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 posses 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 $T = 180\,°C - 210\,°C$ for LDPE and $T = 150\,°C - 190\,°C$ 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 $60\,\mu m \pm 10\,\mu m$ and width $5 \pm 2\,\mu m$) 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 (~23 °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.
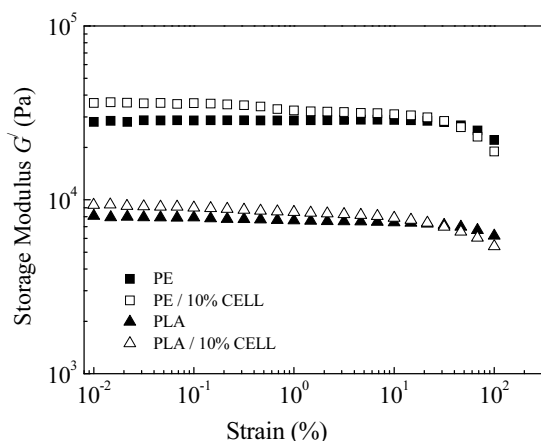
Fig. 1. Amplitude sweep (190 °C, $\omega = 10$ rad/s) for matrix polymers PLA and PE and their composites with 10 wt% of cellulose
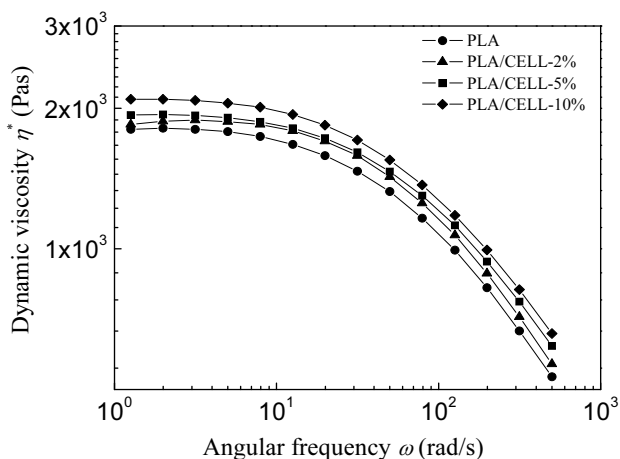
Fig. 2. Dynamic viscosity η^* as a function of angular frequency ω for PLA/CELL composites with different content of cellulose

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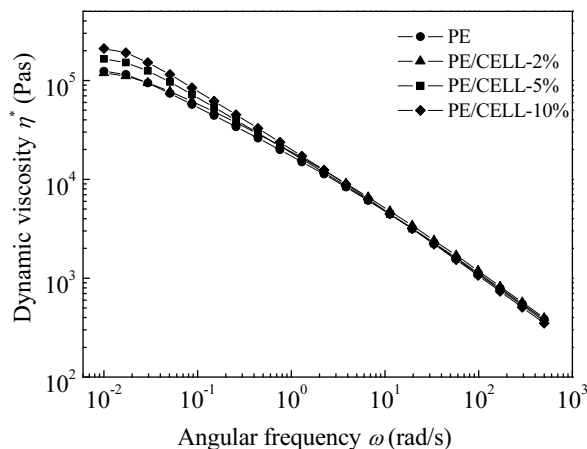
Fig. 3. Dynamic viscosity η^* as a function of angular frequency ω for PE/CELL composites with different cellulosic content

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.
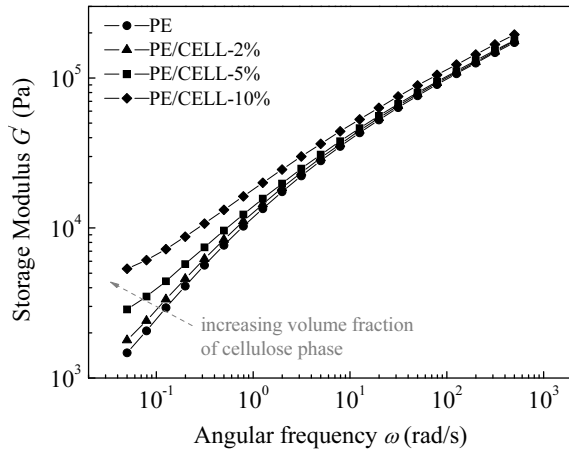

Fig. 4. Frequency dependence of storage modulus G' for PE/CELL composites with different content of cellulose. Arrow shows the increasing volume fraction of cellulosic phase in the matrix melt

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, % (± 7 %)	Tensile strength σ_b, MPa (± 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.
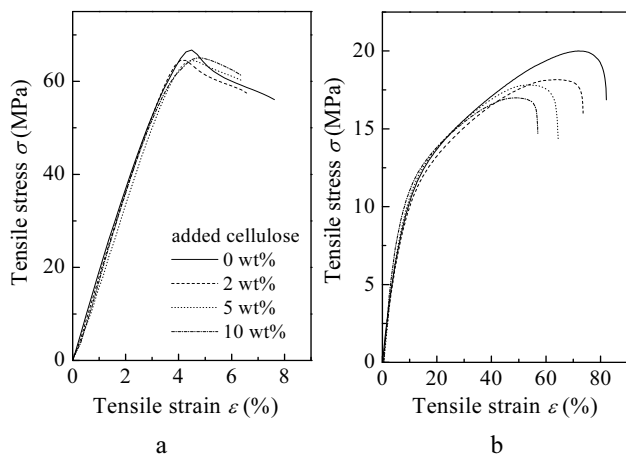

Fig. 5. Stress-strain curves for composites containing various content of cellulose: a – PLA/CELL, b – PE/CELL

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 pertubation 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.

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