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Polymer/lignin blends: interactions, structure, properties

Thesis book

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2019

1. Introduction

Lignin is a major component of all plants. After cellulose, it is the second most abundant natural polymer on Earth. The lignin available on the market is mainly produced by the bioethanol and the paper industry in which it is treated as a side-product forming during the extraction of the targeted valuable product, cellulose. The capacity of world-wide lignin production is estimated to be 50 million tons/year; however, approximately 98 % of this amount is burnt immediately to provide heat and power for cellulose production. In 2014 the isolated and commercially available amount of lignin was only 1.1 million tons¹.

The potentials of lignin are shown by the continuously increasing number of papers published on the characterization, modification and possible application of lignin. The interest in other natural polymers like cellulose and starch also grows but the number of the published papers is much larger. The difference can be explained by the more diverse applications of the two natural polymers, and by the difficulty and complexity of the valorization of lignin, which involves not only scientific, technological, but also economic aspects. Finding ways to improve the handling and properties of lignin and the development of technologies to process it would undoubtedly increase the interest in this natural polymer further.

Since lignin is a side product available in relatively large quantities and its price is quite low, the utilization of lignin in any value added application would result in considerable economical gain. The plastic industry might be one of the potential areas for such a purpose, and an obvious route to use lignin is blending it with polymers to create novel materials with new properties.

The Laboratory of Plastics and Rubber Technology (Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics) together with the Polymer Physics Group (Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences) have considerable experience in the study of interactions, structure

¹ Zion Research. *Lignin Market (Lignosulfonates, Kraft Lignin and Others) for Concrete Additive, Animal Feed, Dye Stuff, and Other Applications: Global Industry Perspective, Comprehensive Analysis and Forecast 2014 – 2020*; Market Research Store: Deerfield Beach, 2015.

and properties in polymer blends and composites. Following the international trends in polymer science and industry, several projects related to natural polymers have been started and completed at the Laboratory in recent years. The main goal of this Thesis was to show a comprehensive study about polymer/lignin blends, with a particular focus on the relationships among interactions, structure and properties.

2. Background

2.1. Blend or composite?

There is a considerable confusion in the literature about the definition of polymer/lignin combinations since some authors call it composite, while others identify it as blend. Occasionally, some confuse terms completely calling the material combination composite, and then discussing miscibility. A blend is a mixture of at least two polymers interacting through interdiffusion, while in a composite the polymer and the filler interact through adsorption at a definite interface. The extent of interdiffusion is determined by the interaction of the components, by their mutual miscibility. As a result, interaction determines the thickness of the interphase and the size of the dispersed particles^{2,3,4}.

In composites a polymer with mobile chains adsorbs on the solid, well-defined surface of a filler. Usually mineral fillers or fibers are dispersed in composites as the second component, but polymers, like lignin could also act as a filler. Cross-linked polymers do not melt, retain their size and possess the necessary well-defined surface, but the powder of a glassy polymer homogenized below its glass transition temperature (T_g) may also meet this condition. The adsorption of the matrix polymer on the surface of the filler results in the formation of an interphase; its thickness as well as interfacial adhesion depend on the surface energy of the components⁵.

Although the definitions presented above seem to be straightforward, it is still quite difficult to decide if lignin acts as a filler or forms a blend. Lignin is originally a cross-linked or highly branched polyphenol with high molecular mass, thus the extraction of lignin is usually impossible without the cleavage of

² Kammer, H. W. Z. *Phys. Chem. (Leipzig)* **1977**, 258, 1149–1161.

³ Taylor, G.I. *Proc. R. Soc. London, Ser. A* **1934**, 146, 501–523.

⁴ Fortelný, I.; Kamenická, P.; Kovar, J. *Angew. Makromol. Chem.* **1988**, 164, 125–141.

⁵ Móczó, J.; Fekete, E.; Pukánszky, B. *J. Adhesion* **2002**, 78, 861–875.

bonds. Most commercially available lignins are produced by vigorous pulping and their molecular mass is relatively small as a consequence. These lignins mainly consist of branched chains and most of them are soluble in some solvent. Moreover, the T_g of lignin is usually lower than the usual processing temperatures of thermoplastics⁶. Accordingly, the homogenization of lignin with thermoplastics results in a blend in most cases.

2.2. Lignin blends

Lignin has been added to a wide variety of polymers from natural to synthetic materials. As the self-interactions among lignin molecules are very strong because of the large number of polar functional groups in the molecule, interactions play a decisive role in the determination of the structure and properties of polymer/lignin blends. Moreover, much contradiction surrounds the issue of interaction, compatibility and miscibility in the literature.

Polyolefins are commodity polymers used in very large quantities in industrial practice. Polyolefins are usually quite apolar, thus they can enter only into weak dispersion interactions with other polymers. Considering the strong polarity and functionality of lignin, one would expect complete immiscibility with polyolefins, but some literature references claim otherwise. The conclusions drawn from these results about compatibility are also quite diverse. Pouteau et al.⁷ observed poor compatibility between low-density polyethylene (LDPE), polypropylene (PP) and Kraft lignin. Good compatibility was found between PP and organosolv as well as prehydrolysis lignin by Košíková et al.⁸, while Jeong et al.⁹ claimed complete miscibility of lignin with several polymers including LDPE, PP, polystyrene (PS) and poly(ethylene terephthalate) (PET). Unfortunately, these claims were supported by very little experimental evidence. In spite of such claims, we expect only weak interactions and immiscibility of lignin with polyolefins, which was proved also by the numerous attempts to modify lignin chemically or by adding a coupling agent.

Polymers containing aromatic rings can form also stronger, π stacking interactions, thus better compatibility, partial miscibility and better properties can be expected upon the blending of the two components. The controversy

⁶ Feldman, D.; Banu, D. *J. Appl. Polym. Sci.* **1997**, *66*, 1731–1744.

⁷ Pouteau, C.; Baumberger, S.; Cathala, B.; Dole, P. C. *R. Biologies* **2004**, *327*, 935–943.

⁸ Košíková, B.; Demianová, V.; Kačuráková, M. *J. Appl. Polym. Sci.* **1993**, *47*, 1065–1073.

⁹ Jeong, H.; Park, J.; Kim, S.; Lee, J.; Cho, J.W. *Fiber. Polym.* **2012**, *13*, 1310–1318.

characterizing the study of polyolefin/lignin blends can be observed also in the case of aromatic polymers. PS can develop π interactions with the polyaromatic lignin, but the components cannot form other interactions except weak dispersion forces. One would expect limited compatibility and relatively poor interactions as a result, and Barzegari et al.¹⁰ found indeed that all mechanical properties including modulus, strength and elongation deteriorated upon the addition of lignin. The properties of PS/lignin blends prepared by Pucciariello et al.¹¹ were also quite poor. On the other hand, Pouteau et al. added Kraft lignin to a number of polymers including PS and found that the compatibility of this latter is much better than that of the rest of the polymers and they explained the difference with the partial solubility of the components and chemical reaction.

A wide variety of other polymers containing aromatic rings were blended with lignin and the conclusions drawn from the results ranged widely also for them. Canetti et al.¹², for example, observed the good dispersion of lignin in PET, while Kadla and Kubo¹³ found the two components immiscible and explained immiscibility with the lack of hydrogen bonding compared to poly(ethylene oxide) (PEO). Jeong et al., on the other hand, found PET and lignin completely miscible.

Hydrogen bonds are considerably stronger than van der Waals and π stacking interactions, thus better compatibility is expected when hydrogen bridges can develop between the components. PEO was found to be miscible with lignin. Kadla and Kubo drew this conclusion from Fourier-transform infrared (FTIR) spectra and the composition dependence of the T_g of the blends which possessed a single T_g . The contradiction related to the role of hydrogen bonds is demonstrated quite well by poly(vinyl alcohol) (PVOH)/lignin blends. These blends were claimed to be heterogeneous¹⁴, which is rather surprising, since the number of active OH groups is considerable in PVOH. Only the combination of several measurements and quantitative analysis may resolve the contradiction about the interaction, compatibility and miscibility of lignin blends. Even scanning electron microscopy (SEM) cannot supply unassailable proof because of possible artifacts and sometimes insufficient magnification.

¹⁰ Barzegari, M.R.; Alemdar, A.; Zhang, Y.; Rodrigue, D. *Polym. Compos.* **2012**, *33*, 353–361.

¹¹ Pucciariello, R.; Villani, V.; Bonini, C.; D'Auria, M.; Vetere, T. *Polymer* **2004**, *45*, 4159–4169.

¹² Canetti, M.; Bertini, F. *Compos. Sci. Technol.* **2007**, *67*, 3151–3157.

¹³ Kadla, J.F.; Kubo, S. *Composites Part A* **2004**, *35*, 395–400.

¹⁴ Kubo, S.; Kadla, J.F. *Biomacromolecules* **2003**, *4*, 561–567.

2.3. Miscibility-structure-property correlations

Miscibility is usually determined by microscopy, differential scanning calorimetry (DSC) measurements or FTIR spectroscopy. All three approaches have advantages and drawbacks and the results obtained by them must be always treated with care. Microscopy seems to be straightforward, but dispersed particles can be very small, thus resolution is important, and of course sample preparation and possible artifacts also might complicate evaluation.

During the evaluation of DSC traces, a frequent mistake is caused by following the general rule that complete miscibility results in a single T_g , while partial miscibility in two T_g values¹⁵. Most technical lignins consist of short and stiff molecules thus the determination of their T_g , particularly when they are blended and diluted with other polymers, is usually very difficult or even impossible. As a consequence, immiscible polymer/lignin blends often exhibit only one T_g which belongs to the thermoplastic forming the matrix.

An apparent shift in a characteristic band of the FTIR spectrum can also be interpreted falsely. Several papers on polymer/lignin blends treat the shift of the absorbance peak of a functional group, like hydroxyl or carbonyl, as an evidence for the formation of strong component interactions or even a homogeneous system. Unfortunately, these claims are mostly not verified by the proper analysis of the infrared spectra, e.g. by the deconvolution of the absorbance peaks. Thus, in many cases the infrared spectrum of a blend is only the superposition of the spectra of the two components.

In spite of the contradictory conclusions drawn by various authors, it is clear that the main factor determining miscibility, structure and properties is the interaction of the components. Although interactions are crucial, very few papers discuss the correlations among miscibility, structure and properties and even less estimate them quantitatively. A rare exception is the work of Pouteau et al. who added Kraft lignin to a number of polymers and studied the relationship between the miscibility of the components and the structure of the blends. The authors recorded micrographs on their blends and then determined the surface area of the dispersed lignin particles in each photo. Plotting the measured areas against the Hildebrand solubility parameter of the studied polymers resulted in a correlation with a minimum. The minimum was located very close to the solubility parameter of Kraft lignin.

¹⁵ Olabisi, O.; Robeson, L.M.; Shaw, M.T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.

2.4. Modification of interactions

Several approaches can be used for the modification of interactions including plasticization, the chemical modification of lignin and the use of coupling agents. Plasticization is an easy and economical way to decrease the strong interactions acting among lignin molecules which prevent their mixing with other polymers. Feldman et al.¹⁶ investigated the plasticizing efficiency of different substances in the blends of lignin and poly(vinyl chloride-co-vinyl acetate). The results revealed a close correlation between the homogeneity of the blend and the Hildebrand solubility parameter (δ) of the plasticizer.

Lignin is often modified chemically to improve its dispersability in a polymer matrix or to enhance its miscibility with polymers. Attaching aliphatic, or less polar moieties to the lignin molecule decreases the strength of self-interactions, but does not necessarily improve miscibility or compatibility with polymers. The final outcome depends on the balance of competitive forces among all components. Gordobil et al.¹⁷ added acetylated and unmodified soda lignin, respectively, to polylactic acid (PLA) at different compositions. According to microscopic images recorded on the blends, the particle size of the dispersed acetylated lignin was much smaller than that of the unmodified lignin. Based on the results, stronger interfacial interactions were claimed for the PLA/acetylated lignin blends, but taking into account that very polar hydroxyl groups were replaced by less polar ester groups, better dispersion must have resulted from weaker interactions among lignin molecules and not from strong-matrix/lignin interactions.

Blend properties may be improved also by compatibilization that modifies mainly interfacial adhesion. In the work of Luo et al.¹⁸ two series of LDPE blends were prepared with lignin in a relatively wide composition range: one with and another without maleic anhydride grafted polyethylene (MAPE). Strength decreased monotonously with increasing lignin content in the absence of MAPE, while it increased in the presence of the coupling agent. Obviously, the compatibilizer increased interfacial adhesion and the load bearing capacity of the dispersed lignin particles considerably.

¹⁶ Feldman, D.; Banu, D. *J. Adhes. Sci. Technol.* **2003**, *17*, 2065–2083.

¹⁷ Gordobil, O.; Delucis, R.; Egüés, I.; Labidi, J. *Polym. Degrad. Stabil.* **2014**, *108*, 330–338.

¹⁸ Luo, F.; Ning, N.; Chen, L.; Su, R.; Cao, J.; Zhang, Q.; Fu, Q. *Chin. J. Polym. Sci.* **2009**, *27*, 833–842.

3. Experimental

In our study commercially available sodium- and calcium-lignosulfonates were used as the lignin component of the blends. All grades applied are the by-products of paper production, and they are contaminated by various amounts of carbohydrates and inorganic salts. Whenever in further discussion lignin is mentioned, we always mean lignosulfonate under this term.

Lignin was added to several types of thermoplastics including PP, PS, glycol modified PET (PETG), PC, PLA, PMMA and ionomer. The interactions in PP/lignin blends were modified by the addition of maleic anhydride grafted PP (MAPP) coupling agents. LDPE and ethylene-vinyl alcohol copolymers (EVOH) with various vinyl alcohol content were also applied as matrix polymers. Furthermore, ionomer/lignin blends were studied in detail using several commercially available ethylene-methacrylic acid copolymers partially neutralized by sodium or zinc salts.

The components were homogenized in an internal mixer. Torque and temperature were recorded during mixing and used in further analysis. The amount of lignin increased from 0 to 60 or 70 vol% in 10 vol% steps in the blends. Plates of 1 mm thickness were compression molded from the homogenized blends. Subsequently, tensile bars were machined from the plates for further testing.

In order to determine the relaxation transitions and glass transition temperature (T_g) of the polymer, dynamic mechanical thermal analysis (DMTA) was carried out in tensile mode. Transitions were also studied by DSC in two heating and one cooling runs.

Mechanical properties were characterized by tensile testing, while local deformation processes were followed by acoustic emission testing. SEM micrographs were recorded on the fracture surfaces created during tensile testing in order to obtain information about micromechanical deformation and failure processes.

The structure of the blends was also analyzed by SEM. Thin slices were cut from the 1 mm thick plates followed by the complete dissolution of lignosulfonate from the slices by soaking them in distilled water. The average size and the size distribution of dispersed lignin particles were determined by image analysis. FTIR spectroscopy was applied to determine the functional groups in the films of the blends.

4. Results

4.1. Compatibilization of polypropylene/lignosulfonate blends

Our first study revealed that the structure of PP/lignin blends forms during processing by the breakup of large lignin particles which soften at the high temperature of processing. This result confirms indisputably that polymer/lignin systems are blends, indeed. Although a wide range of opinions have been published about the miscibility or compatibility of lignin and polyolefins, all evidence implies that weak interactions develop between PP and lignin. The interactions among lignin molecules are much stronger and prevent any mixing of the two components, therefore, dispersed structure forms in the entire composition range studied. Interfacial adhesion can be improved by approximately one order of magnitude through the addition of MAPP. The strength of interfacial adhesion determines the local deformation processes of the blends which fail either by debonding or the fracture of the lignin particles. Also, there is a close correlation between the tensile strength of the blends and the stress expressing the initiation of micromechanical deformation processes. Coupling enhances the stiffness and even more the tensile strength of PP/lignin blends (**Fig. 1**); however, deformability is very small especially at larger lignin content representing the largest obstacle of practical application.

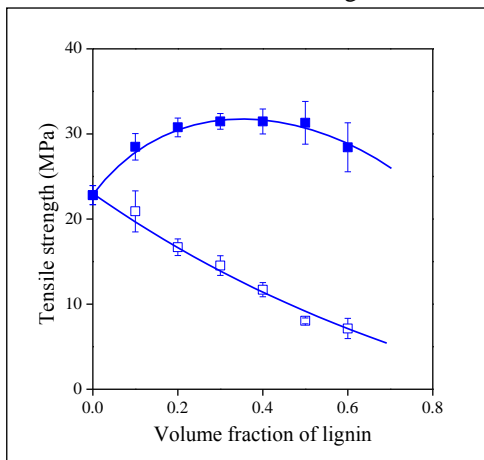


Figure 1. Tensile strength of PP/lignin blends plotted as a function of lignin content; (□) no coupling, (■) MAPP.

4.2. Competitive interactions in aromatic polymer/lignin blends

The abundant amount of aromatic rings in lignin provides the possibility to utilize π electron interactions in polymer/lignin blends. The results of blending experiments carried out with lignin and three thermoplastic polymers containing aromatic rings in their structure (PS, PC and PETG) have shown that π

electron interactions improve compatibility compared to that created by dispersion forces acting in PP blends. After PP, polystyrene containing only aromatic rings and no other functional groups forms the weakest interaction with lignin. Polycarbonate and especially glycol modified poly(ethylene terephthalate) are capable of forming also hydrogen bonds, thus interactions in their blends are even stronger. **Fig. 2** proves the existence of close correlations among miscibility, structure and properties, therefore, it can be stated that the combined effect of competitive interactions determines the structure and properties of the blends. Although stronger interactions develop between lignin and the aromatic polymers studied, heterogeneous structure containing dispersed lignin particles was observed. Debonding is the dominating micromechanical deformation process in PP, but mainly the fracture of the particles occurs at stronger interactions. Deformability expressed by elongation-at-break is still very small for all the blends studied, and they are very brittle.

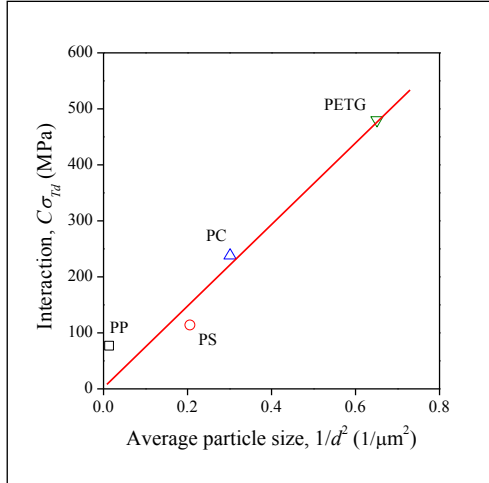


Figure 2. Correlation between quantities characterizing tensile strength (parameter C) and dispersed structure (particle size, d), both being determined by interactions. Lignin content: 30 vol%.

4.3. Hydrogen bonding interactions in EVOH/lignin blends

Lignin contains also a number of polar functional groups which can form hydrogen bridges. The role of hydrogen bonds was studied in the compatibility and structure of EVOH/lignin blends in detail. The results unambiguously proved that strong hydrogen bonds form between the two components, indeed. The development of strong interactions was proved by several approaches, such as by the shift of relaxation temperatures and by the decrease of crystallite size and crystallinity with increasing lignin content. Despite the strong interactions, heterogeneous structure forms in the studied blends, since self-

interactions within the neat components are also very strong. The structure of the blends is determined by competitive interactions; therefore, the increasing vinyl alcohol content of EVOH results in the formation of smaller lignin droplets (**Fig. 3**). The competitive character of interactions is shown also by the increased mobility of the matrix polymer and the decreased viscosity of the blends at certain compositions. Although hydrogen bonds are very strong indeed, miscible blends may be prepared from the lignin used in the study only by applying other approaches like plasticization or chemical modification.

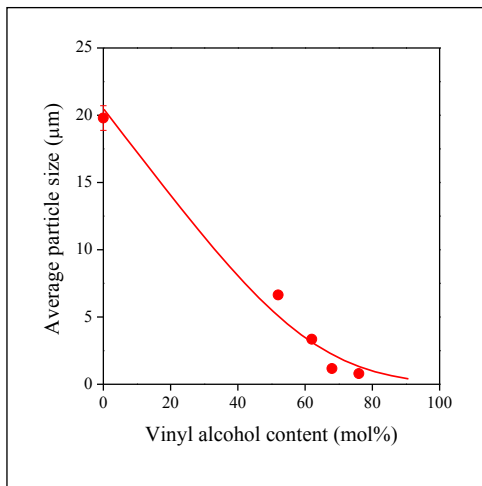


Figure 3. Effect of vinyl alcohol content on the average size of dispersed lignin particles in polymer/lignin blends at 30 vol% lignin content.

4.4. Competitive interactions in ionomer/lignin blends

Lignosulfonate is a special type of lignin which contains functional groups capable of forming ionic bonds. Blends were prepared from industrial lignins and ionomers for the first time in order to investigate the role and importance of ionic bonds. All properties of the blends indicate the development of strong interactions between the components compared to the dispersion forces forming in the LDPE/lignin blend used as reference. Strong interactions result in the increase of strength, the decrease of deformability, shift in the transition temperature of the matrix polymer and the decrease of the melting temperature as well as the heat of fusion of the latter. The simultaneous action of hydrogen bonds of partially neutralized methacrylic acid moieties and ionic bonds results in the formation of small, dispersed lignin particles of the size of several tenth of a micron; however, complete miscibility cannot be achieved. Also, unambiguous correlations could not be established among the chemical composition of the ionomers, the ions used for their neutralization, the counter

ion of the lignin and structure, as well as properties. Hydrogen bridges apparently improve interactions and compatibility somewhat more than ionic bonds. The properties of the blends cover a wide range and materials with a reasonable combination of properties can be produced at moderate lignin contents especially if we compare them to blends prepared from other thermoplastic polymers.

4.5. Miscibility-structure-property correlations in polymer/lignin blends

The final goal was to draw general conclusions about the role of interactions in polymer/lignin blends. For this purpose, we used data from our previous projects and prepared additional thermoplastic/lignin blends. Lignin contains various types and number of functional groups which can enter into different interactions with other polymers. Only weak dispersion forces develop in polypropylene, so the properties of these blends are poor. Aromatic, π electron interactions are stronger and combining them with hydrogen bonds results in reasonable compatibility and mechanical properties. The best properties were achieved with the ionomer as matrix in which the combination of hydrogen bridges and ionic bonds result in good compatibility and properties. Good correlations were found among miscibility, structure and properties, which could be described by using simple theories (**Fig. 4**). Although blends with acceptable properties could be prepared from the ionomer and lignin, for most blends a severe limiting factor of application is their poor deformability. The plasticization or chemical modification of lignin may lead to materials which can be used in industrial practice.

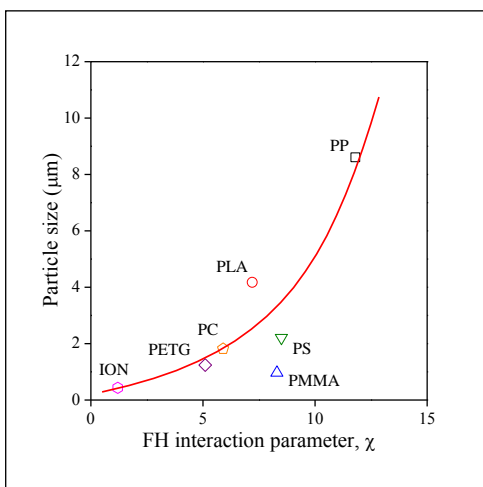


Figure 4. Correlation between the average size of dispersed lignin particles and the strength of interaction (Flory-Huggins interaction parameter). Lignin content: 30 vol%.

5. New scientific results

1. We proved with several approaches that only weak van der Waals interactions can develop at most at the interface between the components of polypropylene/lignosulfonate blends. The energy of these interactions is far lower than that of the self-interactions of lignosulfonates. The application of maleic anhydride grafted polypropylene can increase interfacial adhesion by approximately one order of magnitude, thus the compatibility of the components can be improved as well [2].
2. Based on the study of structure and properties, we showed that compatibility is improved significantly by π electron interactions in the blends of lignosulfonate and thermoplastic polymers containing aromatic rings, compared to polypropylene/lignosulfonate blends. If the thermoplastic polymer contains also polar functional groups such as ether and ester groups, hydrogen bonds may be formed, which enhances further the compatibility [3].
3. The investigations on poly(ethylene-co-vinyl alcohol)/lignosulfonate blends revealed that the competition of van der Waals forces and hydrogen bonding determines their structure and properties. The increasing vinyl alcohol content of the copolymer increases the amount of functional groups capable of forming hydrogen bonding, thus the miscibility of the components is improved. However, complete miscibility cannot be achieved since the energy of the interactions forming at the interface is lower than that of the self-interactions of lignosulfonate [4].
4. We showed for the first time that hydrogen and ionic bonds forming at the interface of ionomer/lignosulfonate blends increase considerably the compatibility, compared to low density polyethylene/lignosulfonate blends in which weak van der Waals forces may develop at most. Miscibility and compatibility is determined mostly by the acid content of the ionomer, which proves that hydrogen bonds determine the properties of the blends studied in the first place, and ionic bonds only in the second place [5].
5. The detailed analysis of thermoplastic/lignosulfonate blends revealed that close correlations exist among the interactions forming between the components, the structure of the blends, and their mechanical properties, which can be explained by simple models. The integration of these models shows that, among the polymers studied, polypropylene forms the weakest (van

der Waals forces), while the ionomer the strongest interactions (hydrogen bridges and ionic bonds) with lignosulfonate. As a consequence, the smallest extent of reinforcement can be achieved in polypropylene while the largest one in the ionomer [6].

6. Possible applications

A German compounding company, TECNARO has already utilized lignin in thermoplastics that can be processed by extrusion, injection molding, thermoforming, etc. Their trade mark, ARBOFORM® includes grades in which lignin is combined with natural fibers, natural resins and waxes. ARBOFORM® is also referred to as 'Liquid Wood' due to its properties similar to those of wood and the fact that it can be melted. These grades have been applied in the construction industry, electronics, jewelry, furniture, and musical instruments.

Our comprehensive study has provided many valuable results regarding component interactions and miscibility-structure-property relationships in polymer/lignin blends. We believe that these results may ease the development of products similar to 'Liquid Wood' in the future.

7. Publications

7.1. Papers used for the preparation of the Thesis

(IF: impact factor, IC: independent citation)

1. Kun, D.; Pukánszky, B. Polymer/lignin blends: Interactions, properties, application. *Eur. Polym. J.* **2017**, *93*, 618-641. (IF: 3.741, IC: 25)
2. Bozsódi, B.; Romhányi, V.; Pataki, P.; Kun, D.; Renner, K.; Pukánszky, B. Modification of interactions in polypropylene/lignosulfonate blends. *Mater. Des.* **2016**, *103*, 32-39. (IF₂₀₁₆: 4.364, IC: 21)
3. Szabó, G.; Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. Competitive Interactions in Aromatic Polymer/Lignosulfonate Blends. *ACS Sustain. Chem. Eng.* **2017**, *5*, 410-419. (IF: 6.140, IC: 6)
4. Podolyák, B.; Kun, D.; Renner, K.; Pukánszky, B. Hydrogen bonding interactions in poly(ethylene-co-vinyl alcohol)/lignin blends. *Int. J. Biol. Macromol.* **2018**, *107A*, 1203-1211. (IF: 3.909, IC: 3)

5. Szabó, G.; Kun, D.; Renner, K.; Pukánszky, B. Structure, properties and interactions in ionomer/lignin blends. *Mater. Des.* **2018**, *152*, 129-139. (IF: 4.525, IC: 1)
6. Romhányi, V.; Kun, D.; Pukánszky, B. Correlations among Miscibility, Structure and Properties in Thermoplastic Polymer/Lignin Blends. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14323-14331. (IF: 6.140, IC: 0)

7.2. Other publications

1. Szabó, G.; Romhányi, V. Pataki, P.; Horváth, Zs.; Kun, D.; Pukánszky, B. A szerkezet és a kölcsönhatások szerepe lignoszulfonáttal társított polipropilénben. *Műanyag és Gumi* **2013**, *50*, 443-448.
2. Szabó, G.; Kun, D.; Pukánszky, B. Ionomer/lignoszulfonát keverékek: tulajdonságok, szerkezet, kölcsönhatás. *Műanyag- és Gumiipari Évkönyv* **2015**, *13*, 42-48.
3. Bozsódi, B.; Szabó, G.; Romhányi, V.; Pataki, P.; Kun, D.; Pukánszky, B. Határfelületi kölcsönhatások jellemzése polimer/lignin keverékekben. *Polymer* **2016**, *2*, 64-68.
4. Fekete, E.; Kun, D.; Móczó, J. Thermoplastic starch/wood composites: Effect of processing technology, interfacial interactions and particle characteristics. *Period. Polytech. Chem. Eng.* **2018**, *62*, 129-136. (IF: 0.877, IC: 1)
5. Nagy, S.; Csiszár, E.; Kun, D.; Koczka, B. Cellulose nanocrystal/amino-aldehyde biocomposite films. *Carbohydr. Polym.* **2018**, *194*, 51-60. (IF: 5.158, IC: 1)
6. Móczó, J.; Kun, D.; Fekete, E. Desiccant effect of starch in polylactic acid composites. *Express Polym. Lett.* **2018**, *12*, 1014-1024. (IF: 3.064, IC: 0)

7.3. Conference oral presentations

1. Kun, D.; Pukánszky, B. Lignin felhasználása társított polimer rendszerekben. *AKI szeminárium*, **11 June 2013**, Budapest, Hungary
2. Renner, K.; Imre, B.; Kun, D.; Pukánszky, B. Improving the property profile of poly(lactic acid) by modification with biofillers and elastomers. *Eurofillers 2013*, **25-29 August 2013**, Bratislava, Slovakia
3. Romhányi, V.; Kun, D.; Pukánszky, B. Physicochemical Characterization of Lignin/polymer Blends. *YoungChem2013 International Congress of Young Chemists*, **9-13 October 2013**, Poznan, Poland
4. Romhányi, V.; Pataki, P.; Kun, D. Pukánszky, B. A kölcsönhatások szerepe termoplasztikus polimer/lignin keverékek tulajdonságainak meghatározásában. *XXXVI. Kémiai Előadói Napok*, **28-30 October 2013**, Szeged, Hungary
5. Dénes, P.; Kun, D.; Horváth, Zs.; Pukánszky, B. Lignoszulfonátok felhasználása polimer keverékekben. *Fiatal Diplomások Fóruma*, **20 November 2013**, Budapest, Hungary
6. Bozsódi, B.; Dénes, P.; Kun, D.; Pukánszky, B. Polypropylene/lignin blends: Comparison of reactive and physical processing. *SMLKI X Meeting of Young Chemical Engineers*, **20-21 February 2014**, Zagreb, Croatia
7. Szabó, G.; Kun, D.; Pukánszky, B. Lignin filled polymers: Composites or blends? *X International Conference 'Students for Students'*, **9-13 April 2014**, Cluj Napoca, Romania
8. Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. Thermoplastics/lignin blends: interactions, structure, properties. *BPPA14*, **19-21 May 2014**, Budapest, Hungary
9. Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. Thermoplastics/lignin blends: interactions, structure, properties. *BiPoCo 2014*, **24-28 August 2014**, Visegrád, Hungary
10. Szabó, G.; Kun, D.; Horváth, Zs.; Pukánszky, B. Interactions, structure and properties in ionomer/lignoszulfonate blends. *MoDeSt 2014*, **31 August - 4 September 2014**, Portorož, Slovenia

11. Kárpáti Z.; Kun, D.; Faludi, G.; Móczó, J. Természetes töltőanyagok határfelületi kölcsönhatásainak vizsgálata politejsav alapú polimer kompozitokban. *XXXVII. Kémiai Előadói Napok*, **3-5 November 2014**, Szeged, Hungary
12. Szabó, G.; Kun, D.; Horváth, Zs.; Pukánszky, B. Mikromechanikai deformációs folyamatok ionomer/lignin keverékekben. *Fiatal Diplomások Fóruma*, **25 November 2014**, Budapest, Hungary
13. Szabó, G.; Kun, D.; Horváth Zs.; Pukánszky, B. Ionomer/lignoszulfonát keverékek: kölcsönhatás, szerkezet, tulajdonságok. *Kálmán Erika Doktori Konferencia*, **10-12 December 2014**, Budapest, Hungary
14. Szabó, G.; Bozsódi, B.; Podolyák, B.; Kun, D.; Pukánszky, B. Ionomer/lignoszulfonát keverékek: tulajdonságok, szerkezet, kölcsönhatás. *Oláh György Doktoráns Konferencia*, **5 February 2015**, Budapest, Hungary
15. Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. Competitive interactions in polymer/lignin blends. *Eurofillers and Polymer Blends 2015*, **26-30 April 2015**, Montpellier, France
16. Józó, M.; Bozsódi, B.; Kun, D.; Pukánszky, B. Ethylene glycol-lignin block copolymers: preparation and characterization. *BiPoCo 2016*, **28 August - 1 September 2016**, Szeged, Hungary
17. Szabó, G.; Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. The role of π electron interactions in polymer/lignin blends. *MoDeSt 2016*, **4-8 September 2016**, Krakow, Poland

7.4. Conference poster presentations

1. Szabó, G.; Kun, D.; Pukánszky, B. Lignin/polymer Blends: Interactions and Mechanical Properties. *15. Österreichische Chemietage 2013 - Joint Meeting of the Hungarian and Austrian Chemical Societies*, **23-26 September 2013**, Graz, Austria
2. Szabó, G.; Podolyák, B.; Kun, D.; Pukánszky, B. Lignin/ionomer Blends: Preparation and Characterization. *YoungChem2013 International Congress of Young Chemists*, **9-13 October 2013**, Poznan, Poland

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3. Romhányi, V.; Kun, D.; Pukánszky, B. Lignoszulfonát szerkezetének szerepe polimer keverékekben. *Oláh György Doktoráns Konferencia*, **6 February 2014**, Budapest, Hungary
 4. Romhányi, V.; Kun, D.; Pukánszky, B. Lignosulfonate/polymer blends: experimental design and optimization of processing, *SMLKI X Meeting of Young Chemical Engineers*, **20-21 February 2014**, Zagreb, Croatia
 5. Szabó, G.; Kun, D.; Pukánszky, B. Utilization of lignin in polymer blends, *SMLKI X Meeting of Young Chemical Engineers*, **20-21 February 2014**, Zagreb, Croatia
 6. Bozsódi, B.; Dénes, P.; Kun, D.; Pukánszky, B. The effect of reactive coupling on the mechanical properties of polypropylene/lignin blends, *ChemCYS 2014 Chemistry Conference for Young Scientists*, **27-28 February 2014**, Blankenberge, Belgium
 7. Szabó, G.; Romhányi, V.; Podolyák, B.; Kun, D.; Pukánszky, B. The role of structure and interfacial adhesion in lignosulfonate filled polymers, *ChemCYS 2014 Chemistry Conference for Young Scientists*, **27-28 February 2014**, Blankenberge, Belgium
 8. Szabó, G.; Romhányi, V.; Kun, D.; Pukánszky, B. Correlation between the micromechanical deformation processes and tensile properties of polymer/lignin blends, *ChemCYS 2014 Chemistry Conference for Young Scientists*, **27-28 February 2014**, Blankenberge, Belgium
 9. Bozsódi, B.; Kun, D.; Pukánszky, B. The effect of methylene diphenyl diisocyanate on the properties of poly(ethylene terephthalate)/lignin blends. *XI International Conference 'Students for Students'*, **9-13 April 2014**, Cluj Napoca, Romania
 10. Parázsó, J.; Józó, M.; Kun, D.; Pukánszky, B. Rheological characterization of polymer/lignin melts. *XI International Conference 'Students for Students'*, **9-13 April 2014**, Cluj Napoca, Romania
 11. Romhányi, V.; Kun, D.; Pukánszky, B. Structure and interactions in polymer/lignin blends. *XI International Conference 'Students for Students'*, **9-13 April 2014**, Cluj Napoca, Romania

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12. Podolyák, B.; Szabó, G.; Kun, D.; Pukánszky, B. Characterization of structure and interfacial adhesion in ionomer/lignin blends. *XI International Conference 'Students for Students'*, **9-13 April 2014**, Cluj Napoca, Romania
 13. Romhányi, V.; Kun, D.; Faludi, G.; Renner, K.; Pukánszky, B. Interfacial interactions in lignin and wood flour filled polylactic acid. *BPPA14*, **19-21 May 2014**, Budapest, Hungary
 14. Bozsódi, B.; Dénes, P.; Kun, D.; Pukánszky, B. The effect of coupling on the structure, interfacial interactions and mechanical properties of polypropylene/lignin blends. *BiPoCo 2014*, **24-28 August 2014**, Visegrád, Hungary
 15. Szabó, G.; Podolyák, B.; Kun, D.; Pukánszky, B. Ionomer/lignosulfonate blends: interaction and mechanical properties, *BiPoCo 2014*, **24-28 August 2014**, Visegrád, Hungary
 16. Romhányi, V.; Kun, D.; Pukánszky, B. Polymer/lignin blends: structure, interaction, properties, *BiPoCo 2014*, **24-28 August 2014**, Visegrád, Hungary
 17. Romhányi, V.; Kun, D.; Renner, K.; Pukánszky, B. Micromechanical deformation processes in polymer/lignosulfonate blends – effect of interfacial adhesion, *BiPoCo 2014*, **24-28 August 2014**, Visegrád, Hungary
 18. Bozsódi, B.; Dénes, P.; Kun, D.; Pukánszky, B.: The effect of coupling on the structure, interfacial interactions and mechanical properties of polypropylene/lignin blends. *Bimate Conference*, **15-17 April 2015**, Slovenj Gradec, Slovenia
 19. Kárpáti, Z.; Kun, D.; Faludi, G.; Móczó, J.; Pukánszky, B.: Interfacial interactions in poly(lactic acid)/lignocellulosic composites. *Bimate Conference*, **15-17 April 2015**, Slovenj Gradec, Slovenia
 20. Szabó, G.; Bozsódi, B.; Romhányi, V.; Kun, D.; Pukánszky, B.: Polymer/lignin blends: structure, interaction, properties. *Bimate Conference*, **15-17 April 2015**, Slovenj Gradec, Slovenia
 21. Szabó, G.; Bozsódi, B.; Podolyák, B.; Kun, D.; Pukánszky, B.: Ionomer/lignosulfonate blends: interaction, structure, properties. *Bimate Conference*, **15-17 April 2015**, Slovenj Gradec, Slovenia

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22. Podolyák, B.; Kun, D.; Pukánszky, B. The role of hydrogen bonding in polymer/lignin blends. *BiPoCo 2016*, **28 August - 1 September 2016**, Szeged, Hungary
 23. Szabó, G.; Kun, D.; Renner, K.; Pukánszky, B. The effect of moisture content on the structure and properties of polypropylene/lignosulfonate blends. *BiPoCo 2016*, **28 August - 1 September 2016**, Szeged, Hungary
 24. Józó, M.; Bozsódi, B.; Kun, D.; Pukánszky, B. Ethylene glycol-lignin block copolymers: preparation and characterization. *BiPoCo 2016*, **28 August - 1 September 2016**, Szeged, Hungary
 25. Podolyák, B.; Kun, D.; Pukánszky, B. Poly(vinyl alcohol-co-ethylene)/lignin blends: interaction, structure, properties. *MoDeSt 2016*, **4-8 September 2016**, Krakow, Poland

