Modification of interactions in polypropylene/lignosulfonate blends

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ABSTRACT

Polypropylene (PP)/lignin blends were prepared in a wide composition range (0–70 vol%) from a PP homopolymer and two lignosulfonates of different compositions by homogenization in an internal mixer and compression molding. Thermodynamic considerations and dynamic mechanical analysis (DMTA) were used for the estimation of interactions and miscibility, while mechanical properties were characterized by tensile testing. Local deformations were followed by acoustic emission measurements, and structure was analyzed by scanning electron microscopy (SEM). The results showed that the structure of the blends form during processing by the breakup of large lignin particles which soften at the high temperature of processing. Weak interactions develop between PP and lignin, since lignin molecules interact with each other strongly and prevent the mixing of the two components. Dispersed structure forms in the entire composition range studied, co-continuous structure cannot develop at all. Interfacial adhesion can be improved through the addition of a maleic anhydride grafted polypropylene (MAPP) coupling agent. Depending on the strength of interfacial adhesion the blends fail either by debonding or by the fracture of lignin particles. Although coupling improves the strength of the blends, deformability is very small especially at larger lignin contents hindering practical application.

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1. Introduction

After cellulose, lignin is the second most abundantly available material in nature [1]. It is a basic constituent of all lignocellulosic materials and industry produces it in increasing amounts as a side product of cellulose and bioethanol production [2]. The chemical structure and properties of lignin depend very much on the technology (e.g. Kraft, sulfite, organosolv, steam explosion process) used to extract it from plants and thus its application also depends somewhat on this process. Kraft lignin is mainly used to produce energy [3], while lignosulfonates are applied in various areas as additive for concrete [4], animal feed pelleting [5] and dust control [6], raw material for the production of certain chemicals [7–9], etc. Because of its quantity and being a side product, lignin is very cheap thus using it in any value added application would result in considerable economical gain. Blending with polymers could be a potential application and several attempts have been reported in the literature about the structure, interactions and properties of polymer/lignin blends [10–30].

Polyolefins, including polypropylene, are commodity polymers used in very large quantities in industrial practice. They are very cheap, but possess good, balanced properties resulting in a wide range of applications. Polypropylene can be further modified in various ways to extend its range of properties and applications. Its stiffness is increased by the incorporation of fillers or fibers [31], impact resistance by modifying it with elastomers [32], nucleation results in larger stiffness [33], but often also in good optical properties [34]. Combining PP with lignin might result in blends with an advantageous property combination at an acceptable price.

The properties of blends depend on their structure, which, on the other hand, is determined by the interaction of the components. Complete miscibility usually results in properties in between those of the components, while the characteristics of immiscible blends often go through a minimum [35], although heterogeneous structure may result in increased fracture resistance [36]. Obviously the interaction of the components is a key factor determining the properties of blends; weak interactions result in immiscibility and poor properties. Lignin is a very polar, while polyolefins are apolar polymers, thus the strong interactions developing among lignin molecules are expected to result in a very poor miscibility of these two polymers.

In spite of the prediction stated above, a wide range of opinions have been published about the miscibility or compatibility of lignin and polyolefins. Some authors found significantly different compatibility in high density and low density polyethylene (LDPE) [37], which is difficult to understand in view of the very similar chemical structures and interactions developing in the two kinds of blends. Although Doherty et al. [2] explained the difference with the possible unfavorable entropic effect of short chain branches, the explanation is very difficult to believe. Kadla

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and Kubo [38] found that PP and Kraft lignin formed immiscible blends as no specific interactions developed between the components. Pouteau et al. [39] observed poor compatibility between LDPE, PP and unmodified Kraft lignin. The authors also blended PP with different molecular weight fractions of lignin and claimed a significant improvement of compatibility as the molecular weight of lignin decreased. Good compatibility was found between PP and organosolv as well as prehydrolysis lignin by Košiková [40], while Jeong et al. [41] claimed complete miscibility of lignin with several polymers including LDPE, PP, polystyrene and poly(ethylene terephthalate). Unfortunately, these claims were supported by very little experimental evidence. In spite of the claims about good compatibility and even miscibility, properties were shown to deteriorate upon blending lignin with most polymers including polyolefins. Although stiffness usually increases in larger or smaller extent [41–46], tensile strength and deformability decrease in most cases [41–47], which indicates poor interactions and the development of a heterogeneous structure. The inferior compatibility of lignin with polyolefins is shown also by the numerous attempts to improve interactions and miscibility in such blends. Lignin has been modified by stearoyl chloride [48], grafted with ethylene monomers [49], esterified with phthalic [45] and maleic anhydride [46], alkylated by dichloroethane [46] and dodecane bromide [47], or compatibilized by a third component. Ethylene-vinyl acetate copolymer [42–44,50] or maleated polyethylene [44,45] was added to the blend to modify structure and improve properties in the latter case. Some of these modifications were claimed to improve blend properties significantly and make possible the production of films for practical applications [42–45,49,50].

In spite of these attempts and claims, considerable controversy surrounds the preparation of polymer/lignin blends, the interactions developing among the components, as well as the resulting structure and properties. Since polypropylene is a cheap commodity polymer available in large quantities, it seemed to be obvious to use it as a matrix for lignin blends. In view of the controversies mentioned above the goal of our study was to prepare PP/lignin blends in a wide composition range, estimate interactions in them, modify those interactions by coupling, if possible, and determine the resulting structure and properties. We also intended to study the deformation and failure mechanism of the blends in order to obtain further information about structure and interactions, and draw conclusion about the possible use of these materials in practical applications.

2. Experimental

The polypropylene used as matrix in the experiments was the Tipplen H 649 FH grade homopolymer supplied by Tisza Chemical Works Ltd., Hungary. It has an MFR of 2.5 g/10 min at 230 °C and 2.16 kg and a nominal density of 0.9 g/cm^3. The two lignin samples used in the experiments were kindly supplied by Burgo Cartiere SpA, Italy. The Bretax C grade is the primary by-product of cellulose production and the counter ion of the sulfonate groups is calcium. The Bretax SRO2 is a modified product, in which calcium ions are exchanged to sodium ions and a significant part of its sugar content is oxidized. Both grades have small molecular weight (1400–2400 g/mol), and they contain various amounts of inorganic salts and sugar. Whenever in further discussion lignin is mentioned, we always mean lignosulfonate under this term. Interactions were modified by the addition of MAPP coupling agents. The Polybond 3200 grade (MA content: 1 wt%, MFR: 106 g/10 min at 190 °C and 2.16 kg, M_n: 33,000 g/mol) produced by Chemtura, USA, was used together with the Bretax C lignin, while the Orevac CA100 grade of Arkema, France (MA content: 1 wt%, MFR: 112 g/10 min at 190 °C and 2.16 kg, M_n: 25,000 g/mol) was applied in blends containing the SRO2 grade. The amount of lignin increased from 0 to 70 vol% in 10 vol% steps in the blends, while that of MAPP was always 20% related to the quantity of lignin added.

The components were homogenized in a Brabender W 50 EHT internal mixer at 190 °C set temperature, 42 cm^3 charge volume, 42 rpm and

10 min mixing time after the addition of lignin. Plates of 1 mm thickness were compression molded from the homogenized blends at 190 °C using a Fontijne SRA 100 machine. After one week storage at room temperature, tensile bars were machined from the plates for further testing.

Dynamic mechanical thermal analysis (DMTA) was carried out on specimens with 60 × 5 × 1 mm dimensions between −50 and +200 °C at 1 Hz frequency, 10 μm amplitude and 2 °C/min heating rate. Mechanical properties were further characterized by tensile testing using an Instron 5566 universal testing machine. Gauge length was 80 mm and the test was done at 10 mm/min cross-head speed. Local deformation processes were followed by acoustic emission testing. The signals were detected with a Sensophone AED-40 type equipment at 20 dB threshold level. The structure of the blends was analyzed by scanning electron microscopy (SEM) using a Jeol JSM 6380 LA apparatus. Thin slices were cut from the 1 mm thick plates with a Leica EM UC6 microtome at −60 °C and then the lignosulfonate was dissolved from the slices by soaking them in distilled water for 24 h at ambient temperature. Micrographs were recorded on fracture surfaces created during tensile testing in order to obtain information about local deformation and failure processes.

3. Results and discussion

The results are presented in several sections. First the crucial issue of interactions is discussed, followed by the presentation of the resulting structure. Deformation and failure mechanism as well as the composition dependence of blend properties are analyzed in the next sections and then general correlations and consequences for practice are discussed in the end.

3.1. Interactions

As mentioned in the introductory section, conclusions published in the literature about the compatibility of polyolefins and lignin contradict each other seriously. Considering the structure of lignin that contains a number of aromatic rings and several functional groups including ionic, aliphatic and phenolic hydroxyl, as well as methoxy and acid groups, one would expect the development of very strong interactions among lignin molecules. The existence of these interactions is supported by the fact that lignin in itself cannot be melted and processed by any processing technology. Polypropylene is very apolar containing only carbon and hydrogen atoms and capable of forming only very weak dispersion interactions. As a consequence, any kind of miscibility or compatibility between lignin and PP would be quite surprising.

Interactions and miscibility can be estimated in various ways in polymer blends. The simplest is the determination of solubility parameters. The value of 33.1 MPa$^{1/2}$ derived from solubility tests was published for calcium lignosulfonate by Myrvold [51]. The solubility parameter of polypropylene was calculated from Hoy's group contributions yielding a value of 16.0 MPa$^{1/2}$. The very large difference between the two quantities predicts complete immiscibility for the two materials, i.e. lignin and PP. The Flory-Huggins interaction parameter can be approximately calculated from solubility parameters [52] and a value of 5.8 was obtained, which is also very large and predicts the lack of compatibility. In view of these calculations the claim of partial or even complete miscibility [41] of lignin and polyolefins is difficult to understand.

Another way to estimate miscibility is the determination of the glass transition temperature (T_g) of the components. Usually a single transition temperature is detected in miscible blends, while two T_g's corresponding to that of the two components is expected to appear at complete immiscibility [4]. The temperature dependence of the loss tangent of a blend series is presented in Fig. 1. Storage and loss moduli convey the same message thus we refrain from their presentation here. Similarly, the temperature dependence of tg δ as well as the effect of composition on it was very similar also for the other three series of