Thermal properties of polylactide / recycled lignin and cellulose filler biocomposites

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Bio-based polymer composites were prepared using poly-L-lactide (PLLA) as a matrix and three different types of natural fillers. Waste paper from regular office paper, cellulose from Tetra Pak® recycling industry and lignin waste from paper manufacturing industry were chosen as fillers. Density, crystallinity and melting/crystallization behavior of PLLA biocomposites loaded with different filler contents (20, 30, 40 wt.%) were compared and discussed.

1. Introduction
Polymer products based on renewable biomass feedstock including agricultural crops, forestry residues, biomass processing residues can form the basis for eco-efficient, sustainable and competitive solutions to substitute partially, and to some extent totally petroleum-based products on a technical and cost-performance values [1]. To further increase value and environmental impact of bio-economy, the use of sustainable polymer materials based on various bio-based oils, bio-based polymers derived from corn and starch and biopolymers lignin, cellulose are encouraged for further intensive investigations [2,3]. Cellulose and lignin are sustainable, biodegradable and relatively cheap materials for the bio-based materials preparation due to their availability from various waste streams, especially involving paper production industry. While cellulose is desirable filler due to its potential reinforcing properties to increase final mechanical characteristic of the composite’s material [4]. We have chosen three filler types obtained as common waste products: waste paper filler (WPF) particles from recycled office paper, recycled cellulose filler (RCF) particles from Tetra Pak recycling industry and lignin waste filler (LWF) from paper production plant. Density measurements and differential scanning calorimetry analysis were performed for the obtained PLLA /recycled natural filler biocomposites.

2. Methodology
2.1. Materials and sample preparations
Poly-L-lactide with trademark PLLA-Biomer L9000 produced by Biomer® was chosen. The main parameters of PLLA are melt flow index 5.3 g/10 min, tensile strength 70 MPa, tensile deformation 2.4%, elastic modulus 3600 MPa.
LWF filler with the particles size bellow 0.25 mm, while WPF and RCF fillers with the particles size bellow 2 mm were used to produce biocomposites. RCF and WPF were used as received from the companies. Cellulose was separated from aluminum and polymer components during industrial processing by the recycling company. The PLLA and fillers were dried at 100 °C for 72 hours in a vacuum oven. Polymer biocomposites were prepared by blending with the thermoplastic mixer Brabender® Mixer 50EHT. PLLA biocomposites were processed with fillers contents of 20, 30, 40 wt%. PLLA biocomposites were obtained by melt blending at 170 °C for 5 min and screws velocity of 70 rpm. Pure PLLA sample was processed in the same conditions for comparison analysis.

2.2. Differential Scanning Calorimetry

Mettler DSC-1 instrument was used to investigate thermal properties. Specimens about 10 mg in weight were scanned in the temperature range from 25 to 250°C by using nitrogen as a purge gas. The DSC heating/cooling rate of 10°C/min was used. Enthalpies (ΔH), melting (T_m) and glass transition (T_g) temperatures were calculated from the experimental heating curves. Degree of crystallinity was calculated from the equation 1

$$\chi = \frac{\Delta H_{\text{exp}}}{\Delta H_{100\%}}$$  \hspace{1cm} (1)

\(\chi\) - degree of crystallinity of sample, where \(\Delta H_{\text{exp}}\) is experimental melting enthalpy of crystalline phase, J/g; \(\Delta H_{100\%}\) is theoretical melting enthalpy of PLLA crystalline phase, 93.7 J/g [5,6].

2.3. Density measurements

For density measurements a simple hydrostatic weighing equipment Sartorius YDK 01 was used. Ten measurements were performed for every sample composition and density was calculated from the equation 2

$$\rho = \frac{W(a)}{0.99983 (W(a) - W(C_2H_5OH))] + 0.0012} + 0.0012$$  \hspace{1cm} (2)

where, \(\rho\) – density of the sample (g/cm³), \(W(a)\) – weight of the sample in air (g), \(W(C_2H_5OH)\) – weight of the sample in ethanol (g), \(\rho(C_2H_5OH)\) – density of ethanol (g/cm³).

3. Results and discussions

3.1. Density measurements

Density data for PLLA /recycled lignin and cellulose filler biocomposites are compared with pure PLLA density 1.219 g/cm³ and the results are summarized in Figure 1.
Figure 1. Density of PLLA biocomposites with lignin and cellulose fillers in comparison to pure PLLA.

The lignin filler loading increases density of composites materials; while the cellulose fillers loading decreases the density of composites materials. For example, at the concentration of 40 wt% of the filler, the lignin composite density is 1.292 g/cm$^3$, but the density of the waste paper composite is only 1.165 g/cm$^3$. Observed density decrease can be explained with the uneven melt blending and formation of the voids in the composite material at high filler loading concentrations.

3.2. Differential Scanning Calorimetry

The second heating and cooling DSC thermograms of the processed PLLA compositions are shown in Figure 2. The characteristic parameters are calculated and summarized in the Table 1. The cooling and heating curves indicate that the addition of lignin and cellulose fillers slightly effect the glass transition temperature $T_g$ of the polymer matrix. The $T_g$ of the PLLA is 62.6 °C, while the $T_g$ of the composite filled with 20 wt% of WPF is 64.7 °C. This could be attributed to the possible some interactions between hydroxyl groups of cellulose with polymer chains through hydrogen bonding development, which can reduce the overall flexibility of the polymer chain mobility [7,8].

The obtained results show that the melting temperature $T_m$ of the composites with the fillers higher loading decreases. $T_m$ of the pure PLLA is 168.8 °C, while the $T_m$ of the PLLA biocomposites loaded with 40 wt% of RCF and WPF are 166.4 °C and 168.0 °C, respectively.

Table 1. Thermal properties obtained from second heating and cooling DSC thermograms

|        | $T_g$ (°C) | $T_{cc}$ (°C) | $\chi_{cc}$ (%) | $T_m$ (°C) | $\chi_m$ (%) | $T_g$ (°C) | $T_c$ (°C) | $\chi_c$ (%) |
|--------|------------|---------------|-----------------|------------|--------------|------------|------------|--------------|
| PLLA   | 58.6       | 98.3          | 23.4            | 168.8      | 53.1         | 62.6       | 95.4       | 4.8          |
| LWF 20%| 58.8       | 105.9         | 30.3            | 169.0      | 43.8         | 63.0       | 95.9       | 3.0          |
| LWF 30%| 58.8       | 103.3         | 20.8            | 168.7      | 48.9         | 62.3       | 95.9       | 7.0          |
| LWF 40%| 58.4       | 102.0         | 19.2            | 168.1      | 49.4         | 61.3       | 96.8       | 10.5         |
| RCF 20%| 57.9       | 98.6          | 7.9             | 168.7      | 48.3         | 62.9       | 100.3      | 25.0         |
| RCF 30%| 58.8       | -             | -               | 168.8      | 52.7         | 63.0       | 117.5      | 41.2         |
| RCF 40%| 58.0       | -             | -               | 166.4      | 47.8         | -          | 128.1      | 41.3         |
| WPF 20%| 57.5       | -             | -               | 169.1      | 46.4         | 64.7       | 100.6      | 34.6         |
| WPF 30%| 57.4       | -             | -               | 169.0      | 42.6         | -          | 103.9      | 35.4         |
| WPF 40%| -          | -             | -               | 168.0      | 35.4         | -          | 103.5      | 28.6         |
Figure 2. Heating and cooling thermograms of the biocomposites: a) cooling curves of LWF biocomposites, b) heating curves of LWF biocomposites, c) cooling curves of RCF biocomposites, d)
heating curves of RCF biocomposites, e) cooling curves of WPF biocomposites, f) heating curves of WPF biocomposites.

Most notable changes are observed for the melting and crystallization of the PLLA. Pure PLLA is characterized from the 2nd heating thermogram with the degree of the crystallinity ($\chi_m$) – 53.1%, cold crystallization process ($T_{cc}$) at about 98.3 °C and degree of the cold crystallization ($\chi_{cc}$) – 23.4%, but during cooling the polymer is characterized by almost amorphous structure and degree of the crystallinity ($\chi_c$) – 4.8%. Lignin filler containing biocomposites also show the cold crystallization process during the cooling; while the other biocomposites show the absence of it. Crystallinity degree for the cold crystallization process decrease to 20.8% and 19.2% for 30 and 40 wt% loading of LWF. PLLA biocomposites with the cellulose based fillers RCF and WPF show almost no cold crystallization process. During cooling stage PLLA filled with the 40wt% of RCF and WPF fillers show degree of crystallinity 41.3% and 28.6%. Crystallization temperature of the PLLA biocomposites increase from 95.4 °C for the pure PLLA till 128.1 °C for the PLLA biocomposites filled with the 40 wt% of RCF. The increase of degree of crystallinity during cooling can be explained with nucleating effect of fillers towards PLLA matrix, which is especially strong for cellulose fillers RCF and WPF. This could be explained with very strong intermolecular interactions developed between the composite’s components [7,8,9].

3. Conclusions

The PLLA biocomposites density increases after loading with lignin filler; while, PLLA biocomposites density decreases after loading with cellulose fillers. This behavior can be related to the formations of the voids at very high filler loading contents. Differential scanning calorimetry analysis show that cellulose fillers slightly effect the glass transition temperature, which decreases by almost 2 degrees. The fillers incorporation into the polymer matrix also increases the crystallinity degree of the PLLA biocomposites. Finally, it can be concluded that the cellulose fillers show more pronounced interaction with polymer matrix in comparison with the lignin filler, which relates to the nature of the fillers.

4. References

[1] Madbouly S, Zhang C, Kessler M R 2016 Bio-Based Plant Oil Polymers and Composites 10-217
[2] Gaidukova G, Ivdre A, Fridrihsone A, Verovkins A, Cabulis U and Gaidukovs S 2017 Ind Crops Prod 102 133–143
[3] Garrison T F, Murawski A and Quirino R L 2016 Polymers 8(7) 262
[4] Sutka A, Sutka A, Gaidukov S, Timusk M, Gravitis J and Kukle S 2015 Holzforschung 69(6) 737-743
[5] Leng J, Kang N, Wang D Y, Wurm A and Schick C 2017 A. Polymer (Guildf) 108 257-264
[6] Saeidlou S, Huneault M A, Li H and Park C B 2012 Prog. Polym. Sci. 37 (12) 1657-1677
[7] Ghanbaria A, Tabarsaa T, Ashorib A, Shakeric A and Mashkour M 2018 Carbohydr Polym. 197 305-311
[8] Lei W, Fanga C, Zhoua X, Li Y and Pub M 2018 Carbohydr Polym. 197 385-394
[9] Gaidukov S, Danilenko I and Gaidukova G 2015 Int J Polym Sci art. no. 123469