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분쇄된 율피로 충전된 Poly(lactic acid) 복합재료의 유변학적 및 가공 특성

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Rheological and Processing Properties of Poly(lactic acid) Composites Filled with Ground Chestnut Shell

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Abstract: Rheological behavior of the poly(lactic acid) (PLA) composites filled with ground chestnut shell (CN) was investigated. Application of various measuring techniques: small amplitude oscillatory shearing rheometry and capillary rheometry, allowed to determine in detail changes of rheological behavior and potential processing limitations of fully biodegradable composites modified by an organic waste filler. Different influence of the ground chestnut shell filler on PLA-based composites flow behavior was observed during rotational and capillary rheometry. Incorporation of particle-shaped natural filler resulted in strong increase of composites' complex viscosity. However, due to occurrence of significant wall slip during capillary flow, materials containing ground chestnut were characterized by improved processability which result in increased melt flow index (MFI).

Keywords: poly(lactic acid), chestnut, composite, rheology.

Introduction

Nowadays, polymers are one of the most widely used materials. They play a significant role in production of packaging, consumer products or automotive parts. Ever growing utilization of plastics brings about increasing production of non-biodegradable waste. Although extensive development of novel highly efficient recycling methods, tons of plastic waste are dumped on landfills every year. In the era of rapidly decreasing amount of non-renewable resources a new class of environmentally-friendly materials needs to be employed in mass production, even though the petrol-based polymers comprise of a small percent of overall crude oil consumption (4-6%). Utilization of bio-based, biodegradable polymers, including poly(lactic acid) (PLA), polyhydroxyalkanoate (PHA), poly(butylene adipate-*co*-terephthalate) (PBAT) and thermoplastic starch, has recently gained a lot of attention of researchers and producers alike, yet the market share of those biopolymers still remains little.[1-8] The reason of this situation is relatively high price and low thermomechanical stability and in some cases brittleness of aforementioned materials.[6-8]

Polymeric composites have always been developed to improve materials' properties, give them a defined characteristics or lower the price. Apart from using conventional, inorganic fillers, incorporation of organic fillers into polymeric matrix is another way to lower the impact of plastics on the environment. Lignocellulosic fillers, i.e. particles and fibers originating from different parts of plants are reported to increase mechanical and physicochemical properties as well as decrease density of thermoplastic and thermosetting polymeric composites.[7,9-13] Natural-based fillers also lower the price of composite final products, in comparison to pure polymeric materials,[14] they are fully renewable and their environmental impact is considerably low.[15] Furthermore, the possibilities of implementation are very wide, as there are various types of natural fillers, which can be used in polymeric composites.

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Different examples of chemically modified[16] and raw,[17] fibrous[18] and particle-like,[19] specially prepared and originating from agricultural waste fillers are described in the literature. The latter is especially interesting from economical and ecological point of view. What's more, composites comprising of waste filler and polymeric resin may reveal advantageous properties.[17,19,20] An example of a agricultural waste filler is horse chestnut shell powder. Horse chestnut (Aesculus hippocastanum) is a large tree, cultivated in parks and gardens of northern hemisphere. Shells of its fruits contain a saponin called aescin, used in production of medicines. Several papers describe application of horse chestnut powder in polyester[21] and polypropylene[22] composites. In a previous study, we described thermal and mechanical properties and morphology of ground chestnut shell powder-filled PLA.[23] Even though the results of our investigation were promising, further insight into the characteristics of the researched material is needed. Apart from mechanical and thermal stability of composites, rheological and processing properties are crucial in assessment of the possibilities of industrial utilization of composites. Therefore, the aim of this study is a complex evaluation of rheological properties of biodegradable, bio-based composites comprising of horse chestnut powder embedded in PLA matrix.

Experimental

Materials and Sample Preparation. Commercial poly(lactic acid) Ingeo^{TM} 3001D with MFI of 22 g/10 min (2.16 kg, 210 ºC) and density of 1.24 g/cm^3 was delivered by Nature Works (USA). This biodegradable polyester grade was applied in presented studies because of low modification level, lack of lubricants and slip agents.

Ground chestnut shell (CN, Aesculus hippocastanum) was used as a filler for preparation of biocomposites. The mean arithmetic size of particle-shaped filler, determined by Fritsch Analysette 22 apparatus was 10.7 μm. Microscopic images of the ground filler were used for determination of organic particles aspect ratio (Figure 1). Digital images were acquired using a Nikon Eclipse E400 microscope equipped with an Opta-Tech digital camera. Using the pictures, the particles' dimensions in two perpendicular directions were measured to assess the mean aspect ratio of the filler. The mean arithmetic aspect ratio of the particles, based on the dimensions of 25 randomly chosen particles, was 1.55, therefore it may be stated that used natural filler is particle-shaped. Detailed information

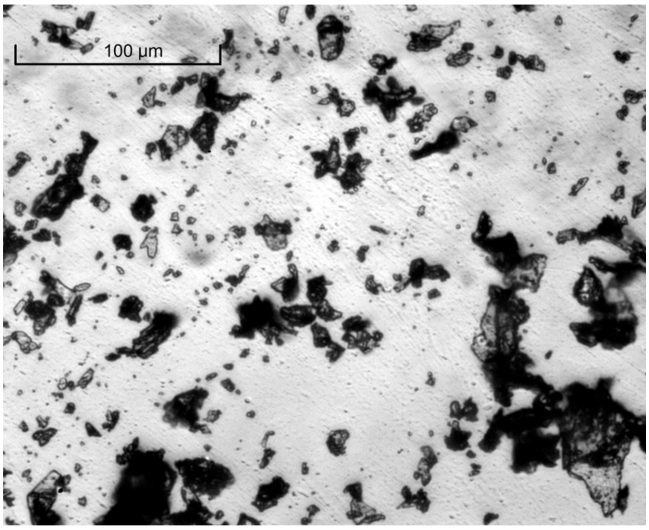

Figure 1. Microscopic image of the filler particles.

about preparation of the filler was published in our former paper.[23] Density of the filler was determined by hydrostatic weighing measurement realized in ethanol, and was equal to 1.15 g/cm^3.

Natural filler was incorporated into polymeric matrix in amounts of 2.5 wt% up to 30 wt%. In the presented study composites were named in reference to the amount of the contained chestnut filler, i.e. 2.5CN, 5CN, 10CN, 20CN and 30CN. PLA-based composites were mixed in a molten state using Zamak 16/40 EHD twin screw co-rotating extruder with maximum temperature setting 190 ºC and screw rotational speed of 100 rpm. The extrudate was pelletized after cooling in a water bath. All composite materials were dried before rheological test in Memmert ULE 500 dryer for 48 h at 60 ºC.

Methods. Rheological investigations in small-amplitude oscillation shearing mode were carried out using an Anton Paar MCR 301 rotational rheometer with 25 mm diameter parallel plates. The experiments were conducted at 190 ºC. In order to realize the dynamic oscillatory measurements, the strain sweep experiments had to be proceeded. Hence, the strain amplitude sweep experiments of all the samples were performed at 190 ºC with a constant angular frequency of 10 Hz in the varying strain window 0.01-100%. The strain value of 0.05% used during the frequency sweep experiments, was determined during the preliminary investigations and it was located in the linear viscoelastic (LVE) region.

Extrusion experiments at high shear rates (100-1500 s^{-1}) were conducted with the use of a capillary rheometer, Dynisco LCR 7000, at a temperature of 190 ºC. The influence of ground chestnut shell addition on rheological properties of PLA composites was determined using a capillary die with a diameter of D=0.762 mm and L/D=30. The Bagley correction was omitted due to a high value of L/D, and the analyses of changes in the rheological behavior were prepared with the use of an apparent shear stress value.[24]

The measurement of melt flow index of PLA and composites was carried out by means of Dynisco LMI 4004 plastometer according to ISO 1133. The measurements were conducted at temperature of 190 °C under 2.16 kg load.

Surfaces of the brittle fractured composites were examined and digitally captured using a scanning electron microscope Zeiss Evo 40, with a magnification of 500×. The electron accelerating voltage of 12 kV was applied. Prior to tests, all specimens were sputtered with a layer of gold.

Results and Discussion

In order to determine parameters for frequency sweep experiments it was necessary to assign linear viscoelastic region (LVE) for molten PLA and PLA-based natural composites. In Figures 2 and 3 the results of amplitude sweep experiments are presented. Changes of the storage (G') and loss (G'') moduli as a function of strain are presented on separate diagrams. It can be seen that incorporation of the particle-shaped filler provides to a significant increase of the elasticity, which results in higher G' values measured for the composite material in comparison to pure PLA. Moreover, with increasing content of the filler, Newtonian plateau was observed in narrower strain range, i.e. shortening LVE region. These phenomena are observed for all composites containing above 5 wt% of the CN filler. Therefore, it can be stated that the presence of the irregularly shaped organic particles creates strain sensitive structures, which are connected with phase separated morphology of the composite structure. This fact is also attributed to mutual interlocking of the agglomerated particles which became steric hindrances in a polymer melt.[1,25] Composite materials containing less than 10 wt% of the filler do not exhibit changes in the rheological behavior, which suggests that low amounts of the filler are well dispersed in polymeric matrix. It should be underlined, that in presented studies the amount of the filler is determined by its weight, the volumetric amount is much higher, therefore the presence of the agglomerated particles is unavoidable. For both polymer and composite samples viscous behavior dominates in the LVE region. This fact suggests a lack of chemical or strong physical formations between polymer and organic particles

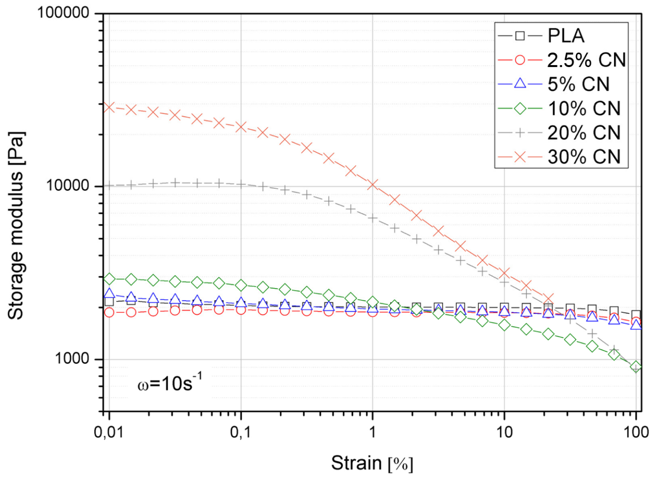

Figure 2. Storage modulus *vs.* strain of PLA and PLA-CN composites (190 ºC).

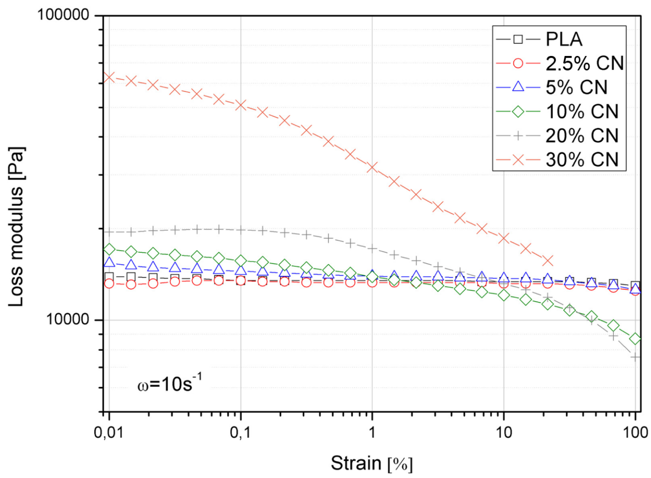

Figure 3. Loss modulus *vs.* strain of PLA and PLA-CN composites (190 ºC).

and samples are not form-stable at rest since creep or flow.[26] Lowered values of G' and G'' at high strains (higher than 5%) observed for composites containing higher amounts of the CN (10 to 30 wt%) in comparison to pure PLA, 2.5CN and 5 CN samples may be interpreted as follows: shearing interlocked organic particles with developed free surface creates physically hindered rigid structures, which provide to occur of macroscopic wall slip between filled polymer and material of the measuring plates.

In Figure 4 results of frequency sweep experiments including changes of complex viscosity as a function of angular frequency are presented. All considered materials, pure PLA and PLA-based composites, reveal shear thinning behavior. Incorporation of more than 10 wt% of the filler caused a significant

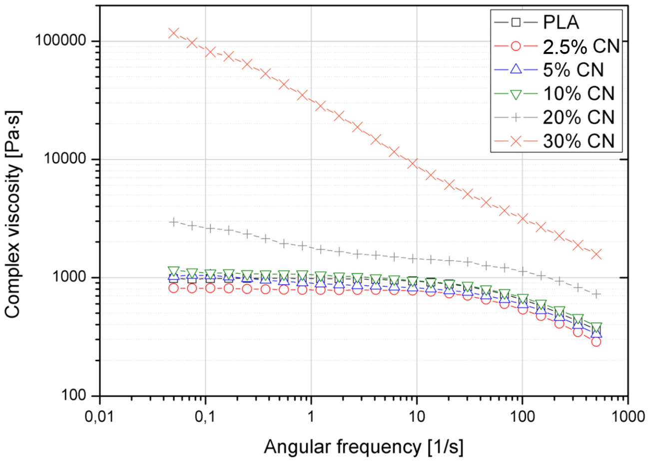

Figure 4. Complex viscosity of pure PLA and PLA-CN composites (190 ℃).

growth of viscosity, while rheological behavior of composites which contain lower amount of the CN, i.e. 2.5, 5 and 10 wt% exhibit similar course of the viscosity curve. The difference between low and highly filled composites is especially distinct at low angular frequencies. Moreover, only in case of PLA-CN composites containing 20 and 30 wt% of the filler no Newtonian plateau at low frequencies was observed. For PLA-based composites with filler amount up to 10 wt% Newtonian plateau may be noted in similar frequency range as for pure PLA matrix. Despite differences in rheological behavior of the sample containing 20 wt% of CN, in comparison with pure PLA and the samples containing lower amounts of the filler, only the composite with maximum 30 wt% of CN reveals significant changes of flow character which may provide to strong limitations during its melt processing. Strong increase of the viscosity at low shear rates may result in problems with proper filling of a mold cavity and shorts during injection molding.

Changes of G' and G'' as a function of angular frequency were presented in Figure 5. Both loss and storage moduli increase after incorporation of 20 and 30 wt% of CN. Well dispersed particle-shaped ground chestnut shells, in case of 2.5CN-10CN samples, do not provide to creation of polymer-filler network which presence causes changes of relaxation time spectrum and affects viscoelastic properties of composite materials.[25,27] In case of the samples containing high amounts of the filler (20CN and 30CN), aggregated filler particles provide to occurrence of discontinuities in molten composite which cause squeezing polymer on the agglomerates surface. The higher amount of the filler, the bigger discontinuities occur

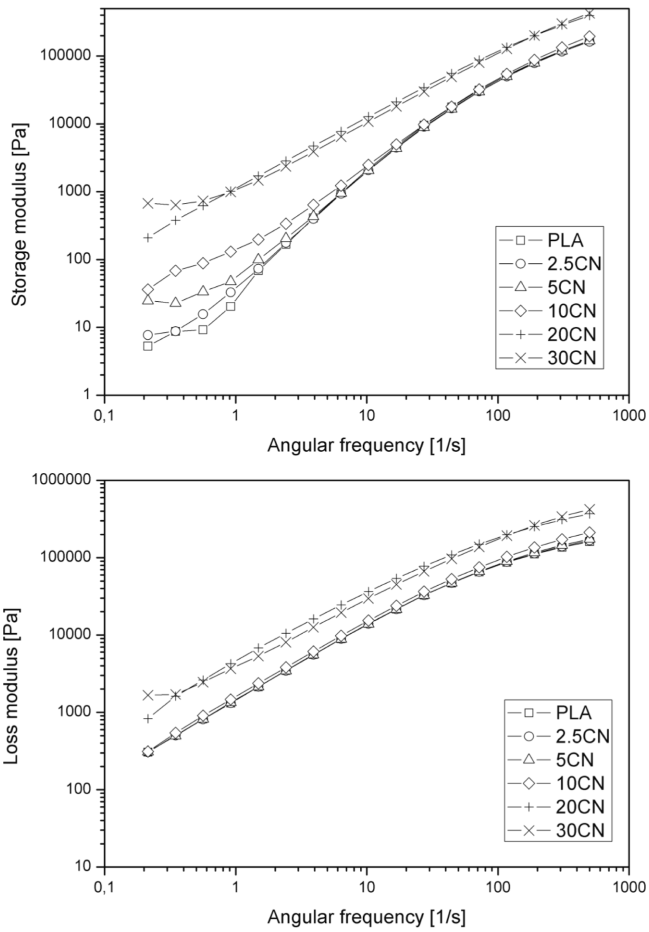

Figure 5. Storage and loss modulus *vs*. angular frequency of PLA and PLA-CN composites.

because of different polarity between PLA and CN. This phenomenon results in an increase of composite melt elasticity in comparison to unmodified polymer.[27,28]

In order to assess information about presence of physical network formation between organic filler particles incorporated in PLA matrix, additional analysis of phase angle (δ) *vs*. complex modulus (G^*) curves (i. e. van Gurp-Palmen plots) was realized (Figure 6).[29] The phase angle is the phase difference between applied strain and measured stress. In case of fully elastic material, the stress and strain waves are in phase (δ=0°), whereas strictly viscous material reveals two waves out of phase (δ=90°). In reference to data presented in Figure 5, for all considered materials, PLA and PLA-based composites, G'' dominates over G'. If phase angle is above 45° viscous behavior dominates. In van Gurp-Palmen plot PLA, 2.5CN and 5CN samples approach a phase angle of 90°, which indicates strongly viscous-like behavior of molten material. First devi-

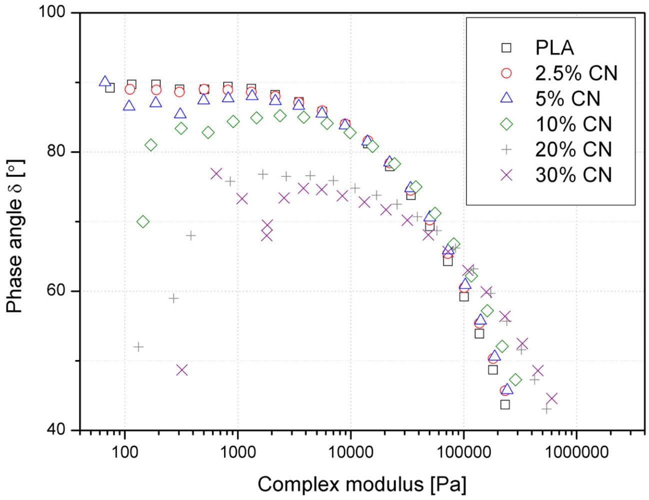

Figure 6. Van Gurp-Palmen curve of PLA and PLA-CN composites.

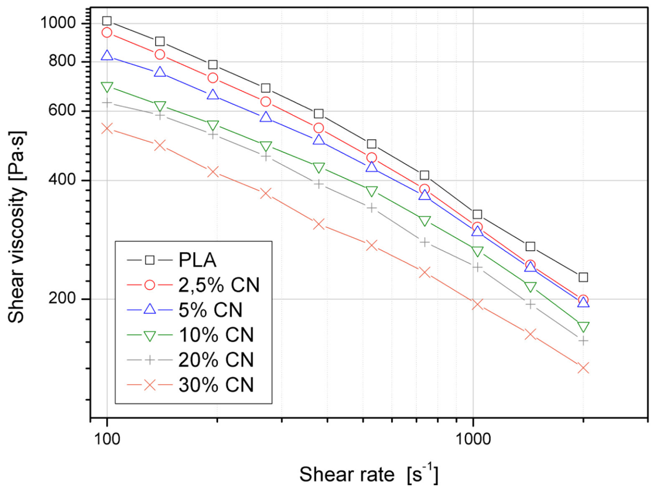

Figure 7. Viscosity curves of PLA and PLA-CN composites obtained from capillary rheometer, *L*/*D*=30 *D*=0.762 mm.

ation can be observed for a composite sample containing more than 5 wt% of the filler, however 10CN still exhibit similar shape of the curve as for pure PLA. For 20CN and 30CN samples significant differences in curve shape are denoted. The drop in phase angle observed for low complex viscosity values is an effect of development of solid-like structures in polymeric matrix, by physically interlocked ground chestnut particles.[30,31]

Results of rheological experiments realized at high shear rates, which are obtained from capillary rheometer, are presented in Figure 7. In comparison to results from frequency sweep experiments realized by rotational rheometry different tendencies in rheological behavior of composite materials can be observed. The higher amount of the filler incorporated into polymeric matrix, the lower measured values of apparent shear viscosity. Mentioned decrease of the viscosity can be observed in the whole measured shear rate range, i.e. from 100 s^{-1} up to 1500 s^{-1}. The apparent shear viscosity of the composite material containing the highest amount of the CN (30 wt%) in comparison to pure PLA was 46% at the 100 s^{-1} and 41% lower at 1500 s^{-1} respectively. Therefore, it can be stated that modification efficiency of CN filler on PLA-based composites rheological behavior is shear independent during capillary flow. Contrarily to the results of frequency sweep experiments, incorporation of the particle-shaped filler does not provide to changes of the flow curve shape and the character of the flow. All curves presented in Figure 6 are in non-Newtonian flow region. Observed gradual lowering of apparent viscosity corresponding to increased amount of the filler may be attributed to changes of interfacial wall slip caused by presence of the natural filler. Increased amount of a lignocellulosic filler, for example wood flour, usually provides to significant changes of the composite wall slip in comparison to unmodified thermoplastic polymeric matrix, which provide to dominant plug flow during capillary flow.[32-34] Similar wall slip behavior was also observed during oscillatory rheometry experiments, where it resulted in lowering of G' and G'' values measured for 10CN, 20CN and 30CN samples in high strain region (Figures 2, 3). It cannot be excluded that observed phenomenon of lowered apparent shear viscosity is simultaneously caused by presence of lignocellulosic organic particles as well as saponins and another low molecular weight substances contained in ground chestnut that migrate into the surface of the extrudate.[33] Decreased friction between polymer and die material resulting from formulation of the slip layer provides to decrease of pressure values which are used for shear viscosity calculations.

One of the most important measurements realized in industrial conditions which allows for basic evaluation of thermoplastic polymer processing properties is determination of melt flow index (MFI). In considered case MFI of PLA and its composites was measured at lowered temperature (190 ℃) in comparison to measurement conditions specified in European Standard EN ISO 1133, i.e. 210°C. This change is caused by possibility of natural filler degradation due to high temperature. Gaseous products released from the filler during its decomposition in case of measurement realization at temperature above 200 ℃ may provide to strong deviations in rheological data. The results of the MFI evaluation realized by

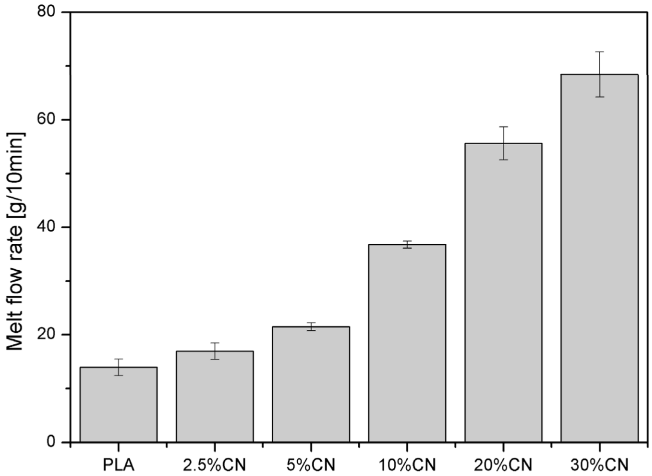

Figure 8. Melt flow index of PLA and PLA-based composites, 190 ºC, 2.16 kg.

gravimetric plastometer are presented in Figure 8. Increasing content of the filler caused significant changes of composites' MFI in comparison to pure PLA. Even at lowest amount of the ground chestnut shell waste incorporated into polymeric matrix an increase of MFI value can be observed, however only in case of composites containing more than 10 wt% of the filler a significant improvement of this processing parameter is denoted. The MFI value grows along with increasing CN content and for the sample containing 30 wt% of the ground chestnut shell it is over 5 times higher than in case of the neat resin. Such a pronounced change is especially important from a manufacturer's point of view, as processing conditions for pure PLA and its composites may significantly vary. Lee *et al.* in their work presented similar results concerning modification of Floreon by kenaf fibers.[35] What's more, it may be seen that

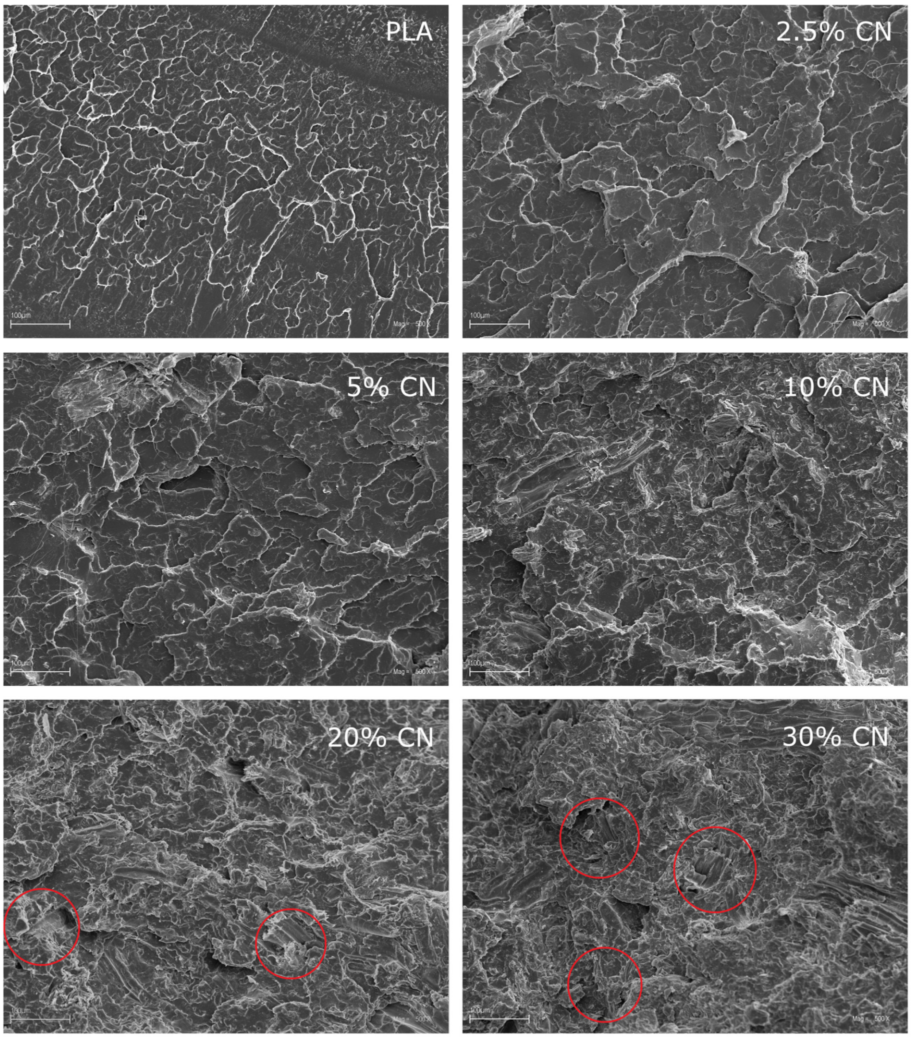

Figure 9. SEM images of PLA and PLA-CN composites (mag. 500×).

obtained results go in line with the outcomes of the capillary rheological experiments. Increasing MFI values are an indicator of growing extrusion throughput, that is, a greater mass of a polymer flows through the die in a certain time. As the apparent viscosity value is inversely proportional to the mass flow rate, increasing value of the latter causes a decrease of the former. Therefore the results of the MFI measurements prove the modifying effect of the ground chestnut shell particles on the PLA processing properties and are in a good agreement with experiments realized at capillary rheometer.

In Figure 9 SEM images of brittle fractured PLA and PLA-CN composites surfaces are presented. Observations were prepared in order to confirm aforementioned explanation of rheological data based on phenomenon of mutual contact of the organic particles and their interlocking, which in effect provides to different rheological behavior of composites containing 20 and 30 wt% of the filler. Images presenting surfaces of composite materials with lower amount of the filler (2.5-10 wt%) showed that organic particles are distributed freely in polymeric matrix without presence of agglomerated structures. In SEM images of composite fractured surfaces with higher than 10 wt% content of the CN in some regions natural particles are close to each other and in some cases (marked by red circles) come into mutual contact. Microscopic analysis of the structures confirms previously assumed theory and it is in a good agreement with rheological data.

Conclusions

The effect of utilization of ground chestnut shell as an organic waste filler on rheological and processing properties of poly(lactic acid) was studied and presented. Application of various measuring techniques (rotational and capillary rheometry) allows for a comprehensive assessment of composite materials flow behavior at a wide range of shear rate. Rotational rheometry experiments realized in strain and frequency sweep showed that incorporation of the filler provides to significant changes of rheological behavior, including increase of complex viscosity and changes of linear viscoelastic region. Oscillatory measurements allowed to establish the critical filler content (10 wt% of CN), incorporation of which gives the opportunity to produce fully biodegradable composites with good dispersion and defined processability. Moreover, it was found that the composite materials reveal different rheological behavior dependent on flow geometry resulting from the measurement type. Rheological characteristics of the molten polymeric composites evaluated by capillary experiments showed that incorporation of the organic waste filler caused a decrease of the apparent shear viscosity of modified materials. Processing properties of PLA-based composites filled with ground chestnut shell were determined by melt flow index (MFI) evaluation. It was found that despite of increasing elasticity of the molten composites and increasing complex viscosity determined by frequency sweep experiments, processability of composite materials became higher in comparison to pure PLA, due to lowered wall slip which provide to occurrence of the plug flow during flow through a capillary.

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