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POLYMER/LIGNIN BLENDS: INTERACTIONS, PROPERTIES, APPLICATIONS

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ABSTRACT

Lignin is a cheap material available in large quantities, thus the interest in its valorization is increasing both in industry and academia. A possible approach towards value added applications is using it as a component in plastics. However, blending lignin with polymers is not straightforward because of the polarity of lignin molecules resulting in strong self-interactions. The structure and properties of lignin depend on the extraction technology used for its production. The structure of lignin is complex and its characterization difficult. Lignin has been added to various polymers in the last few decades and the resulting material was sometimes called blend, while in other cases composite. Based on arguments we show that lignin forms blends, and these are classified and discussed according to the interactions developing in them, since competitive interactions determine the structure and properties of the blends. Usually even strong interactions are not sufficient to result in complete miscibility. As a consequence lignin is often modified chemically or by plasticization to improve its dispersion in plastics, or a compatibilizer is added to increase interfacial adhesion. Lignin can be used also as a reactive component in various resins and polymers.

KEYWORDS

lignin, extraction technology, blend, miscibility, structure, modification, application

1. Introduction

Lignin is a major component of all plants. Grass contains it in 17-24 wt%, softwood in 18-25 wt% and hardwood in 27-33 wt% [1], thus it represents an enormous renewable raw material source. 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. The isolated and commercially available amount of lignin was only 1.1 million tons in 2014 [2]. Global lignin market was valued at approximately 775 million US$ in 2014 and is expected to reach around 900 million US$ in 2020 corresponding to an average annual growth of 2.5 % between 2015 and 2020 [2].

Although the indicated growth rate is not exceptional, the valorization of lignin may increase it considerably. The relatively slow growth rate stems from the established extraction processes, in which lignin is used as fuel, and from the difficulties of handling lignin as discussed also in this article. However, the potentials of lignin are also shown by the continuously increasing number of papers published on the characterization, modification and possible application of lignin (**Fig. 1**). The interest in other biopolymers like cellulose, starch and poly(lactic acid) (PLA) also grows and in the case of starch and cellulose 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 areas in which lignin could be used as an additive or raw material for the production of new plastics. This, however, requires a deeper knowledge of lignin, which may help overcome its drawbacks and exploit its advantages. In this feature article, we attempt to summarize recent trends and achievements in the use of lignin in plastics, with a particular focus on polymer/lignin blends. Because of their importance, we discuss other topics as well, like the effect of extraction technology on the structure of lignin, its chemical modification, and the use of lignin as a reactive component in plastics. Several review papers were published on lignin blends in the last three decades [3-9] listing numerous combinations of lignin with polymers. As a consequence, we do not follow this approach, but pay more attention to interactions because of their importance in the determination of the structure and properties of such blends. According to our knowledge, such an approach has not been followed yet. The possible applications of lignin blends are also discussed briefly at the end of the paper.

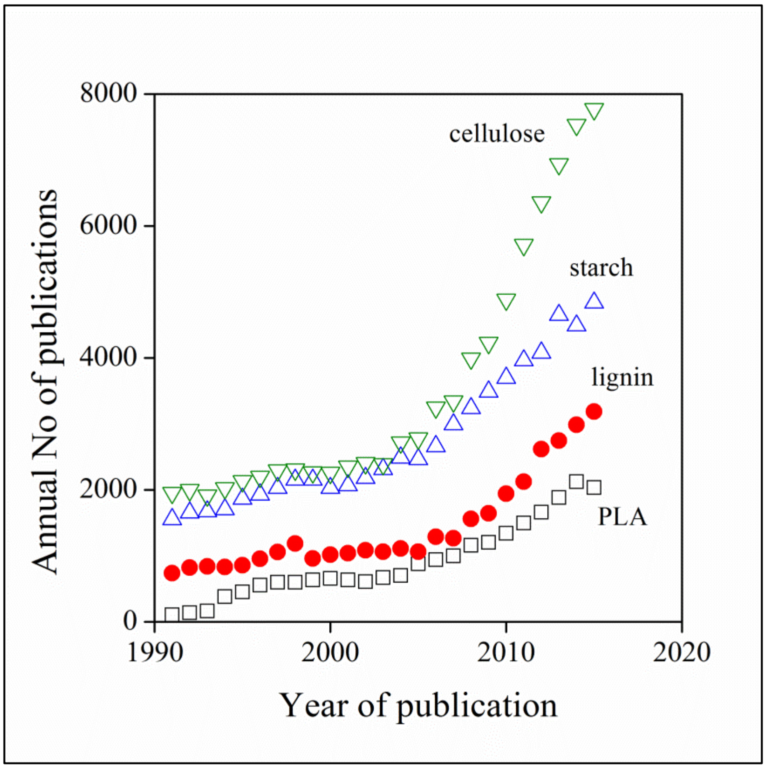


Fig. 1. Annual number of publications on (☐) PLA, (●) lignin, (△) starch and (▽) cellulose.

2. Extraction and characterization of lignin

Lignin is extracted from lignocellulosic substances. The technology of extraction determines the structure of the product, thus its discussion is essential when lignin is used as a component of polymer blends.

2.1. Lignin structure

Lignin is a natural polyphenol which is formed from monolignols through enzymatic dehydrogenative polymerization in plants [10]. The monolignols forming the repeat units of lignin are *para*-coumaryl alcohol (H-type), coniferyl alcohol (G-type) and sinapyl alcohol (S-type) which may be connected with each other through various covalent bonds. The H/G/S ratio is 0-5/95-100/0 in softwood, 0-8/25-50/46-75 in hardwood and 5-33/33-80/20-54 in grasses [11]. Lignin possesses a very complex chemical structure that can only be described by average empirical formulae or model structures. The C_9 formula is the most frequently applied average empirical formula which shows the molar ratio of 9 carbon atoms to the other elements or functional groups of lignin; the formula represents an average repeat unit formed by the constituting monolignols. The C_9 formula of spruce (softwood) lignin is $C_9H_{7.92}O_{2.40}(OCH_3)_{0.92}$, while that of beech (hardwood) lignin is $C_9H_{7.49}O_{2.53}(OCH_3)_{1.39}$ [12]. The differences are caused mostly by the dissimilar ratio of monolignols forming softwood and hardwood.

Model structures were created for spruce lignin by Freudenberg [10], Adler [13], Brunow [14], and Gellerstedt [15], respectively, and for beech lignin by Nimz [16]. We present the structural models based on the results of Adler [13] and Gellerstedt [15] **in Fig. 2**. Gellerstedt el al. [15,17] revealed that two main types of lignin called type 1 (Fig. 2a) and 2 (Fig. 2b) form in plants. 48 w/w% of softwood lignin is type 1, while 40 w/w% type 2 [15,17]. Type 1 lignin is located in a glucomannan-lignin-xylan (w/w=9:9:1) complex which is directly bonded to the cellulose fibrils through hydrogen bridges. The different linkages connecting the repeat units of type 1 are indicated in the figure. Type 2 lignin is present in a xylan-lignin-glucomannan (w/w=2:3:1) complex which is located around the cellulose fibrils embedded in type 1 lignin. In type 2 lignin mostly β-O-4’ ether bonds form between the repeat units, which makes β-O-4’ ether bond the most frequent linkage not only in softwood, but also in hardwood lignin representing approximately 50 % and 60 % of the bonds, respectively [18].

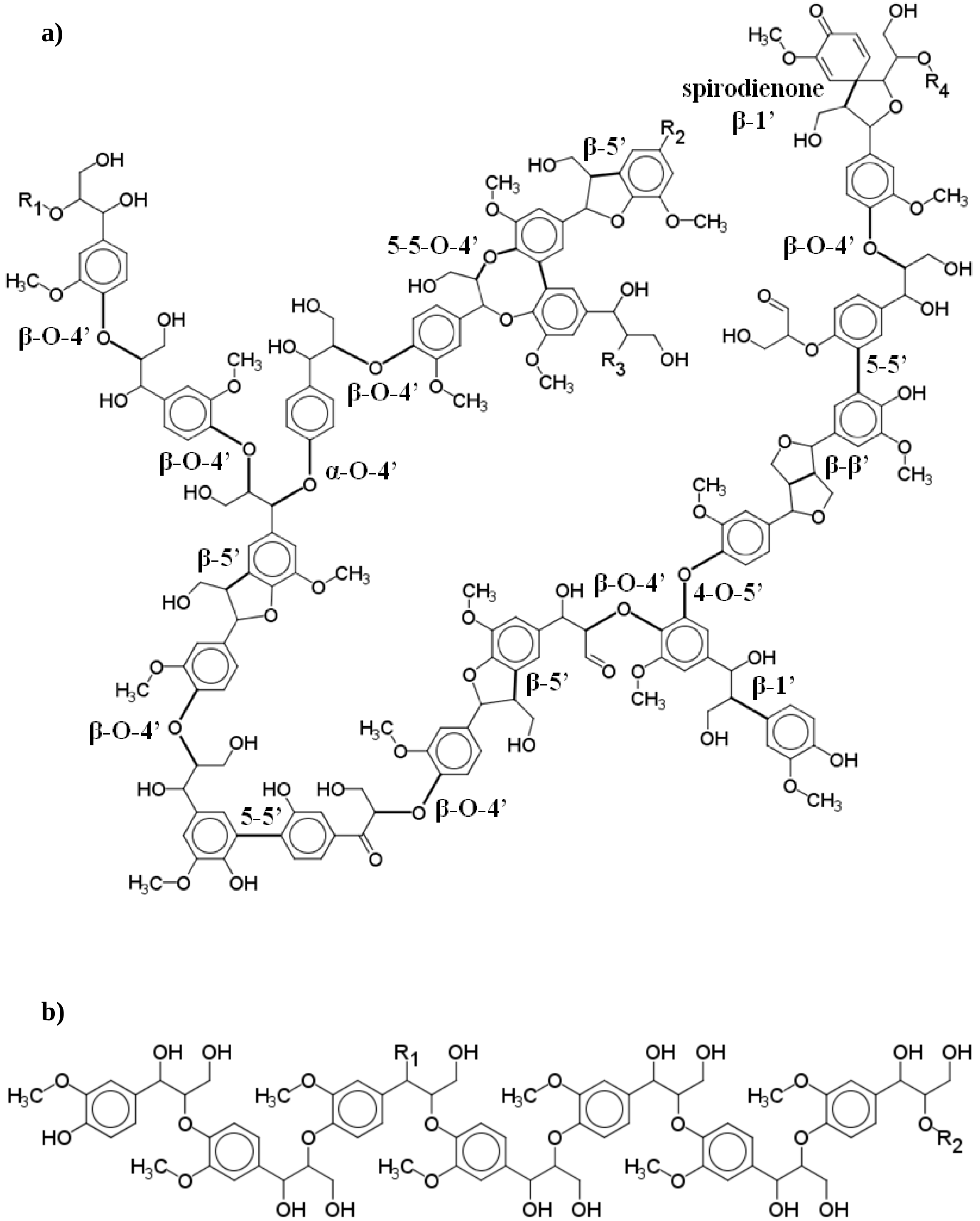


Fig. 2. The model structures of spruce lignin based on [13,15]. a) Type 1 lignin, b) Type 2 lignin.

2.2. Extraction

At the industrial level lignin must be extracted to obtain the cellulose needed for paper or bioethanol production. In the paper industry this step is called pulping, which may include physical and chemical methods. Today mostly chemical processes are applied, thus in most cases chemicals are used to degrade the cross-linked or highly branched structure of lignin, while cellulose remains intact. As a result, lignin usually becomes soluble in the reaction medium, from which cellulose fibers can be easily separated by filtration. Accordingly, the extraction of lignin from plants is impossible without the modification of its chemical structure. In the following sections we present the most important procedures used for the extraction of lignin from lignocellulosic materials.

2.2.1. Soda process

The soda process patented by Watt and Burgess in 1854 [19] was the first chemical pulping method. Today it is applied mostly to produce cellulose from agricultural crops with relatively small lignin content like wheat straw and bagasse. During the soda process wood chips are cooked in alkaline aqueous medium (conditions in **Table 1**) [18]. Sodium hydroxide deprotonates the phenolic hydroxyl groups of lignin in the process, which initiates a consecutive reaction resulting in the cleavage of the most frequent bonds among the repeat units of lignin, the α-O-4-ether and β-O-4-ether links.

2.2.2. Kraft process

At present the Kraft process [20] is the most often used pulping method. The Kraft process can be considered as a development or improvement of the soda process. Besides sodium hydroxide the cooking liquor contains also sodium sulfide which accelerates the degradation of lignin further. In a typical Kraft process wood chips are cooked in alkaline aqueous medium (conditions in **Table 1**) [18]. Similarly to the soda process, most of the α-O-4-ether and β-O-4-ether bonds of lignin are cleaved by the end of the cooking procedure. The weight average molecular weight of softwood (spruce) and hardwood (eucalyptus and mixture of other species) Kraft lignins are 19800 and 3700-3900 g/mol, respectively [21]. Kraft lignins are soluble in alkaline solutions ($pH > 10.5$), dioxane, acetone, dimethylformamide, and 2-methoxyethanol. The structural model of softwood Kraft lignin is presented in **Fig. 3**. Most Kraft lignin is burnt during cellulose production and is not available on the market. The amount of the commercially available Kraft lignin was 100 thousand tons in 2014 [2].

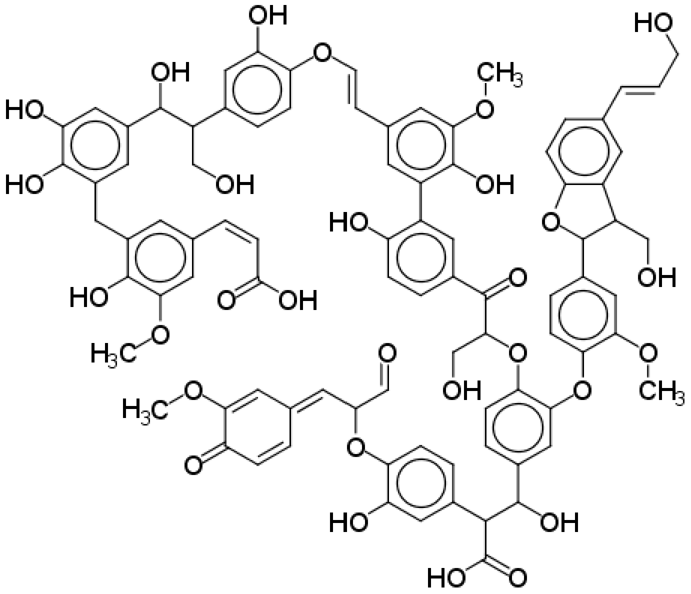


Fig. 3. The model structure of softwood Kraft lignin based on the structural model of Adler [13] and the reactions taking place during pulping [22].

2.2.3. Sulfite process

Today the sulfite process [21] is the main source of commercially available lignin, the amount of which was 1.0 million tons in 2014 [2]. The amount of the sulfite, bisulfite and dissolved sulfur dioxide used depends on the pH of the reaction medium, which determines the mechanism of lignin degradation. Four main variations exist in this technology the acid bisulfite (pH = 1-2), the bisulfite (pH = 3-5), the neutral sulfite (pH = 5-7) and the alkaline sulfite (pH = 9-13) process [18]. In the industry, the sulfite process is carried out mainly under acidic conditions, thus the conditions of acid bisulfate and bisulfate process are given in **Table 1**. In the pH range used, the main reaction is the sulfonation of the α-carbon atoms of lignin, which leads to the cleavage of the α-O-4-ether bonds. As only a minor part of the most frequent β-O-4-ether bonds react in the process, the molecular weight of lignosulfonates is larger than that of the Kraft lignin. The weight average molecular weight of softwood (two species of spruce) and hardwood (two species of eucalyptus) lignins are 36000-61000 g/mol and 5700-12000 g/mol, respectively [24]. Lignosulfonates are soluble in water, ethylene glycol and dimethyl sulfoxide. The structural model of softwood lignosulfonate is presented in **Fig. 4**.

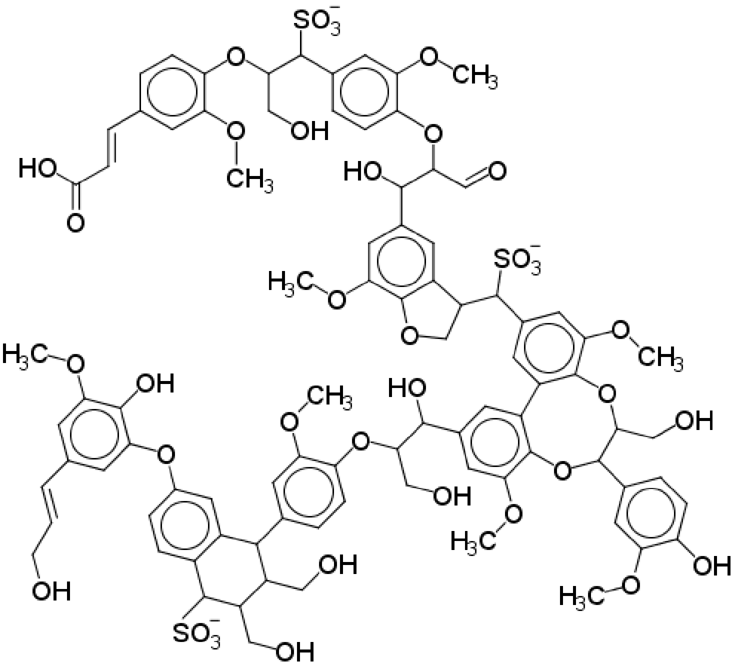


Fig. 4. The model structure of softwood lignosulfonate based on the structural model of Adler [13] and the reactions taking place during pulping [22].

2.2.4. Organosolv process

The organosolv process [25,26] is a widespread technology at the laboratory level, which is based on the extraction of lignin by polar organic solvents like methanol, ethanol, formic acid and acetic acid. As a consequence, the polarity, structure and properties of organosolv lignin depend specifically on the applied solvent. Numerous organosolv processes exist today, however, the Alcell® procedure appears the most often in scientific papers. This method consists of the extraction of lignin with 40-60 wt% aqueous ethanol (conditions in **Table 1**) [27]. The weight average molecular weight of hardwood (mixture of species) organosolv lignin is 4100 g/mol [21]. This lignin is soluble in dilute alkaline solutions and in ethanol-water mixtures [28].

2.2.5. Steam explosion

Steam explosion was first proposed by Mason [29] for the disintegration of wood to produce Masonite board stock. After some modification the technology became a widespread pretreatment method for the production of bioethanol. In such a typical steam explosion procedure biomass is treated with hot steam followed by an explosive decompression step (conditions in **Table 1**) [30]. The sudden pressure release defibrillates the cellulose bundles resulting in cellulose chains easily accessible for cellulase, the enzyme applied to convert cellulose to glucose in aqueous medium. During the enzymatic treatment lignin remains insoluble thus it can be filtrated out from the solution containing the sugar. The weight average molecular weight of softwood (white birch and larch) steam explosion lignin is 1100-2300 g/mol [31].

Table 1
Active agents and conditions of lignin extraction technologies.

Technology	Active agents	Conditions				Reference
		pH	Temp. (°C)	Time (h)	Pressure (MPa)	
Soda	NaOH	13-14	155-175	2-5	VP[a]	18
Kraft	NaOH, Na_2S	13-14	155-175	1-3	VP[a]	18
Sulfite (acid bisulfite)	H^+, HSO_3^-	1-2	125-145	3-7	VP[a]	18
Sulfite (bisulfite)	(H^+), HSO_3^-	3-5	150-170	1-3	VP[a]	18
Organosolv (Alcell®)	40-60 wt% aqueous ethanol	-	180-210	n.d.	2-3.5	27
Steam explosion	water	7	180-240	0.02-0.30	1-3.5[b]	30

a) vapor pressure

b) then explosive decompression

2.3. Characterization

The chemical structure of lignin, including the number and type of functional groups, determines its reactivity and also its compatibility with polymers. Accordingly, the quantitative determination of functional groups is essential to find possibilities for the modification and utilization of lignin. Numerous analytical methods have been applied successfully for the characterization of lignin and for the quantitative determination of its functional groups. Some of these methods are listed in **Table 2** together with the relevant functional groups and related references. Most of the techniques listed are relatively simple, easily available and routinely used including sample preparation, measurement, and evaluation of the results. However, because of the complex structure of lignin and its dependence on the source as well as on the extraction technology, these methods alone are usually not sufficient for the complete characterization of the chemical structure of lignin. Accordingly, further analytical methods must be also applied, when the goal is the generation of model structures.

Table 2
Methods for the quantitative determination of the functional groups of lignin.

Functional group	References for the various methods						
	Titrimetry	GC	^{1}H NMR	^{13}C NMR	^{31}P NMR	UV-VIS	TG-MS
Aromatic hydroxyl	32-34	35-38	39-43	44-46	45,47,48	49-53	54,55
Total hydroxyl	56,57	37,42,58	39-43	44-46	45,47,48		54,55
Methoxyl	59,60	61,62		63,64			54,55
Carboxyl	33,64	65			47,48		
Carbonyl	34,67-69		70			71,72	
Sulfonate	33,73,74						

El Mansouri and Salvadó [75,76], for example, determined the chemical structure and composition of five different technical lignin samples. They carried out elemental analysis first to define the molar ratio of carbon, hydrogen, oxygen, nitrogen and sulfur.

They created the basic C_9 formula for the softwood Kraft lignin and lignosulfonate samples studied, which could be further extended by the quantitative determination of methoxyl [62], phenolic hydroxyl [52], total hydroxyl [38,43,44], carbonyl [72], carboxyl [33] and sulfonate groups [33]. Although the authors [76] claim that the expanded formulae contain all the necessary information about the structure of their technical lignins, these do not give the molecular weight of the samples, or the ratio of the different repeat units (H/G/S).

Molecular weight distribution can be determined by gel permeation chromatography (GPC) [75,77-79]. One of the key issues of the technique is reliable calibration. Since monodisperse lignin standards are not available, Glasser et al. [21] used commercially available monodisperse polystyrene (PS) standards for calibration. The approach is justified by the fact that the stiffness of PS chains is similar to that of lignin. El Mansouri and Salvadó [75] determined the molecular weight of their softwood Kraft lignin sample using the method proposed by Glasser et al. [21]. The number average molecular weight was found to be 545.2 g/mol thus an average molecule of this lignin contains 3.093 repeat units.

The relative amount of the H/G/S units can be obtained by the cleavage of the lignin backbone and the analysis of the fragments obtained. Faix et al. [80,81], for example, used pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) to determine the repeat units of lignin. They pyrolyzed several types of lignin, separated the degraded products by GC and detected the fragments by MS. However, degradative methods coupled with chromatography supply mostly qualitative information, since the degradation of lignin is very complex and a number of side reactions occur. Non-degradative techniques like two-dimensional (2D) NMR are more accurate and Sette et al. [82] could determine quantitatively the number of β-O-4’, β-5’, β-1’, β-β’, 5-5’-0-4’ linkages both in native and technical lignins by ^{13}C, ^{1}H-correlated NMR. However, the determination of certain linkages requires high resolution and thus can be tedious, time-consuming and expensive; 2D NMR should be combined with the degradative methods mentioned above to obtain a comprehensive picture of covalent linkages in lignin. Only the thorough characterization of the actual lignin sample and the creation of a model structure can lead to the successful modification and application of lignin as an additive or a constituent of polymer blends.

3. Thermoplastic/lignin blends

Lignin is added to a number of polymers, but even the definition of the resulting material is unclear; some term it as blend, some others as composite, thus we first have to clarify definitions and then discuss the various classes of materials prepared. Interactions play a crucial role in the determination of blend properties, thus they will be discussed in detail in this section, while methods used for their modification will be presented subsequently.

3.1. Blend or composite?

There is a considerable confusion in the literature about the definition of polymer/lignin combinations, thus the question must be discussed in some extent. 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. Weak interaction results in a thin interphase and a heterogeneous blend with large dispersed particles, while strong interactions lead to a homogeneous blend with no observable particles [83-85]. Accordingly, interactions determine the mutual solubility of the phases and the strength of interfacial adhesion in heterogeneous blends.

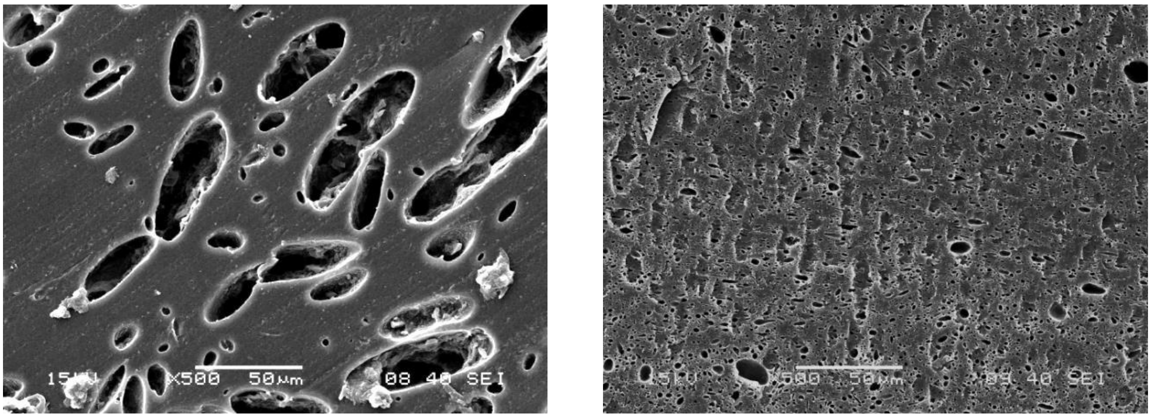
In composites a polymer with mobile chains adsorbs on the solid, well-defined surface of a filler. Usually mineral fillers or fibers are dispersed in composites as the second component, but polymers, like lignin could also act as a filler. Cross-linked polymers do not melt, retain their size and possess the necessary well-defined surface, but the powder of a glassy polymer homogenized below its 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 components [86]. Accordingly the term "filler" should not be used for blends, while the term "miscibility" is not relevant in the case of composites.

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 polymer with high molecular weight, thus the extraction of lignin is usually impossible without the cleavage of bonds. Most commercially available lignins are produced by vigorous pulping and their molecular weight 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 thermoplastics as demonstrated by the data listed in **Table 3**. Accordingly, the homogenization of lignin with thermoplastics results in a blend. This statement is further supported by the scanning electron micrographs (SEM) recorded on polymer/lignosulfonate blends (**Fig. 5**). Lignosulfonate was dispersed in low density polyethylene (LDPE) and poly(ethylene-co-vinyl alcohol) (EVOH), respectively, and then the lignosulfonate was dissolved with water from the cut surfaces of the blends. The average particle size of the lignosulfonate particles is much larger in LDPE (**Fig. 5a**) than in EVOH (**Fig. 5b**) indicating the strong effect of interactions. Accordingly these combination of materials can be clearly considered as blends indeed. The statement is further corroborated by the fact that the original particle size of lignin was around 80 μm which broke up to smaller particles of around 30 μm in LDPE and 1 μm in EVOH during homogenization.

Table 3
Glass transition temperatures of different lignins determined by differential scanning calorimetry.

Type of lignin	Glass transition temperature (°C)	Reference

Softwood Kraft lignin	162	87
	141	88
	153	89
Hardwood Kraft lignin	108	90
Kraft lignin	165	91
Alcell® (organosolv) lignin	97	88
Hardwood organosolv lignin	95	92
Rice straw soda lignin	155	91
Wheat straw soda lignin	150	88
Softwood sodium-lignosulfonate	138	88
Hardwood sodium-lignosulfonate	127	88



a) b)

Fig. 5. Heterogeneous structure of polymer/lignosulfonate blends. Lignosulfonate content: 30 vol%. a) LDPE; b) EVOH, vinyl alcohol content: 68 mol%.

3.2. Blends

Lignin has been added to a wide variety of polymers from natural to synthetic materials. Several review papers [3-9] give account of these blends listing the polymer or group of polymers according to their chemical structure and describe the most important findings of the selected papers. In their excellent paper Doherty et al. [7], for example, present a long list of polymers including proteins, starch and other biopolymers, polyolefins, vinyl polymers, polyesters, etc. Since these reports are available for the reader, we refrain from giving a similar account of the published papers, but discuss matrix polymers mainly according to their polarity and the interactions that they can develop with lignin instead. The self-interactions among lignin molecules are very strong because of the large number of polar functional groups in the molecule, thus 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, which definitely needs clarification.

3.2.1. Poliolefins

Polyethylene (PE), polypropylene (PP) and their copolymers are usually quite apolar. They can enter only into weak dispersion interactions with other polymers due to the lack of any functional groups in the molecules. Considering the strong polarity and functionality of lignin, one would expect complete immiscibility with polyolefins, but some literature references claim otherwise. Since the phenolic OH groups of lignin are able to scavenge free radicals, considerable number of attempts are made to use it as a stabilizer and protect the matrix polymer against oxidation. Most of these attempts were successful and proved the antioxidant effect of lignin. Pucciariello et al. [93] showed that steam-explosion lignin protects LDPE, HDPE and linear low density polyethylene against UV radiation, while Levon et al. [94] found that the thermal oxidative stability of PE improves considerably when it is blended with lignosulfonate. Most other studies [95-100] indicated almost invariably that lignin stabilizes polyolefins, unfortunately less attention was paid to the effect of lignin type on stabilization efficiency and to the comparison to existing stabilizer systems. Although phenolic hydroxyl groups scavenge radicals and improve stability indeed, because of their relatively small molar number, less efficiency is expected from them than from traditional, small molecular weight stabilizers.

Another important issue in stabilization is the homogeneity of polymer/lignin blends.

When lignin is added in small amounts for stabilization, the quality of dispersion is not always easy to determine. Good dispersion and compatibility was claimed in several cases [97,101], which is difficult to understand in view of the considerable differences in the chemical structure of the two types of polymers. Homogenization and compatibility are even more important when a larger amount of lignin is added to the polymer to modify mechanical properties. A wide variety of effects were observed on different properties as a result of blending with lignin. Modulus usually increases, because of the stiffness of lignin molecules [101-106], but strength and deformability often decreases [101-107]. The conclusions drawn from these results about compatibility are also quite diverse. As mentioned above, Kosikova et al. [97] found good compatibility between organosolv and prehydrolysis lignin and PP, while Jeong et al. [101] claimed outright complete miscibility with several polymers including LDPE and PP. Unfortunately these claims are rarely supported by real experimental evidence and reflect mainly the hopes and belief of the authors. 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.

3.2.2. Polymers with aromatic rings

Polyolefins can enter only into weak dispersion interactions with lignin, thus immiscibility and poor properties are expected in their blends. On the other hand, plastics 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. Numerous papers have been published on such blends and the controversy characterizing the study of polyolefin/lignin blends can be observed also for aromatic polymers. The drawing of generally valid conclusions is practically impossible and evaluation is complicated by the differences in the polymers, lignin samples and modifications used in these experiments.

The simplest polymer containing aromatic rings is PS. It 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. [108] found indeed that all mechanical properties including modulus, strength and elongation deteriorated upon the addition of lignin. The authors explained the poor properties and rough fracture surface of the blends by poor wetting and interaction between the lignin particles and PS. The properties of PS/lignin blends prepared by Pucciariello et al. [93] were also quite poor, which was explained by the authors with the poor compatibility of the components. On the other hand, based on changes in the T_g of PS, Lispergauer et al. [109] assumed some degree of miscibility between lignin and PS, although they modified lignin with maleic anhydride, which might have improved interactions. Pouteau et al. [110] 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. The exceptional behavior and especially the reaction are difficult to understand and accept without further proof.

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. [111], for example, observed the good dispersion of lignin in poly(ethylene terephthalate) (PET), while Kadla and Kubo [90] found the two components immiscible and explained immiscibility with the lack of hydrogen bonding compared to poly(ethylene oxide) (PEO). Jeong et al. [101], on the other hand, found PET and lignin completely miscible. Their results were based on the evaluation of mechanical properties including tensile strength shown in **Fig. 6**. However, some doubts might arise about their conclusion, since they found all four polymers studied miscible with their Kraft lignin including LDPE, PP and PS. Miscibility was claimed also for a number of other polymers containing aromatic rings, like poly(4-vinyl pyridine) [112,113] and polyaniline [114], but most of the polymers including PET form not only π electron interactions, but also H-bonds with lignin.

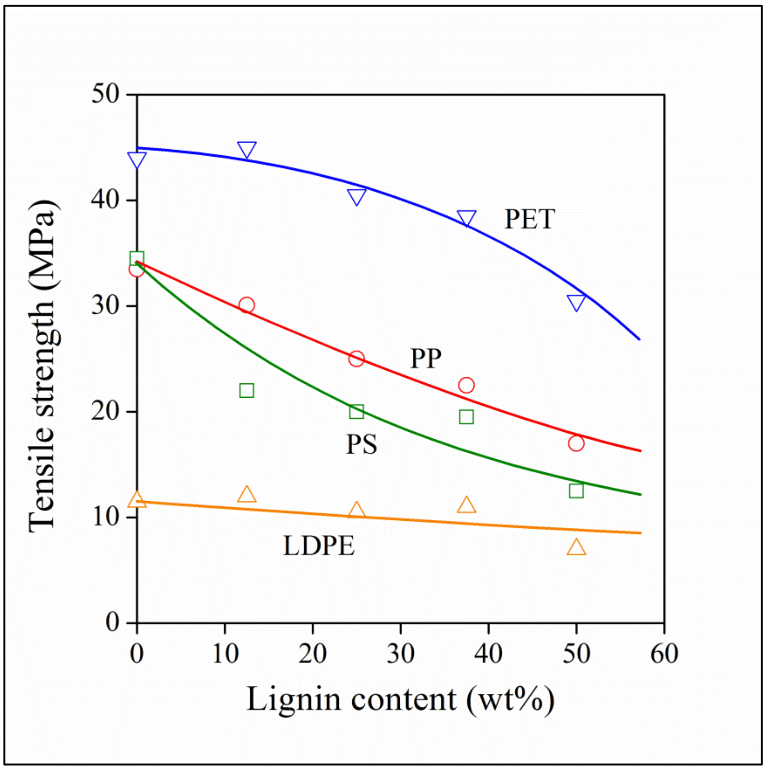


Fig. 6. Composition dependence of the tensile strength of polymer/softwood Kraft lignin blends. Symbols: (△) LDPE, (☐) PS, (○) PP, (▽) PET. Data were taken from the work of Jeong et al. [101].

Considering all the information offered in the papers published on aromatic polymer/lignin blends, we can conclude that interactions are generally stronger in these blends than in polyolefin/lignin combinations [115]. However, compatibility and properties cover a wide range and depend on the characteristics of the specific polymer and lignin used in the experiments. In spite of the claims of several authors, complete miscibility is rarely achieved, the blends usually have heterogeneous structure and their properties, especially deformability are not exceptionally good.

3.2.3. Other polymers, H-bonds

Hydrogen bonds are considerably stronger than the interactions discussed in the previous two sections, thus better compatibility and properties are expected in such blends. Blends were prepared from lignin and a large number of polymers capable of such interactions. The conclusions are similarly contradictory as before. One of the polymers was found to be miscible with lignin is poly(ethylene oxide). Kadla and Kubo [90,116-119] carried out extensive experiments on such blends and explained miscibility with the formation of H-bonds. They drew this conclusion from FTIR spectra and the composition dependence of the T_g of the blends which possessed a single T_g.

Miscibility was claimed for other polymers as well. Liu et al. [120,121] found that poly(4-vinylpyridine) is miscible with lignin and a similar conclusion was drawn about poly(vinylpyrrolidone)/lignin blends by Silva et al. [122], as well as about polypolyanlinine/lignin blends by Rodrigues et al. [114]. This latter group studied its blends with FTIR spectroscopy and cyclic voltammetry and drew this conclusion from the results. Unfortunately, SEM micrographs recorded on their samples indicated the presence of lignin particles (**Fig. 7**). Although these latter are rather small proving that interactions are quite strong due to the formation of hydrogen bonds, the heterogeneity of the structure is clear.

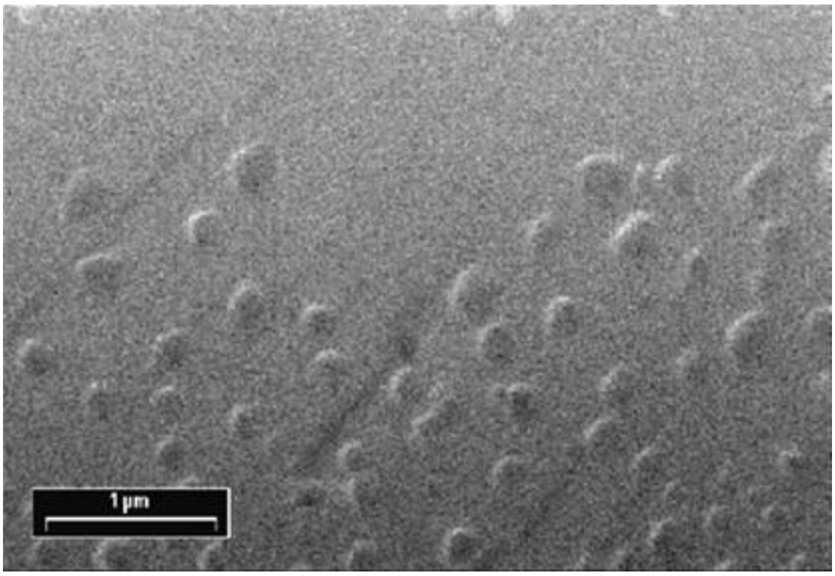


Fig. 7. Dispersed Kraft lignin particles in polyaniline blends claimed to be miscible. Lignin content: 36 wt% [114].

The contradiction related to the interpretation of experimental results and the conclusions drawn about interactions and miscibility are amply demonstrated by the publications on poly(vinyl chloride) (PVC)/lignin blends. Feldman et al. [88,123-127] studied these blends quite extensively. They observed two T_g values on DSC traces, one of which disappeared after annealing at higher temperature [123]. Although the authors mention the likelihood of homogeneous PVC/lignin blends, they do not claim miscibility firmly in this and in their subsequent papers even when they used plasticized PVC for better dispersion and to improve impact resistance. In spite of the detailed studies and conclusions of Feldman et al. [123-127], El-Raghi et al. [128] came to the conclusion that PVC and lignin are miscible due to interactions between the α hydrogen of PVC and the hydroxyl groups of lignin. The conclusion is based on the fact that they see only one transition on the DSC trace of the blend.

The contradiction related to the role of hydrogen bonds in the interaction of lignin with polymers is demonstrated quite well by poly(vinyl alcohol) (PVOH)/lignin blends. Quite a few studies have been carried out on this combination of materials and most of the authors concluded that they form heterogeneous blends [129-132], which is rather surprising, since the number of active OH groups is considerable in PVOH. Only further studies may resolve the contradiction, which shows that only the combination of several measurements and quantitative analysis can offer sufficient proof about the interaction, compatibility and miscibility of lignin blends. Even microscopy cannot supply unassailable proof because of possible artifacts and sometimes insufficient magnification. The development of hydrogen bridges was observed also in biopolymer/lignin blends with the same result. PLA seems to be immiscible with lignin [133,134], but based on SEM micrographs, Ouyang et al. [135] claimed the formation of a homogeneous, single-phase structure in their blends. The compatibility of poly(butylene adipate-co-terephthalate) with lignin seems to be much better because the two polymers can form also π electron interactions. Polyhydroxybutyrate (PHB) was claimed to form miscible blend up to 40 wt% lignin content, but phase separation occurred at large concentrations [136,137]. The conclusion was drawn again from DSC traces and SEM micrographs. Considering the less polar structure of PHB compared to PLA, the result is quite surprising.

3.3. Miscibility-structure-property correlations

The analysis of papers published on polymer/lignin blends shows that a wide variety of structures and properties were observed by various research groups and the most contradictory statements were made about the compatibility or miscibility of lignin with different polymers. Practically no polymer/lignin blend exists which was not rated miscible and immiscible at the same time by one group or another. Miscibility is usually determined by microscopy, 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 values [138]. According to this approach a polymer/lignin blend must be homogeneous at the segmental level when only one T_g is determined in the blend. However, 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. The main reason is that the flexibility of these molecules changes only in a small extent as they go through glass transition, the related increase in specific heat is small and appear only as a slight change on the DSC trace. As a consequence, immiscible polymer/lignin blends often exhibit only one T_g which belongs to the thermoplastic forming the matrix [115].

An apparent shift in a characteristic band of the FTIR spectrum can also be interpreted falsely. First of all such a shift indicates only the existence of interactions and definitely does not prove miscibility. Nevertheless, several papers on polymer/lignin blends treats the shift of the absorbance peak of a functional group, like hydroxyl or carbonyl, as an evidence for the formation of strong component interactions [114,116-119] or even a homogeneous system [101,90,139]. Unfortunately, these claims are mostly not verified by the proper analysis of the infrared spectra, e.g. by the deconvolution of the absorbance peaks. False conclusions drawn in the absence of adequate investigation are demonstrated well by the following example. EVOH/lignosulfonate blends were prepared in a wide composition range, and then infrared spectra were recorded on them. Since EVOH may form hydrogen bridges with a lignosulfonate sample, it is obvious to follow changes in the absorbance peak of the hydroxyl groups between 3600 and 3300 cm^{-1} (**Fig. 8**). This absorbance peak shifts significantly with the increasing amount of lignosulfonate in the blend, the shift might be regarded as a proof for the presence of hydrogen bonds between the components or even for the formation of a miscible blend. However, the deconvolution of the corresponding peak and mathematical analysis revealed that the infrared spectrum of the blends is the superposition of the spectra of the two components. Both components contain hydroxyl groups, but in different environments, thus the corresponding absorption bands appear at different wavelengths leading to the shift observed in Fig. 8. Immiscibility and heterogeneous structure was confirmed by SEM micrographs (Fig. 5). Nevertheless, the result presented above does not necessarily mean that hydrogen bridges do not form between the components. Since the components interact at the interphase, their concentration in the blend is relatively small and difficult to detect by FTIR spectroscopy.

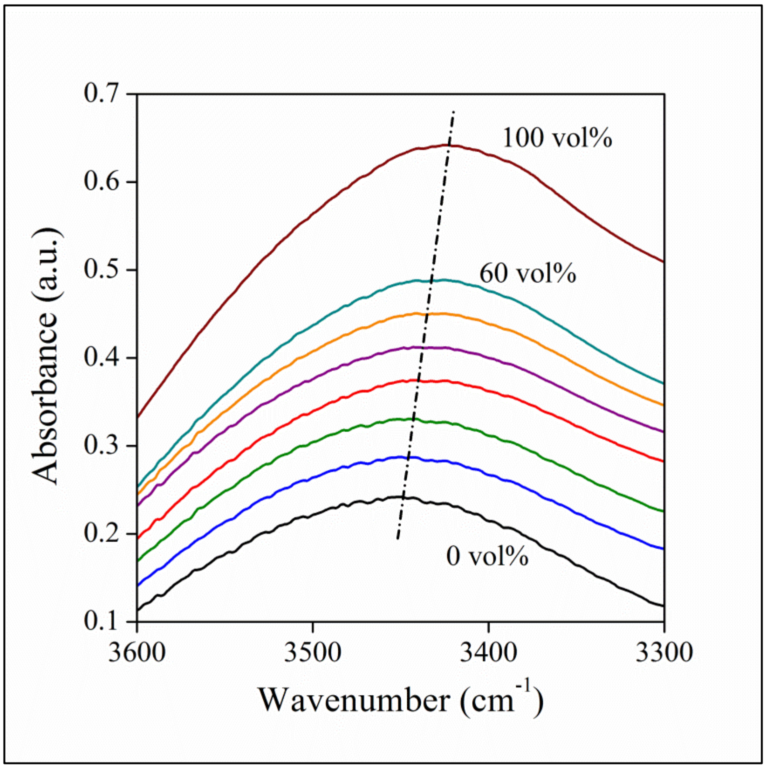


Fig. 8. The absorption band of hydroxyl groups in the infrared spectra of a series of EVOH/lignosulfonate blends. Vinyl alcohol content of EVOH: 68 mol%. Lignosulfonate content increases in 10 vol% steps from bottom to top.

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. Simple approaches may offer valuable information about these relationships and help create guidelines for further development.

A rare exception is the work of Pouteau et al. [110] 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 (δ) of the studied polymers results in a correlation with a minimum as shown in **Fig. 9**. The minimum is located very close to the solubility parameter of Kraft lignin. To support the assumption presented above the Hildebrand solubility parameters of several lignin samples are listed in **Table 4**. The values were taken from a number of papers using lignins from different sources and applying dissimilar approaches for the determination of the solubility parameter. The δ value of Kraft lignin derived from the results of Pouteau et al. [110] is somewhat smaller than the value estimated by Thielemans and Wool [139], but it is in the same range.

The analysis of the results published by Kadla and Kubo [116] offers another good example, which proves the benefits of the quantitative estimation of interactions and structure-property correlations. The authors [116] blended the same Kraft lignin as Pouteau et al. [110] with PEO in the whole composition range (from 0 to 100 % lignin content) and determined the properties of the blends. The addition of lignin enhanced both the stiffness and the strength of the blends. Only one T_g was observed for each blend and a significant shift was observed in the position of the absorption of hydroxyl groups in the infrared spectra of the blends compared to pure lignin. Based on these results they claimed that the two components are miscible in the entire composition range because of the formation of strong hydrogen bonds between them. However, the statement needs further corroboration because of the inherent uncertainty of the methods used by the authors.

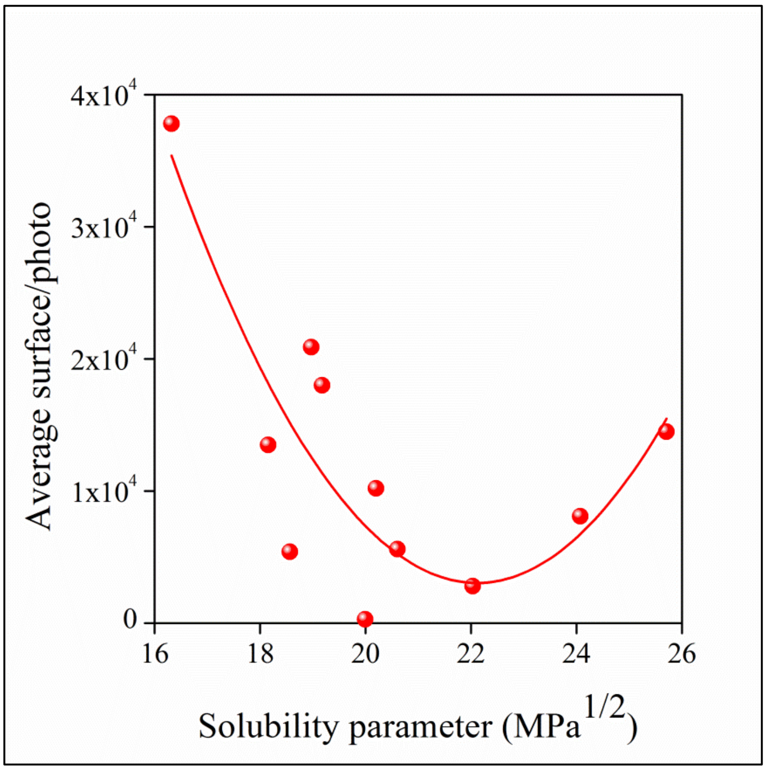


Fig. 9. Estimation of the Hildebrand solubility parameter of organosolv lignin from the area of dispersed particles in polymer/lignin blends. Data were taken from the work of Pouteau et al. [110].

Table 4

Estimation of the Hildebrand solubility parameters of several lignin samples.

Lignin type	δ ($MPa^{1/2}$)	Method	Reference
Hardwood	22.7[a]	Hoy's group contribution	this work
Softwood	23.3[a]	Hoy's group contribution	this work
Hardwood Kraft	22.1	image analysis of blends	110
Hardwood Kraft	24.3	Hoy's group contribution	139
Softwood Kraft	24.6	Hoy's group contribution	139
Hardwood Ca lignosulfonate	32.3	solubility testing	140
Softwood Ca lignosulfonate	33.1	solubility testing	140
Alcell® (organosolv)	28.0	Fedors' group contribution	28
Hardwood organosolv	22.7	–	92

a) Solubility parameters were calculated in this work for the chemical formulas given by Nimz [16] and Adler [13], respectively.

The conclusion of the authors [116] can be analyzed with models which relate interfacial interactions, structure and the mechanical properties of blends and thus connect miscibility and strength directly [141-144]. The composition dependence of tensile strength can be expressed in the following form [143]

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

where σ_{Tred} is the reduced tensile strength of the blend, σ_T and $\sigma_{T\mathrm{m}}$ 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, which, among other factors, depends also on interfacial adhesion. However, in blends the load bearing capacity of the dispersed phase, i.e. parameter B is not affected only by component interactions but also by the inherent properties of the components [144]

$$B = \ln\left(\frac{C\sigma_{Td}}{\sigma_{Tm}}\right) \tag{2}$$

where σ_{Td} and σ_{Tm} are the true tensile strength of the dispersed particles and the matrix, respectively, and parameter C is related to the stress carried by the dispersed component. This latter was found to be inversely proportional to the Flory-Huggins interaction parameter (χ) [144]

$$C = \frac{k}{\chi} \tag{3}$$

where k is a constant. There are several experimental methods to determine the χ value of two polymers, e.g. from the composition dependence of the T_g [145,146] or the melting temperature [147,148], from solvent uptake measurements [149,150], or from Hildebrand solubility parameters

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

where V_r is a reference volume with the value of 100 cm^3/mol [151], δ_1 and δ_2 the solubility parameters of the components, R the universal gas constant, and T the absolute temperature.

The δ values of the polymers can be estimated using group contributions according to the approach of Small [152], Hoy [153], van Krevelen [154] or others [155,156,157].

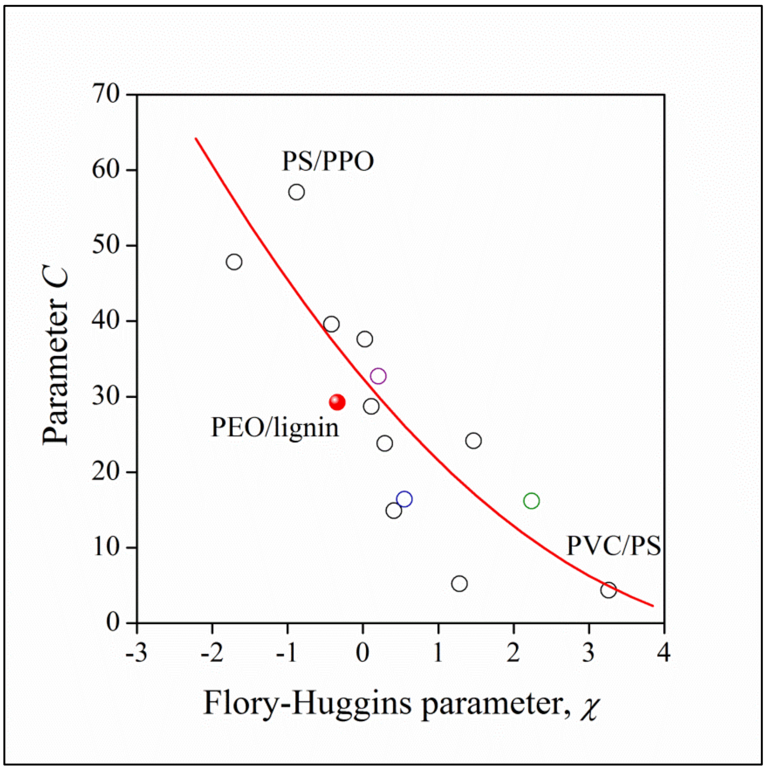


Fig. 10. Correlation of miscibility and mechanical property in polymer blends; relationship between parameter *C* derived from tensile strength and the Flory-Huggins parameter expressing polymer-polymer interaction. Symbols: (○) reference blends [158-160], (●) PEO/lignin blend [116].

For the PEO/lignin blends discussed above [116] the χ value was estimated from the composition dependence of T_g, while parameter C was calculated from the strength data of Kadla and Kubo [116]. The correlation predicted by **Eq. 3** is presented in **Fig. 10** for a number of polymers with a wide range of miscibility from the completely immiscible PVC/PS blend to the completely miscible PS/polypropylene oxide (PPO) pair. The data for most polymers were taken from our previous research and publications [158-160]. In spite of the simplifications used and some neglected factors, the correlation between the two quantities (*C* and χ) is surprisingly good. In **Fig. 10** the miscible blend of PS and PPO can be seen at the left end of the correlation, while the immiscible blend of PVC and PS at its right end. As it was mentioned earlier, Kadla and Kubo [116] had found PEO/lignin blends to be miscible. The point for the pair is located somewhere in the middle of the correlation, closer to the PS/PPO blend. As a consequence, we may not confirm the conclusion of Kadla and Kubo [116] about the miscibility of their blend, but we may expect strong interaction and some mutual solubility of the components at least. Obviously, the quantitative estimation of interactions as well as the analysis of experimental results offer valuable information about miscibility-structure-property correlations and help the utilization of lignin in polymers.

3.4. Modification of interactions

The previous sections confirm without any doubt that component interactions determine the structure and properties of polymer/lignin blends. As a consequence, the way to prepare materials with a well-defined structure and acceptable properties is to control lignin-lignin, as well as lignin-polymer interactions that can be achieved by modification. Several approaches can be used for the modification of interactions including plasticization, the chemical modification of lignin and the use of coupling agents.

3.4.1. Plasticization

Plasticization is an easy and economical way to decrease the strong interactions acting among lignin molecules which prevent their mixing with other polymers. As a result of plasticization the processability and dispersion of lignin in thermoplastic polymers may improve considerably together with the toughness and deformability of the resulting blends. Plasticizers are small molecular weight substances that replace polymer-polymer interactions with those between the polymer and the plasticizer. This process increases the mobility of polymer chains resulting in a decrease of both the glass transition and the processing temperature of the blend.

Various compounds can be used for plasticization, but their efficiency depends very much on the structure of the lignin used, i.e. on the extraction technology. Bouajila et al. [161] compared a series of plasticizers in Kraft lignin in order to check their efficiency. The plasticizing effect was estimated by the decrease of T_g as a function of plasticizer content.

The T_g of plasticized lignin is plotted against plasticizer concentration in **Fig. 11**. Water proved to be the best plasticizer in this study, while the plasticizing efficiency of ethylene glycol was surprisingly small in Kraft lignin. The results clearly prove that plasticizers can decrease the T_g of lignin, and probably improve properties as well.

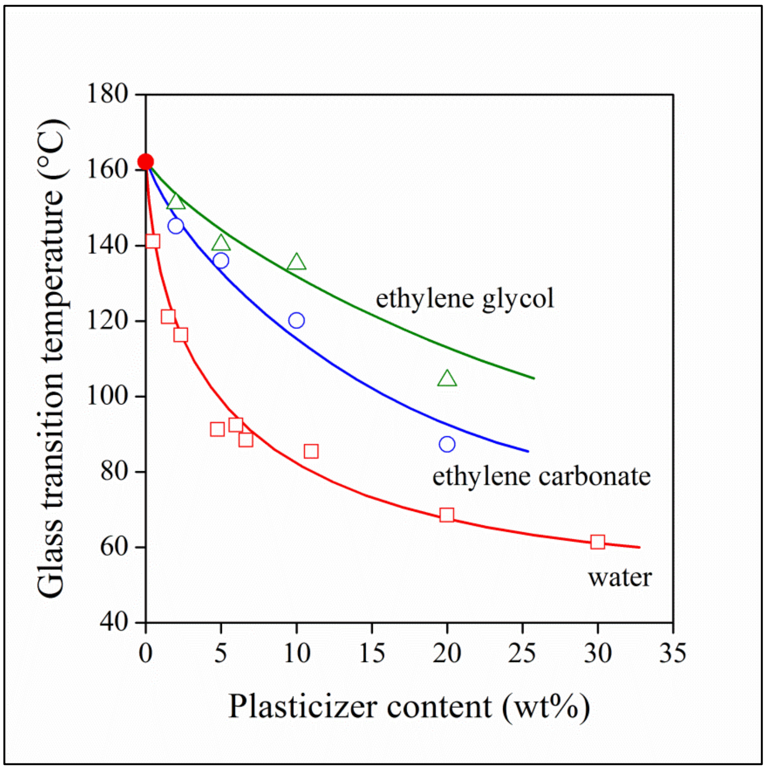


Fig. 11. Glass transition temperature of Kraft lignin as a function of plasticizer content. Plasticizers: (☐) water, (○) ethylene carbonate, (△) ethylene glycol. Data were taken from the work of Bouajila et al. [161].

Several papers demonstrate the positive effect of plasticization in polymer/lignin blends. Glycerol was found to be an efficient plasticizer in PVOH/lignin blends [162]. Su et al. [162] combined PVOH with soda lignin in the presence of glutaraldehyde as cross-linker and glycerol as plasticizer. According to the authors, the compatibility between PVOH and soda lignin was good. As expected, increasing glycerol content resulted in the decrease of tensile strength and the increase of elongation-at-break in the studied range of plasticizer content. The mechanical properties of neat PVOH were improved significantly through the addition of soda lignin, glutaraldehyde and glycerol. PEO is an efficient plasticizer improving properties in the combination of PLA and lignin [163]. Rahman et al. [163] improved the compatibility between PLA and PEO by a transesterification catalyst under reactive mixing conditions. The deformability of the PLA/PEO binary blend increased and its strength decreased with increasing PEO content. When the catalyst was applied, the formation of PLA-PEO block copolymers increased deformability further. PLA/lignin binary blends had larger stiffness and strength compared to the PLA/PEO binary blends, however, their deformability was significantly smaller. A good balance of stiffness and strength was achieved in PLA/PEO/lignin ternary blends in which lignin particles provided strength, while PEO increased deformability.

Feldman et al. [126] investigated the plasticizing efficiency of different substances in the blends of lignin and poly(vinyl chloride-co-vinyl acetate). The mechanical properties of the blends were influenced strongly by the particle size distribution of lignin; finer dispersion resulted in larger strength and deformability. The results also revealed a close correlation between the homogeneity of the blend and the Hildebrand solubility parameter (δ) of the plasticizer. This correlation is demonstrated by **Fig. 12**, in which the particle size distribution of lignin plasticized by diethylene glycol dibenzoate (δ = 20.7 MPa$^{1/2}$) and dioctyl phthalate (δ = 16.8 MPa$^{1/2}$) is presented. The δ value of diethylene glycol dibenzoate is closer to that of the applied lignin (δ = 28.0 MPa$^{1/2}$ [28]) than that of dioctyl phthalate, thus the size of dispersed lignin particles is smaller and their distribution is narrower in the presence of diethylene glycol dibenzoate than with the other plasticizer.

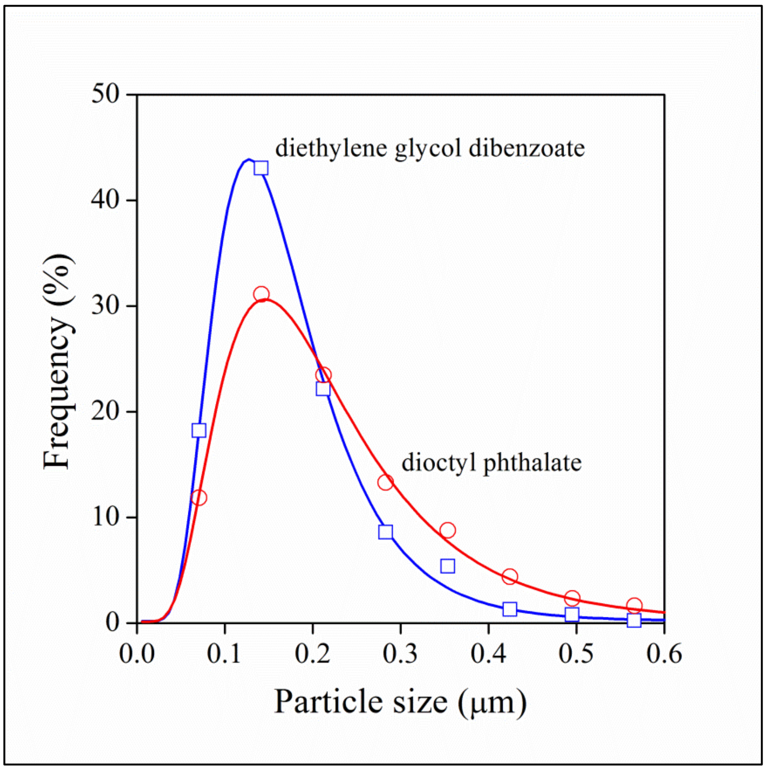


Fig. 12. Effect of plasticization on the particle size distribution of lignin in poly(vinyl chloride-co-vinyl acetate). Plasticizer: (☐) diethylene glycol dibenzoate, (○) dioctyl phthalate. Plasticizer content is 35 phr in the vinyl chloride-vinyl acetate copolymer. The plasticized polymer contains 23 wt% lignin. Data were taken from the work of Feldman et al. [126].

3.4.2. Chemical modification

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. A large number of papers claim that the chemical modification of lignin improves significantly the homogeneity and/or the mechanical properties of its blends with polyolefins and PLA. Lignin has been esterified with stearoyl chloride [164], acetic [101,165,166], phthalic [167] and maleic anhydride [168], alkylated with dichloroethane [168], dichloromethane [169] and dodecane bromide [170], arylated with chlorobenzene [169], reacted with propylene oxide [103,129,171,172], as well as grafted with ethylene monomers [173]. Nevertheless, it is often difficult or even impossible to ascertain the positive effect of these chemical modifications as the authors often do not present the results of the blends containing unmodified lignin as reference [103,129,167-172].

A good example is supplied for this approach by Maldhure et al. [168,169] who modified lignin in several ways to enhance its compatibility with PP. Lignin was esterified with maleic anhydride [168], alkylated with dichloroethane [168], dichloromethane [169] and arylated with chlorobenzene [169], respectively. Subsequently they prepared PP/modified lignin blends up to 25 wt% lignin content. Unfortunately, the properties of the blends containing unmodified lignin were not presented in these papers [168,169], therefore, we can only guess the real effect of the various modifications.

Chen et al. [170] alkylated lignin with bromododecane and then prepared PP/lignin blends. Long aliphatic chains are attached to lignin as a result of the reaction, thus they expected a positive effect on the compatibility of PP and lignin. Unfortunately, we cannot be certain about the outcome in this case either, since the authors did not present mechanical properties and morphology for the blends containing the unmodified lignin. Nevertheless, Chen et al. [170] claimed improvement in compatibility.

Sailaja and Deepthi [167] esterified lignin with phthalic anhydride and then blended the product with LDPE in the presence of a maleic anhydride grafted LDPE (MALDPE) compatibilizer. The changes in mechanical properties indicated that the addition of MALDPE improved interfacial adhesion between the components, which was corroborated also by SEM micrographs recorded on the fracture surfaces of the blends. However, deformability decreased monotonously with increasing lignin content, which might hinder the application of these blends.

Contrary to many of the works published, Gordobil et al. [165] added both acetylated and unmodified soda lignin to PLA at different compositions. The acetylation reaction is presented in **Fig. 13.** 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 stronger matrix/lignin interactions.

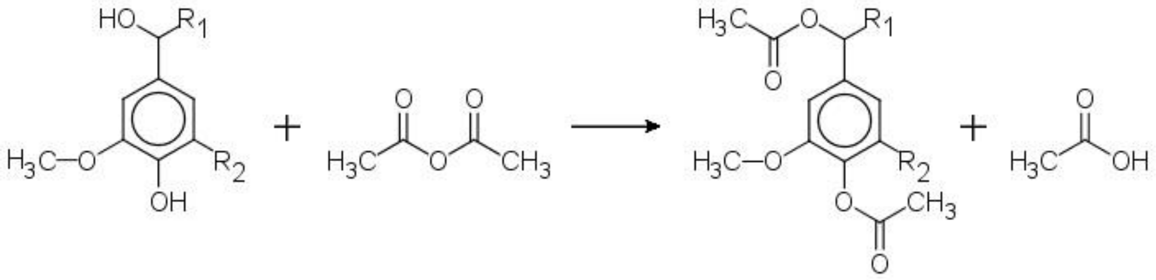


Fig. 13. Esterification of lignin by acetic anhydride.

Mechanical properties measured at larger deformations depend considerably on component interactions [141-144]. This statement is strongly corroborated by **Fig. 14** in which the tensile strength of the two series of blends is plotted against the volume fraction of lignin. Tensile strength decreases with increasing lignin content in both cases, however, the extent of decrease is much smaller for blends containing acetylated lignin [165]. The tensile strength of heterogeneous materials depends on the strength of interfacial adhesion which is determined by the contact surface of the phases, i.e. particle size and the strength of interaction. The first increases with decreasing particle size, while the second probably decreases with modification. Debonding stress also increases with decreasing particle size, thus the formation of voids becomes more difficult and premature failure less probable. The changes observed in the composition dependence of tensile strength in PLA/lignin blends is the combined effect of all factors and not only that of the strength of interaction. However, the results presented above clearly prove that the chemical modification of lignin can be beneficial and improve the properties of its blends.

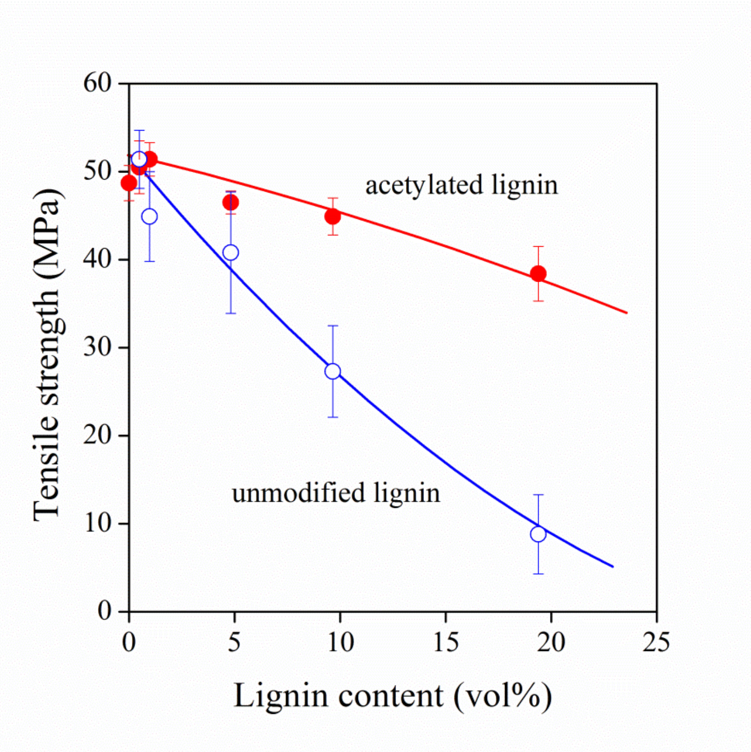


Fig. 14. Tensile strength of PLA/lignin blends plotted as a function of lignin content; (○) unmodified lignin, (●) acetylated lignin.

Wei et al. [171] propoxylated lignin based on the method of Glasser et al. [174,175]. The as prepared hydroxypropyl lignin was blended with soy protein to develop a potential biodegradable plastic with better mechanical performance than the pure soy protein applied. The addition of just 2 wt% hydroxypropyl lignin resulted in tensile strength of 16.8 MPa, 2.3 times that of pure soy protein, with no accompanying decrease in elongation at break as a result of strong interaction between the components. Compared with other soy protein/lignin blends, the propoxylation of lignin plays a key role in the improvement of mechanical properties since this modification increases the steric availability of the hydroxyl groups of lignin, thus hydrogen bonding may develop more easily between the polymer matrix and lignin.

3.4.3. Compatibilization

Lignin, including commercially available lignin samples, is a polar substance which is immiscible and often even incompatible with most polymers, but especially with apolar ones like PE, PP or PS. Plasticization and chemical modification change the properties of the lignin phase, but blend properties may be improved also by compatibilization that modifies mainly interfacial adhesion [108,167,176-183].

Ethylene-vinyl acetate (EVAc) random copolymers were successfully applied as compatibilizers in LDPE/lignin blends by Alexy et al. [176]. The addition of 10 wt % EVAc increased the tensile strength by about 200 % and the elongation-at-break approximately by 1300 % compared to corresponding properties of the non-modified samples.

PS/lignin blends were studied over a wide range of lignin content (0–80 wt%) in the work of Barzegari et al. [108]. Blends were compounded with and without the addition of a linear styrene-hydrogenated butylene-styrene block copolymer and all properties deteriorated with increasing lignin content in both of them. At 60 wt% lignin content the compatilizer improved the dispersion of lignin and enhanced interfacial adhesion leading to the increase of strength and deformability compared to the blend not containing the compatibilizer, but all mechanical properties including stiffness, strength and deformability were inferior to the corresponding properties of neat PS.

An effective approach was presented by Oliveira and Glasser [177] for the compatibilization of PS and lignin. Star-like lignin-PS copolymers were synthesized by grafting isocyanate-capped PS segments onto hydroxypropyl lignin in their work, and then these copolymers were added to PS/hydroxypropyl lignin blends. The compatibilizing effect of the copolymers was corroborated by the analysis of the fracture surfaces of the blends. The results revealed that the applied copolymers reduced the particle size of dispersed lignin significantly, which might be an important evidence for improved interfacial adhesion [177].

Lignin contains a number of reactive functional groups, which offer the possibility for reactive compatibilization as well. In this case, the copolymers acting as compatibilizers form in situ during blending. Polymers with reactive groups [167,178,179, 183] or small molecular weight chemicals [180-182] can be reacted with lignin to form the compatibilizer. Methylene diphenyl diisocyanate [180] and polymeric methylene diphenyl diisocyanate [181,182] proved to be efficient coupling agents in polybutylene succinate/lignin blends.

Polyethylene and lignin were compatibilized by maleic anhydride grafted polyethylene in other works [167,178]. A similar approach was used to improve interfacial adhesion in polypropylene/lignosulfonate blends through the addition of maleic anhydride grafted polypropylene (MAPP) to the PP/lignin blend [179]. Two series of polypropylene blends were prepared with sodium-lignosulfonate in a wide composition range: one with and another without the compatibilizer. Strength decreases monotonous with increasing lignin content in the absence of MAPP, while it increases in the presence of the coupling agent (**Fig. 15**). Obviously the compatibilizer increased interfacial adhesion and the load bearing capacity of the dispersed lignin particles considerably. The improvement, i.e. the extent of compatibilization can be expressed quantitatively with the help of the simple model presented earlier (see **Eq. 1**). If the natural logarithm of reduced tensile strength is plotted against the volume fraction of the dispersed phase, a straight line should be obtained, the slope of which is equal to parameter B. The tensile strength of the two blend series of **Fig. 15** was plotted in this way in **Fig. 16**. Both correlations are linear indeed, furthermore, the slope, i.e., parameter B of the compatibilized blends is much larger than that of the blends which do not contain the compatibilizer. This result confirms unambiguously the beneficial effect of the compatibilizer and the fact that the MAPP coupling agent improves interfacial adhesion significantly in PP/lignosulfonate blends. Nevertheless, we must call the attention here to the fact that although the strength of the blends increased, their deformability decreased at the same time in an extent which would considerably hinder their practical application. This calls the attention to the importance of property optimization and also to the proper selection of the approach used for the modification of lignin and its blends.

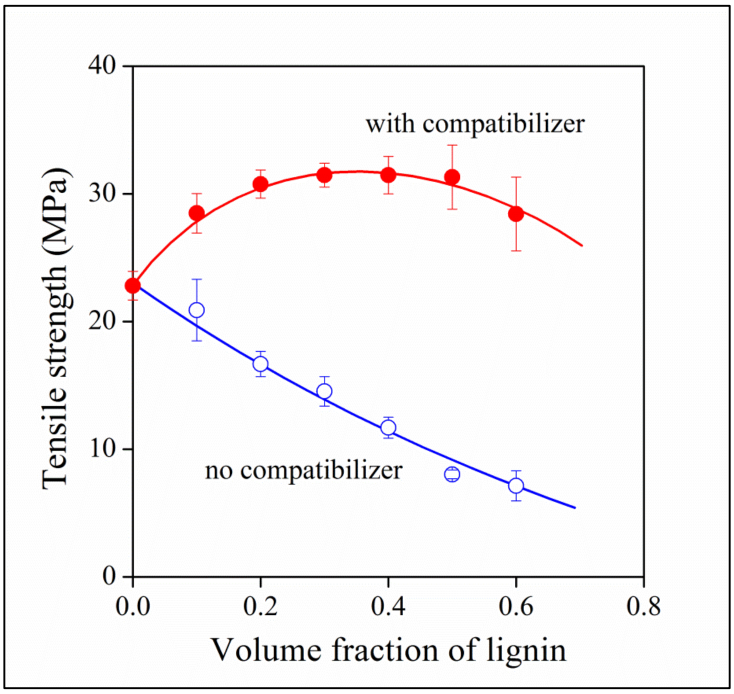


Fig. 15. Tensile strength of PP/lignosulfonate blends plotted against their lignin content; (○) no compatibilizer, (●) MAPP [179].

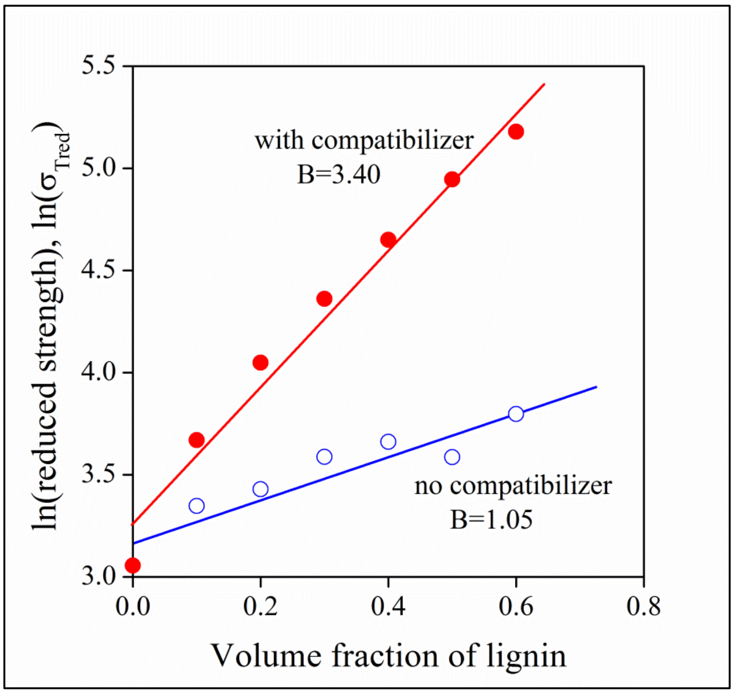


Fig. 16. Reduced tensile strength of PP/lignosulfonate blends plotted against lignin content in the linear form of **Eq. 1**. Effect of MAPP on interfacial interactions. (○) no compatibilizer, (●) MAPP [179].

4. Lignin as a reactive component

Because of its large number of functional groups, lignin is often used as reactive component for the preparation of cross-linked resins and other polymeric materials. Although this is an important approach and possibility for the utilization of lignin, the issue is out of the scope of our paper, since we focus mostly on blends here. Nevertheless, we summarize the main aspects of the reactive use of lignin in polymers, point out major factors and list a few examples. The preparation of lignin-based polymers follows two general approaches. In the first lignin is modified chemically by phenolation, oxypropylation, esterification, etc. in order to enhance the reactivity of lignin. Modification increases cost and environmental impact and thus reduces the competitive edge of lignin over conventional systems prepared on traditional petroleum basis. In the second approach, the traditional components of a resin system are substituted partially by unmodified lignin. Both approaches are only partial solutions as they do not eliminate completely the use of substances based on crude oil. Polymers in which lignin is used as a reactive component are presented very briefly in subsequent paragraphs.

4.1. Phenol-formaldehyde resins

Considering the polyphenolic structure of lignin and its similarity to phenolic resins, the use of lignin for the preparation of these latter seems to be obvious. The urge to use different types of lignin in phenolic-formaldehyde resins is further supported by the need for low cost adhesives of reliable supply and durability mainly for engineered wood like plywood, chip, fiber and wafer board. The direct substitution of phenol with lignin in a phenol-formaldehyde resin resulted in large excess of formaldehyde [184] because of the smaller functionality of lignin, which could be overcome by the adjustment of stoichiometry. The prepared adhesives containing lignin proved to be suitable for the preparation of plywood panels. However, direct substitution often leads to the deterioration of properties proportionally to the amount of lignin used [184] often because of impurities in lignin [185]. As mentioned above, lignin can be modified chemically to increase its functionality or reactivity [185-188].

4.2. Epoxy resins

Lignin can be applied both as the epoxy component and as the curing agent (hardener) in epoxy resins. In the first case, lignin must be modified to create epoxide groups on the molecule first, which is mostly done by reacting the hydroxyl groups of lignin with epichlorohydrin, and by epoxide (oxirane) ring formation in alkaline medium subsequently. Steam exploded bamboo lignin was functionalized in this way [189]; the thermal stability of the resin prepared with lignin was worse than that of the petroleum-derived epoxy, but passed the dip-solder resistance test (250–280 °C) [189,190]. The flexural strength of lignin-based epoxy resins was also smaller than that of the petroleum-derived epoxy. Epoxy resins can be cross-linked with curing agents containing reactive hydrogen atoms in the form of amine, anhydride, carboxyl or hydroxyl groups. Unmodified lignin contains both carboxyl and hydroxyl groups so it may be an adequate curing agent without any chemical modification. Lignin modified with anhydride groups was used as curing agent for epoxy and it increased both the stiffness and the fracture resistance of the resin [191].

4.3. Polyurethanes

Polyurethanes are usually synthesized through the reaction of isocyanate and hydroxyl groups. Because of its structure lignin can provide the hydroxyls and replace traditional polyols. Papers on polyurethanes which use lignin as one of the components mostly describe the preparation of films as well as rigid and flexible foams. Lignin is often modified also for this purpose to improve reactivity or solubility in the reaction medium [192,193]. When lignin is used for the replacement of traditional polyols, one must take into account that its functionality exceeds two. The effect is demonstrated well by **Fig. 17** showing that increasing lignin content results in the increase of both the tensile strength and the deformability of polyurethane films [194] due to their increased cross-link density. Similar results were obtained by others [195] confirming the importance of the proper characterization of lignin and the need for the optimization of stoichiometry and reaction conditions in such applications.

4.4. Graft copolymers

A promising way for the chemical modification of lignin is to attach polymer chains to it through its reactive, mostly hydroxyl functional groups. Lignin graft copolymers can be obtained both by the "grafting from" and the "grafting to" approaches. Usually the first approach is preferred since it can produce larger graft density compared to the second route. Grafting from is frequently carried out either by ring opening polymerization using the hydroxyl groups of lignin as a macroinitiator, or by forming a lignin macroradical which acts as an active center for the radical polymerization of monomers. Many examples have been published for the first approach. The most frequently polycaprolactone or polylactide is attached to lignin to produce, for example, UV protective films or coatings [196-198] or an impact modifier for PLA [199]. Chemical modification is an obvious way to increase the value of lignin and to make it suitable for various applications.

5. Application

Most commercial applications are related to lignosulfonates, since they are available in the largest quantity in the industry [2]. Lignosulfonates are mostly used as a dispersant, particularly in the production of concrete admixtures for reducing the amount of necessary water, for faster development of strength, and for the improvement of workability [200]. This type of lignin is commonly applied also as a binder [201], a component of adhesives [202], or a raw material for the production of chemicals including vanillin [203], dimethyl sulfide [204] and methyl mercaptane [204]. Lignosulfonates are used in animal feeds as a binder to improve pellet durability, abrasion resistance and as lubricant decreasing extruder wear [201]. They are widely used in oil well drilling muds mostly as mud thinner, clay conditioner, viscosity control agent and fluid loss additive [205]. Concentrated spent sulfite liquors are applied directly for dust control in road and mineral ore dedusting [206]. Lignosulfonates are also applied as dispersants in water-based paints and inks [207].

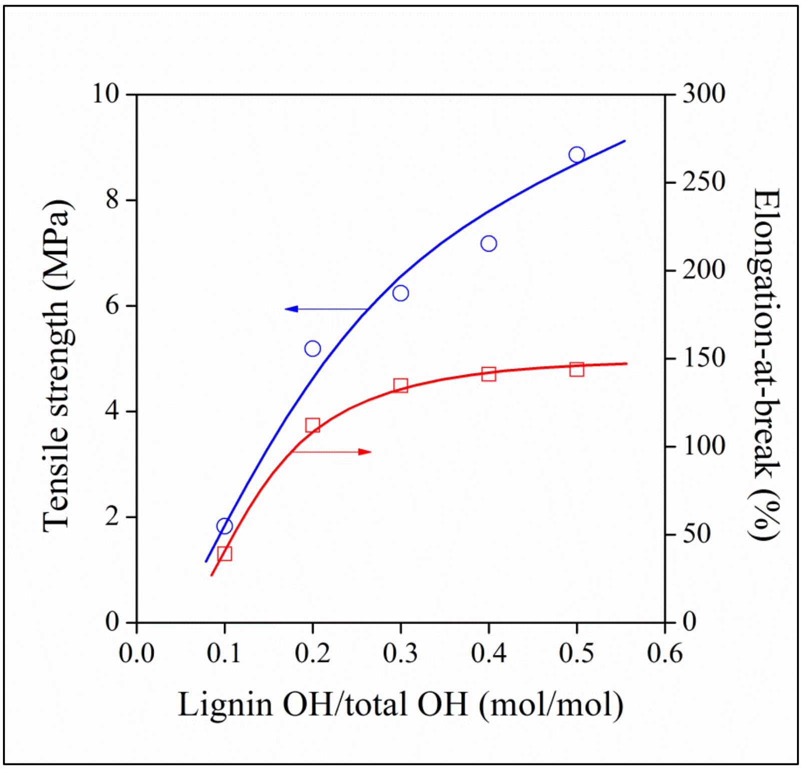


Fig. 17. Mechanical properties of polyurethane plotted against the lignin OH/total OH ratio. Effect of cross-link density. Symbols: (○) tensile strength, (☐) elongation-at-break [194].

Bioethanol production yields mostly steam explosion lignin, thus more and more attention is paid to the utilization of other industrial lignins as well. A German compounding company, TECNARO has already utilized lignin in thermoplastics that can be processed with 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, musical instruments etc. **Fig. 18.** shows a pair of commercially available headphones with earcups made of 'Liquid Wood’.

Fig. 18. AudioQuest® NightHawk headphones with earcups made of ARBOFORM®

Cicala et al. [208] found that the component which makes ARBOFORM® a thermoplastic is PLA. This result is strongly corroborated by the DSC thermograms of ‘Liquid Wood’ [183,208,209] showing the glass transition and the cold crystallization of PLA. Therefore, we can conclude that ARBOFORM® is actually a PLA/lignin blend reinforced with hemp, flax or other natural fibers.

The potential use of lignin as a stabilizer has already been discussed in section 3.2.1. Due to the presence of phenolic hydroxyl groups in its polyphenol structure, lignin has a radical scavenging and stabilizing effect in polymers. The crucial role of the phenolic hydroxyl groups in the stabilization was proved by Sadeghifar and Argyropoulos [210] who showed that selective methylation of the phenolic hydroxyls decreases antioxidant activity. The antioxidant and stabilizing characteristics of lignin have been studied in several polymers mainly in PE [93,94,981,210], PP [93,95-100] and PLA [165,166]. Most experiments indicated that lignin is usually inferior to commercial additive packages, and it also discolors the polymer, thus further work must be done before its industrial application.

The polyaromatic structure of lignin makes it a promising precursor for carbonization. Carbonized lignin can be applied in catalysis, energy storage and fibers. Li et al. [211] fabricated a lignin-derived catalyst for biodiesel production, which had large catalytic activity with excellent cycle performance.

The carbonization of lignin leads to products for electrical applications. Wang et al. [212] produced fibrous carbon mats from Alcell® lignin/PEO blends by electrospinning, carbonization and thermal annealing in the presence of urea. The mats were found to be efficient anodes in lithium ion batteries. Hu et al. [213] prepared high energy density supercapacitors from activated submicron carbon fibers derived from lignin. The excellent performance of the material demonstrates the potential of lignin-based carbons for electrical energy storage.

Kadla et al. [214] fabricated carbon fibers from the blends of lignin and PEO through thermal spinning followed by carbonization. The tensile strength of the fibers was 300–450 MPa and their modulus 30–60 GPa corresponding to general performance grades. Schreiber et al. [215] produced carbon fibers from blends of hardwood organosolv lignin and cellulose acetate by electrospinning. The fibers were treated with iodine to facilitate carbonization and to help retain fiber morphology. Compared to carbon fibers produced from neat polyacrylonitrile (PAN), the fibers derived from biopolymers had a smaller degree of overall graphitization, but formed larger in-plane graphitic crystals. Liu et al. [216] prepared composite fibers containing lignin, PAN and carbon nanotubes (CNT) by gel-spinning and then carbonization at the temperatures of 1000 and 1100 °C, respectively. The fibers made from PAN/lignin blends had a strength of 1720 MPa and modulus 230 GPa, properties very similar to those of neat PAN fibers (strength 1600 MPa, modulus 223 GPa). The addition of CNT resulted in a slight deterioration of properties (strength 1400 MPa, modulus 200 GPa).

Responsive materials change their properties significantly upon an external stimulus which can be a change in temperature, pH, light, magnetic or electric field, etc., and the property responding can be color, transparency, volume, shape, etc. The response usually must be fast for practical, mainly medical applications like controlled drug release [217-221]. Kim and Kadla [222] grafted N-isopropylacrylamide (NIPAM) onto modified hardwood Kraft lignin, which was used as a macroiniciator for atom transfer radical polymerization. Depending on the degree of substitution of the macroinitiator, the grafted copolymers were either fully or partially soluble in water. Both the soluble and the suspended copolymers precipitated from aqueous solutions at 32 °C and above. Feng et al.

[223] prepared hydrogels by the graft polymerization of organosolv lignin and NIPAM in the presence of N,N'-methylenebisacrylamide as the cross-linker and hydrogen peroxide as the initiator to produce temperature-sensitive hydrogels. Gao et al. [224] used softwood Kraft lignin for the preparation of pH-responsive hydrogels. Relatively strong hydrogels formed under neutral conditions, which collapsed or reformed on the increase or decrease of pH. Duval et al. [225] synthesized a pH- and light-responsive polymer from softwood Kraft lignin in a two-step procedure by the incorporation of diazobenzene groups onto lignin. The Kraft lignin derivatives containing diazobenzene changed their color as a function of pH in solution and responded to light by the cis-trans photoisomerization of the diazobenzene groups.

6. Conclusions

The chemical structure of lignin is complex and depends very much on the extraction technology used for its production. Because of the complicated structure, the proper characterization of lignin is difficult and requires the use of a number of methods. Besides the number of functional groups, the ratio of monomers and molecular weight must be also determined for the complete characterization of lignin. The combination of lignin with thermoplastics should be treated as blend and not composite. Because of their large number of polar functional groups, lignin molecules interact strongly with each other. As a consequence, competitive interactions determine the structure and properties of the blends, and most polymers are immiscible with lignin, because of weaker interactions forming between lignin and the matrix polymer than among lignin molecules. Apparently none of the interactions developing in the blends, including hydrogen bridges, is sufficient to result in complete miscibility. Nevertheless, strong interactions, like the combination of aromatic π-electron interaction and hydrogen bonds, lead to very small dispersed particles and relatively good properties. However, the deformability of the blends is usually poor which might be compensated by the chemical modification of lignin, plasticization, or the use of coupling agents. Lignin can act also as a reactive component in the preparation of various resins and polymers.

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