

Effect of competitive interactions on the structure and properties of blends prepared from an industrial lignosulfonate polymer

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ABSTRACT

To explore the possibility of applying lignin in practice, an industrial lignosulfonate (0–50 vol%) was blended with four ionomers. The concentrations of carboxyl and carboxylate groups were systematically varied in the ethylene-acrylic acid copolymers to study the competition of hydrogen and ionic bonds forming between the components. The mechanical properties of the blends were determined by tensile testing. The structure was investigated by scanning electron microscopy, while deformation and failure processes were studied by acoustic emission measurements and microscopy. Interfacial interactions were quantitatively characterized by analyzing local deformation processes and by evaluating the composition dependence of the tensile strength using appropriate models. Molecular dynamics simulations indicated that carboxylate groups preferably form clusters in the ionomer phase, consequently, the increasing degree of neutralization results in ionomers with more and more self-interactions of components deteriorating ionomer-lignin interactions. The novel combination of experiments, modeling, and simulation was done for the first time on such materials, and it pointed out that the role of hydrogen bonds is more critical in determining blend properties. Blends can be prepared for practical applications with a good combination of stiffness (0.8 GPa), tensile strength (22 MPa), and elongation-at-break (25 %) at 30 vol% lignosulfonate content and 33 % neutralization.

1. Introduction

The world oil industry is undergoing a considerable transformation, as the need for fossil fuels will diminish in the coming decades due to the spread of renewable energy and electromobility. Large oil companies have accumulated such enormous capital that they could emerge as new players outside the chemical industry, even in renewable energy or electric vehicle technology [1,2]. In addition, refineries are increasingly focusing on sustainability, i.e., they are using more and more renewable energy sources to provide a more significant part of the energy needed to run their processes and are using increasing amounts of renewable raw materials [1]. This process results in the transformation of oil refineries, at least partly into biorefineries.

Of all renewable feedstocks, lignocellulose is the most abundant on

Earth, and it is already the primary raw material for many biorefineries [3,4]. The main constituents of lignocellulose are cellulose, hemicelluloses, and lignin, which can be separated by the conversion of lignocellulose [5,6]. Lignin is an aromatic polymer with a cross-linked or hyperbranched structure, which is impossible to extract in its original form [7,8]. The molecular weight and structure of the lignin produced by the pulping process depend on the particular technology used [8]. The most common technologies are the Kraft and the sulfite processes [9]. Still, steam explosion is also becoming more common at the industrial scale, and intensive research is being carried out on organosolv processes as well [10–12]. When lignocellulose is treated with a sulfite solution, sulfonated lignin, i.e., lignosulfonate, is produced. The typical counter-ions of the sulfonate groups are sodium, magnesium or calcium [13]. The sulfonate groups in lignosulfonates are prone to form ionic

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interactions, but the molecule also contains several other functional groups that can participate as donors or acceptors in hydrogen bonding.

Using lignin as a component of polymer systems is challenging due to its complex structure and strong self-interactions. Several attempts have been made to produce polymer blends and composites using lignin [14,15]. Numerous synthetic polymers have been applied as matrix materials, which are able to form different types of interactions with lignin. Polyethylene and polypropylene develop only weak van der Waals interactions with lignin; thus, blends with poor properties have been obtained [16–20]. The interfacial adhesion between polyolefins and lignin can be significantly improved using compatibilizers that can bind to lignin by chemical or hydrogen bonding [18–21]. Polystyrene can form aromatic interactions with lignin, resulting in stronger interfacial interactions compared to polyolefin/lignin blends [17,22]. Polyethylene terephthalate can develop not only aromatic interactions but also hydrogen bonds with lignin, which further improves the interfacial adhesion between the components [17,23]. Interactions are quite strong between lignin and polymers that can form only hydrogen bonds in addition to van der Waals interactions, such as polylactic acid [17,24], polyamides [25] or polyhydroxybutyrate [26]. Research to date has demonstrated that the strongest possible interactions must be created between the polymer matrix and lignin to obtain a useful material [17].

Among synthetic polymers, ionomers have considerable similarities with lignosulfonates. Most commercially available ionomers are ethylene-acrylic acid or ethylene-methacrylic acid copolymers, in which the acid groups are partially neutralized, i.e., deprotonated to form a salt. In ionomers, the protons are replaced by a metal ion, most commonly sodium or zinc, resulting in the formation of ionic and hydrogen bonds in the ionomers [27], which is a common feature of lignosulfonates as well. A further particular characteristic of ionomers is that several ionic groups can align parallel to each other due to the flexibility and mobility of the methylene moieties, thus forming ionic multiplets. The ionic multiplets act as cross-links and are so stable that they do not break up even above the melting point of the polymer [28–30]. Moreover, electrostatic attraction develops among the multiplets, resulting in the formation of clusters. In fact, clusters create a new phase in ionomers in addition to the amorphous and crystalline phases of the copolymer, and together they determine properties [28,29,31].

Recently, our group produced blends from lignosulfonate and commercially available ionomers for the first time [16]. The basic concept was to create strong ionic and hydrogen bonds between the components and to combine the beneficial properties of ionomers and lignosulfonates. Furthermore, we expected that stronger ionic interactions would dominate over hydrogen bonds, thus further improving properties. Contrary to the expectations, increasing concentration of the ionic groups in the ionomer resulted in a weaker reinforcing effect of the lignosulfonate. Moreover, reinforcement increased with increasing the concentration of acid groups capable of forming hydrogen bonds. In commercially available ionomers, several variables (type of monomers, molecular weight, carboxylate counter-ion, concentration of carboxyl and carboxylate groups) change simultaneously, thus preventing the accurate quantitative analysis of the competition between ionic and hydrogen bonding [16].

For this reason, ionomers were prepared from an ethylene-acrylic acid copolymer (EAc) by neutralizing the acid groups with sodium carbonate in different ratios. Consequently, only the concentrations of carboxyl and carboxylate groups differed in the ionomers used [28]. The structure of the ionomers changed significantly with an increasing degree of neutralization, leading to the increased size and number of clusters, which thus also influenced the crystallization of the polymer [28]. The goal of the present study was to use these tailor-made ionomers for the preparation of lignin blends to obtain a more accurate and reliable picture of the competition between hydrogen and ionic bonding. We also wanted to determine the optimum degree of neutralization which leads to materials with high practical applicability. The lignin content of the blends changed in a wide range, and the mechanical

properties, structure, as well as the failure of the blends were studied in detail. The interactions between the components were also characterized using independent approaches. Interactions were interpreted also through molecular dynamics simulations. The combination of experiments, modeling and simulation led to important new information about interfacial interactions in ionomer/lignin blends. The practical relevance of the results is also discussed briefly in the final section of the paper.

2. Experimental

2.1. Materials

The ethylene-acrylic acid copolymer (EAc) Nucrel 31001 (Dow, USA) was used to prepare the ionomers. According to the datasheet of the product, the copolymer had a density of 0.94 g/cm³ and a melt flow rate (MFR) of 1.3 g/10 min at 190 °C and 21.6 kg. The nominal acrylic acid content was 9.5 %, but according to our Fourier transform infrared spectroscopy (FTIR) measurements, the true acrylic acid content of the batch used was 8.5 %. The method of determination was described in detail in our previous publication [28]. Anhydrous sodium carbonate with a purity of ≥99.5 %, purchased from Molar Chemicals (Hungary), was used for neutralization. According to the datasheet of the product, it contained max. 50 ppm sulfur, max. 10 ppm phosphates, max. 0.025 % chlorides, max. 30 ppm silicates; its Al, Fe, Mg, and Pb content was below 20 ppm, and the Ca and K content did not reach 0.01 %. In addition, 2000 ppm Irganox 1010 (BASF, Germany) and 2000 ppm Irgafos 168 (BASF, Germany) antioxidants were added to the copolymer during neutralization. The former is a primary stabilizer, and the latter is a secondary antioxidant. The degree of neutralization of the polymers, i.e., the relative number of acidic hydrogens replaced by sodium ions, was 0, 17, 33, 50, and 67 % of the total number of acidic groups.

The Bretax CRO2 lignosulfonate used for the preparation of the blends was supplied by the Burgo Group (Italy). The counter-ion of the lignosulfonate is calcium, and its C9 formula is C₉H_{8.44}O_{3.88}S_{0.32}. The lignosulfonate used was an industrial lignin grade, hence it had a relatively low molecular weight ($M_n = 1400\text{--}2400$ g/mol). It also contained various salts and reducing sugars as impurities. The concentration of functional groups capable of forming hydrogen bonds was determined by ³¹P NMR [32,33]. The lignosulfonate contained 2.73 mmol/g aliphatic hydroxyl, 0.70 mmol/g phenolic hydroxyl, and 0.54 mmol/g carboxyl groups. The sulfonate groups capable of forming ionic interactions were determined by titrimetry, and their concentration was 1.75 mmol/g. The average diameter of the lignosulfonate particles before blending was 80 μm. For the sake of simplicity, hereafter, the term lignin will be used instead of lignosulfonate. The lignin content in the blends was varied between 0 and 50 vol% in 10 vol% increments.

2.2. Sample preparation

The ionomers were prepared using a Brabender 350 internal mixer (Brabender, Germany) with a nominal volume of 370 cm³ attached to a Brabender Plasti-Corder Lab-Station (Brabender, Germany). The temperature of the internal mixer was set to 150 °C for the neutralization reaction, and the rotational speed of the mixer was 50 rpm. The EAc copolymer was added to the mixer first. The primary and secondary stabilizers were introduced immediately after the melting of the copolymer. The anhydrous sodium carbonate was gradually fed to the mixer from minute 5 to minute 10. The total mixing time was 35 min from the time of EAc addition. According to the torque vs. time curves, this time was sufficient for the neutralization reactions to take place. After removing the polymer melt from the mixer, it was cooled under air and rested for one day. The material was then placed into liquid nitrogen and ground to pieces smaller than 1 mm in a Fritsch 4ERKK90 mill (Fritsch, Germany).

Ionomer/lignin blends were prepared using a Brabender W 50 EHT

internal mixer (Brabender, Germany) with a volume of 42 cm³. The temperature of the mixer was set to 190 °C, and the mixing speed to 50 rpm. The EAc copolymer or the ionomer was added first, and then lignin was introduced 3 min after the melting of the polymer. The components were then homogenized for 10 min. Subsequently, the mixtures were compression molded into 1 mm thick plates at 190 °C using a Fontijne SRA 100 apparatus (Fontijne, The Netherlands). The samples were preheated for 3 min, compression molded for 2 min, and cooled slowly to room temperature while maintaining the pressure. The plates were stored at room temperature for at least 2 weeks before testing. Five dog bone-shaped test specimens were fabricated from the plates of each material using a Charlyrobot Charly 4 U CNC milling machine (Charlyrobot, France).

2.3. Characterization

The mechanical properties of the specimens were determined by tensile testing using an Instron 5566 (Instron, USA) apparatus. The gauge length was 80 mm, and the samples were deformed with a cross-head speed of 10 mm/min. Acoustic emission (AE) testing was carried out simultaneously using a Sensophone AED-40 (Geréb & Társa, Hungary) apparatus. The AE device records elastic waves generated by local processes during deformation. The threshold level was set to 20 dB. The structure of the blends was investigated using a JEOL JSM 6380 LA scanning electron microscope (JEOL, Japan). Thin slices of 50–100 µm thickness were cut from the 1 mm thick plates using a Leica EM UC6 (Leica, Austria) microtome at −100 °C. Thereafter, the lignosulfonate was completely removed from the slices by dissolving it in distilled water for 24 h at ambient temperature. Before taking the micrographs, the slices were coated by sputtering them with gold/palladium alloy. The average size and the size distribution of dispersed lignin particles were determined by image analysis. SEM images were also recorded on fractured surfaces created in tensile testing. In this latter case, the samples were not etched by any solvent. Images were recorded at the accelerating voltage of 15 kV, the spot size of 40–50 V, and the working distance of 10–20 mm. The surface of the samples was previously sputter-coated with gold. The blends were also studied by FTIR measurements, but these results will not be discussed in the paper, because no significant shift of characteristic bands or correlations were observed, i.e., the estimation of interactions directly from FTIR data was not possible. Moreover, the shift in the wavelength of the absorbance of a characteristic band can be often misleading and may not express interactions quantitatively in lignin-based blends [34].

2.4. Molecular dynamics simulations

The interactions within an EAc/lignin and an ionomer/lignin blend were analyzed by classical molecular dynamics simulations. Two model systems were composed of two lignosulfonate molecules and 250 copolymer chains. In the EAc/lignin system, all chains were ethylene-acrylic acid copolymers, which contained 38 ethylene and two acrylic acid units. In the ionomer/lignin blend, 125 copolymer chains were the same as in the EAc/lignin blend, and the remaining 125 chains were deprotonated ethylene-acrylate copolymers consisting of 38 ethylene and two acrylate units. The inclusion of sodium ions ensured the charge neutrality of the systems. Details about the physical size and composition of the periodic simulation boxes are summarized in Table 1.

Molecular dynamics simulations were performed with the LAMMPS program [35] using the OPLS-AA force field [36]. The initial geometries of the simulation boxes were created with PACKMOL, based on the data listed in Table 1. The cutoff for intermolecular interactions was set to 10 Å. Beyond this distance, Coulomb interactions were estimated with the particle-particle particle-mesh method with an accuracy of 10^{−5}. The timestep was set to 1 fs. To obtain the box sizes listed in Table 1, initial simulations were performed in the NpT ensemble at a pressure of 1 bar and a temperature of 500 K. The pressure and temperature were controlled by a Nosé–Hoover barostat and thermostat, respectively, employing a coupling constant of 100 fs [37–39]. These systems were simulated for 7.7 ns, and the cell volume was averaged over the last 6 ns to obtain the final box sizes. The subsequent production runs were performed in the NVT ensemble employing the temperature of 500 K. The settings for the thermostat remained the same as in the NpT runs. The trajectories were analyzed with the TRAVIS software [40,41].

3. Results and discussion

The results are presented and discussed in several sections. First, the properties of the polymer/lignin blends are described, followed by an analysis of the local processes taking place during deformation. Subsequently, the interactions between the components are evaluated quantitatively using two independent methods. Finally, the results obtained by these methods are interpreted with the help of molecular dynamics simulations.

3.1. Properties

Preparing polymer blends and composites is generally a cheap, simple, and efficient way to produce materials with beneficial properties. The characteristics and properties of polymer blends are determined by the quality of the components chosen, composition, the formed structure, and the interactions between the components [34,42,43]. The mechanical properties of ionomer/lignin blends were determined by tensile testing. Fig. 1 shows the Young's modulus of the blends as a function of lignin content. Stiffness increased significantly with increasing lignin content due to the aromatic structure and the strong ionic and hydrogen bonds acting within the lignin, which create particles with large stiffness [17,21,44–47]. In contrast, the methylene units provide flexibility for the molecular chains of the EAc copolymer and ionomers; the stiffness of the ionomer matrix is comparable to that of elastomers. The increase in modulus is very similar at different degrees of neutralization; thus, only one trend line has been drawn in Fig. 1. In this and the subsequent figures, the trend line indicates the general correlation, and is intended only to guide the eye.

The degree of neutralization influences the composition dependence of tensile strength (Fig. 2) especially at smaller lignin contents. The strength of the blends prepared from ionomers with 0 and 17 % degree of neutralization exhibit a minimum at 10 vol% lignin content (red line), while at other degrees of neutralization, only a slight minimum appears at 20–30 vol% (blue line). The presented lines are intended only to guide the eye. Although significant reinforcement was not achieved in either case, the strength of the blends was practically the same at 40–50 vol% lignin content as that of the matrix, which is very advantageous from the practical point of view. However, the deformability of the blends decreased monotonically with increasing lignin content (not shown), i.

Table 1

Composition, cell parameters of the cubic simulation boxes, and simulation times for the two blends modeled.

Blend	Number of molecules and ions included in the simulation boxes				Cell parameter (Å)	Simulation time (ns)
	Lignin	Ethylene-acrylic acid	Ethylene-acrylate	Sodium ion		
EAc/lignin	2	250	0	6	89.37	255
Ionomer/lignin	2	125	125	256	89.25	247

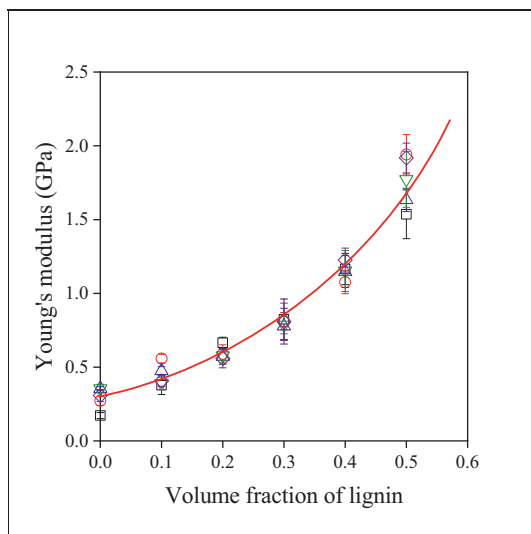


Fig. 1. Young's modulus of ionomer/lignin blends plotted as a function of lignin content. Degree of neutralization: (□) 0 %; (○) 17 %; (△) 33 %; (▽) 50 %; (◇) 67 %.

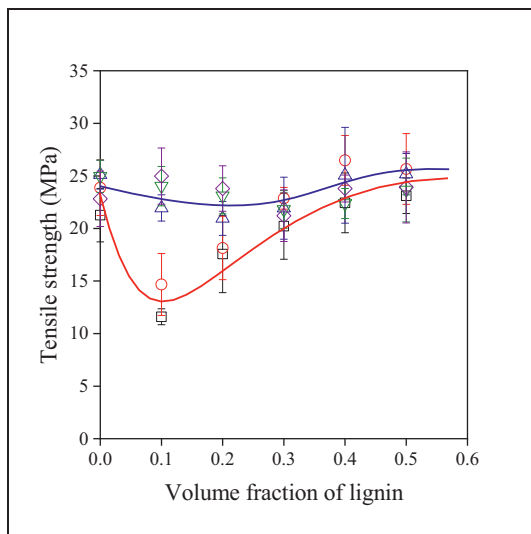


Fig. 2. Composition dependence of the tensile strength of ionomer/lignin blends. Degree of neutralization: (□) 0 %; (○) 17 %; (△) 33 %; (▽) 50 %; (◇) 67 %.

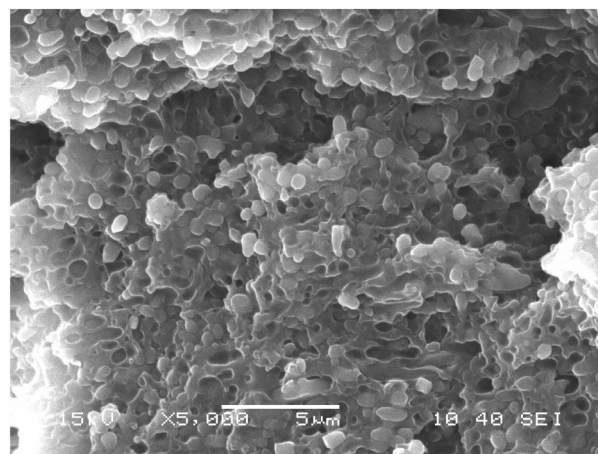
e., acceptable strength is accompanied by brittleness.

Although there is precedent for drawing conclusions regarding interactions directly from the composition dependence of the tensile strength of polymer blends and composites, this approach might be very misleading. In principle, we cannot draw conclusions about interactions between components from the composition dependence of modulus or other properties measured at small deformations either [48]. Accordingly, no attempt is made here to explain the effect of the degree of neutralization on the interactions developing between the components. It has been shown earlier [16–18,49–51] that only the use of appropriate models allows the estimation of the strength of interfacial adhesion. Moreover, due to the complexity of polymer systems, virtually all models use simplifying assumptions. For this reason, in our opinion, the best solution is to investigate blends and composites using several independent approaches and to draw final conclusions from their combined results.

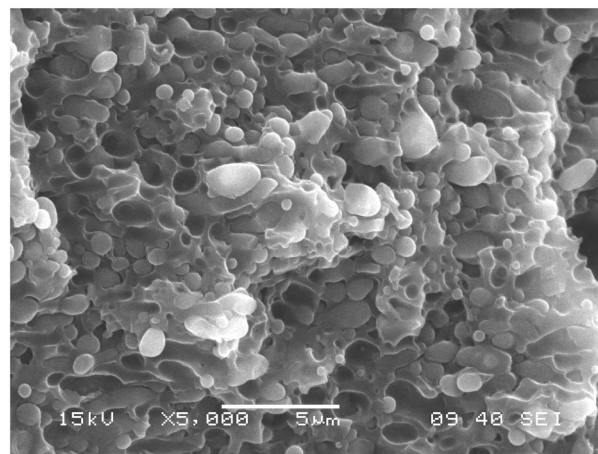
3.2. Local deformation processes

The deformation processes occurring at the microscopic level frequently cause the macroscopic failure of the materials under load. In polymer blends, the deformation processes are determined by the inherent strength of the components and interfacial adhesion. If the strength of the dispersed particles is smaller than the strength of interactions, the fracture of the particles is often observed. Conversely, the typical local deformation process is the separation of the matrix/dispersed particle interface, i.e., debonding, if interactions are weak. This suggests that particle fracture is often considered as evidence of strong and debonding as proof of weak interfacial interactions [52]. Fig. 3 shows electron micrographs of the fractured surface of ionomer/lignin blends. Both blends contained 30 vol% lignin, the degree of neutralization was 17 % for one ionomer matrix (Fig. 3a), and it was 50 % for the other (Fig. 3b). No fractured lignin particles appeared on the surfaces, only intact particles and cavities left behind. It is clear that the dominant deformation process during tensile testing was the separation of interfaces around lignin particles.

Local deformation processes can be monitored by detecting acoustic emission signals during tensile testing. Deformation processes initiated by the dispersed particles generate elastic waves with frequencies in the



a)



b)

Fig. 3. SEM micrographs demonstrating debonding in ionomer/lignosulfonate blends. Magnification: 5000×. Lignin content: 30 vol%. Degree of neutralization: a) 17 %, b) 50 %.

ultrasonic range, which a piezoelectric sensor can record. Usually, the dominant deformation process is identified by the simultaneous use of acoustic emission measurements and the microscopic analysis of fractured surfaces. With the microscope the actual process can be identified, but micrographs usually show only a small part of the sample. In contrast, acoustic emission measurements provide information about the entire sample indirectly. In the case of ionomer/lignin blends, SEM micrographs already provided clear evidence that the dominant deformation process was the separation of the interface between lignin and the ionomer. Thus, the results of acoustic emission measurements can be interpreted with their help. A typical acoustic emission pattern recorded during the tensile testing of an ionomer/lignin blend is shown in Fig. 4. 20 vol% lignin was dispersed in an ionomer with a 17 % degree of neutralization in the given sample. Circles represent individual signals, and their height is proportional to the amplitude of the waves generated during debonding. The solid blue line represents the cumulative number of acoustic events, i.e., the total number of events recorded up to a given deformation, and the red line shows the stress vs. deformation curve. Debonding is characterized by a step-like curve; the processes take place in a relatively narrow deformation and stress range. In Fig. 4, a large number of signals generated by debonding appeared in a short time at the start of the tensile test, and the curve of cumulative number of events rose steeply. At larger deformations, acoustic signals became less frequent as the interfaces have separated around most particles. At this stage, mainly the cavities expanded around debonded lignin particles, which did not produce further detectable acoustic signals. Consequently, the cumulative number of events corresponds to a saturation function.

Previous studies on ionomer/lignin blends reported strong interfacial interactions between the components [16,17]. In contrast, at the beginning of this section, we stated that debonding usually implies weaker interactions, i.e., an explanation is needed here. In spite of strong ionic and hydrogen bonds, lignin formed a separate phase in the polymer matrix. However, the diameter of dispersed lignin particles was around 1 μm (Fig. 3.), indicating the formation of strong interactions between the ionomer and lignin. In comparison, in polyethylene, in which only weak van der Waals interactions can develop between the components at most, the diameter of the dispersed lignin particles is 10–20 μm [16,53]. The size of dispersed lignin particles gave some indications about the interactions developing between lignin and the

matrix polymer, although particle size is influenced also by processing conditions. Despite the strong interactions, interfacial adhesion was still weaker than the inherent strength of lignin particles. The diameter of dispersed particles was very small; thus, the number of defects initiating fracture was also small. Moreover, ionic and hydrogen bonds among lignin molecules resulted in large inherent strength, which was definitely larger than the strength of interfacial adhesion. Accordingly, debonding dominated over the fracture of lignin particles.

3.3. Interfacial adhesion

Examining the number of events registered during tensile test as a function of the elongation, the characteristic deformation and stress values where the emission processes occur can be determined. Assuming that each acoustic emission signal is generated by the separation of an interface surrounding a particle, we can easily read off the corresponding debonding stress (σ^D) from the stress vs. deformation curve in the way shown in Fig. 4 (see red signal). The interface around a lignin particle separates when the external stress reaches σ^D , defined by Eq. (1)

$$\sigma^D = -C_1\sigma^T + C_2\left(\frac{EW_{AB}}{d}\right)^{1/2} \quad (1)$$

where σ^T is the thermal stress, E is matrix modulus, W_{AB} is the reversible work of adhesion, d is the diameter of the lignin particle, and C_1 and C_2 are constants [54]. Thus, debonding stress σ^D can be calculated even from particle size using Eq. (1). In blends and composites, the particle size of the dispersed component has a specific distribution. Fig. 5 shows the particle size distribution of lignin in a blend containing 20 vol% lignin in the ionomer matrix with a 17 % degree of neutralization. Debonding stress distribution can be derived from the particle size distribution using Eq. (1), if all the required parameters are known.

The $C_1\sigma^T$ and $C_2(EW_{AB})^{1/2}$ terms cannot be calculated from the characteristics of individual particles because of the lack of sufficient degrees of freedom; however, they can be determined by iteration. The $C_1\sigma^T$ term was assumed to be the same for all matrices, while different $C_2(EW_{AB})^{1/2}$ terms were determined at each degree of neutralization by minimizing the sum of squares of the difference between the distribution of debonding stresses calculated from Eq. (1) and the distribution of σ^D determined by acoustic emission. The distributions of the measured (red line) and calculated (blue line) σ^D values are shown in Fig. 6 for the lignin/ionomer blend having a matrix with a degree of neutralization of 17 %. The agreement between the calculated and measured distributions

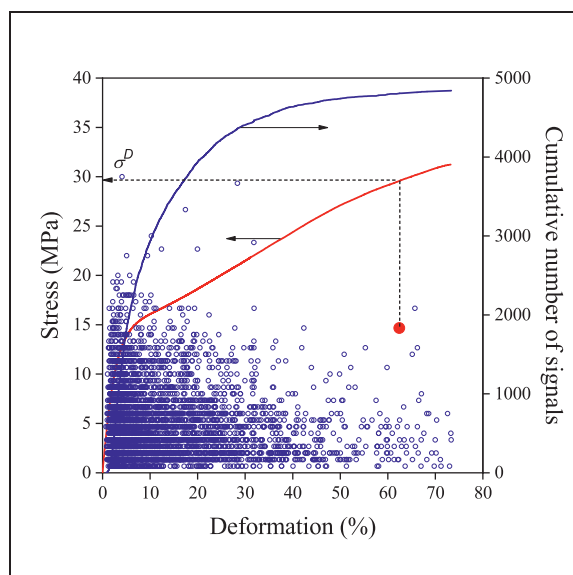


Fig. 4. Determination of the debonding stress from acoustic emission testing demonstrated by the example of a selected signal (see red dot). Degree of ionomer neutralization: 17 %. Lignin content: 20 vol%.

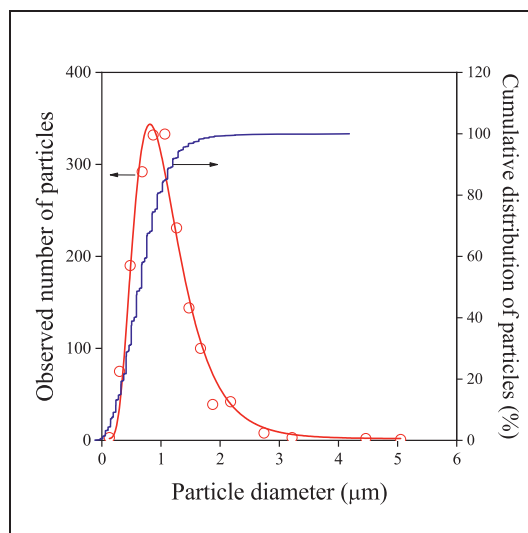


Fig. 5. Particle size distribution of lignin dispersed in an ionomer/lignin blend. Degree of neutralization: 17 %. Lignin content: 20 vol%.

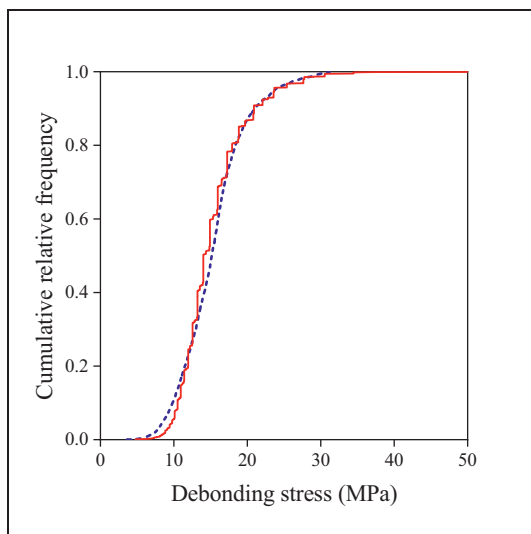


Fig. 6. Comparison of the distribution of debonding stresses determined by acoustic emission testing (—) and calculated from particle size distribution (---). Degree of neutralization: 17 %. Lignin content: 20 vol%.

is excellent. The discrepancies between the two correlations may be due to the simplifying assumptions used and the uncertainties in the determined particle size distribution.

The values obtained by the least squares method are summarized in Table 2. The value of the $C_2(EW_{AB})^{1/2}$ term decreased monotonically with increasing degree of neutralization, as shown by Fig. 7. If we assume that the C_2 constant is the same and matrix modulus does not change significantly with the degree of neutralization, the results show the decrease of W_{AB} with increasing neutralization. This may seem surprising at first, since one would expect an increase of electrostatic interactions with an increasing number of ions in the matrix polymer. Because of this unexpected result, the effect of neutralization on interfacial adhesion had to be verified by another approach as well.

3.4. Reinforcement, stress transfer

Component interactions in polymer blends and composites strongly influence mechanical properties determined at large deformations. Using a previously established model, the interactions between components can be estimated quantitatively from either yield stress, tensile strength, or impact resistance [50,55,56]. The relationship between the true tensile strength (σ_T) of polymer blends and their composition is expressed by Eq. (2) [50].

$$\sigma_T = \sigma_{Tm} \lambda^n \frac{1 - \varphi}{1 + 2.5\varphi} \exp(B\varphi) \quad (2)$$

where σ_{Tm} is the true tensile strength of the matrix, λ is the relative elongation of the blend, n is the strain-hardening factor defined for the matrix, φ is the volume fraction of lignin, and B is the load carrying capacity of the dispersed phase, which expresses the degree of reinforcement. The transformation of Eq. (2) yields the reduced tensile

Table 2

Quantities characterizing debonding stress in ionomer lignin blends calculated from Eq. (1).

Degree of neutralization (%)	$C_1\sigma^T$ (MPa)	$C_2(EW_{AB})^{1/2}$ (MPa $\mu\text{m}^{1/2}$)
0	2.7	18.3
17		16.8
33		12.8
50		12.3
67		11.1

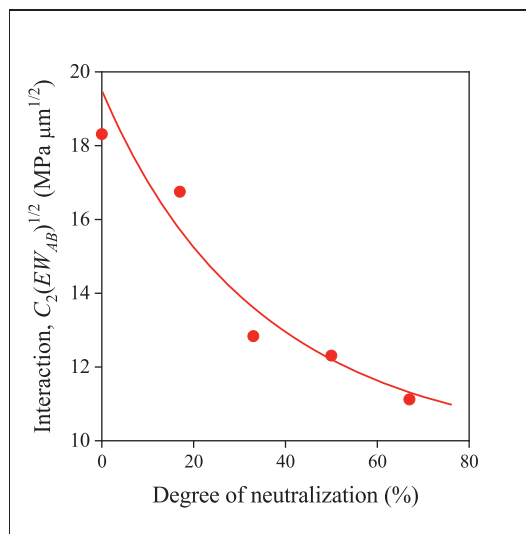


Fig. 7. Effect of the degree of neutralization on the term containing the reversible work of adhesion [$C_2(EW_{AB})^{1/2}$, Eq. (1)].

strength (σ_{Tred})

$$\ln\left(\sigma_T \frac{1 + 2.5\varphi}{1 - \varphi} \frac{1}{\lambda^n}\right) = \ln(\sigma_{Tred}) = \ln(\sigma_{Tm}) + B\varphi \quad (3)$$

depending linearly on the volume fraction of the second component. If we plot the natural logarithm of relative tensile strength against the volume fraction of the dispersed component, the slope of the straight line is proportional to the load-bearing capacity of the second component, i.e., the dispersed lignin particles, and under certain conditions to the strength of interactions. The tensile strengths of the blends prepared from the ionomer with a 17 % degree of neutralization were plotted in the representation of Eq. (3) in Fig. 8, and a least squares line was fitted to the data. The calculations were carried out for all matrices, and the results are summarized in Table 3. The determination coefficient characterizing the quality of the fit was above 0.98 in all cases, and the value of parameter B decreased from 6.40 to 5.54 with increasing degree of neutralization. In a previous study, parameter B was compared in different polymer/lignin blends. Interactions were weak in the polypropylene blends generated only by weak dispersion forces, resulting in

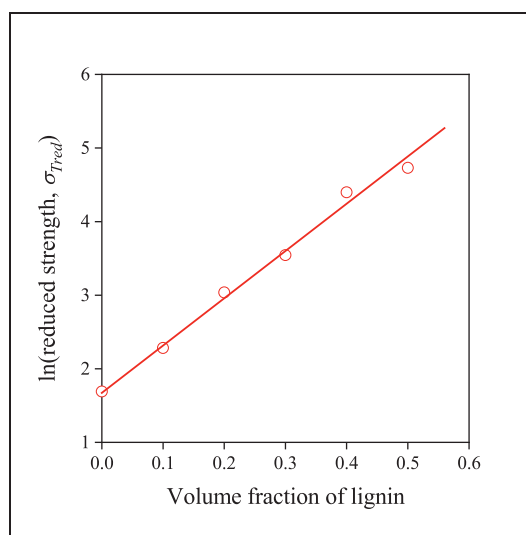


Fig. 8. Tensile strength of ionomer/lignin blends plotted against lignin content in the representation of Eq. (3). Degree of neutralization is 17 %.

Table 3

Load bearing capacity of lignin (Parameter B) and stress transfer coefficient ($C\sigma_{Td}$) characterizing interactions in ionomer/lignin blends.

Degree of neutralization (%)	Matrix strength (MPa)		B	R^{2b}	$C\sigma_{Td}$
	measured	calculated ^a			
0	21.3 ± 2.5	22.8 ± 6.5	6.40	0.9807	67,800
17	23.9 ± 2.7	24.8 ± 5.8	6.30	0.9920	65,400
33	25.1 ± 1.4	26.3 ± 5.3	6.03	0.9904	43,700
50	25.0 ± 1.5	25.9 ± 5.0	5.86	0.9932	32,000
67	22.8 ± 2.6	25.3 ± 4.4	5.64	0.9923	22,000

^a Calculated from the intersection of the $\ln(\sigma_{Tred})$ vs. φ lines (see Eq. (3) and Fig. 8).

^b Determination coefficient indicating the quality of the fit.

a smaller parameter B value (0.74). The presence of aromatic interactions (polystyrene, $B = 1.48$), hydrogen bonds (poly (methyl methacrylate), $B = 1.55$) or hydrogen bonds and aromatic interactions (glycol modified poly(ethylene terephthalate), $B = 1.76$) resulted in increasing parameter B values. However, this comparison must be treated with care since parameter B depends also on the properties of the matrix [17].

The value of parameter B does not depend only on interactions but also on the relative strength of the components, as described by Eq. (4) [51]

$$B = \ln\left(\frac{C\sigma_{Td}}{\sigma_{Tm}}\right) \quad (4)$$

where σ_{Td} is the true strength of the dispersed phase, and C is the stress transfer coefficient, which can be directly related to interfacial interactions. Accordingly, interfacial interactions estimated by parameter B can be compared only for blends for which the relative strength of the components is approximately constant. This condition is more or less valid for the ionomer/lignin blends studied here. The stress transfer coefficient C offers a more reliable estimate of interfacial interactions than parameter B . According to Eq. (5), parameter C is inversely proportional to the Flory-Huggins interaction parameter χ [51]

$$C = \frac{K}{\chi} \quad (5)$$

where K is a proportionality factor. The equation implies that smaller Flory-Huggins interaction parameters, i.e., better miscibility of the components lead to larger stress transfer coefficients. Unfortunately, parameter C cannot be derived from Eq. (4), since the tensile strength of lignin was not known. If we assume that the tensile strength of lignin was constant in the blends, then the value of $C\sigma_{Td}$ showed the effect of neutralization on stress transfer and thus on interactions. According to the last column of Table 3, $C\sigma_{Td}$ decreased significantly with an increasing degree of neutralization. The tendency is demonstrated by Fig. 9. Accordingly, the calculation of the stress transfer coefficient C also confirmed that the ionomers formed weaker and weaker interactions with lignin with an increasing degree of neutralization. To understand this unexpected phenomenon, interactions developing in the ionomer/lignin blends were analyzed by molecular dynamic calculations as well.

3.5. Molecular dynamics, interactions

EAC/lignin and ionomer/lignin periodic model systems were set up and studied by molecular dynamics simulations. One of the key questions to answer was whether sodium ions interact with the sulfonate

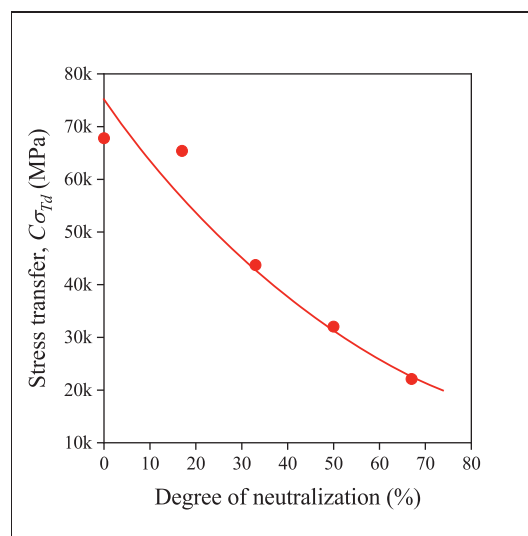


Fig. 9. The effect of neutralization on the stress transfer between the components ($C\sigma_{Td}$).

groups of lignin and the carboxylate groups of the copolymer. Thus, the resulting trajectories were analyzed in terms of combined distribution functions, representing the simultaneous occurrence of distances between chosen atoms in a heat map. The sodium ion was selected as the reference particle, and the distances to the oxygen atoms in the sulfonate groups of lignin, $O(SO_3)$, the oxygen atoms in the carboxyl group of the ethylene-acrylic acid copolymer chain, $O(\text{Carboxyl})$, and the oxygen atoms in the carboxylate group of the ethylene-acrylate copolymer chain, $O(\text{Carboxylate})$ were calculated in the process. Fig. 10 shows the resulting plots and presents the heat maps of the $Na \cdots O(\text{Carboxyl})$ vs. $Na \cdots O(SO_3)$ distance on the top (Fig. 10a and b), and the $Na \cdots O(\text{Carboxylate})$ vs. $Na \cdots O(SO_3)$ distance on the bottom (Fig. 10c). A strong correlation can be seen at distances of around 250 pm in all cases. This result indicates that the sodium ion takes part in the formation of salt bridges between the SO_3 group of lignin and the acrylate units of the ionomers, and the interactions between the SO_3 group of lignin and the acid groups of the copolymer can also be mediated by a sodium cation.

Fig. 10 reveals that the $O(SO_3) \cdots Na \cdots O(\text{Carboxyl})$ arrangement is less frequent in the ionomer/lignin system (Fig. 10b) than in the EAC/lignin blend (Fig. 10a). However, the probability for the occurrence of an $O(SO_3) \cdots Na \cdots O(\text{Carboxylate})$ arrangement is much larger than that of the $O(SO_3) \cdots Na \cdots O(\text{Carboxyl})$ interaction. These observations indicate that sodium cations preferably take part in salt bridges. The three-body analysis of combined RDFs corroborated our initial hypothesis that ionic interactions must develop between lignin and the ionomers. However, it did not explain the deteriorating effect of EAC neutralization on the interfacial adhesion between the blend components.

The blends investigated here have an amphiphilic character, as the polar carboxyl and carboxylate groups are attached to a non-polar chain. In contrast, the lignosulfonate particles have sulfonyl and other polar groups as well. A well-known behavior of amphiphilic liquids, e.g., ionic liquids [57], is their separation into microphases, in which the polar and nonpolar parts aggregate to form a microheterogeneous structure. Since the basic building blocks for such a nanostructural organization can also be recognized in the present blends, one must consider whether microphases also form in this case. One way to characterize such behavior and the possible aggregation of different species in a trajectory is based on Voronoi analysis [58]. The Voronoi analysis starts by assigning all points in space to an atom, based on a distance criterion that also considers the van der Waals radii of the atoms. In turn, a cell for each atom will be defined by the points assigned to the given atom. The volume and surface of these atomic Voronoi cells and the contact area to

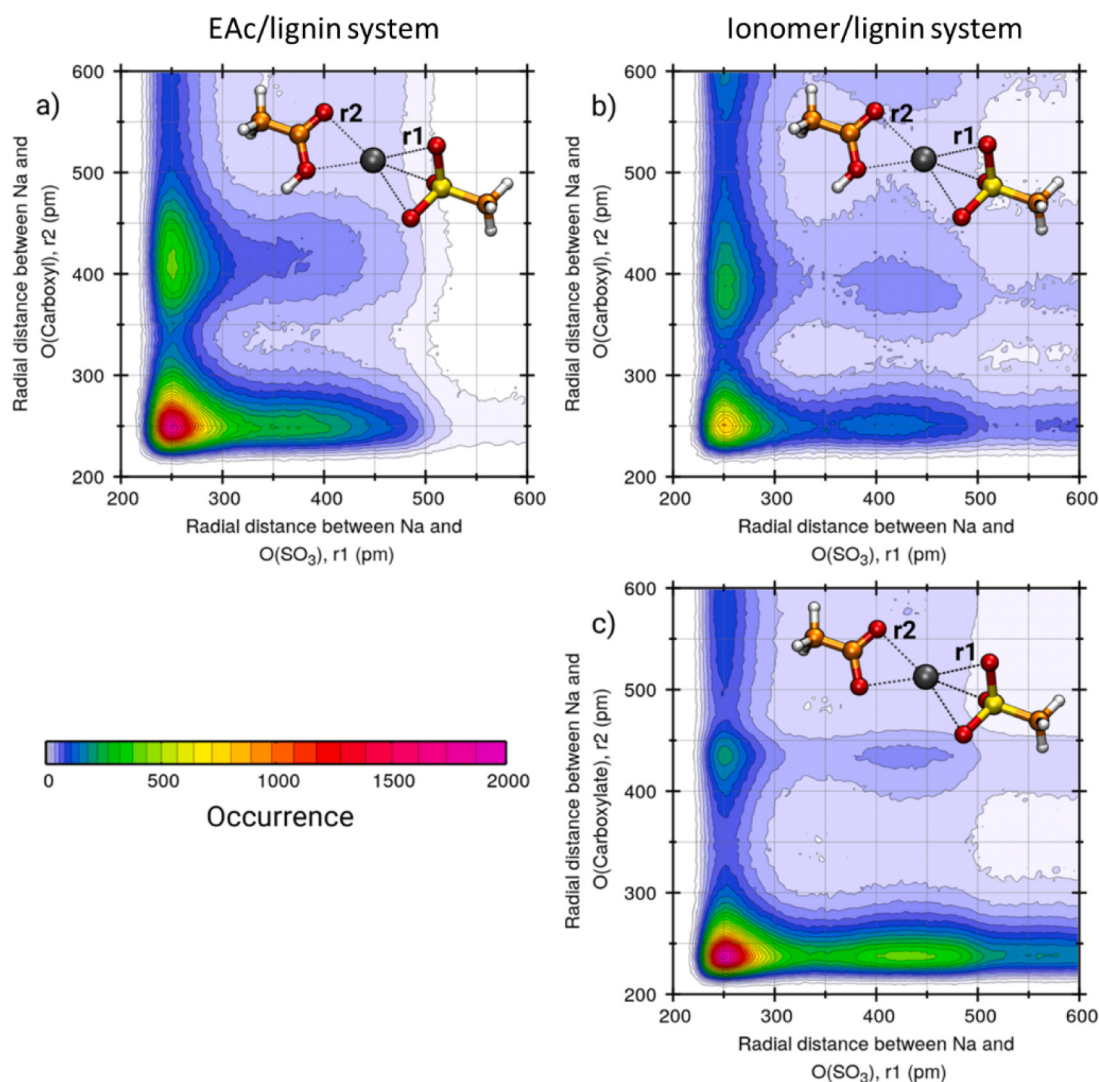


Fig. 10. Combined radial distribution functions obtained by three-body analysis: a) Na⁺···O(Carboxyl) vs. Na⁺···O(SO₃) in EAc/lignin; b) Na⁺···O(Carboxyl) vs. Na⁺···O(SO₃) in ionomer/lignin; c) Na⁺···O(Carboxylate) vs. Na⁺···O(SO₃) in ionomer/lignin.

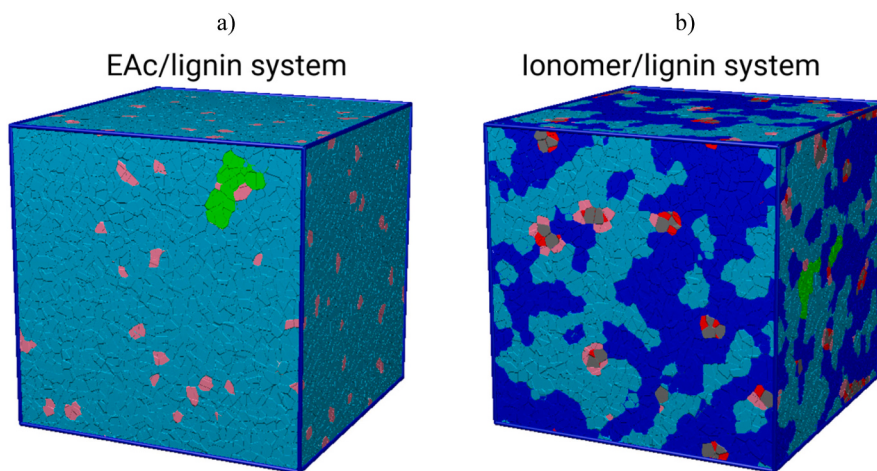


Fig. 11. Voronoi decomposition of simulation boxes: a) EAc/lignin system; b) ionomer/lignin system. Colour code: green: atoms of lignin molecules; red: carboxylate groups of the ethylene-acrylate copolymer; pink: carboxyl groups of the ethylene-acrylic acid copolymer; dark blue: carbon chain of the ethylene-acrylate copolymer; light blue: carbon chain of the ethylene-acrylic acid copolymer; gray: sodium ions.

the neighboring atoms, with which the cells share at least one face, are valuable information regarding the structure of the system.

Voronoi analysis was performed on both model blends. Coloring all atoms of the lignin molecules green, all sodium cations gray, the carboxylate groups of the ethylene-acrylic acid copolymer red, the carboxyl groups of the ethylene-acrylic acid copolymer pink, the carbon chain of the ethylene-acrylate copolymer dark blue, and the carbon chain of the ethylene-acrylic acid copolymer light blue, the snapshots presented in Fig. 11 can be obtained. A striking difference can be observed between the two blends when the Voronoi cells belonging to the carboxylate and carboxyl groups, i.e., the pink and red entries, are compared. The number of such cells is much larger in the EAc/lignin system, indicating a much more dispersed distribution of these groups. The number of pink and red areas is substantially smaller in the ionomer/lignin blend, and the association of sodium cations with the carboxyl and carboxylate groups can be observed as well. This observation clearly supports the assumption that the clustering of the polar copolymer parts increases with an increasing degree of neutralization. The formation of such clusters is a well-known fact in the world of ionomers [27–29,31,59].

Using the results of the Voronoi analysis, domain analysis can quantify the distribution of the different subsets within a simulation. As the Voronoi analysis determines which atomic cells are in contact with each other, this information can be used to partition the system into so-called domains. First, the atomic cells, which consist of the atoms that belong to the same domain, e.g., all carbon and hydrogen atoms of all non-polar moieties, are grouped into subsets. If two atoms from the same subset share a common Voronoi face, they belong to the same domain [58]. Accordingly, a small number of domains indicates the clustering of the respective species, while a large number indicates that the respective species are dispersed and widely distributed within the simulation box.

Two different domain analyses have been carried out. Only two subsets were defined in the first, one of them including the polar units and the other containing the nonpolar parts of all molecular species. The sulfonate groups of lignin, the carboxyl and carboxylate groups of the copolymers, as well as all sodium cations have been chosen as polar components. All other parts of the molecules are assigned to the nonpolar subset. Each molecular species defined a subset in the second domain analysis, i.e., all lignin molecules, all sodium cations, as well as all ethylene-acrylic acid and ethylene-acrylate copolymers, belonged to a different subset.

Table 4 summarizes the number of domains obtained from the analyses and the averaged domain volumes. The first set shows that the number of polar domains is considerably smaller in the ionomer/lignin system than in the EAc/lignin blend. This is quantitative proof of cluster formation in ionomers. Another interesting difference is the number of lignin domains in the two blends. The two lignin molecules remain separated in the EAc/lignin system; in the ionomer/lignin blend, they form a single domain. This result implies that the blend is in a thermodynamically more stable state if the lignin molecules interact with each other. A possible driving force for phase separation is the preference of carboxylate groups to form clusters in the ionomer phase. As a consequence, lignin molecules are rejected from the phase. Because the carboxylate groups of the ionomer are present in larger numbers in the clusters than at the interface and the reduced number of carboxyl groups allows the formation of less hydrogen bonds between the components, an increasing degree of neutralization results in ionomers with more and more self-interactions deteriorating ionomer-lignin interactions. Consequently, the role of hydrogen bonds is more critical in determining blend properties presented in this study.

4. Conclusions

The functional groups of ionomers and lignosulfonate are capable of forming hydrogen and ionic bonds; thus, in their blends, strong interactions form at the interface between the components. The effect of

Table 4

Domain analysis of phase separation in ionomer/lignin blends.

Blend	First domain analysis		Second domain analysis			
	Polar	Nonpolar	Lignin	Ethylene-acrylic acid	Ethylene-acrylate	Sodium
EAc/lignin	265.4	1.0	2.0	1.0	–	4.6
Ionomer/lignin	77.4	1.0	1.0	1.0	1.0	53.7

the competition between hydrogen and ionic bonding has been studied through the correlation of local deformation processes, structure, and the composition dependence of tensile strength in blends containing an industrial lignosulfonate and ionomers prepared from an ethylene-acrylic acid copolymer neutralized with sodium carbonate in different ratios. The results were analyzed quantitatively using appropriate models. Contrary to the expectations, if the acid groups in the ionomer matrix are neutralized to a larger extent, i.e., the number of carboxylate groups increases, the interactions are weaker than in the acrylic-acid copolymer/lignin blends. Molecular dynamics simulations indicate that ionic moieties in the components strongly interact with each other; thus, decreasing interfacial adhesion may be caused by other factors. The Voronoi and domain analysis performed on the results of molecular dynamic simulations showed that the ionomer rejects lignin molecules because of increased self-interactions of the components. A reduced number of carboxyl groups in the ionomer allows the formation of less hydrogen bonds between the ionomer and lignin. The carboxylate groups of the ionomer are present in larger numbers in the clusters than at the interface between the components. Consequently, the optimization of the degree of neutralization and thus interactions allow the production of structural materials from ionomer/lignin blends containing about 30 vol% lignin, which possess an acceptable combination of modulus, tensile strength, and elongation-at-break.

CRedit authorship contribution statement

Emese Pregi: Investigation, Data curation, Visualization, Writing – review & editing. **Jan Blasius:** Conceptualization, Resources, Visualization, Writing – original draft, Project administration. **Dávid Kun:** Validation, Investigation, Writing – original draft. **Oldamur Hollóczki:** Validation, Investigation, Writing – original draft. **Béla Pukánszky:** Conceptualization, Validation, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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