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Synthesis and characterization of polymer biocomposites with lignin

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Abstract: A new method of synthesis of polymer biocomposites with lignin using the photopolymerization method has been proposed. Bisphenol A glycerolate (1 glycerol/phenol) diacrylate (BAGDA) was used as a main monomer and 2-ethylhexyl acrylate (EHA) as a reactive diluent. Lignin (L) was applied as an eco-filler. The influence of the increasing lignin content (0; 2.5; 5; 10; 20% w/w) on the properties of the obtained biocomposites was investigated. The chemical structure of biomaterials was investigated by the attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR) method while the thermal properties were studied by the differential scanning calorimetry (DSC) and thermogravimetric analysis (TG/DTG). Their hardness was measured by the Shore D method. Incorporation of the biopolymer into the structure of polymer composites could be a promising alternative to synthetic materials and would contribute to better lignin utilization. The results of the study are of practical importance in prospective applications of biocomposites with lignin.

Keywords: lignin, biocomposites, physicochemical properties, eco-filler, photopolymerization

1. Introduction

In recent years the development of polymeric materials based on renewable natural resources has attracted the growing interest of scientists (Thangavel et al., 2015; Klapiszewski et al., 2013; Ramos et al., 2019). This is a result of two main problems, which are the dwindling of available natural resources derived from fossil fuels and the global environmental problem connected with generated wastes (Mohanty et al., 2002). Both of these problems have attracted more and more attention to identify renewable and sustainable alternatives which can reduce the overdependence of society on fossil fuels and can solve the environmental problem associated with the increasing generation of wastes (Ghozali et al., 2017). Incorporation of renewable materials as substitutes and fillers can promote sustainability for the existing plastic industry (Klapiszewski et al., 2012; Bula et al., 2015; Borysiak et al., 2016; Klapiszewski et al., 2017).

Lignocellulosic biomass has been considered as an alternative feedstock to replace traditional fossil resources as one of the most accessible forms of carbon (Stewart, 2008; Lora and Glasser, 2002). Lignin, a polymeric component of biomass is the second most abundant biopolymer next to cellulose. Chemically it is an amorphous macromolecular aromatic polymer composed of three phenylpropanoid monomers: coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol. Its structure and molecular weight depend on the origin and extraction processes (Vanholme et al., 2010). Lignin is a by-product from the paper and pulp industry. Moreover, many attempts have been made to use lignin wastes as a filler component to improve properties of the products and to reduce their production costs (Upton and Kasko, 2016; Ikeda et al., 2017; Goliszek et al., 2019; Thakur et al., 2014; Klapiszewski et al., 2019). This available and low-cost renewable biopolymer can be a promising raw material for the production of environmentally friendly polymer composites (Spiridon and Tanase, 2018; Grzabka-Zasadzińska et al., 2018).

UV-curing is a widely accepted technology owing to its numerous advantages: low-energy consumption, rapid cure rates and solvent-free formulations. Photopolymerization of monomer

acrylates to create thermosetting materials is a commonly used UV-system for numerous applications such as protective coatings, dental materials, adhesive, printing inks and composites (González et al., 2015; Yagci et al., 2010).

The aim of this study was to obtain polymeric biocomposites with lignin as a filler using the photopolymerization method and detailed characterization of the products.

2. Materials and methods

2.1. Materials

Bisphenol A glycerolate (1 glycerol/phenol) diacrylate, 2-ethylhexyl acrylate, kraft lignin and 2,2-dimethoxy-2-phenylacetophenone were obtained from Sigma-Aldrich.

2.2. Preparation of composites

Bisphenol A glycerolate (1 glycerol/phenol) diacrylate (BAGDA) was heated in a laboratory dryer to 60°C. Then its appropriate amount was weighed into a glass vessel. In the next step, 2-ethylhexyl acrylate (EHA) was added dropwise to this vessel while stirring. The ratio of BAGDA to EHA was 10:3. Then the adequate amount of lignin (L) (2.5; 5; 10; 20% w/w) was added and stirring was continued to obtain a homogeneous mixture. Finally, 1.2% w/w of 2,2-dimethoxy-2-phenylacetophenone (IQ), as a photoinitiator, was added and after stirring the mixture was placed in a glass form and cured under the UV lamp for 0.5 h. As a result, a composite in the form of a brown plate was obtained. For comparison the synthesis of composite without lignin addition was also performed. The chemical structure of monomers is presented in Fig. 1. The experimental parameters of the synthesis were collected in Table 1.

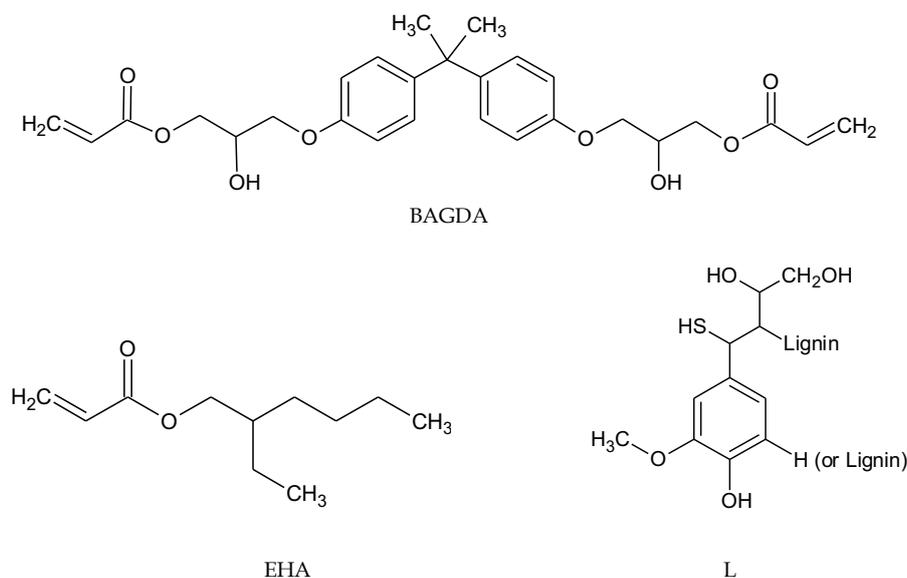


Fig. 1. Chemical structures of monomers

Table 1. Experimental parameters of the synthesis

Composite	BAGDA (g)	EHA (g)	L (% w/w)	L (g)	IQ (% w/w)	IQ (g)
EHA + 0%L	4.588	1.376	0	0	1.2	0.071
EHA + 2.5%L	4.332	1.299	2.5	0.141	1.2	0.069
EHA + 5%L	4.423	1.327	5	0.287	1.2	0.072
EHA + 10%L	4.219	1.266	10	0.548	1.2	0.072
EHA + 20%L	4.167	1.250	20	1.083	1.2	0.078

2.3. Methods

The FTIR spectra were recorded with a Bruker Tensor 27 FTIR spectrometer (Germany) using the attenuated total reflectance (ATR) technique. All spectra were obtained within the range of 600-4000 cm^{-1} in the absorbance mode. The spectral resolution was 4 cm^{-1} with 32 scans taken for each spectrum. The calorimetric measurements were carried out using Netzsch DSC 204 calorimeter (Selb, Germany) operated in a dynamic mode. The dynamic scans were performed at a heating rate of $10^\circ\text{C min}^{-1}$, the first scan being from 20°C to a maximum of 110°C to remove any adsorb moisture, and the second from 25°C to 550°C in a nitrogen atmosphere ($30 \text{ cm}^3 \text{ min}^{-1}$). The sample mass was $\sim 5\text{-}10 \text{ mg}$. An empty aluminum crucible was used as a reference. Thermal analysis was conducted using STA 449 Jupiter F1, Netzsch (Germany). The samples were heated from 30 to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$, in a dynamic atmosphere of helium ($25 \text{ cm}^3 \text{ min}^{-1}$). The sensor thermocouple of S TG-DSC type and an empty Al_2O_3 crucible as a reference were used. The materials hardness was measured by the Shore D method using a Zwick 7206/H04 analog hardness testing apparatus (Germany) at 23°C . Readings were taken after 15s.

3. Results and discussion

3.1. ATR/FT-IR analysis

The ATR/FT-IR spectra of the obtained materials are presented in Fig. 2. The spectroscopic evaluation proved a successful synthesis of biocomposites with lignin, that is proved from the presence of characteristic bands of appropriate functional groups. The broad band at 3454 cm^{-1} is assigned to the stretching vibrations of hydroxyl groups. The bands around 2960, 2930 and 2870 cm^{-1} are from the stretching vibrations of C-H in $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The absorption band at 1725 cm^{-1} is due to the stretching vibrations of C=O groups which is characteristic for acrylates. The stretching vibrations of ester group C-O-C give a doublet at 1181 and 1240 cm^{-1} . The signals at 1600 and 1509 cm^{-1} are from aromatic C=C vibrations in the aromatic rings. The band at 1041 cm^{-1} is assigned to the stretching vibrations of C-O bonds in alkyl-aryl ethers. The signals at 809 cm^{-1} are from the CH out-of-plane deformation vibrations. The increasing content of lignin reflected in the increasing intensity of these bands confirmed completely the predictions.

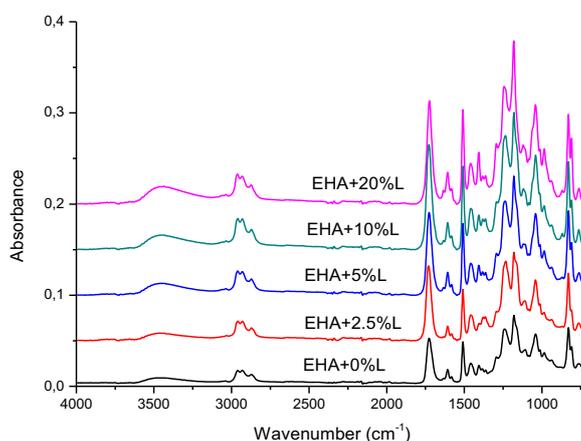


Fig. 2. ATR/FT-IR spectra of the composites

3.2. DSC analysis

The DSC curves of composites are presented in Fig. 3. Additionally, the DSC results are collected in Table 2. They reveal the presence of endothermic peaks with the maximum at $387\text{-}396^\circ\text{C}$. This is associated with their total thermal degradation. The enthalpy of decomposition (ΔH_d) values ranges from 58.9 to 101.2 J/g , depending on the amount of lignin used during synthesis. The broad exothermic effect at around $200\text{-}320^\circ\text{C}$, which is particularly visible for the lignin-containing composites, is from the lignin intermolecular crosslinking and repolymerization of smaller lignin molecules formed via the bond cleavage (Jiang et al., 2018). The temperature of total thermal degradation (T_d) among lignin-

containing composites is similar. The highest values of T_d were obtained for the biocomposites with 2.5 and 5% w/w addition of lignin. This can be a result of potential interactions between the carbonyl groups of acrylates and the hydroxyl groups of lignin (Spiridon and Tanase, 2018). However, when higher concentration of lignin was used (10, 20%), its dominant role in the composite material was filler.

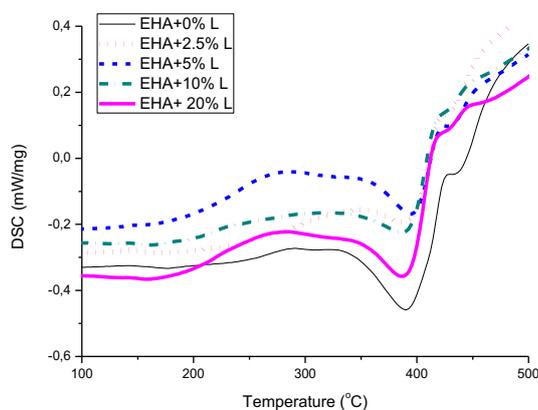


Fig. 3. DSC curves of the composites

Table 2. DSC data of the composites

Composite	T_d (°C)	ΔH_d (J/g)
EHA + 0%L	390.3	101.2
EHA + 2.5%L	387.3	48.4
EHA + 5%L	394.5	47.8
EHA + 10%L	386.8	58.9
EHA + 20%L	387.0	82.8

3.3. TG/DTG analysis

Thermal properties of composites were studied by means of thermogravimetry. The TG/DTG curves of composites are shown in Fig. 4. Temperatures related to weight loss of 5 and 50% ($T_{5\%}$ and $T_{50\%}$, respectively), temperatures of maximum decomposition (T_{max1} , T_{max2}) with adequate values of weight loss (W_{loss1} , W_{loss2}) and values of residual mass (RM) are collected in Table 3. Thermal decomposition of the composite without lignin proceeds in a one-step process whereas decomposition of the biocomposites proceeds in a two-step process. The first peak on the DTG plot observed only for a lignin-containing material in the temperature range of 185-192°C (T_{max1}) can be associated with the degradation of aliphatic fragments and oxygen functionalities from lignin. These species decompose very easily when heated (Sobiesiak et al., 2016). The second decomposition peak is connected with the degradation of crosslinked polymer network of composites. It is in the temperature range of 409-425°C (T_{max2}). The increasing lignin content results in the decreased T_{max2} values. According to the presented results the composite without lignin is characterized by the highest degree of crosslinking, because it is the most thermally stable. The addition of lignin to the polymer network results in the reduction of thermal resistance due to crosslinking degree reduction. The residual mass increases with the increasing content of lignin in the composite. It is in the range of 8.77-15.07%, which indicates possible application of obtained biocomposites as potential precursors for carbon materials preparation.

3.4. Shore hardness

According to the results of Shore-D hardness test (Fig. 5), the hardness values show slight changes with the increasing lignin content. The highest Shore-D hardness values were obtained for the biocomposites with 2.5 and 5% w/w addition of lignin. When 20% w/w of lignin was applied, the decrease in the hardness value was observed. This can be due to the decrease of composite homogeneity with the increasing lignin content and homopolymerization process.

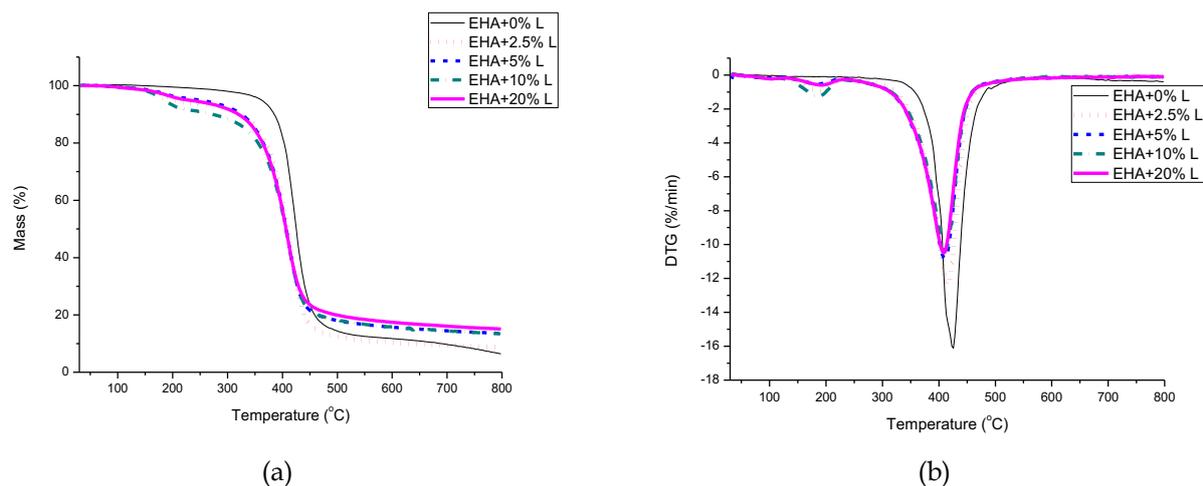


Fig. 4. TG (a) and DTG (b) curves of the synthesized composites

Table 3. TG/DTG data of the composites

Composite	T _{5%} (°C)	T _{50%} (°C)	T _{max1} (°C)	T _{max2} (°C)	W _{loss1} (%)	W _{loss2} (%)	RM (%)
EHA + 0%L	362	425	-	425	-	93.65	6.35
EHA + 2.5%L	204	409	188	416	8.28	84.67	8.77
EHA + 5%L	249	410	185	410	4.68	81.32	13.51
EHA + 10%L	185	406	186	411	8.64	74.63	13.28
EHA + 20%L	192	407	192	409	4.09	78.83	15.07

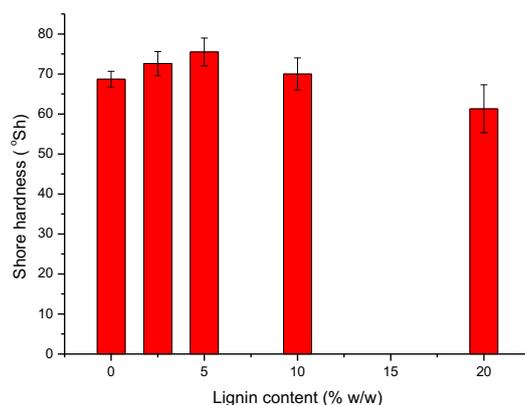


Fig. 5. Hardness of the composites

4. Conclusions

New biocomposites with lignin addition were obtained by the environmentally friendly UV curing process due to the solvent-free technology. Bisphenol A glycerolate (1 glycerol/phenol) diacrylate was applied as main monomer and 2-ethylhexyl acrylate as a reactive diluent. The spectroscopic evaluation proved the successful synthesis of lignin-containing biocomposites, which was confirmed by the presence of characteristic bands of appropriate functional groups. Thermal properties of the obtained biomaterials were investigated by the DSC and TG/DTG methods. The addition of lignin to the polymer network is probably related with reducing their degree of crosslinking which results in their thermal resistance reduction. When a small lignin amount was added to the composite (2.5 and 5% w/w), potential interactions between the carbonyl groups of acrylates and the hydroxyl groups of lignin can take place whereas when a higher amount of lignin was used (10 and 20% w/w), a filler is a dominant role of lignin. This prediction is confirmed by the obtained thermal (DSC, TG/DTG) and mechanical (Shore D test) results. The formation of char during the pyrolysis process increases with the increasing

lignin content. The application of UV curing together with incorporation of natural biopolymer into the structure of polymer composites results in obtaining materials which are more environmentally friendly than the synthetic composites and contribute to better utilization of lignin.

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