures. However, with increasing CS, melting enthalpies of PLA in composites decrease proportionally to weight fraction of added CS, however melting enthalpies of peaks related to CS, respectively, increase. As can be seen from Fig. 2 the higher the CS content the higher is the crystallization enthalpies of CS in composites. CS crystallisation peak grows gradually and already at ratio of 50/50 PLA glass transition region crossovers with crystallization peak of CS.

All these facts points out that PLA and CS crystallize independently in composite and no co-crystallization can be seen. Therefore it can be suggested that PLA and CS surfaces are not fully compatible, in spite of both polymers has similar esters groups.

Rheology

First of all, the linear viscoelastic range characterized by the onset of the strain dependent behaviour for all composites was detected. The dynamic modulus of PLA remains linear up to 10% of strain. Addition of CS to PLA slightly reduces the linear viscoelastic range. Therefore, the strain of 5% was chosen as constant for the dynamic frequency sweeps of all composites samples.

Fig. 3 demonstrates the dynamic frequency sweeps for PLA and its composites with CS. Native PLA shows Newtonian flow till 100 rad/s, while for its composites the Newtonian flow is hardly observed and yielding may occur in this case.

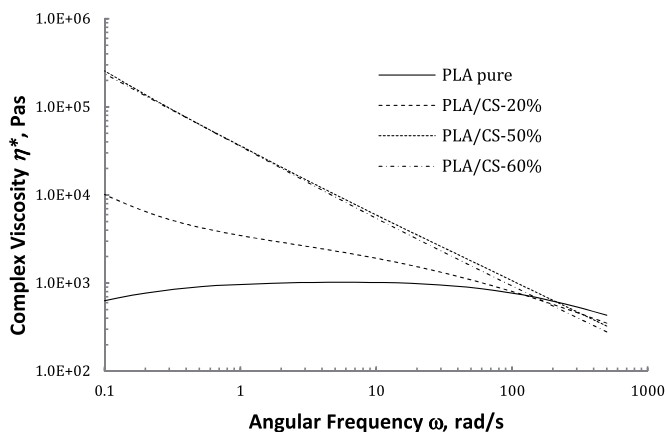


Figure 3. Dynamic viscosity η^* as a function of angular frequency ω for PLA/CS composites with different cellulose stearate content

As can be seen from the Fig. 3 the processability of composites is affected by the addition of CS to the polymer melts. In comparison to matrix PLA the PLA/CS composites have higher melt viscosity, especially, at low angular frequencies ω where contribution of CS phase becomes apparent. The increase of the viscosity depends on the CS content: the higher the CS content in composites, the higher is the values of melt viscosity η^* . Taken into account the fact that PLA and CS have weak compatibility, as was defined from DSC behaviour, the presence of CS particles perturbs normal polymer flow and hinders the mobility of chain segments. Therefore, the higher the amount of the CS, the worse is the dispersion of the minor phase in the melt and the higher is the viscosity of the composite.

Fig. 4 shows the angular frequency dependences of storage (circles) and loss (squares) moduli of PLA/CS composites with various content of CS. Pure PLA shows classical viscoelastic behaviour and at lower angular frequencies loss modulus is higher than the storage modulus. Addition of CS

leads to the increase of storage modulus. As can be seen from the Fig. 4 when CS content becomes higher than 20 wt% the storage modulus begins to dominate over loss modulus values: with high CS content behaviour of dynamic moduli is becoming similar to pure CS, for which storage modulus exceeds loss modulus by one order of magnitude. The enhancement observed in dynamic modulus is significantly higher at low ω than at high ω . For storage moduli the slope of the modulus curves diminish with increasing amounts of CS. The higher the CS content, the higher is the volume fraction of CS phase, and the higher is the G' at low. At high ω the effect of CS decreases and the matrix contributions dominate. Finally, based on G' and G'' data serving as the measure of molecular rigidity we can conclude that when CS content is higher 20% the composite materials loses its viscoelastic properties and become more rigid than native polymer.

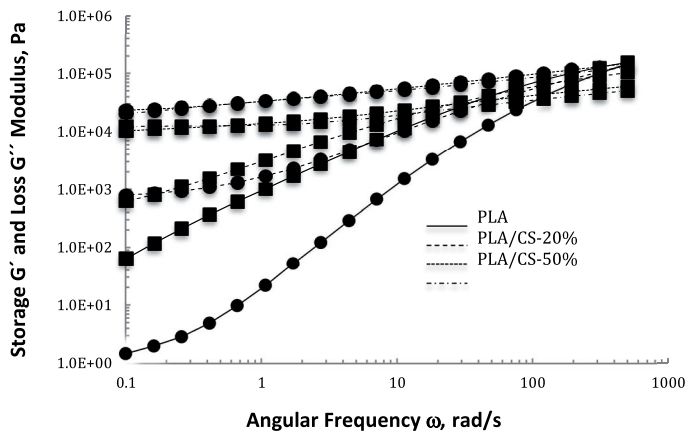


Figure 4. Frequency dependence of storage modulus G' and loss modulus G'' for PLA/CS composites with different content of cellulose stearate.

CONCLUSIONS

Studies on the non-isothermal crystallization and melting behavior of PLA/CS composites prepared by compounding in twin-screw extruder were carried using DSC. Native PLA has cold crystallisation and melting peaks on endotherm, which are clearly decreasing with growing content of CS. It is confirmed that CS has no impact on PLA glass transition and melting temperature. However, addition of CS decreases melting enthalpies of PLA in composites proportionally to weight fraction of added CS. This means that PLA and CS surfaces are not fully compatible.

Rheology measurements of PLA/CS composites were performed in the dynamic oscillatory mode. In certain range of shear rate PLA shows viscoelastic behaviour with loss modulus being higher than the storage modulus. With addition of CS, storage modulus is increasing and overrides loss modulus values and behaviour of dynamic moduli curves is becoming similar to pure CS. Dynamic viscosity of PLA/CS composites increases with addition of CS. As a result, due to poor compatibility of PLA and CS, the presence of cellulose stearate particles perturbs normal polymer flow and hinders the mobility of chain segments. Therefore, ≤ 20 wt% of CS in composite is the optimum amount for composites to reserve their plasticity.

Acknowledgements

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Baltic Polymer Symposium

10.4028/www.scientific.net/KEM.559

Influence of Cellulose Stearate (CS) Content on Thermal and Rheological Properties of Poly(lactic acid)/CS Composites

10.4028/www.scientific.net/KEM.559.99

PAPER IV

Tarasova, E.; Šumigin, D.; Kudrjašova, M.; Krumme, A. (2013). Preparation of Cellulose Stearate and Cellulose Acetate Stearate in 1-Butyl-3-Methylimidazolium Chloride. J. Zicans, R. M. Meri. *Key Engineering Materials* 559 (2013) 105–111. Trans Tech Publications Ltd

Preparation of Cellulose Stearate and Cellulose Acetate Stearate in 1-Butyl-3-Methylimidazolium Chloride

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Keywords: ionic liquid BMIMCl, modification of cellulose, cellulose stearate, cellulose acetate stearate

Abstract: Cellulose stearates were prepared in a 1-butyl-3-methylimidazolium chloride ionic liquid. The addition of base pyridine as well as catalyst Tin octoate sufficiently increases the degree of hydroxyl group substitution. The new path for preparation of cellulose mixed esters, namely cellulose acetate stearate (CAS), is performed. The ¹H NMR data confirmed the structure of obtained mono- and mix- cellulose esters.

Introduction

One of the most interesting aspects of cellulose chemical modification is the production of cellulose fatty acid esters. Long-chain aliphatic acid esters of cellulose have been identified as potential biodegradable plastics due to the enzymatically labile ester bond and the natural abundance of both cellulose and fatty acids [1]. However, due to its high crystallinity, cellulose is difficult to dissolve in common solvents. Recently, ionic liquids (ILs) have been shown to be a perfect solvent for cellulose that can also be a reaction media for homogeneous modification of cellulose. In particular 1-butyl-3-methylimidazolium chloride (BmimCl) seems to be the most popular and efficient ionic solvent for cellulose. One of the perspective ways for development of cellulose thermoplastic materials is the synthesis of high cellulose esters, CEs, in which OH-groups of cellulose are substituted by long-chain fatty acids $-\text{CO}(\text{CH}_2)_n\text{CH}_3$ with $n \geq 12$. By employing a homogeneous reaction, the whole cellulose chain is accessible for modification and problems related to two-phase (industrial) reactions are avoided. However, it was shown that the obtainable degree of substitution, DS, of high cellulose esters (in particular, cellulose laurate, $n=10$) in BmimCl is not higher than 1.5 [2]. This value is even lower, usually less than 1, for cellulose stearates with $n=16$. In our work we used BmimCl as a reaction media for homogeneous esterification of cellulose with the focus to produce high cellulose esters with larger DS. Another perspective way for development of cellulose thermoplastic materials is the preparation of mixed cellulose esters where some of cellulose OH-groups is substituted with acetyl groups and others with long-chain fatty acids. However, most of publications are still focused on mono-substituted esterification of cellulose in ILs. The preparation of mix-substituted CEs in ionic liquids are only mentioned in literature for commonly used cellulose acetate propionate [3] and cellulose acetate butyrate [4] and is completely absent for cellulose acetate stearate or other higher fatty acids. In present paper we are going to report a homogeneous mix-acylation of cellulose in ionic medium with the focus to prepare cellulose acetate stearate.

Experimental procedure

Chemicals and Materials. All the chemicals used are commercially available. Cellulose used was acid-free α -cellulose (chemically clean, no lignin) supplied by Hahnemuhle FINEART. Reagents used in synthesis of ionic liquid (chlorobutan and 1-methylimidazole) and cellulose stearates (stearoyl chloride, SC, acetyl chloride, AC, Tin II octoate, pyridine) were purchased from Sigma-Aldrich Company.

BmimCl synthesis. The BmimCl was synthesized in the laboratory using reported procedure [5]. In typical preparation, 1.5 mole of chlorobutan and 1 mole of 1-methylimidazole were added to a round-bottomed flask fitted with a reflux condenser for 3 days at 80°C with stirring. The top phase of the two phases formed contains starting material, which is removed by washing several times with ethyl acetate. The yellowish IL product of BmimCl was further heated to 50°C under vacuum to eliminate any dissolved ethyl acetate solvent.

Dissolution of cellulose in BmimCl. Microcrystalline cellulose as well as ionic liquid was dried under vacuum at 105°C for 24 h prior the use. 1 g of cellulose was dissolved in 50 g BmimCl by stirring at 100°C for 12 h under vacuum.

Measurements. ¹H and ¹³C NMR spectra were acquired on a Bruker AV-300 spectrometer. The cellulose esters were measured in deuterated chloroform (CDCl₃) at 25°C and referenced to trimethylsilane (TMS) as an internal standard.

Molecular weight distribution of cellulose stearates was obtained by PL-GPC-220. Trichlorobenzene, TCB, was used as eluent (160°C, 0.5ml/min). Polystyrene standards were used for calibration.

Intrinsic [η] and reduced viscosities η/η_0 (where η is the viscosity of solution at certain temperature and concentration, η_0 is the viscosity of pure solvent at the identical temperature) of cellulose esters in chloroform were measured using Ubbelohde viscometer, holding the temperature at 25°C. Molar mass (MM) of pure cellulose was determined at 25°C from the intrinsic viscosity of cellulose solution in cupriethylenediamine hydroxide, CuEn, according to a standard procedure [6]. The MM was then calculated by Mark-Houwink equation [7]. The obtained MM was 100 000 g/mol.

Results and discussion

Cellulose stearates (CS)

The synthesis of cellulose stearates were done according to common procedure [8]: stearoyl chloride (5 moles per anhydroglucose unit, AGU) was carefully added to the solution of cellulose in BmimCl. The temperature was kept at 80°C for 3 h. All reactions were carried out under nitrogen atmosphere and with the use of reflux condenser. Isolation was carried out by precipitation into 200 ml of methanol, washing with large amount (2 liters) of methanol and drying under vacuum at 70°C for 12 h. After that the samples were dissolved in chloroform and precipitated by adding of methanol. Again it was dried, and the same procedure was repeated twice to remove any intermediate products and unreacted materials. A series of cellulose stearates has been successfully produced by linking aliphatic acid chlorides (C18) onto cellulose backbone. The DS of cellulose stearates was analyzed by titration method [7]. The details of the synthesis and DS values of obtained products are listed in Table 1.

Table 1. Condition and results of acylation of cellulose dissolved in BmimCl.

Sample	details	DS
CS-I	Molar ratio AGU:SC=1:5, no base, no catalyst	0.4
CS-II	Molar ratio AGU:SC:pyridine=1:5:6	1.0
CS-III	Molar ratio AGU:SC=1:5. One drop of Tin octoate is added.	1.6
CAS-I	Molar ratio AGU:AC:SC=1:3:6	NA
CAS-II	Molar ratio AGU:AC:SC=1:3:3	NA

Firstly we conduct acylation of cellulose with stearoyl chloride without any base or catalyst. Such cellulose stearates are named as CS-I in Table 1.

Structure analysis by means of ^1H NMR after acylation revealed the introduction of the alkyl chains into cellulose. As can be seen from the fig. 1, the protons of stearate moiety appear at 2.3 (H-8), 1.2-1.6 (H-10-23) and for methyl end of stearate is 0.8 (H-24) ppm. These peaks are absent for pure cellulose. The ^{13}C NMR spectra (not presented here) show peaks at 14 ppm attributed to C24 of the methyl groups, C8 carbon atoms are indicated by the peaks from 33 to 35 ppm. The peaks between 22 and 30 ppm include the signals of C9-C23. These results are in very good agreement with the NMR spectra reported for cellulose stearates [8-10].

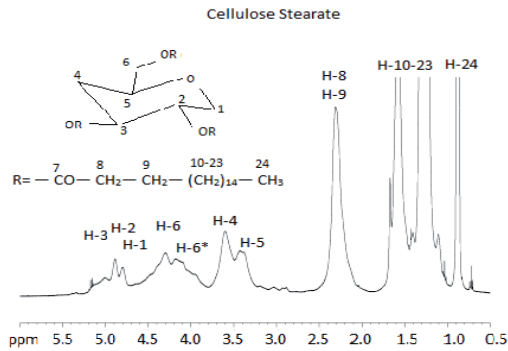


Figure 1. ^1H NMR spectrum of CS-I in CDCl_3

As it is mentioned in literature [11], in the absence of any base, the HCl formed in the synthesis of cellulose stearates can cause the degradation of the cellulosic backbone during reaction. Therefore, the GPC was applied to investigate hydrolytic degradation of the polymer chain. As can be seen from the fig. 2a no sufficient degradation (only negligible part of de-polymerization can be seen) is found in CS-I without a base. If degradation would take place, the additional peak in GPC curves at low MM had to be observed, or whole peak had to shift to lower MM. However, such effects are not observed. Additionally, the number-averaged MM of cellulose stearate calculated from molar mass distribution is comparable with viscosity-averaged MM of pure cellulose. The possible degradation process can also be checked by well-known method, namely, differential scanning calorimetry, DSC. Fig. 2b shows the

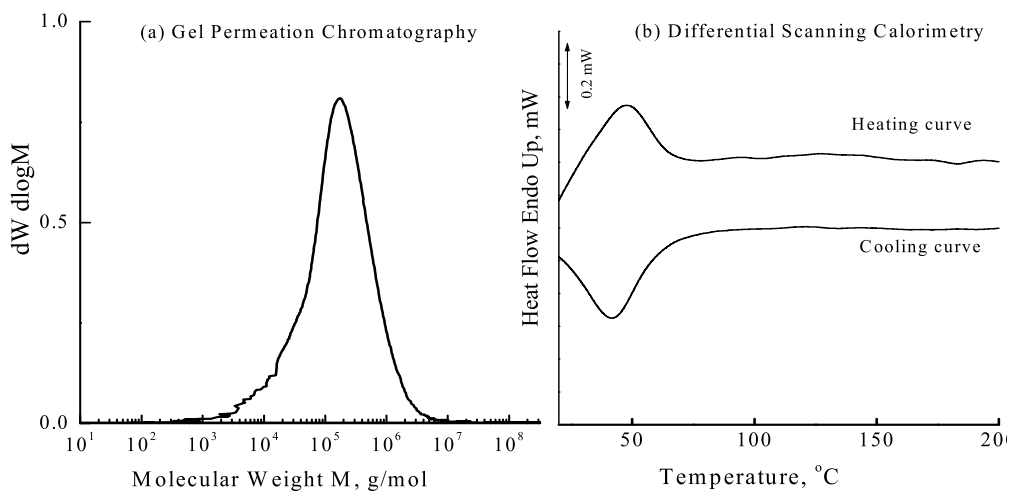


Figure 2. (a) Molar mass distribution of CS-I, obtained by GPC. (b) Non-isothermal heating and cooling curves of CS-I, obtained by DSC at $10^\circ\text{C}/\text{min}$.

non-isothermal DSC heating and cooling scans of chosen CS-I. Endotherm as well as exotherm of CS does not show any pronounced peak of degradation in the range of temperatures from 50°C up to 200°C , as seen in fig. 2b. The peaks observed in DSC scans at 34°C and 40°C are related, respectively, to crystallization of the alkyl chains (fatty acid groups) and consequent melting of these crystals. This effect is well-known for high cellulose esters as side chain crystallization. The

absence of sufficient degradation during modification of cellulose in IL can be a consequence of that the HCl formed during reaction are fixed by ionic liquid due to the fact that BmimCl itself is a tertiary amine.

It has been reported by several authors that acylation with long-chain fatty acids in ionic liquids gives only moderate DS less than unity [10, 13]. Unfortunately, in our hands also in the absence of any base or catalyst only moderate DS (0.4, see Table 1 sample SC-I) has been achieved. With the focus to produce highly substituted cellulose esters, it was decided to use catalysts to increase DS. Therefore, the effect of catalyst on efficiency of esterification of cellulose in BmimCl has also been studied. As a possible efficient catalysts pyridine and **Tin(II) octoate** was chosen. **Tin(II) octoate** is widely used in polymerization of different esters (polylactide, polyglucolide etc.), but was never used before for esterification of cellulose, at least for cellulose in ILs.

It was found that addition of low amount of pyridine (3 equivalents of pyridine to AGU) does not affect DS strongly, while already a molar ratio AGU:pyridine of 1:6 is sufficient to achieve $DS \cong 1$, see CS-II in Table 1.

In the presence of Tin octoate the efficiency of cellulose esterification is significantly increased and obtained values of $DS > 1$: for example, obtained values of DS for CS-III was 1.6. Moreover, the time of synthesis in the presence of Tin octoate can be significantly decreased up to 1.5-2 hours preventing possible degradation process.

It should be noticed that addition both pyridine and Tin octoate to reaction media does not cause the degradation of polymers, as indicated by intrinsic viscosity measurements of all samples.

Cellulose acetate stearate (CAS)

Little attention has been given to the synthesis of mixed esters in ILs. Cellulose acetate (CA) is the most widely produced cellulose ester, because of its good physical properties. However it is not water resistant and has a poor solubility in wide range of organic solvents. By introducing the stearyl group into CA, it is possible to overcome these limitations of CA and obtained mixed cellulose ester, cellulose acetate stearate, keeping the good properties of CA but also exhibits better solubility in organic solvents due to its higher hydrophobicity. However, the preparation of mix-substituted cellulose esters in ILs is only mentioned for cellulose acetate butyrate and propionate, and no information available for synthesis of mix-substituted higher esters, such as cellulose acetate stearate (CAS). In this work the homogeneous mix-acylation of cellulose in BmimCl was studied.

In principle, the composition of cellulose mixed esters can be controlled by the ratio and order of addition of the acylating agents. Due to rather low chemical reactivity of stearyl chloride in comparison with acetyl chloride, the stearyl chloride was introduced first, left to react for 6 h; next it was precipitated, washed (by similar procedure described in previous section for cellulose stearate) to remove any unreacted materials and dried. Then the obtained CS was again dissolved in BmimCl and after that acetyl chloride was introduced and whole mixture was left for further reaction for 2 h. After that the product was precipitated with methanol, washed several times and dried. The molar ratios of components AGU:AC:SC were varied. The obtained samples were well dissolved in chloroform and some other organic solvents. A representative ^1H NMR spectrum of obtained product (sample CAS-I) recorded in CDCl_3 is shown in fig. 3. Comparing the given spectrum with the spectrum of CS-I of the fig. 1, the differences in NMR peaks of CS and CAS can be easily observed.

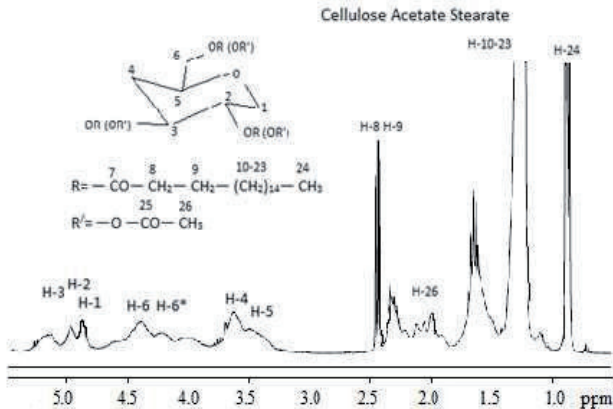


Figure 3. ^1H NMR spectrum of CAS-II in CDCl_3

substituted acetate groups in CAS-II is less than in CAS-I or CAS-II was much better purified from impurities.

Due to poor spectral resolution the spectra of cellulose esters do not provide impeccable confirmation of CAS production. Therefore we conducted additionally the intrinsic viscosity measurements of all our samples. Figure 4 represents the reduced viscosity Wolf plot for solutions of CS and CAS in chloroform.

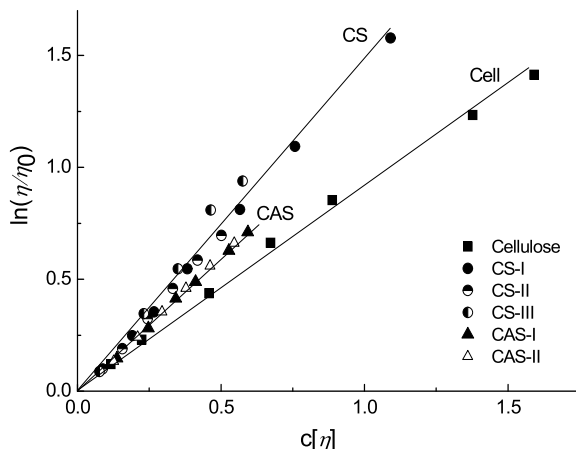


Figure 4. Reduced Wolf plot for solutions of CS and CAS in chloroform at 25°C

it can mean that chemical structure of obtained products is dissimilar from CS. Taken into account the NMR results we can suggest that at least low-substituted cellulose mix-esters can be produced by offered method. To our knowledge, this is one of the first experimental attempts to synthesize cellulose acetate stearates in ILs.

Conclusions

The results of our work shows that without any base and catalysts the cellulose stearates with low DS less than 0.5 can be easily synthesized in BmimCl ionic liquid. However, DS of cellulose stearate can be sufficiently increased up to 1.6 using either the base pyridine in large amount or small amount of special catalyst Tin octoate.

The protons of stearate moiety appear at approximately the same position as for pure CS-I: 2.2-2.4 (H-8, H-9), 1.2-1.6 (H-10-23) and for methyl end of stearate 0.9 (H-24) ppm. The acetate methyl group leads to the clearly seen signal at 2.0 ppm (H-26). The position of this signal for acetate methyl group in CAS is identical to that observed for cellulose diacetate (done by us), cellulose acetate laurate [11] and cellulose acetate butyrate [4]. The CAS-I and CAS-II show identical NMR spectra, however peaks related to acetate methyl groups in CAS-I are not so clear pronounced. Hence, it can be speculated that either the content of

acetate methyl groups in CAS-I are not so clear pronounced. Hence, it can be speculated that either the content of

acetate methyl groups in CAS-I are not so clear pronounced. Hence, it can be speculated that either the content of

In our work the preparation of novel mixed cellulose esters, namely cellulose acetate stearate, was successfully conducted and confirmed by means of NMR spectroscopy.

Acknowledgments

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Preparation of Cellulose Stearate and Cellulose Acetate Stearate in 1-Butyl-3-Methylimidazolium Chloride

10.4028/www.scientific.net/KEM.559.105

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