

# International Journal of Biological Macromolecules

Volume 107, Part A, February 2018, Pages 1203-1211

<https://doi.org/10.1016/j.ijbiomac.2017.09.098>

## Hydrogen bonding interactions in poly(ethylene-co-vinyl alcohol)/lignin blends

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## **Abstract**

Blends were prepared from lignin and ethylene-vinyl alcohol (EVOH) copolymers to study the effect of hydrogen bonding interactions on compatibility and structure. The vinyl alcohol (VOH) content of the copolymers changed between 52 and 76 mol%, while the lignin content of the blends varied between 0 and 60 vol%. Low density polyethylene (LDPE) with 0 mol% VOH content was used as reference. The components were homogenized in an internal mixer and they were characterized by various methods including Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The results of the experiments proved that strong hydrogen bonds form between the two components shown by FTIR spectroscopy, a shift in the relaxation temperatures of the matrix polymer and by the decrease of crystallite size and crystallinity with increasing lignin content. In spite of the strong interactions, heterogeneous structure forms in the studied blends since self-interactions within the neat components are also very strong. The size of dispersed lignin particles is determined by competitive interactions in the blends; stronger EVOH/lignin interactions result in smaller particle size. Although hydrogen bonds are very strong, miscible polymer/lignin blends can be prepared only by applying other approaches like plasticization or chemical modification.

**Keywords:** lignin blends; Flory-Huggins interaction parameter, quantitative analysis

## 1. Introduction

After cellulose, lignin is the second most abundantly available natural polymer [1]. It is a basic constituent of all lignocellulosic materials and industry produces it in increasing amounts as a side product of cellulose and bioethanol production [2]. The chemical structure and properties of lignin depend very much on the extraction technology (e.g. Kraft, sulfite, organosolv, steam explosion) used for its production. The major part of Kraft lignin is used to produce energy [3], while liginosulfonates are applied in a variety of niche areas [4-8], but in much smaller amounts. Because of its quantity and being a side product, lignin is inexpensive thus using it in any value added application would result in considerable economic advantage. Blending with polymers could be a potential application and a large number of papers can be found in the open literature about the structure, interactions and properties of polymer/lignin blends [9-22].

Experiments carried out with polypropylene (PP)/lignin blends showed that the weak dispersion interactions developing in such blends result in dispersed structure, large lignin particles and poor properties [23]. Although interfacial interactions could be improved by the use of a coupling agent, the miscibility of the components did not improve much. Polymers containing aromatic moieties formed much stronger interactions with lignin [24]. The size of dispersed lignin particles decreased and properties improved considerably because of the formation of aromatic,  $\pi$ -electron interactions. However, differences were considerable in the structure and properties among the three polymers, i.e. polystyrene (PS), polycarbonate (PC) and poly(ethylene-terephthalate (PET) used as matrix in the study. These results indicated that the possibility of forming hydrogen bridges further improves the compatibility of the components.

Numerous papers have been published on blends prepared from lignin and polymers capable of forming H-bonds. The conclusions about interaction, miscibility and structure are often

rather contradictory or surprising like in the case of PVC/lignin blends. Feldman et al. [25-30] studied these blends quite extensively. In their first paper they reported the appearance of two glass transitions on the DSC traces, one of which disappeared after annealing at higher temperature [25]. Although the authors mention the likelihood of homogeneous PVC/lignin blends, they do not claim miscibility definitely in this and in their subsequent papers even when they used plasticized PVC for better dispersion. In spite of the detailed studies and conclusions of Feldman et al. [25-30], El-Raghi et al. [31] came to the conclusion that PVC and lignin are miscible as a result of interactions between the  $\alpha$  hydrogen of PVC and the hydroxyl groups of lignin. The development of hydrogen bridges was observed also in the blends of lignin and several biopolymers such as poly(lactic acid) (PLA), polyhydroxybutyrate (PHB) and poly(butylene adipate-co-terephthalate) (PBAT). PLA seems to be immiscible with lignin [32-34], but based on SEM micrographs, Ouyang et al. [35] claimed the formation of a homogeneous, single-phase structure in their blends. PHB was claimed to form miscible blend up to 40 wt% lignin content, but phase separation occurs at large concentrations [36,37]. Since the chemical structure of these biopolymers is quite similar, their dissimilar behavior in the blends is rather surprising. The compatibility of PBAT with lignin is better because the two polymers can form also  $\pi$  electron interactions [33]. Miscibility was claimed for other polymers as well. Liu et al. [38,39] found that poly(vinyl pyrrolidone) is miscible with lignin. A similar conclusion was drawn about polyaniline/lignin blends by Rodrigues et al. [40] by the analysis of Fourier transform infrared (FTIR) spectra and the results of cyclic voltammetry, but unfortunately, SEM micrographs recorded on their samples clearly indicated the formation of heterogeneous structure, the presence of lignin particles. Another polymer found to be miscible with lignin was poly(ethylene oxide) (PEO). Based on FTIR spectra and the composition dependence of the glass transition temperature ( $T_g$ ) of the blends Kadla and Kubo [41-45]

concluded that miscibility is the result of the formation of H-bonds. As the ether groups of PEO form H-bridges only with the hydroxyl and carboxyl groups of lignin, polymers containing hydrogen-donor groups in large numbers should be able to form even more hydrogen bonds with lignin. Poly(vinyl alcohol) contains numerous hydroxyl groups capable of donating hydrogens to the oxygen-containing functional groups of lignin, thus it is expected to be miscible, but at least compatible with lignin. Quite a few studies have been carried out on this combination of materials and most of the authors concluded that they form heterogeneous blends [43,46-49], which contradicts the expectations and is quite surprising.

In view of our previous results on polymer/lignin blends [23,24] and the contradictory information related to interaction and miscibility, as well as to the role of hydrogen bonds in the determination of structure and properties in such blends, we decided to study this question more in detail. We prepared EVOH/lignin blends in a wide range of lignin contents. In order to study the effect of H-bonds quantitatively, we changed the vinyl alcohol content of the copolymers from 52 to 76 mol%. Several approaches were used for the estimation of the strength of interactions, and both structure and interactions were analyzed quantitatively. Conclusions about the significance of hydrogen bonding interactions are drawn in the last section of the paper, in which consequences for practice are also mentioned.

## **2. Experimental**

### *2.1. Materials*

The type, source and most important characteristics of the polymers used in the experiments are summarized in **Table 1**. The ethylene-vinyl alcohol copolymers supplied by Kuraray Europe GmbH had various vinyl alcohol content in order to study the effect of hydrogen bonds quantitatively. Low density polyethylene (MOL Group, Hungary) with zero amount of vinyl

alcohol was used as a reference. The lignosulfonate sample was kindly supplied by the Burgo Group, Italy. The Bretax SRO2 grade is a product in which sugar content was reduced; the counter ion of the sulfonate groups is sodium. The lignin used has small molecular weight (number average molecular mass 2260 g/mol) and it contains various amounts of inorganic salts and a small amount of remaining reducing sugars. Whenever in further discussion lignin is mentioned, we always mean lignosulfonate under this term. The amount of lignin in the blends was changed from 0 to 60 vol% in 10 vol% steps.

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

Polymer	Grade	Vinyl alcohol (mol%)	Density (g/cm <sup>3</sup> )	Melt flow rate (g/10 min)
LDPE	Tipolen FA 244-51	0	0.92	0.3 <sup>a</sup>
Evoh52	Eval G156B	52	1.12	6.4 <sup>a</sup>
Evoh62	Eval H171B	62	1.17	1.7 <sup>a</sup>
Evoh68	Eval F101B	68	1.19	1.6 <sup>a</sup>
Evoh76	Eval M100B	76	1.22	2.2 <sup>b</sup>

a) 190 °C/2.16 kg

b) 220 °C/2.16 kg

## 2.2. Sample preparation

The components were homogenized in a Brabender W 50 EHT internal mixer at 220 °C set temperature, 42 cm<sup>3</sup> charge volume, 50 rpm and 10 min mixing time after the addition of lignin. Torque and temperature were recorded during mixing and used in further analysis. Plates of 1 mm and films of 100 µm thickness were compression molded at 220 °C using a Fontijne SRA 100 machine. The plates and films were stored for one week at room temperature (23 °C and 50 % RH) before further testing.

### *2.3. Characterization*

Interactions were estimated with different approaches. FTIR spectroscopy was applied to determine the functional groups in the films by using a Bruker Tensor 27 spectrophotometer in the wavelength range of 4000-400  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution with 16 scans. Relaxation transitions and glass transition temperature were determined by dynamic mechanical thermal analysis (DMA) on specimens with 60 x 5 x 1 mm dimensions between -150 °C and the melting of the sample at 1 Hz frequency, 10  $\mu\text{m}$  deformation and 2 °C/min heating rate. The equipment used was a Perkin Elmer Diamond DMA apparatus. The melting and crystallization of the LDPE and EVOH components were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 apparatus. The measurements were done in two heating and one cooling runs between 30 and 220 °C with heating and cooling rates of 10 °C/min. The weight of the samples was 3-5 mg in each case. The structure of the blends was analyzed by scanning electron microscopy (SEM) using a Jeol JSM 6380 LA apparatus. Thin slices were cut from the 1 mm thick plates using a Leica EM UC6 microtome at -120 °C for LDPE and -60 °C for EVOH blends, and then the lignosulfonate was dissolved from the slices by soaking them in distilled water for 24 hours at ambient temperature. The average particle size and particle size distribution of the dispersed lignin particles were determined by image analysis.

### **3. Results and discussion**

The results are presented and discussed in several sections. The effect of composition on the structure of the blends is shown in the first section, and then interactions are discussed in detail in the next one. Correlations between structure and interactions are analyzed quantitatively in the subsequent section followed by a discussion including relevance for practice.

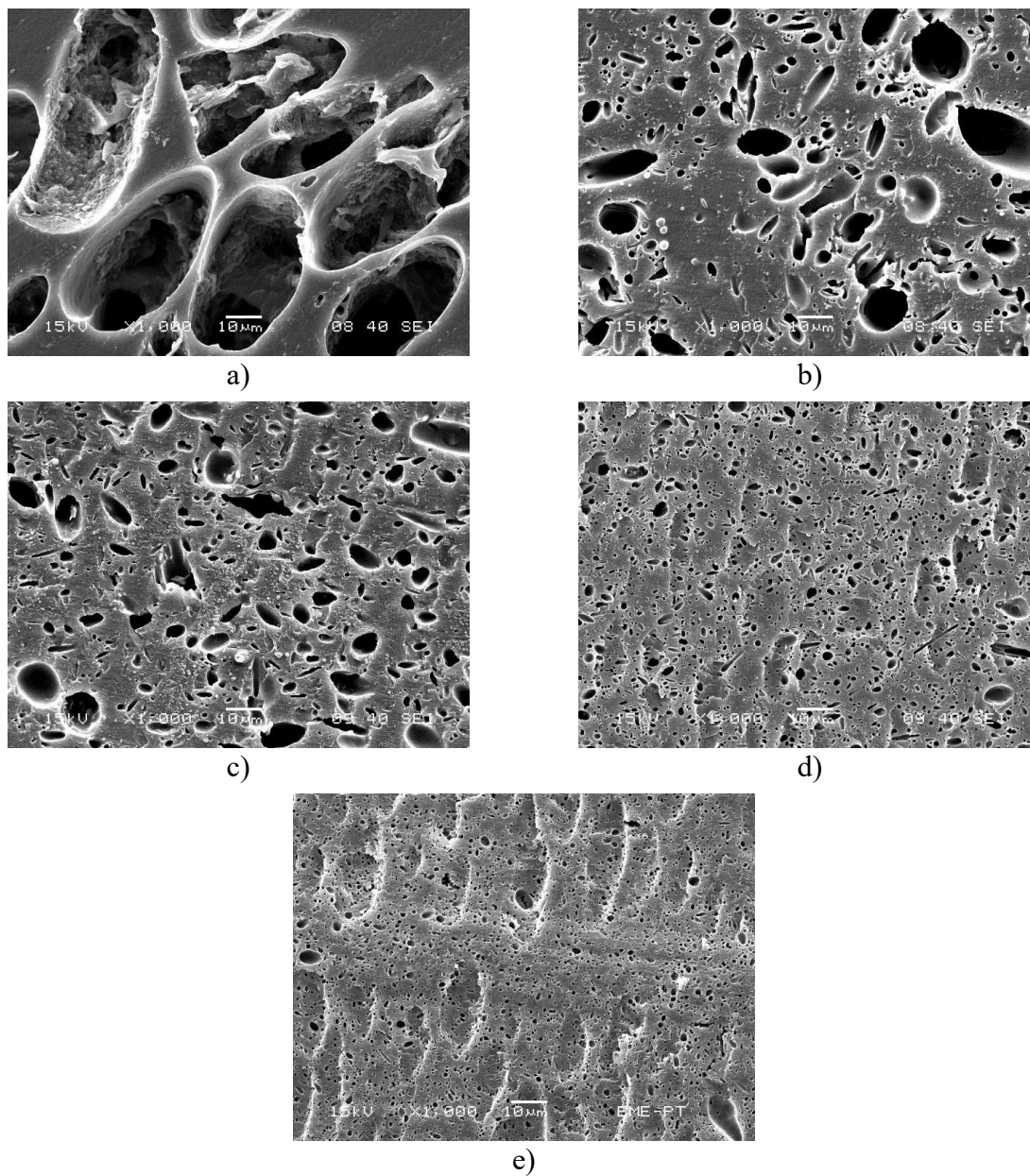
### 3.1. Structure

As described in the introductory part, the opinions on the structure of polymer/lignin blends differ considerably among groups and authors. Miscibility was claimed even for polyolefin/lignin blends [50], while heterogeneous structure was found for example for the PVOH/lignin pair [46-49] although both components of the latter are capable of forming strong hydrogen bonds with each other. Structure is a good indicator for interactions, since complete immiscibility leads to heterogeneous structure and dispersed particles of one component in the other, while complete miscibility to a homogeneous, one phase material. The effect of the vinyl alcohol content of the polymers on the structure of their blends with lignin is demonstrated in **Fig. 1** at 30 vol% lignin content. The figure allows the drawing of two important conclusions. It is completely clear that structure is heterogeneous in all cases, the matrix polymer contains dispersed lignin particles. On the other hand, the size of these particles decreases significantly with increasing vinyl alcohol content indicating that the number of OH groups and thus interactions influence structure considerably. We must also emphasize here that heterogeneous structure was observed in the entire composition range, phase inversion or co-continuous structure did not develop in any of the blends.

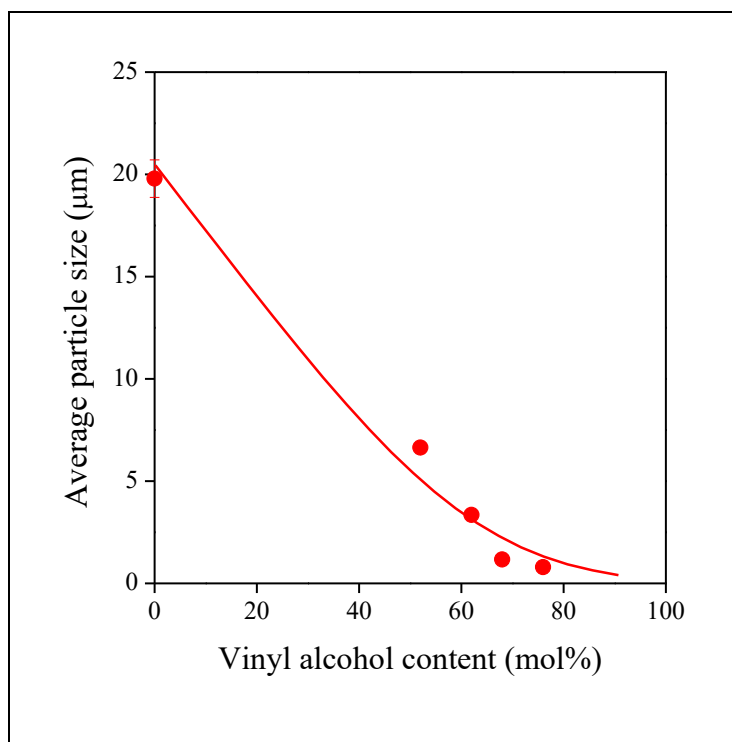
The qualitative observation is shown quantitatively in **Fig. 2** in which the average size of the lignin particles is plotted against the vinyl alcohol content of the polymers used as matrix. The considerable effect of OH content is clearly demonstrated by the figure. Since the original size of the lignin particles was around 80  $\mu\text{m}$ , they must have broken up during homogenization. However, the extent of attrition is very different. Quite large particles with a size of around 20  $\mu\text{m}$  form in polyethylene, while much smaller ones are present in the blend with large vinyl alcohol content. These results question very strongly the claims about the miscibility of polyolefins and lignin [50], on the one hand, and prove that hydrogen bonds are very efficient in increasing



compatibility and even resulting in partial miscibility, on the other. In accordance with our earlier experience, competitive interactions determine the structure and properties of polymer lignin blends [24], thus they must be investigated more in detail.



**Figure 1.** The structure of polymer/lignin blends at 30 vol% lignin content. Matrix polymer: a) LDPE, b) EVOH52, c) EVOH 62, d) EVOH 68, e) EVOH76.



**Figure 2.** Effect of vinyl alcohol content on the average size of dispersed lignin particles in polymer/lignin blends at 30 vol% lignin content.

### 3.2. Interactions

The strength of interactions can be estimated in various ways in polymer blends. Since EVOH forms hydrogen bridges with lignin, one obvious way is to follow changes in the absorbance of the hydroxyl groups between the wavenumbers of 3600 and 3300  $\text{cm}^{-1}$  and quite a few groups do that [33,35,38,41-45,47]. The peak usually shifts significantly with increasing amount of lignin in the blend, which is often regarded as a proof for the presence of hydrogen bonds between the components or even for the formation of a miscible blend. We recorded spectra on our EVOH/lignin blends and analyzed changes in the absorbance of the hydroxyl group at 4350  $\text{cm}^{-1}$  (the full spectra and the enlarged section of the hydroxyl vibration are included into the supplementary information). As shown by [Fig. 3](#), a shift was observed in the position of the peak indeed. However, this result must be treated with care, since deconvolution and mathematical

analysis revealed that the infrared spectrum of the blends is the practically the superposition of the spectra of the two components [2]. Both components contain hydroxyl groups, but in different environments, thus the corresponding absorption bands appear at different wavelengths leading to the shift observed. Consequently, we must need further proof and confirmation for the existence of strong interactions and for the estimation of their strength.

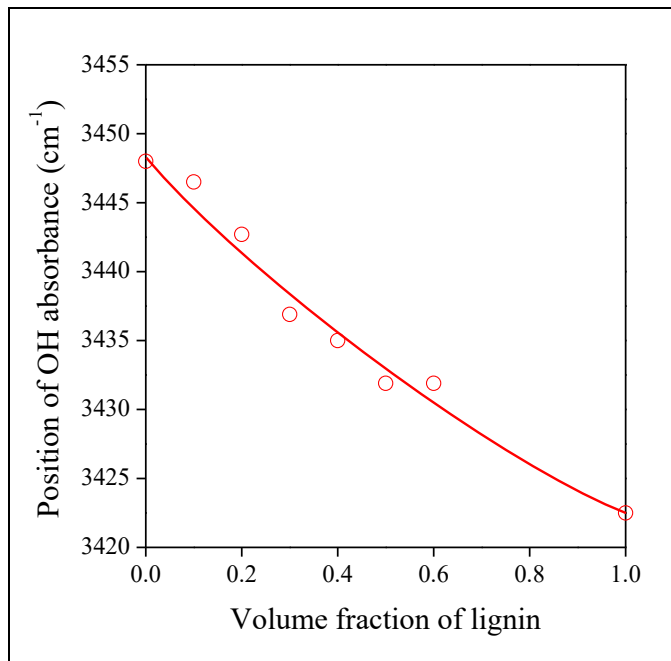
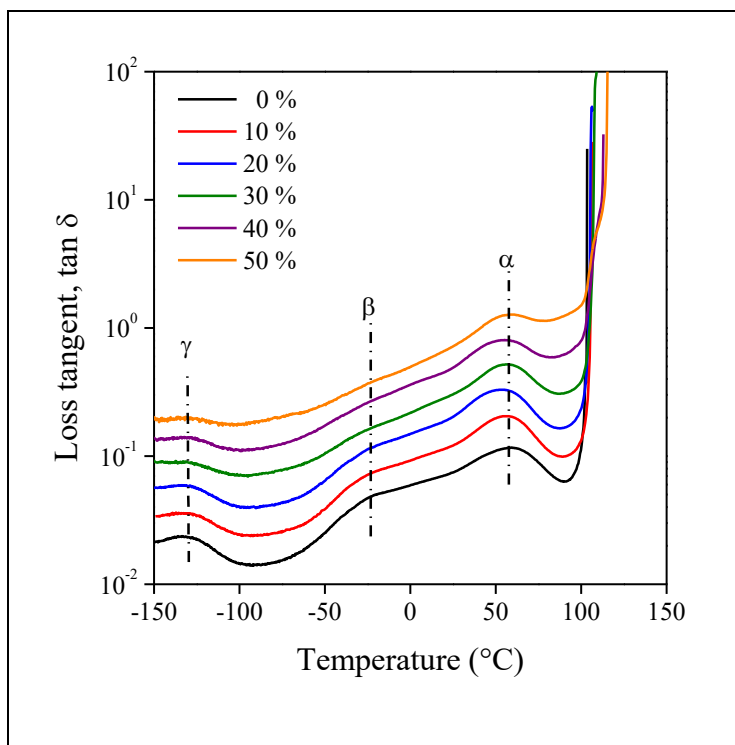


Fig. 3 Shift in the position of the absorbance of the hydroxyl groups in the region of 3420-3450  $\text{cm}^{-1}$ . Possible effect of hydrogen bonding interactions.

Strong interactions result in a shift in the temperature of relaxation transition of the components and usually a single transition is observed in the case of complete miscibility. Relaxation transitions and changes in them can be followed by dynamic mechanical analysis quite well. The temperature dependence of the loss tangent of LDPE/lignin blends is presented in Fig. 4. Three transitions can be observed in the spectra. The transition detected at the lowest temperature is assigned to the movement of methylene units [x], the one appearing at around -25

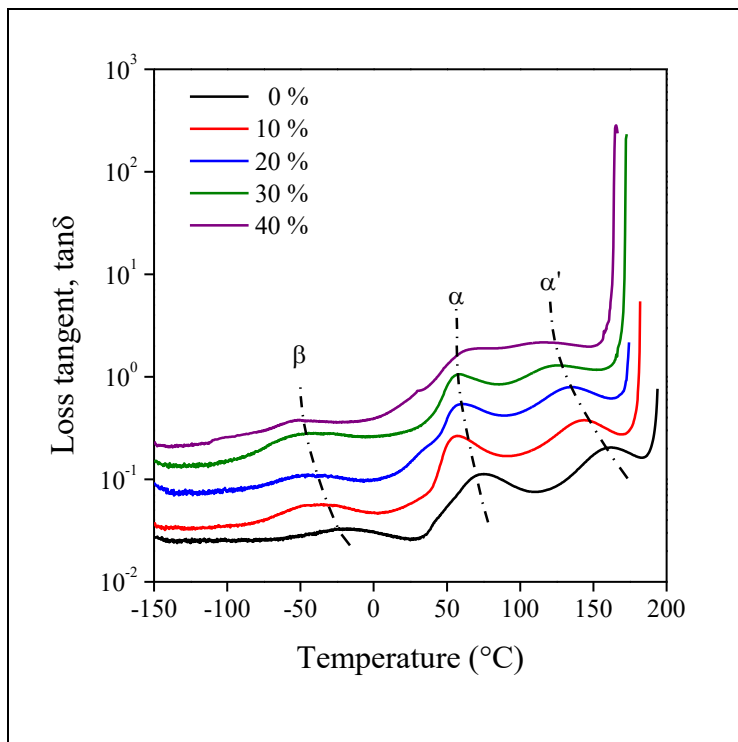
°C to that of chain branches [x], while the transition detected at the highest temperature is usually related to segments attached to the crystalline phase of polyethylene [x]. No transition can be associated with the lignin phase in spite of the fact that quite a few papers report glass transition temperatures for lignin [27,35,51-53]. These have been determined mostly by DSC, which is quite surprising since lignin molecules are small and very stiff, thus their mobility changes very little during the glass transition. We could not detect a  $T_g$  for the lignin used in any of the blends prepared by us up to now [23,24, this work]. Nevertheless, the most notable fact related to Fig. 4 is that none of the transitions change their position with increasing lignin content indicating an almost complete lack of interaction.



**Figure 4.** Temperature dependence of the loss tangent recorded on LDPE/lignin blends at various lignin contents.

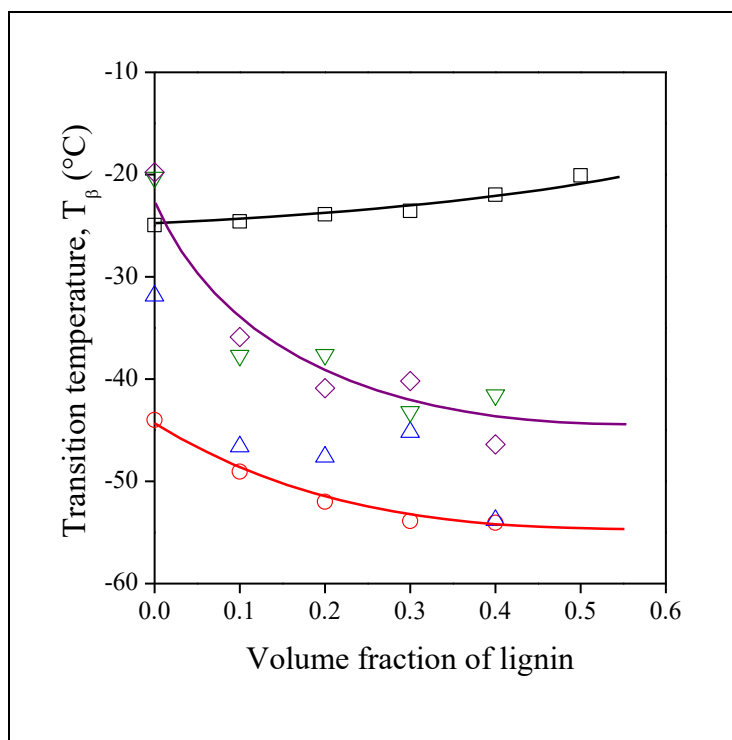
DMA spectra differ considerably for the EVOH/lignin blends (Fig. 5). Three transitions can be observed in these spectra as well, but the transitions appear at different temperatures. The

identification of the transitions is more difficult here, the lowest one might be related to ethylene-vinyl alcohol units ( $T_{\beta}$ ) [x], the second one to amorphous vinyl alcohol segments ( $T_{\alpha}$ ) [x], while the one appearing at the highest temperature to units attached to PVOH crystals ( $T_{\alpha'}$ ) [x]. The transitions of the methylene segments cannot be detected in the spectra, and polyethylene crystallites were not observed in the DSC traces either. Contrary to the spectra presented in Fig. 4, all three transitions move towards lower temperatures with increasing lignin content in EVOH/lignin blends. Although the downward shift is slightly surprising, it indicates that interactions develop between the two components and they increase the mobility of the EVOH phase. The extent of the shift increases with increasing lignin content proving that it results from the interaction of the two components.



**Figure 5.** Effect of lignin content on the dynamic mechanical spectra (loss tangent) of EVOH76/lignin blends.

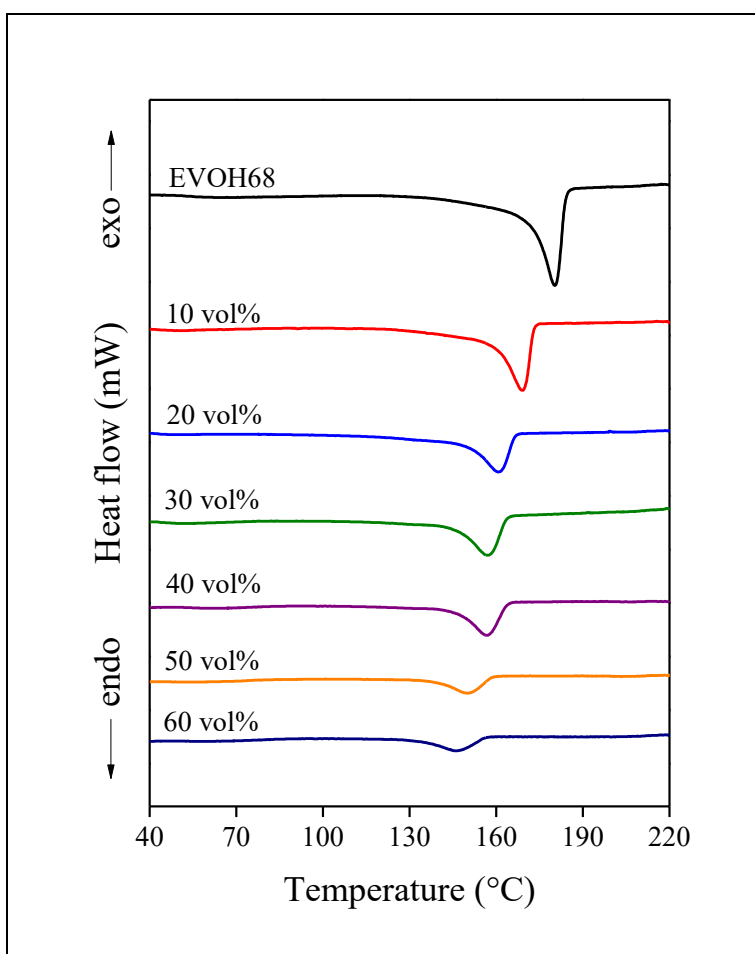
The shift in the transition temperature of the polymer component was determined quantitatively and the values are plotted against lignin content in **Fig. 6**. The temperature of the  $\beta$  transition was plotted for all blends for the sake of comparison. Transition temperature does not change in the LDPE blend, as shown earlier, or increases slightly at most. Considerable decrease is observed for the EVOH blends indicating quite strong interactions. Both the transition temperature and the extent of the decrease depend on the vinyl alcohol content of the copolymer, and both increases with increasing amount of VOH.



**Figure 6.** Composition dependence of the  $\beta$  transition of polymer/lignin blends. Effect of VOH content. Symbols: ( $\square$ ) 0 (LDPE), ( $\circ$ ) 52, ( $\triangle$ ) 62, ( $\nabla$ ) 68, ( $\diamond$ ) 76 mol%.

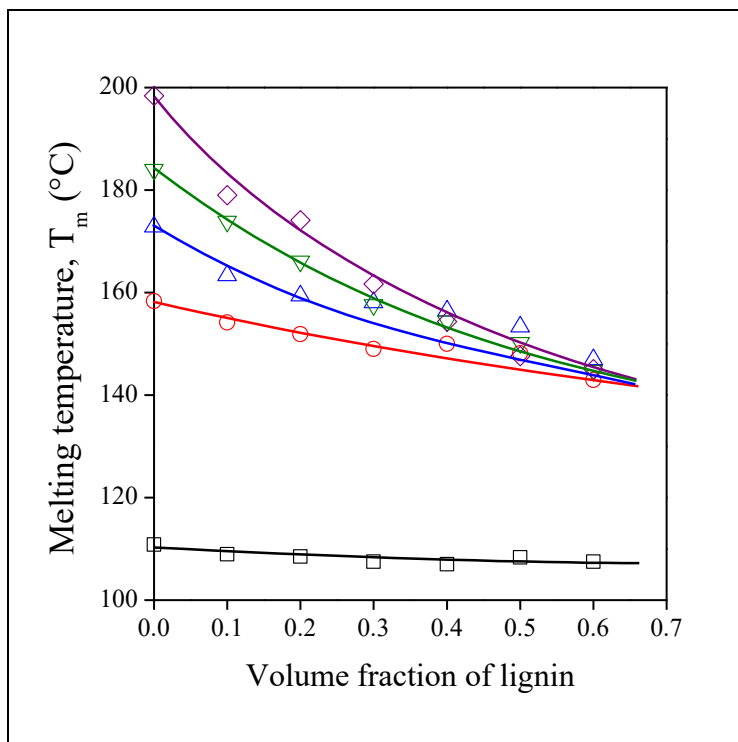
In semi-crystalline polymers interactions influence also crystallization. Usually both the thickness of the lamellae and crystallinity decreases as a result, thus the study of the melting and crystallization of blends also offers information about interactions. The melting traces of

EVOH68/lignin blends are presented in **Fig. 7**. The melting peak of the crystalline phase appears quite clearly in the traces, and the peak temperature of melting shifts quite strongly towards lower temperatures with increasing lignin content. As mentioned earlier, the melting of methylene segments in the copolymer cannot be detected by DSC at all, probably because a crystalline polyethylene phase does not form. The strong shift of the melting peak of the vinyl alcohol crystals confirms the formation of quite strong interactions between EVOH and lignin.



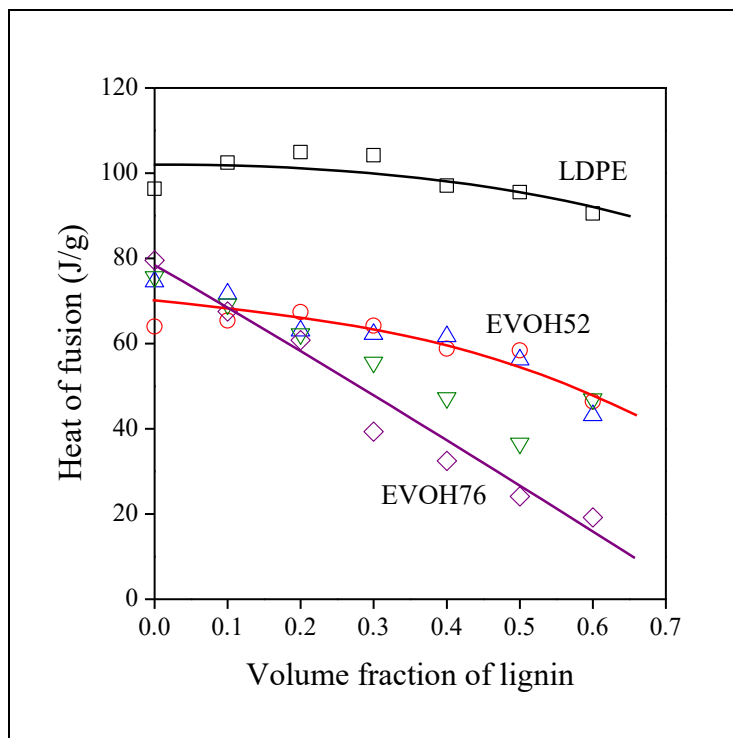
**Figure 7.** Melting traces recorded in the second heating run on EVOH68/lignin blends at various lignin contents.

The changes mentioned above can be seen much better if we plot characteristic values against lignin content. The composition dependence of melting temperature is presented in **Fig. 8**. We can see that similarly to the transition temperatures determined by DMA (see **Figs. 4** and **6**), the peak temperature of melting does not change in the polyethylene blends basically at all. On the other hand, characteristic temperatures, including the temperature of crystallization, decrease considerably with increasing lignin content and the effect becomes stronger with the increasing VOH content of the copolymers. Similarly to the melting temperature, the heat of fusion of the matrix polymer also decreases with increasing lignin content, as shown by **Fig. 9**. The same relationships can be observed in the figure as in the previous ones; no change in LDPE and increasing effect with increasing VOH content. The changes clearly prove the development of strong interactions between the components resulting in less regular crystals and smaller crystallinity.





**Figure 8.** Dependence of the peak temperature of melting of the crystalline EVOH phase on lignin content in EVOH/lignin blends. Second heating run. Symbols: ( $\square$ ) 0 (LDPE), ( $\circ$ ) 52, ( $\triangle$ ) 62, ( $\nabla$ ) 68, ( $\diamond$ ) 76 mol%.



**Figure 9.** Effect of composition on the heat of fusion of the crystalline EVOH phase in EVOH/lignin blends. Second heating run. Symbols: ( $\square$ ) 0 (LDPE), ( $\circ$ ) 52, ( $\triangle$ ) 62, ( $\nabla$ ) 68, ( $\diamond$ ) 76 mol%.

### 3.3. Quantitative analysis, correlations

The results presented in the previous section indicate that lignin and EVOH polymers enter into strong interaction with each other. The methods used for the characterization of the blends yield only qualitative estimate of interactions. However, interactions can be characterized quantitatively with the help of appropriate models. The easiest way is the calculation of the Flory-Huggins interaction parameter ( $\chi$ ) from solubility parameters ( $\delta$ ) using [Eq. 1](#)

$$\chi = \frac{V_r (\delta_1 - \delta_2)^2}{RT} \quad (1)$$

where  $\delta_1$  and  $\delta_2$  are the solubility parameters of the components,  $V_r$  is a reference volume taken as  $100 \text{ cm}^3$  [54],  $R$  the universal gas constant, and  $T$  the absolute temperature. Solubility parameters can be easily calculated from the group contributions of Small [55], Hoy [56] or van Krevelen [57].

Solubility parameters calculated for the polymers applied and Flory-Huggins interaction parameters derived from them are listed in **Table 2**. The solubility parameter of lignin was determined experimentally by Myrvold [58] for sodium liginosulfonate and its value is  $32.7 \text{ MPa}^{1/2}$ . The large difference between the solubility parameters of the matrix polymers and lignin forecasts immiscibility which was confirmed by the SEM study (see **Fig. 1**). However, solubility and interaction parameters change with composition, the first increases, while the second decreases with increasing VOH content, reflecting stronger interactions which result in smaller size of the dispersed lignin particles (**Figs. 1** and **2**). The very close correlation of **Fig. 2** indicates that interactions determine the structure of the blends and that hydrogen bonds create strong interactions between the components indeed.

**Table 2** Quantities characterizing the interaction between lignin and the polymers used in this study.

Polymer	Vinyl alcohol (mol%)	$\delta$ ( $\text{MPa}^{1/2}$ )	Interaction parameter, $\chi$	
			from $\delta^a$	Nishi-Wang <sup>b</sup>
LDPE	0	17.6	9.2	-0.001
EVOH52	52	22.8	4.0	-0.035
EVOH62	62	23.7	3.3	-0.054

EVOH68	68	24.2	2.9	-0.095
EVOH76	76	24.9	2.5	-0.123

a) at of 25 °C.

b) at 220 °C.

The results presented in [Section 3.2](#) offer us another way to estimate interactions. The Flory-Huggins interaction parameter can be calculated from the melting point depression of the crystalline phase by the approach of Nishi and Wang [59]. The model is based on the Flory-Huggins lattice model and relates the melting point of the crystalline component to the interaction parameter in the following way

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = -\frac{RV_2}{\Delta H_2 V_1} \chi (1 - \varphi_2)^2 \quad (2)$$

where  $T_{m0}$  and  $T_m$  are the melting points of the crystalline component alone and in the blend, respectively,  $V_1$  and  $V_2$  the molar volume of the repeating units of the two components,  $\Delta H_2$  the enthalpy of fusion of the crystalline polymer and  $\varphi_2$  its volume fraction in the blend. [Eq. 2](#) can be rearranged to

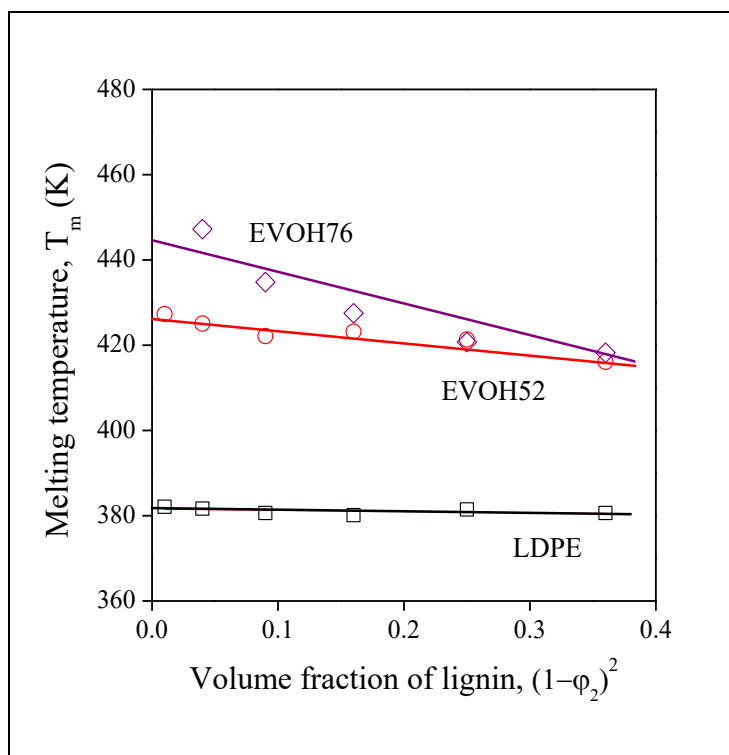
$$T_m = T_{m0} + \frac{BV_2}{\Delta H_2} T_{m0} (1 - \varphi_2)^2 \quad (3)$$

If the experimental values are plotted according to [Eq. 3](#), a straight line should be obtained and  $B$  can be calculated from its slope.  $B$  is related to the Flory-Huggins interaction parameter in the following way

$$\chi = \frac{BV_1}{RT} \quad (4)$$

The melting temperature of the EVOH phase is plotted against composition for selected

blends according to the model in Fig. 10. We obtain very good straight lines with changing slope indicating changing strength of interactions. The calculated Flory-Huggins interaction parameters are listed in Table 2. They correlate well with those derived from solubility parameters, but they have negative values. We must emphasize here that the model of Nishi and Wang [59] yields inherently negative interaction parameters indicating complete miscibility that is obviously not true in our case. Although the tendency is the same in the two cases, the negative values need further considerations.



**Figure 10.** Melting temperature of the EVOH phase plotted against lignin content in the representation of the Nishi-Wang [59] approach (see Eq. 3). Symbols: ( $\square$ ) 0 (LDPE), ( $\circ$ ) 52, ( $\diamond$ ) 76 mol%.

The approaches used supplied quantitative values for the strength of interaction, and a comparison to the results of Fig. 2 indicate close relationship between interaction and structure.

Structure and interaction can be related to each other quantitatively by the use of further models. The simplified approach of Tokita [60] and Fortelný [61] predicts the diameter ( $d$ ) of the dispersed phase forming during the mixing of two immiscible polymers

$$d = \frac{8 \alpha \gamma_{AB} f(\eta_{rel})}{\pi \eta_m} \varphi \quad (5)$$

where  $\gamma_{AB}$  is interfacial tension,  $f(\eta_{rel})$  is a function of the relative viscosity of the two components with a value close to 1 [62],  $\alpha$  is the coalescence probability of colliding particles and  $\eta_m$  is the viscosity of the matrix polymer. Interfacial tension is related to the Flory-Huggins interaction parameter in the following way [63,64]

$$\gamma_{AB} = \frac{b R T \chi^{1/2}}{V_r} \quad (6)$$

where  $b$  is the effective length of a monomer unit. Introducing [Eq. 6](#) into [Eq. 5](#) and combining some of the parameters into a constant ( $k_1$ ) leads to the correlation

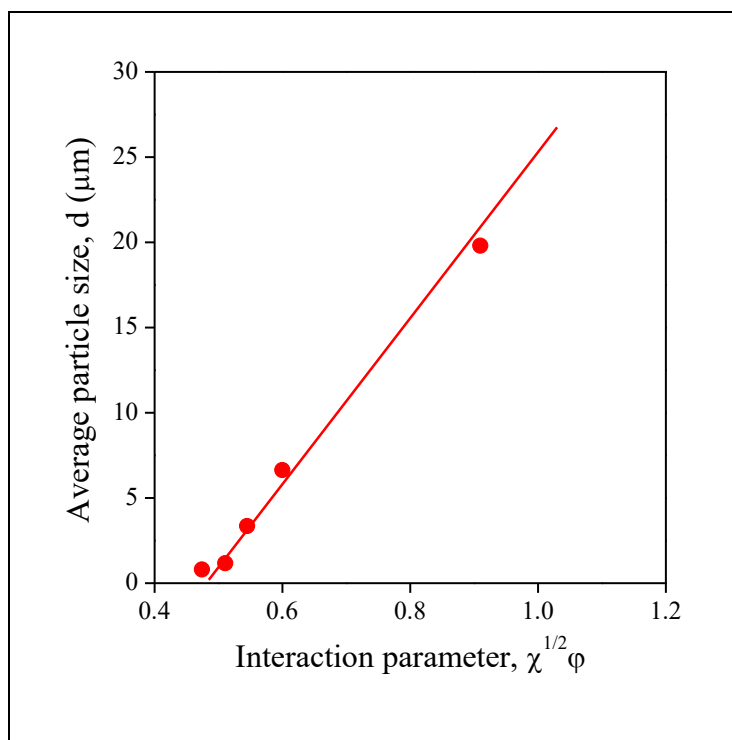
$$d = k_1 \frac{b R T \chi^{1/2}}{V_r} \varphi \quad (7)$$

which can be simplified into the following form

$$d = k_2 \chi^{1/2} \varphi \quad (8)$$

where  $k_2$  is a constant. [Eq. 8](#) relates directly the structure of the blend (dispersed particle size,  $d$ ) to the parameter expressing the strength of interaction (Flory-Huggins interaction parameter,  $\chi$ ).

The results obtained were plotted in the way suggested by the model presented above. One correlation is shown in [Fig. 11](#) for demonstration. We can see that the approach is valid and a very close correlation is obtained between the parameters representing structure and interactions. The blends contained 30 vol% lignin. At constant lignin content the decreasing values of the independent variable mean increasing strength of interaction which results in decreasing particle size. We can conclude that hydrogen bonds generate strong interactions between lignin and EVOH polymers, the strength of interaction increases with increasing VOH content and the structure of the blends is determined by these interactions.



**Figure 11.** Effect of interaction on the structure (average size of lignin particles) of EVOH/lignin blends at 30 vol% lignin content. See [Eq. 8](#).

### 3.4. Discussion

Although we could prove unambiguously the important role of hydrogen bonds in the

determination of compatibility and structure, a few questions remained open. The exact meaning of the interaction parameters determined by the Nishi-Wang [59] approach and their explanation is obviously one of them. In order to help the interpretation of the values listed in **Table 2**, we compare them to literature data in **Table 3**. The blends included into the table are listed in decreasing order of the interaction parameter indicating increasing strength of the interactions. Very small absolute values were obtained for  $\chi$  in blends in which only dispersion forces act, i.e. for PP/polyisobutylene (PIB), linear low density polyethylene (LLDPE)/PIB) and LDPE/lignin. In spite of the large number of functional groups of the lignin molecule, it can enter only into dispersion interactions with polyethylene. Nishi and Wang obtained a value of  $-0.295$  at  $160\text{ }^{\circ}\text{C}$  ( $-0.336$  at  $220\text{ }^{\circ}\text{C}$ ) for the completely miscible blend of poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF). We calculated a value of  $-0.123$  at  $220\text{ }^{\circ}\text{C}$  for the EVOH76/lignin blend. The relatively large absolute value indicates strong interaction, but the components are still immiscible, which is an obvious contradiction. The only explanation of immiscibility is that self-interactions within each component, EVOH and lignin, respectively, are extremely strong and compete with EVOH/lignin interactions. The explanation about the strong self-interaction of the components is supported by the crystallinity of EVOH and the high melting temperature of its crystals, on the one hand, and by the fact that lignin in itself cannot be melted and processed, on the other.

**Table 3** Comparison of Flory-Huggins interactions parameters for various crystalline/amorphous blends

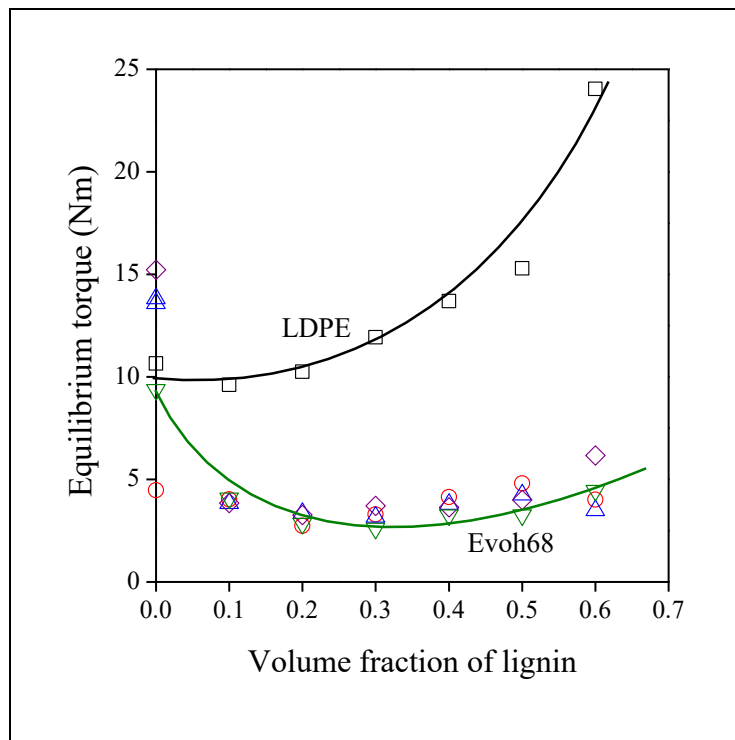
Blend component		Interaction parameter, $\chi$		Ref.
Polymer 1	Polymer 2	from $\delta^a$	Nishi-Wang <sup>b</sup>	
LDPE	lignin	9.20	-0.001	this work
LLDPE	PIB	0.20	-0.024	65

PP	PIB	0.02	-0.104	66
EVOH76	lignin	2.50	-0.123	this work
PVF <sub>2</sub>	PMMA	0.93	-0.336	59

a) at 25 °C.

b) at 220 °C.

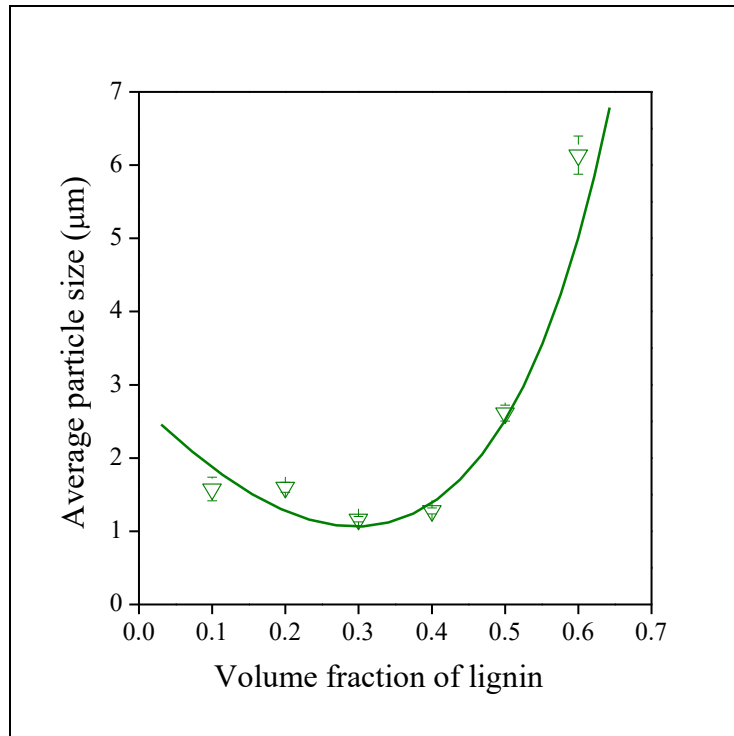
The role of competitive interactions is demonstrated well also by the composition dependence of equilibrium torque recorded during the homogenization of the components. Torque is proportional to viscosity which increases with increasing lignin content in polyethylene (Fig. 12). On the other hand, a minimum appears in the viscosity of the blends prepared from the EVOH polymers. As a result of the interaction of unlike polymers, the mobility of the molecules increases and viscosity decreases. This effect is related also to the chemical composition of the EVOH polymer since it decreases with decreasing VOH content.





**Figure 12.** Dependence of the equilibrium torque measured during homogenization on lignin content. Decrease of viscosity upon blending. Symbols: ( $\square$ ) 0 (LDPE), ( $\circ$ ) 52, ( $\triangle$ ) 62, ( $\nabla$ ) 68, ( $\diamond$ ) 76 mol%.

Increased mobility was observed already during the analysis of DMA spectra showing the shift of transitions towards lower temperatures. The effect of competition is shown also by **Fig. 13** in which the particle size of the EVOH68/lignin blend is plotted against composition; a minimum appears here too. We know that particle size is determined by thermodynamic (interactions) and kinetic (shear) factors, and particle break up and coalescence take place simultaneously. The combined effect of the two factors results in the minimum in particle size at a certain composition. We can conclude that although the interactions between lignin and the polymers containing hydroxyl groups are quite strong, they are not strong enough to compete successfully with the self-interactions of the components and thus do not result in complete miscibility. Obviously the combination of several, different interactions (e.g. aromatic, H-bond, ionic) and/or some other methods (plasticization, chemical modification [2]) are needed if we want to prepare homogeneous blends from the lignin used in this study.



**Figure 13.** Changes of the size of dispersed lignin particles in EVOH68/lignin blends as a function of lignin content. Effect of thermodynamic and kinetic factors.

## Conclusions

The results of the experiments directed towards the study of the role of hydrogen bonds in the compatibility and structure of EVOH/lignin blends unambiguously proved that strong hydrogen bonds form between the two components indeed. The development of strong interactions was proved by FTIR spectroscopy, the shift of relaxation temperatures and by the decrease of crystallite size and crystallinity with increasing lignin content. In spite of the strong interactions, heterogeneous structure forms in the studied blends, since self-interactions within the neat components are also very strong. The size of the dispersed lignin particles is determined by competitive interactions in the blends; increasing EVOH/lignin interactions result in smaller particle size. The competitive character of interactions is shown also by the increased mobility of

the matrix polymer and the decreased viscosity of the blends at certain compositions. Although hydrogen bonds are very strong indeed, miscible blends may be prepared from the lignin used in the study only by applying other approaches like plasticization or chemical modification.

### **Acknowledgements**

The authors are indebted to Brúnó Bozsódi and Gábor Szabó for the evaluation of experimental data. The research on the structure-property correlations of polymeric materials was financed by the National Scientific Research Fund of Hungary (OTKA Grant No. K 120039 and PD 112489).

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