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Competitive Interactions in Aromatic Polymer/Lignosulfonate Blends

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Abstract

Polymer/lignosulfonate blends were prepared from three polymers containing aromatic moiety in their chain: polystyrene (PS), polycarbonate (PC) and a glycol modified poly(ethylene terephthalate) (PETG), in order to study the effect of aromatic, π electron interactions on miscibility, and on the structure and properties of the blends. Polypropylene (PP)/lignin blends were used as reference. The components were homogenized in an internal mixer and compression molded into plates of 1 mm thickness. Structure was characterized by scanning electron microscopy (SEM) and image analysis, while mechanical properties by tensile testing and acoustic emission measurements. Component interactions were estimated from solubility parameters, the composition dependence of glass transition temperature and mechanical properties. The results indicated that π electron interactions result in better compatibility than the dispersion forces acting in PP blends. The average size of the dispersed lignin particles was smaller and properties were better in aromatic polymers than in PP. After PP, PS containing only aromatic rings and no other functional groups formed the weakest interaction with lignin, while interactions in PC and especially PETG capable of forming also hydrogen bonds were much stronger showing that the combined effect of competitive interactions determines the structure and properties of the blends.

Keywords: lignin blends, compatibility, miscibility, aromatic interactions, dispersed structure, mechanical properties, local deformations

Introduction

Lignin is produced in increasing quantities as a side product in the cellulose and bioethanol industries. Because of its complicated, often cross-linked structure the utilization of lignin is restricted to energy production [1], to its use as a raw material for the production of some chemicals [2-4] or as an additive in certain applications [5-7]. However, because of its availability and being a side product, lignin is relatively cheap thus its utilization in value added applications could result in considerable financial gain. The potentials of lignin are shown in the continuously increasing interest in this material, more and more papers are published on the characterization, modification and possible application of lignin. An obvious route to use lignin in the plastics industry is blending it with polymers to create novel materials with new properties.

The structure of the lignin produced by an industrial process or in the laboratory depends very much on the technology used for extraction and differs considerably from the original structure in the lignocellulosic plant. Although the classification is arbitrary, according to the extraction process we can differentiate several types of lignin such as Kraft lignin, lignosulfonate, organosolv and steam explosion lignin. The different structure and interactions of these products are clearly shown by the fact that lignosulfonates are soluble in water, while Kraft lignin can be dissolved only under alkaline conditions [8,9]. The difference is caused mainly by the presence of the sulfonic acid groups. However, the aromatic rings and most of the functional groups present are very similar in all lignins, ionic groups or pH does not play a role in polymer blends anyway. Nevertheless whenever lignin is mentioned in this work, we understand lignosulfonate under the term and use lignin only for the sake of brevity.

A considerable number of papers have been published on the blends of lignin with a wide range of polymers including proteins [10-12], starch [13-15], polyolefins [16-26], vinyl polymers

[18,19,21,27-35] and polyesters [19,21,22,36-43]. The chemical modification of lignin [10,14,16,20-22,27,29,36,40,41] and coupling [16,17,20,24,25,27,28] is often used to achieve better properties in polymer/lignin blends. Lignin may also be applied as a reactive component in epoxy [44,45] and phenol formaldehyde resins [46,47], as well as in polyurethanes [48-50]. Several review papers are available which discuss the attempts to produce new materials by combining lignin with polymers [51-55]. They list the combination of the materials used, the approach applied and the potential applications. However, these and other papers published on lignin blends occasionally offer contradictory information both about the properties obtained and especially about the miscibility of the components. Miscibility was claimed to change from the complete solubility of the components in each other [15,21,22,33,38] to complete phase separation [12,18-20,22,24-32,34-36,39,42] with properties changing accordingly.

In spite of such contradictions one fact becomes evident from the study of the published papers: the key for the successful preparation of polymer/lignin blends lays in the control of interactions. Lignin is a polar compound containing a large number of functional groups interacting with each other. Strong interactions and the usually small molecular weight of commercial lignin samples result in a stiff and brittle material which usually is not miscible with any polymer. The importance of interactions is mentioned in a number of papers published on lignin blends. Several of them emphasize the significance of hydrogen bonds, but Kilpeläinen et al. [56] also showed the role of aromatic, π electron interactions in the complete dissolution of wood in ionic liquids. The authors [56] claim that these interactions help to dissolve also the lignin component of wood which otherwise forms a suspension in the solution of non-aromatic ionic liquids. The possible role of specific interactions generally and that of π-π stacking particularly is mentioned also in several other papers. Chen et al. [57], for example, think that the significant shift in the aromatic group vibration in poly(butylene adipate-co-terephthalate)/Kraft lignin blends is caused by aromatic interactions. Bahl et al. [58] studied the effect of a polybutadiene-g-polypentaflouorostyre coupling agent on the properties of styrene-butadiene rubber/lignin blends and claimed that the coupling agent improved properties through π-π stacking interactions. Such interactions were utilized in the preparation of hybrid fillers by combining lignin and carbon black [59] and were found to be active in lignin/carbon nanotube [60,61] as well as in lignin/graphene [62-64] combinations. Deng et al. [65] studied aromatic interactions specifically in various solvents and found considerable changes in the fluorescent spectra of the solutions with increasing lignin content. Although much evidence indicates the existence and effect of aromatic π-π interactions, Doherty et al. [54] claim that non-covalent interactions are not sufficient to result in the complete solubility of lignin in most polymers.

In a previous publication we discussed the structure, interactions and properties of polypropylene/lignin blends [24]. The results clearly proved that interactions between PP and lignin are very weak resulting in large lignin particles being dispersed in the PP matrix at all compositions, and in very poor properties. Although interfacial adhesion could be increased by the application of a coupling agent, the properties of the blends, especially their deformability, needed further improvement. Based on the results obtained in the previous project, we decided to check the possible role and effect of aromatic, π electron interactions on the miscibility, structure and properties of polymer/lignin blends. A commercial lignosulfonate sample was blended in a wide composition range with polystyrene (PS), polycarbonate (PC) and a glycol modified poly(ethylene terephthalate) (PETG), respectively. Special effort was made to estimate interactions and miscibility quantitatively, but structure and properties were also determined. The PP/lignin blends prepared earlier were used as reference.

Experimental

Materials

The type, source and most important characteristics of the polymers used in the experiments are summarized in **Table 1**. Their melt flow rate (MFR) was measured under different conditions, i.e. PP at 230 °C/2.16 kg, PS at 200 °C/5 kg, PC at 300 °C/1.2 kg and PETG at 250 °C/2.16 kg. The molecular weight of PP, PS and PC was determined by gel permeation chromatography in trichlorobenzene (PP) and tetrahydrofuran (PS, PC), respectively, while that of PETG by the measurement of intrinsic viscosity at 25 °C in the solution of 1,1,2,2-tetrachloroethane (60 %) and phenol (40 %) using the Mark-Houwink constants $K = 0.000372$ and $a = 0.73$ [66]. The lignosulfonate sample used in the experiments was kindly supplied by Burgo Cartiere SpA, Italy. The Bretax C grade is the primary product of cellulose production and the counter ion of the sulfonate groups is calcium. The lignin used has small molecular weight (1400-2400 g/mol), and it contains various amounts of inorganic salts and sugar. Whenever in further discussion lignin is mentioned, we always mean lignosulfonate under this term. The chemical structure of the repeat units of the polymers used and a possible model structure of the lignosulfonate molecule are presented in **Fig 1**. The amount of lignin was changed from 0 to 60 vol% in 10 vol% steps in the blends.

Table 1 The most important characteristics of the polymers used in the study

Polymer	Abbrev.	Producer	Type	M_n (g/mol)	MFR (g/10 min)
Polypropylene	PP	MOL	H 649 F	92620	2.5
Polystyrene	PS	Americas Styrenics	Styron 686 E	127970	2.5
Polycarbonate	PC	Covestro	Makrolon 2658	24730	13.0
Modified poly(ethylene terephthalate)	PETG	SK Chemicals	Ecozen SE	26150	10.9

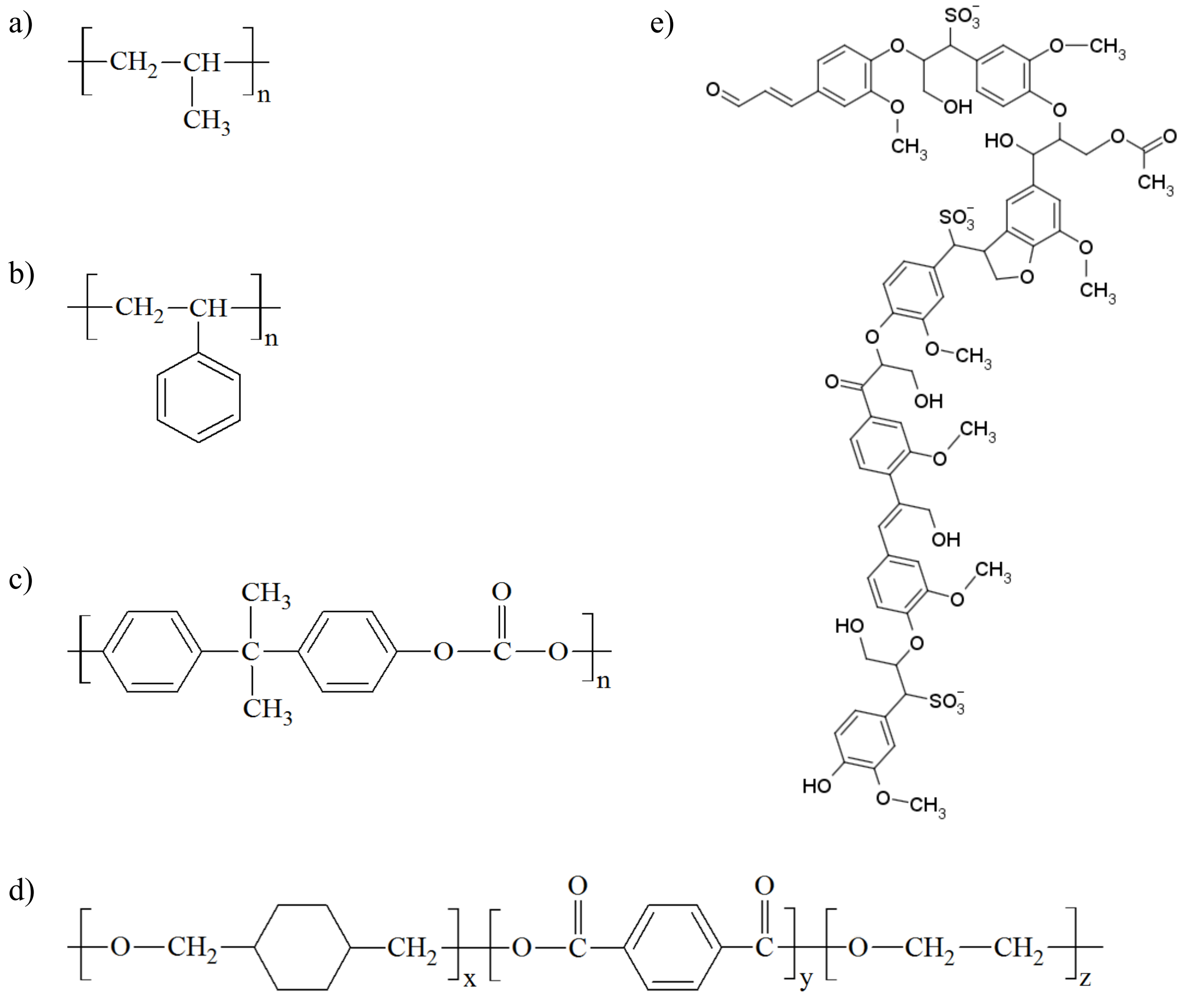


Figure 1. Chemical structure of the repeat units of the polymers used in the experiments and that of a lignosulfonate model molecule, a) PP; b) PS; c) PC; d) PETG; e) lignosulfonate.

Sample preparation

The components were homogenized in a Brabender W 50 EHT internal mixer at 190 °C set temperature with the exception of PC which was processed at 220 °C. Mixing was carried out at 42 cm^3 charge volume, 42 rpm and 10 min mixing time after the addition of lignin. Torque and temperature were recorded during mixing and used in further analysis. Plates of 1 mm thickness were compression molded at 190 °C from three of the polymers and at 220 °C from PC using a Fontijne SRA 100 machine. After storing the plates for one week at room temperature, tensile bars were machined from them for further testing.

Characterization

In order to determine relaxation transitions and glass transition temperature (T_g), dynamic mechanical thermal analysis (DMTA) was carried out on specimens with 60 x 5 x 1 mm dimensions between 30 and 150 °C at 1 Hz frequency, 10 μm deformation and 2 °C/min heating rate. The measurements on PP and its blends were done from -50 °C to include the glass transition temperature of this polymer into the range of the test. Relaxation transitions were studied also by differential scanning calorimetry using a Perkin Elmer DSC 7 apparatus. The measurements were done in two heating and one cooling runs between 30 and 220 °C with heating and cooling rates of 20 °C/min. The weight of the samples was 6-8 mg in each case. Mechanical properties were 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 40/4 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 using 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 hours at ambient temperature. The procedure was thoroughly optimized and checked to avoid the creation of artifacts. Soaking was carried out as a function of time for selected samples: the color of the water was determined, the dissolved lignin content was checked by Fourier transform infrared spectroscopy (FTIR), and the appearance of the sample was studied by microscopy to detect any possible change in the structure and/or composition of the matrix polymer. The average particle size and particle size distribution of the dispersed lignin particles were determined by image analysis. Micrographs were recorded also on fracture surfaces created during tensile testing in order to obtain information about local deformation and failure processes. The blends were also studied by FTIR and rotational viscometry, but these results will not be discussed in the paper thus further details are not included here.

Results and discussion

The results are presented in several sections. The properties and structure of the blends are shown in the first two sections followed by the discussion of the crucial issue of interactions in the subsequent one. Deformation and failure mechanism are analyzed in the next part of the paper, followed by a discussion including comments on the consequences for practice.

Properties

The blending of two polymers can result in various combination or properties. The characteristics of blends produced from miscible components changes more or less additively with composition, while immiscibility usually leads to negative deviation from additivity [67]. The viscosity of the blends studied increases with increasing lignin content, but only limited information can be drawn from the results thus we refrain from their presentation. The stiffness of the aromatic polymer/lignin blends and that of the reference series (PP/lignin) increase monotonously with increasing lignin content (see Supporting Information). The rate of modulus increase is similar for the three aromatic polymers and somewhat smaller for PP. As described previously, the interaction between PP and lignin is very weak, dispersed particles debond under the effect of the slightest load and the resulting blend has a small modulus [24]. In polymers with reasonable interfacial adhesion the very stiff lignin component increases the modulus of the blends considerably and more or less proportionally to lignin content. Much information cannot be obtained about interactions and miscibility from the composition dependence of stiffness.

The tensile strength of the blends depends on lignin content in a more complicated way. The strength of the blends goes through a slight maximum for all three aromatic polymers, but this maximum seems to be absent in PP (**Fig. 2**). The appearance of such maxima indicates the development of relatively good interactions between the components, but it is impossible to draw valid conclusion about interfacial adhesion directly from primary strength data. The only conclusion that we can draw from the direct observation of the composition dependence of tensile strength is that it points toward somewhat stronger interaction between the aromatic polymers used and lignin, than between PP and lignin. The small strength of PS blends is surprising and we think that it results from the processing technology used (compression molding) and from the extreme brittleness of the plates obtained.

The deformability of the blends was a crucial question in PP/lignin blends; lignin made the blends extremely brittle. Although the deformability of neat PP and PETG is quite large, around 100 %, that of the blends is extremely small, below 10 %, already at 10 vol% lignin content (see Supporting Information). Obviously, not only PP but all polymers become quite brittle upon the incorporation of lignin. The composition dependence of the studied properties shows that viscosity and stiffness increase, strength changes moderately, while deformability decreases drastically upon the addition of lignin, but we obtained very limited information about the interaction of the components in this way.

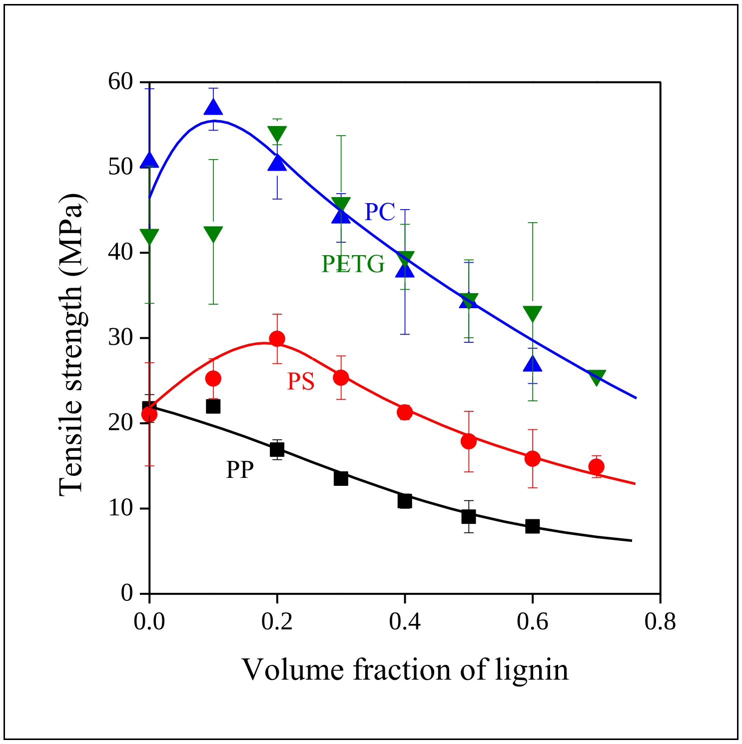
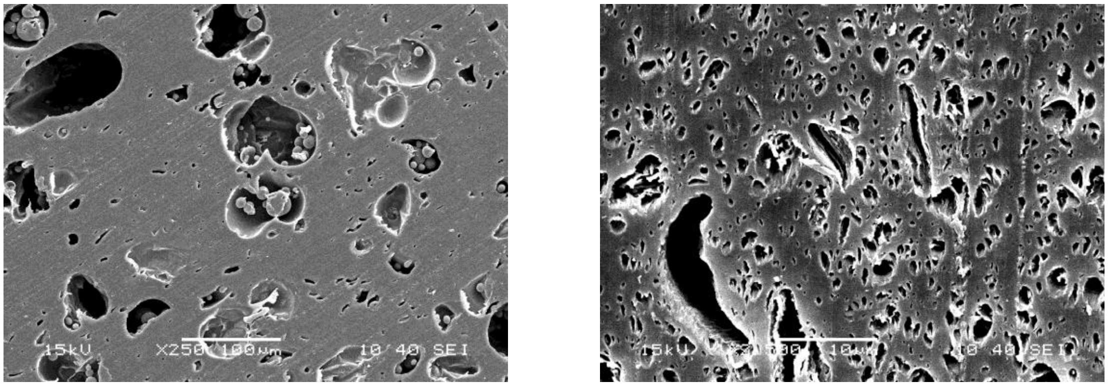


Figure 2. Tensile strength of thermoplastic polymer/lignin blends plotted as a function of lignin content. Symbols: (■) PP, (●) PS, (▲) PC, (▼) PETG.

Structure

The structure of polymer blends depends significantly on the interaction of its components. Complete miscibility results in homogeneous structure, while immiscibility leads to dispersed structure with various morphologies [68-70]. Besides dispersed particles, very often phase inversion and a co-continuous structure are also observed in most blends [68-70]. Quite surprisingly, such phase inversion did not occur in the studied blends even above 50 vol% lignin content; lignin was dispersed in the form of droplets in all blends independently of the type of the polymer matrix or composition. The lack of phase inversion cannot be the result of changing matrix structure or properties during soaking, since the possibility of such changes was thoroughly checked and excluded earlier, as mentioned in the experimental part. Two micrographs are presented in **Fig. 3** demonstrating this dispersed structure. Lignin is distributed in the form of very large particles in PP (**Fig. 3a**), while its particle size is much smaller in PETG (**Fig. 3b**). The attention must be called here to the different scale of the two micrographs in **Fig. 3**. The average size of the dispersed particles differs so much in the two cases that it was impossible to show them on the same scale. The size of the dispersed particles in heterogeneous blends is a clear indicator of interactions. Stronger interactions result in smaller interfacial tension [71,72], thicker interphase [72], better stress transfer [73] and smaller particles [74,75]. According to the micrographs presented in **Fig. 3** the interaction between PETG and lignin is much stronger than between lignin and PP.



a) b)

Figure 3. Dispersed structure of polymer/lignin blends. Cut surfaces etched with water for 24 hours. Lignin content: 20 vol%. a) PP, 250x; b) PETG, 2500x.

Particle size distribution was determined quantitatively by image analysis from the micrographs. The composition dependence of the average particle size is shown in **Fig. 4** for the four blend series. Particle size differs significantly in PP from that observed in the blends of aromatic polymers. π electron interactions are apparently much more effective than the dispersion forces acting in PP blends and result in the small size of dispersed lignin particles. The difference among the three polymers containing aromatic rings is much smaller. According to the size of lignin particles the strongest interaction prevails in PETG, while the weakest in PS. However, this qualitative assessment must be supported with a more quantitative estimation of the strength of component interactions.

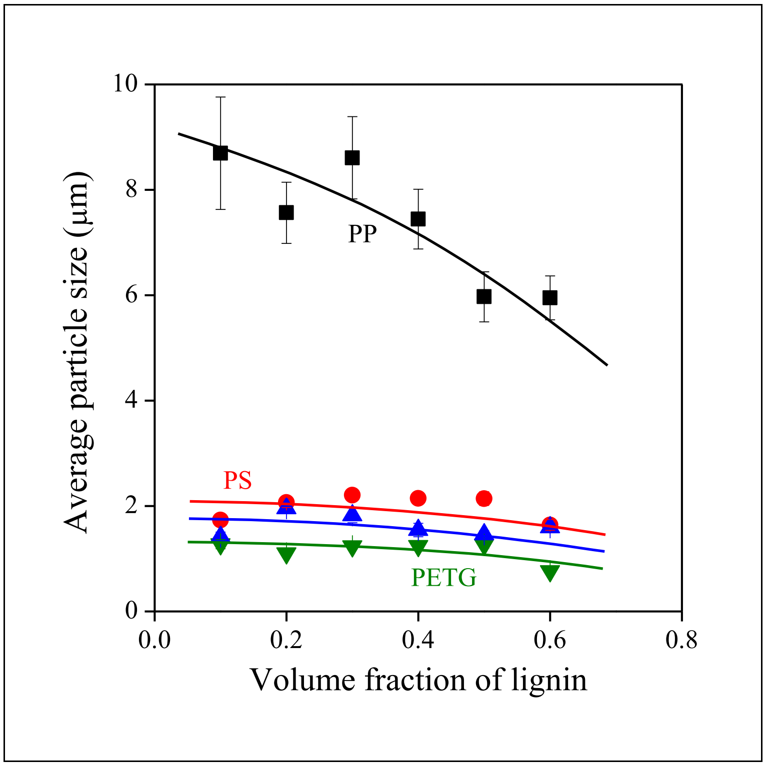


Figure 4. Effect of lignin content on the average size of lignin particles dispersed in the various polymers studied. Symbols are the same as in **Fig. 2**.

During the detailed study of PP/lignin blends we concluded that the original lignin particles of about 80 µm size break up during processing to smaller ones dispersed in the blends (around 6-9 µm) [24]. Particle size is determined by thermodynamic (interactions) and kinetic (shear, time) effects during homogenization. Instead of composition, average particle size is plotted against the equilibrium torque of mixing proportional to the shear stress acting in the internal mixer (**Fig. 5**). The dependence of particle size on shear is very strong in the PP blends, while quite small in the other three blends indicating that kinetics dominates in the first case, and thermodynamics in the second. This result clearly proves that aromatic, π electron interactions are much stronger than dispersion ones and they determine the structure of the blends in polymers containing aromatic rings.

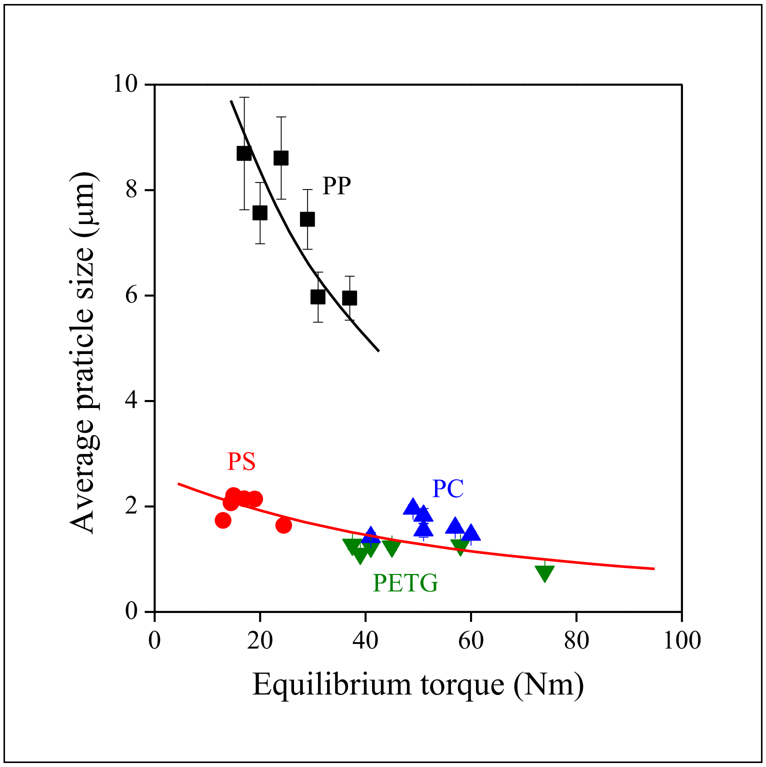


Figure 5. Effect of shear stress (torque) prevailing in the internal mixer during homogenization on the size of lignin particles dispersed in the polymers. Symbols are the same as in **Fig. 2**.

Interactions

The interaction of blend components can be estimated in several ways. Very often miscibility or compatibility is estimated from SEM micrographs or the composition dependence of properties. The decrease of tensile strength is usually interpreted as weak interfacial interaction [76,77], but that statement is completely wrong. The strength of interactions cannot be estimated from the composition dependence of strength directly, because the effect of the dispersed phase is influenced also by the strength of the matrix. A simple model describing the composition dependence of composite or blend strength offers the possibility of estimating the strength of interactions. The model can be expressed in the following form [73,78]

$$\sigma_{Tred} = \sigma_T \frac{1+2.5\varphi}{1-\varphi} \frac{1}{\lambda^n} = \sigma_{T0} \exp(B\varphi) \tag{1}$$

where σ_{Tred} is the reduced tensile strength of the blend, σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$ and $\lambda = L/L_0$, where L is the ultimate and L_0 the initial gauge length of the specimen) of the blend and the matrix, respectively, n is a parameter taking into account strain hardening, φ is the volume fraction of the dispersed component and B is related to its relative load-bearing capacity, i.e. to the extent of reinforcement which, among other factors, depends also on interfacial adhesion. If we plot the natural logarithm of reduced tensile strength against the amount of the dispersed phase, we should obtain a straight line, the slope of which is proportional to the load-bearing capacity of the reinforcement, and under certain conditions to the strength of interactions. The tensile strength of the four series of blends was plotted in this way and all correlations proved to be linear indeed with different slopes (see Supporting Information) showing dissimilar interfacial adhesion.

Quantities characterizing the extent of reinforcement were calculated in the way described above and collected in **Table 2** for all four series. The difference between the calculated and the measured strength of the matrix (see columns 2 and 3) indicates that deformation mechanism changes in the blends, failure occurs by a new mechanism induced by the presence of lignin particles. Parameter B changes between 0.74 and 1.76 showing some difference in interactions. According to the values these are the weakest in PP, as expected, and the strongest in PETG. Among the aromatic polymers PC seems to develop the weakest interaction with lignin, which contradicts somewhat the conclusion drawn from the size of the dispersed lignin particles (see **Fig.**

4). Here we must remind the reader, though, that parameter B depends also on the properties of the matrix and does not reflect the strength of interactions completely correctly [79].

Table 2. Quantities characterizing interaction calculated from the mechanical properties of the blends

Polymer	σ_{T0} (MPa)		B	R^{2b}	$C\sigma_L$
	Measured	Calculated^a			
PP	21.7 ± 1.6	29.5	0.74	0.9641	77
PS	21.0 ± 6.1	37.7	1.68	0.9482	114
PC	50.6 ± 8.6	66.4	1.48	0.9928	238
PETG	42.1 ± 8.0	82.9	1.76	0.9821	480

a) Calculated from the intersection of the lnσ_{Tred} vs. φ lines (see **Eq. 1**).

b) Determination coefficient indicating the goodness of the fit.

Another approach takes the load carried by each component and the properties of the constituents into account and relates mechanical properties to the size of the dispersed particles [73]. The stress carried by the dispersed component is expressed by Parameter C

$$B = \ln\left(\frac{C\sigma_L}{\sigma_0}\right) \tag{2}$$

where σ_L and σ_0 are the tensile strength of the dispersed particles (lignin) and the matrix, respectively. Since we do not know the strength of the lignin particles, which may change also with their actual size [80], we can calculate only the $C\sigma_L$ term expressing the load carried by the lignin phase which is related to the strength of interactions. In **Eq. 2** σ_L, i.e. the strength of lignin particles is assumed to be constant and the same in all blends. The quantity ($C\sigma_L$) is included into the last column of **Table 2** and indicates that the strength of interaction differs indeed for the four polymers, it is the weakest in PP, while the strongest in PETG.

Parameter C depends on the size of the interface and on the thickness of the interphase and it is inversely proportional to the Flory-Huggins interaction parameter (χ) [73]. As mentioned above, the size of dispersed particles is also related to interactions thus a direct correlation can be established between the mechanical properties of the blends and the size of the dispersed particles [73]

$$C = K\frac{\varphi^2}{d^2} \tag{3}$$

where φ is the volume fraction of the dispersed particles, d their average diameter and K is a constant. The correlation is presented in **Fig. 6** at 30 vol% lignin content. The close relationship confirms that both mechanical properties and particle size are determined by the interaction of the components and that this latter is weak for PP and stronger in the aromatic polymers used.

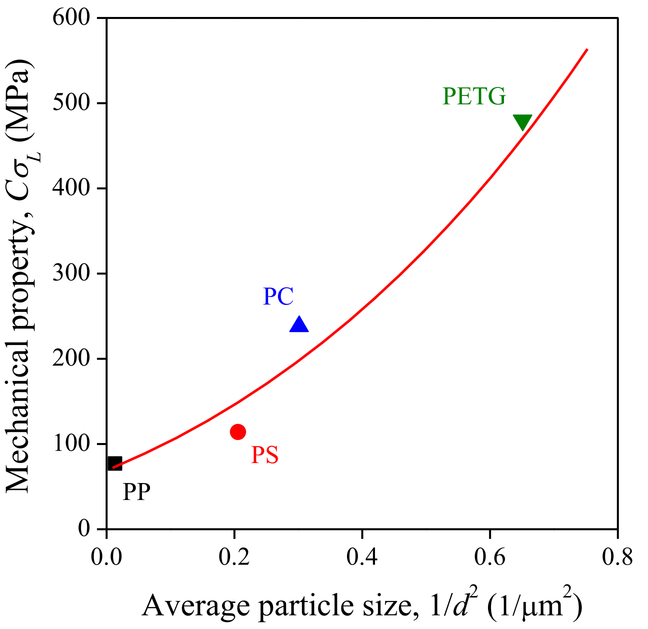


Figure 6. Correlation between quantities characterizing mechanical properties (strength, *C*) and dispersed structure (particle size, *d*) both being determined by interactions.

The Flory-Huggins interaction parameter measures the strength of interactions more directly. It can be obtained by different routes. The simplest way is its estimation from the solubility parameters of the components by the correlation

$$\chi = \frac{V_r(\delta_1 - \delta_2)^2}{RT} \tag{4}$$

where V_r is a reference volume with the value of 100 cm^3/mol [81], δ_1 and δ_2 the solubility parameters of the components, R the universal gas constant and T the absolute temperature. The Hildebrand solubility parameters of the matrix polymers were calculated from the group contributions of Hoy [82]. The solubility parameter of the lignin sample was taken from the literature and was determined experimentally specifically for a lignosulfonate sample by Myrvold [83]. The results of the estimate are collected in **Table 3**. In spite of all the simplifications and neglected factors, they agree well with those derived from mechanical testing; the smallest Flory-Huggins parameter, i.e. the strongest interaction and the largest degree of solubility, was obtained for PETG, while the largest for PP. The interaction of PS with lignin is not very strong, in spite of the aromatic rings in its structure.

Table 3. Flory-Huggins interaction parameters calculated from solubility parameters (T=298 K).

Polymer	Hildebrand solubility parameter δ^a (MPa$^{1/2}$)	Flory-Huggins interaction parameter, χ
PP	16.0	11.8
PS	18.6	8.5
PC	21.0	5.9
PETG	21.9	5.1
Lignin	33.1	–

a) Calculated from Hoy's group contributions, except for lignin which was determined experimentally by Myrvold [83]

Although the estimate presented above agrees well with the results obtained by other measurements, the approach includes a large number of simplifications (constant reference volume, $\chi \geq 0$, average interactions, no H-bridges and specific interactions). Interactions can be estimated also from the number and composition dependence of the relaxation transition temperatures in blends. Complete miscibility results in a single glass transition temperature, while partial or complete immiscibility in two T_g values [67]. The T_g of PP practically does not change as shown in our previous paper [24]. The glass transition temperature of all three thermoplastic polymer phases containing aromatic moieties decreases in different extents indicating the interaction of the phases (see Supporting Information). The T_g of the PS phase changes only slightly (0.4 °C in the entire composition range), while that of PC (11 °C) and PETG (9 °C) much more considerably. The absolute values of these changes indicate the weakest interaction between PS and lignin, while the strongest in the PC blend. However, since the transition of the dispersed lignin phase was very weak and difficult to determine, component interactions cannot be estimated quantitatively from changes in the glass transition temperatures [84].

Deformation and failure

Although aromatic, π electron interactions increased the compatibility of the blends, their deformability is still limited possibly hindering application in certain fields. The large deviation between the calculated and measured strength of the matrix (see **Table 2**) also needs explanation. Deformation and failure processes in heterogeneous polymers can be followed relatively simply by acoustic emission measurements. The dissimilar elastic properties of the components initiate local deformation processes around the inclusions under the effect of external load, which can be detected by piezoelectric sensors. The result of such a measurement is presented in **Fig. 7** for the PETG blend containing 20 vol% lignin. The small circles represent individual acoustic events (signals, hits) and the continuously increasing correlation (right hand axis) indicates the cumulative number of signals detected during the measurement. The stress vs. deformation trace of the blend is also included for reference (left hand axis). The large number of events and the steeply increasing cumulative number of hit trace indicate strong interaction and/or the fracture of the lignin particles [80,85].

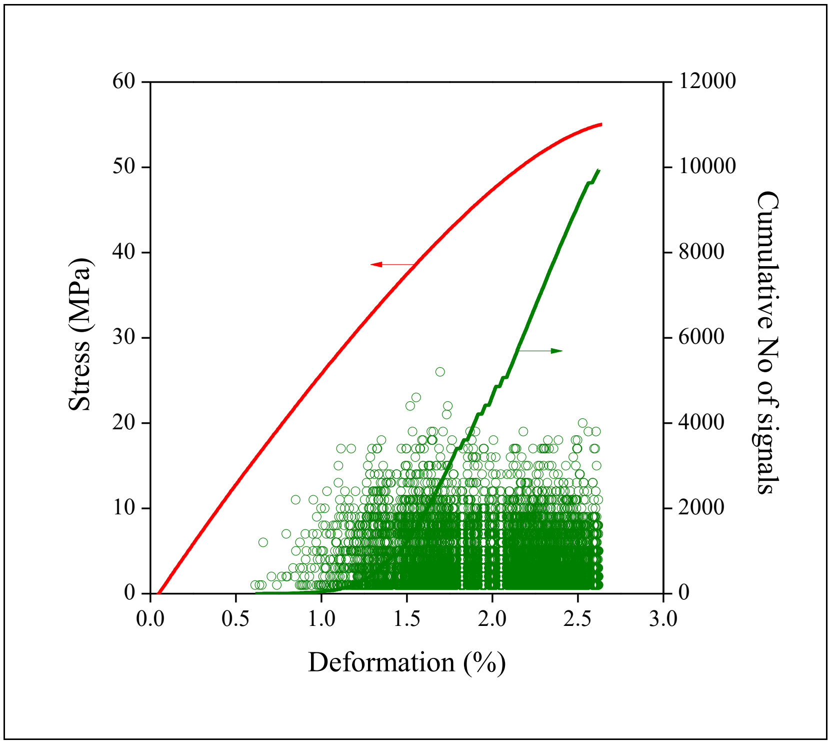


Figure 7. Acoustic emission testing of a PETG/lignin blend. Lignin content: 20 vol%. Stress vs. elongation trace is plotted as reference. ○ individual signals, ——— cumulative number of signals.

The cumulative number of event traces are compared to each other in **Fig. 8**. The trace of a PS blend is not included, because the specimens prepared from this polymer were extremely brittle and broke at very small deformations resulting in a very small number of signals. The traces obtained for the aromatic polymers and PP differ considerably from each other. The latter increases at the beginning of the measurement and then almost flattens out, increasing only slowly at larger deformations. Such traces usually indicate debonding as the dominating local deformation process with subsequent fracture of the particles at larger deformations [85]. In the other two blend series the large number of signals and the steeply increasing cumulative number of hit trace, on the other hand, indicate particle fracture as the dominating mechanism. Although the mechanism of deformation seems to be different in PP and in the other polymers studied, all the blends are very brittle and their elongation-at-break is very small hindering their application in certain fields.

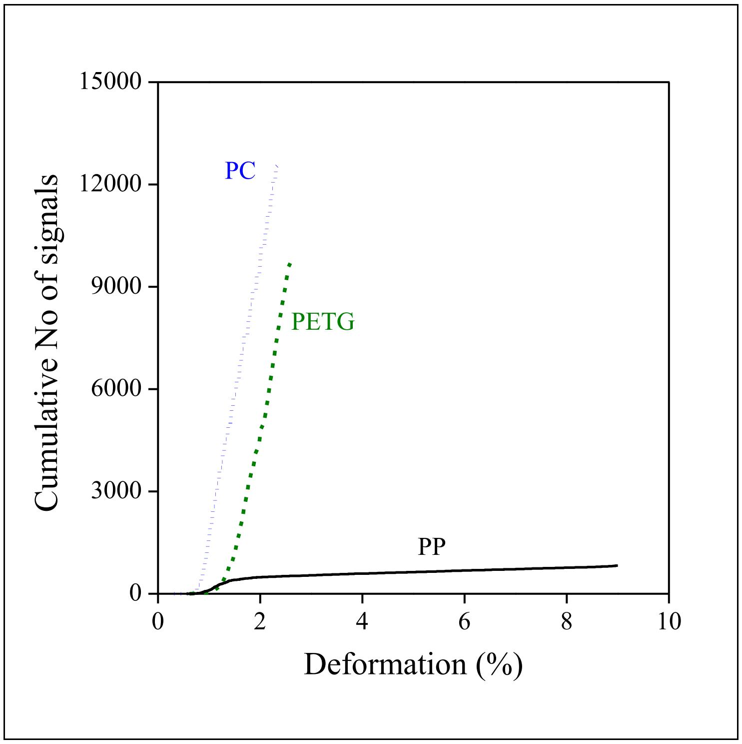


Figure 8. Comparison of the cumulative number of signal traces of three polymer/lignin blends containing 20 vol% of the dispersed phase. ——— PP, •••••• PC, ------- PETG.

The mechanism of deformation and failure can be confirmed further with the help of electron micrographs recorded on fracture surfaces. Two typical micrographs are presented in **Fig. 9.** Extensive debonding and some particle fracture are seen in **Fig. 9a** showing the fracture surface of a PP blend containing 20 vol% lignin. Some plastic deformation and mainly the fracture of the particles occur in the blends prepared from aromatic polymers as shown in **Fig~~s~~. 9b**. Obviously, the stronger interaction between lignin and the aromatic polymers prevent debonding and the particles break in these blends instead. The fracture of lignin particles changes failure mechanism and leads to the dissimilar matrix strengths listed in columns 2 and 3 in **Table 2**. The particles are very brittle and weak; their extrapolated strength is around 10 MPa.

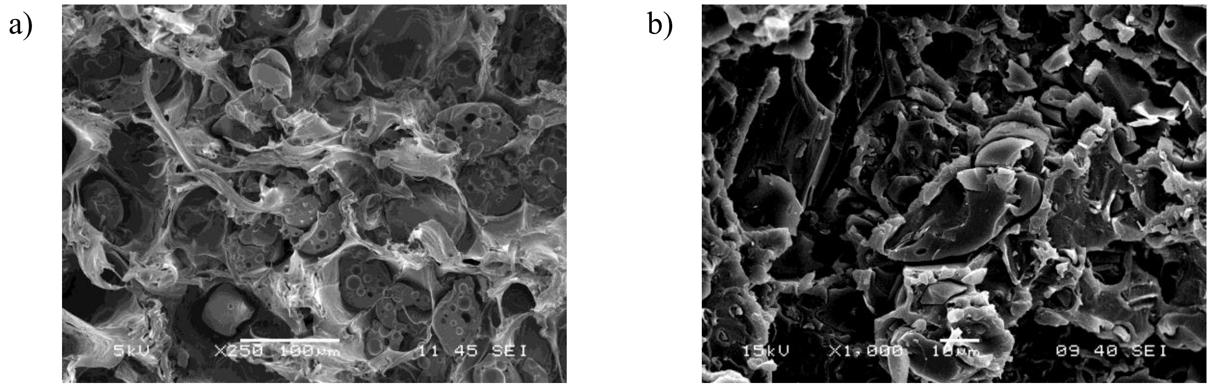


Figure 9. SEM micrographs showing the deformation and failure mechanism of polymer/lignin blends. Lignin content: 20 vol%. a) PP, debonding and some particle fracture; b) PC, particle fracture.

Discussion

All the results presented above agree quite well with each other and show that aromatic, π interactions contribute to the partial solubility of the components and the improvement of properties compared to PP/lignin blends. On the other hand, the differences in the behavior of the three polymers containing aromatic moieties require further considerations and explanation. Although the aromatic rings are there in all three thus they can interact with lignin through π interactions, their structure is quite different. Apart from aromatic, π interactions PS cannot interact with lignin in any other way, except through dispersion forces, but these latter proved to be weak and insufficient in PP blends. The limitations of π electron interactions is clearly shown by the inferior properties of the PS blends, which is in complete agreement with literature references [18,21,28]. On the other hand, PC contains one, while PETG two carbonyl groups in their repeat units, which can form hydrogen bonds with the various functional groups of lignin (see **Fig. 1**). The importance of hydrogen bonds was pointed out in several publications by a number of authors. They were thought to be significant in poly(vinyl chloride) [31,33], poly(vinyl alcohol) [34,35], poly(lactic acid) [37-39], and polyhydroxybutyrate [42,43]. In spite of the importance of hydrogens bonds, Doherty et al. [54] claimed that they alone are not sufficient to compete successfully with the strong interactions among lignin molecules and to result in complete miscibility. It is obvious that π electron interactions may boost properties, but do not solve the problem of insufficient miscibility that is proved by the heterogeneous nature of the blends and by the fact that coupling is used in some cases [27,28].

The results indicate that the miscibility of lignin and thermoplastic polymers can be achieved only through much stronger interactions than those prevailing in the studied polymers. An even larger obstacle before the application of lignin blends is the brittleness of lignin, the fracture of the particles during deformation, which leads to the catastrophic failure of the blends. This problem might be overcome by better dispersion than that achieved in the blends produced in this study or by the modification of lignin through functionalization or plasticization as suggested by some authors [30-32]. Functionalization with more apolar moieties decreases the interaction among lignin molecules, but also those formed with other polymers. Obviously further work and optimization must be done before the practical utilization of thermoplastic polymer/lignin blends.

Conclusions

The results of blending experiments carried out with lignin and three thermoplastic polymers containing aromatic rings in their structure have shown that π electron interactions improve compatibility compared to that created by dispersion forces acting in PP blends. The size of dispersed particles was smaller and properties were better in aromatic polymers than in PP. After PP, PS containing only aromatic rings and no other functional groups formed the weakest interaction with lignin, while interactions in PC and especially in PETG capable of forming also hydrogen bonds was much stronger showing that the combined effect of competitive interactions determine the structure and properties of the blends and lead to the differences observed. In spite of their stronger interactions, the aromatic polymers studied are not miscible with lignin in the composition range studied, heterogeneous structure containing dispersed lignin particles forms at all concentrations. Debonding is the dominating local deformation process in PP, but mainly the fracture of the particles occurs at stronger interactions. Deformability is still very small in all the blends studied and they are very brittle. Further improvement is needed in interactions and deformability for the practical use of thermoplastic polymer/lignin blends.

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Supporting Information

Stiffness and deformability of polymer/lignin blends. Determination of parameter B. Dispersed structure of polymer/lignin blends (PS, PC). Results of DMTA measurements. Glass transition temperature of polymer/lignin blends (PS, PC, PETG). Acoustic emission testing of polymer/lignin blends (PP, PS, PC).

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