STRUCTURE EVOLUTION IN POLY(ETHYLENE-CO-VINYL ALCOHOL)/LIGNIN

BLENDS: EFFECT OF INTERACTIONS AND COMPOSITION

Emese Pregi[1,2], Dávid Kun[1,2], Vi Vu[1,2],

Béla Pukánszky[1,2,*]

[1]Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and

Materials Science, Budapest University of Technology and Economics, H-1521 Budapest,

P.O. Box 91, Hungary

[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences,

Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

*Corresponding author: Phone: +36-1-463-2015, Fax: +36-1-463-3474,

Email: bpukanszky@mail.bme.hu

ABSTRACT

Blends were prepared from lignin and ethylene-vinyl alcohol (EVOH) copolymers to study the effect of component interactions and composition on structure. The vinyl alcohol (VOH) content of the polymers changed between 0 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 the dispersed structure of the blends was characterized by scanning electron microscopy (SEM). As an effect of the strong self-interactions of lignin, this latter forms immiscible blends with ethylene-vinyl alcohol copolymers in spite of the hydrogen bonds acting between the two components. Because of immiscibility, lignin is dispersed in the form of particles in the EVOH phase even at lignin contents as large as 60 vol%. The size of dispersed lignin particles is determined by particle break-up and coalescence, the original lignin particles of around 80 μm size break up to much smaller ones; particle sizes below one micrometer form at large vinyl alcohol contents. As equilibrium thermodynamic factors are stronger than kinetic ones in the studied system, changing shear stresses do not influence particle size much. The coalescence of particles is determined by composition and component interactions, and a simple semi-empirical model was proposed to describe the correlations of these variables quantitatively. Good agreement was found between the prediction of the model and experimental results.

1. INTRODUCTION

Lignin is a constitutional part of plants, thus it is available in very large quantities.

Cellulose and bioethanol production yields large amounts of lignin as a secondary product or waste. Most of it is used for the production of energy and some in niche applications. Nevertheless, lignin is a cheap, natural raw material with possibilities not completely utilized yet [1]. The idea of using it as a component of plastic products seems to be obvious and numerous papers report attempts to utilize it as a component of polymer blends [2–13] or as a constituent of cross-linked resins [14–19]. However, using lignin in such applications raises several questions most of which have not been answered completely yet.

Lignin is a polar substance with a large number of functional groups. These groups are capable of forming strong interactions with each other, thus lignin is not miscible with most of the commercial polymers available. The question of miscibility is rather contradictory. Complete miscibility was reported for a large variety of polymers including polyolefins [20–28], which is very strange in view of the polar character and strong self-interactions of lignin and the weak interactions developing polyolefins and other polymers. In reality, most of the polymer/lignin blends prepared up to now have heterogeneous structure. In spite of the heterogeneous structure, interactions between lignin and the synthetic polymer used as matrix play a crucial role in the determination of compatibility and blend morphology, e.g. in the size of dispersed lignin particles [1–3]. Besides dispersed particles very often phase inversion and a co-continuous structure also occurs in the blends of synthetic polymers [29–32], however, they were rarely observed in polymer/lignin blends. Particle size was shown to determine properties in many blends including impact modified polymers [33,34].

In the blends of two immiscible polymers the size of dispersed particles is determined by two factors: thermodynamics and kinetics. Kinetic effects, mainly shear stresses prevailing during mixing result in the break-up of larger particles, while weak interactions and large amount of the dispersed component lead to coalescence. Many attempts have been made to describe the evolution of particle size during extrusion or mixing, but unambiguous

correlation does not exist yet [35]. Most of the groups working in the field agree that the viscosity of the matrix (kinetics), shear rate (kinetics), interfacial tension (thermodynamics) and composition influence particle size, but the models developed may contain other parameters as well, like the frequency of particle break-up or coalescence probability [36–39]. These models vary in complexity, but most of them regard the components as Newtonian fluids. Many factors are still unknown or undefined and several are completely neglected. Consequently, most of the approaches yield semi-empirical equations the success of which is determined by their agreement with experimental results.

The size of dispersed particles influences properties quite strongly also in polymer/lignin blends. According to our knowledge, the factors influencing blend morphology have never been investigated in these materials, thus it seemed to be worth to pay more attention to this question. Accordingly, we prepared poly(ethylene-vinyl alcohol) (EVOH)/lignin blends in a wide range of lignin contents. The vinyl alcohol content (VOH) of the copolymers varied from 0 to 76 mol% resulting in changing interactions. We determined the size of the dispersed lignin particles as a function of lignin and VOH content. An attempt was made to describe the observed correlations quantitatively and to identify the most important factors determining structure in the studied polymer/lignin blends.

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 contents in order to study the effect of component interactions quantitatively. Low density polyethylene (MOL Group, Hungary) with zero

vinyl alcohol content was used as reference. The lignosulfonate sample used in the experiments 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 low 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. It has 2.73 mmol/g aliphatic hydroxyl, 0.70 mmol/g phenolic hydroxyl, 0.54 mmol/g carboxyl and 1.75 mmol/g sulfonate groups. The concentration of hydroxyl and carboxyl groups was determined by ^{31}P NMR, while that of sulfonate by titrimetry. The density of Bretax SRO2 is 1.63 g/cm^3. 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^3)	MFR (g/10 min)
LDPE	Tipolen FA 244-51	0	0.92	0.3[a]
EVOH52	Eval G156B	52	1.12	6.4[a]
EVOH62	Eval H171B	62	1.17	1.7[a]
EVOH68	Eval F101B	68	1.19	1.6[a]
EVOH76	Eval M100B	76	1.22	2.2[b]

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^3 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 thickness were compression molded at 220 °C using a Fontijne SRA 100 machine. The plates were stored for one week at room temperature (23 °C and 50 % RH) before analysis.

2.3. Characterization

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. The particles were regarded as spheres and their imprint on the micrographs as circles. The equivalent diameter (d_{eq}) was determined accordingly and the procedure was checked by comparing the obtained value to the volume fraction of lignin in the blend. The agreement was very good in most cases. Equivalent dimeter was averaged according to the number of particles and the number average of particle diameter (d) was calculated by the equation $d = (4\,d_{eq})/\pi$.

3. RESULTS AND DISCUSSION

The results will be presented in several sections. The dependence of structure on composition is reported first, followed by the discussion of the main factors determining the size of dispersed lignin particles. A model relating particle size to these factors quantitatively will be described next, followed by coalescence probability, and then the model is compared to approaches published in the literature in the last section of the paper.
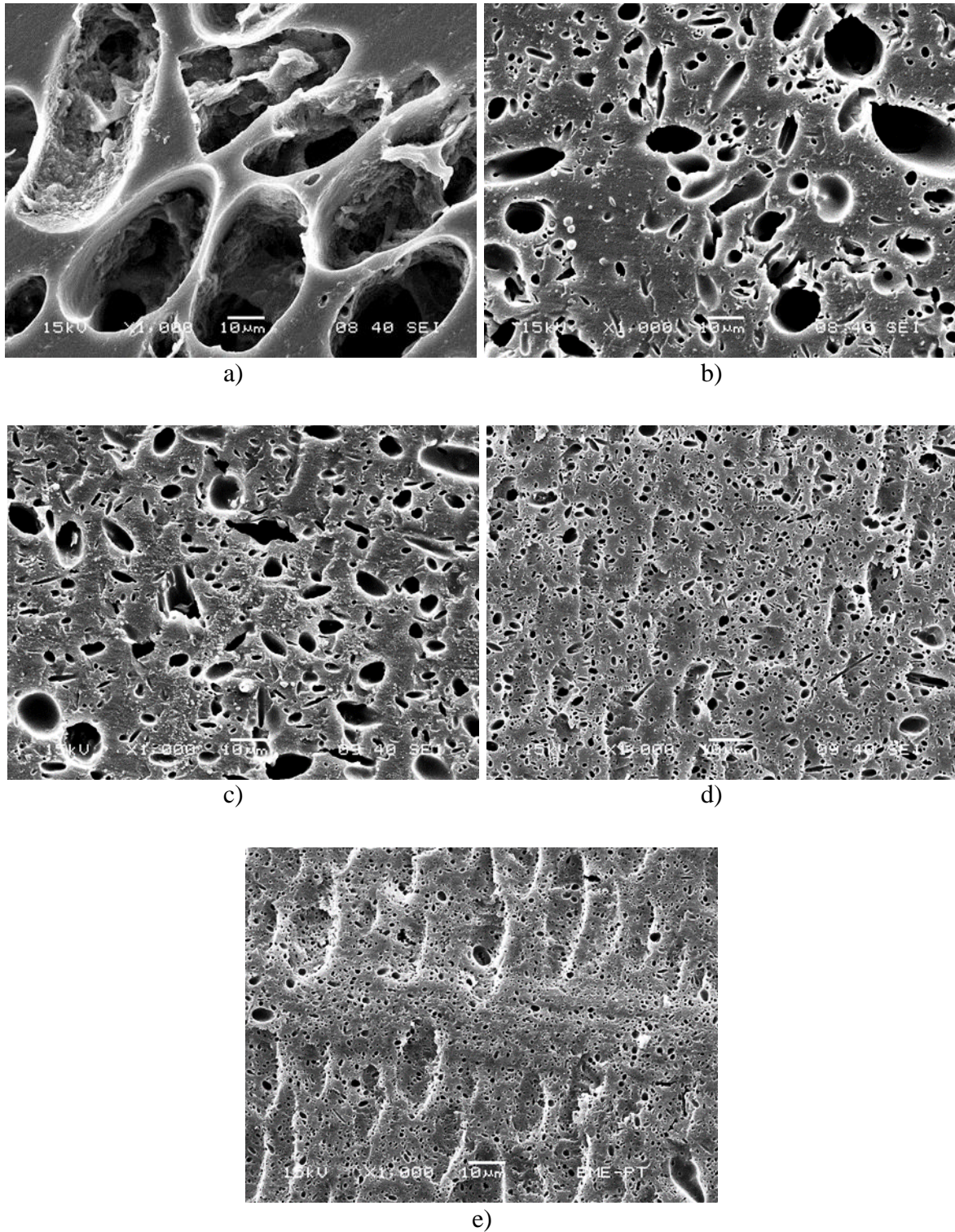
Fig. 1   Effect of the chemical structure of the polymer used as matrix on the structure
of polymer/lignin blends. Lignin content: 30 vol%. a) LDPE, b) EVOH52, c)
EVOH62, d) EVOH68, e) EVOH76.

3.1. Structure

Because of the strong interactions among lignin molecules, the dispersion of lignin in other polymers is difficult, heterogeneous structure forms. As the SEM micrographs of **Fig. 1** show, lignin is dispersed in the form of distinct particles in the matrix polymer. However, the size of the particles depends very much on the chemical composition of the polymer, on its vinyl alcohol content. Particle size decreases drastically from about 30 μm to below 1 μm with increasing VOH content. The original particle size of lignin was about 80 μm thus the particles must break up during homogenization. The extent of break-up depends on the hydroxyl group content of EVOH, and thus possibly on the interaction of the two components.
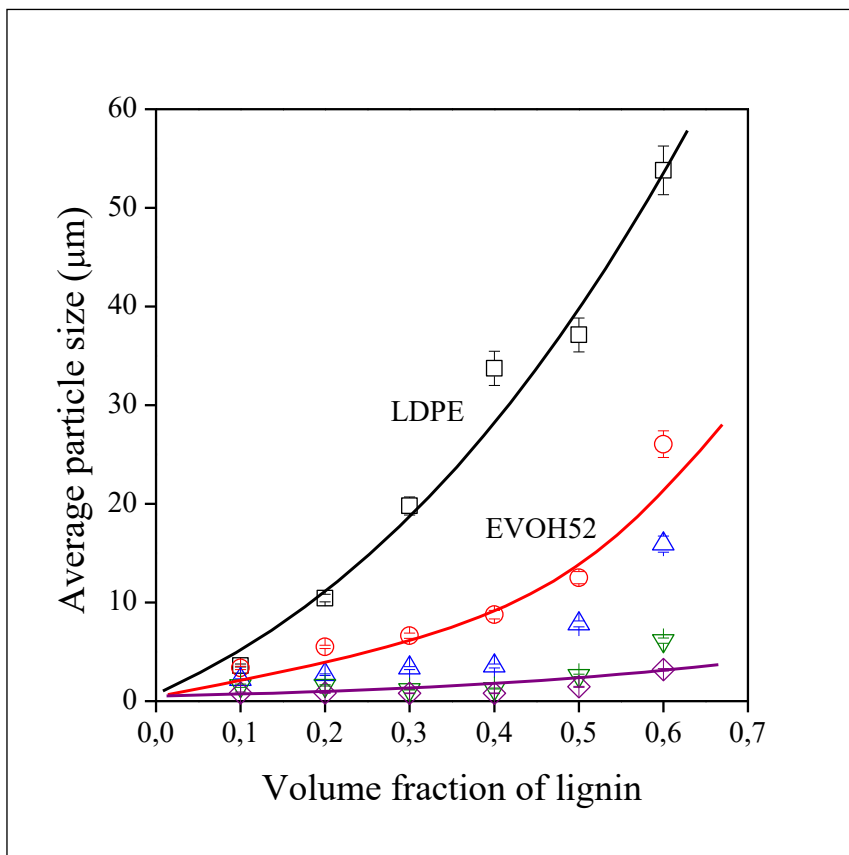

Fig. 2 Composition dependence of the average particle size of polymer/lignin blends. Effect of VOH content. Symbols: (□) LDPE, (○) EVOH52, (△) EVOH62, (▽) EVOH68, (◇) EVOH76.

The SEM micrographs of **Fig. 1** offer only a qualitative view of structure and particle size. The size of the dispersed lignin particles was determined quantitatively by image analysis, and their number average is plotted against the composition of the blends in **Fig. 2**. According to the figure both composition, i.e. lignin content, and the chemical structure of the matrix polymer, i.e. VOH content, influence particle size quite strongly. Decreasing particle size with increasing vinyl alcohol content must be the result of changes in interactions, in the compatibility of the two components. The figure also indicates, although it is not straightforward, that the decrease in particle size with increasing VOH content is not linear. The increase of size with increasing lignin content seems to be obvious; one would expect the formation of larger particles at larger lignin concentrations. The lack of co-continuous structure and phase inversion even at as large lignin content as 60 vol% is slightly surprising and must be the result of the strong self-interactions among lignin molecules and the small molecular weight of the natural polymer.

3.2. Factors

The size of the particles dispersed in the matrix of a polymer blend depends on thermodynamic and kinetic factors. The relative effect of the two factors may change depending on component properties and processing conditions. Thermodynamics is determined mainly by interactions; entropy usually plays a much smaller role. The strength of interactions between two polymers can be estimated in different ways, one of the most often used approach is the interaction parameter (χ) defined by the Flory-Huggins theory. The parameter can be determined experimentally, but also calculated from Hildebrand solubility parameters in the following way

$$\chi = \frac{V_r\,(\delta_1 - \delta_2)^2}{R\,T} \tag{1}$$

where δ_1 and δ_2 are the solubility parameters of the components, V_r is a reference volume taken as 100 cm^3 [40], R the universal gas constant, and T the absolute temperature. The solubility parameter of sodium lignosulfonate was determined experimentally by Myrvold [41], while that of LDPE and the EVOH copolymers was estimated from the group contributions of Hoy [42]. The interaction parameters were calculated at 25 °C for the polymers used in the study, and they are plotted against their VOH content in **Fig. 3**. The figure clearly shows that the value of χ covers a wide range with increasing VOH content. It is very large for LDPE indicating complete immiscibility, while much smaller at larger vinyl alcohol contents predicting better compatibility and even partial miscibility of the components.
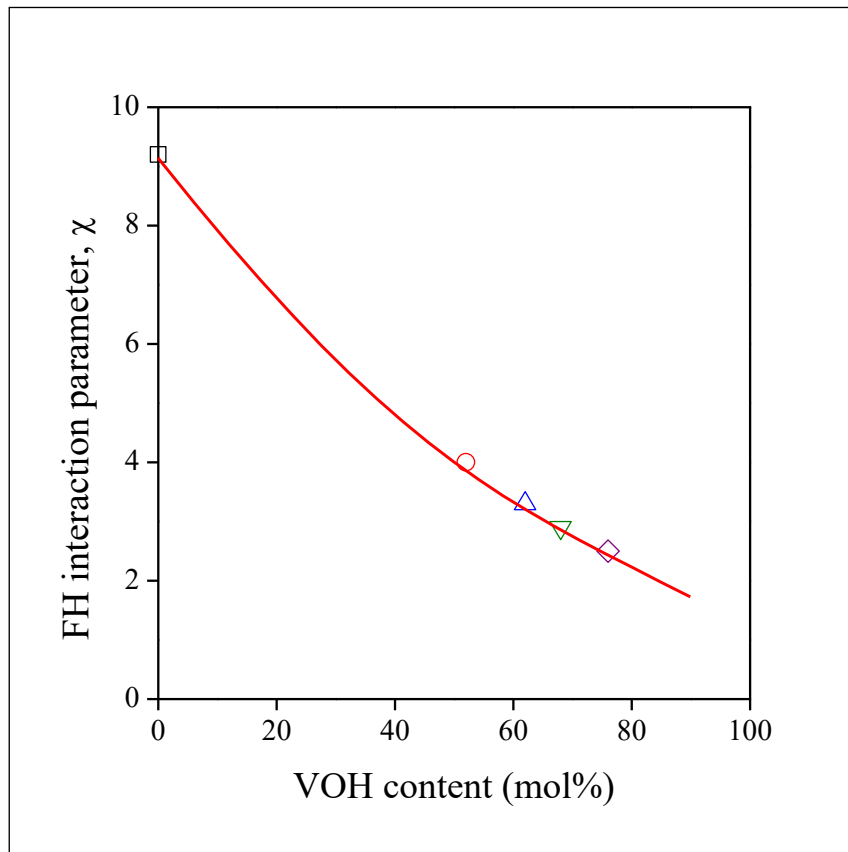

Fig. 3 Dependence of the Flory-Huggins interaction parameter of polymer/lignin blends on the VOH content of the synthetic polymer. Symbols are the same as in **Fig. 2**.
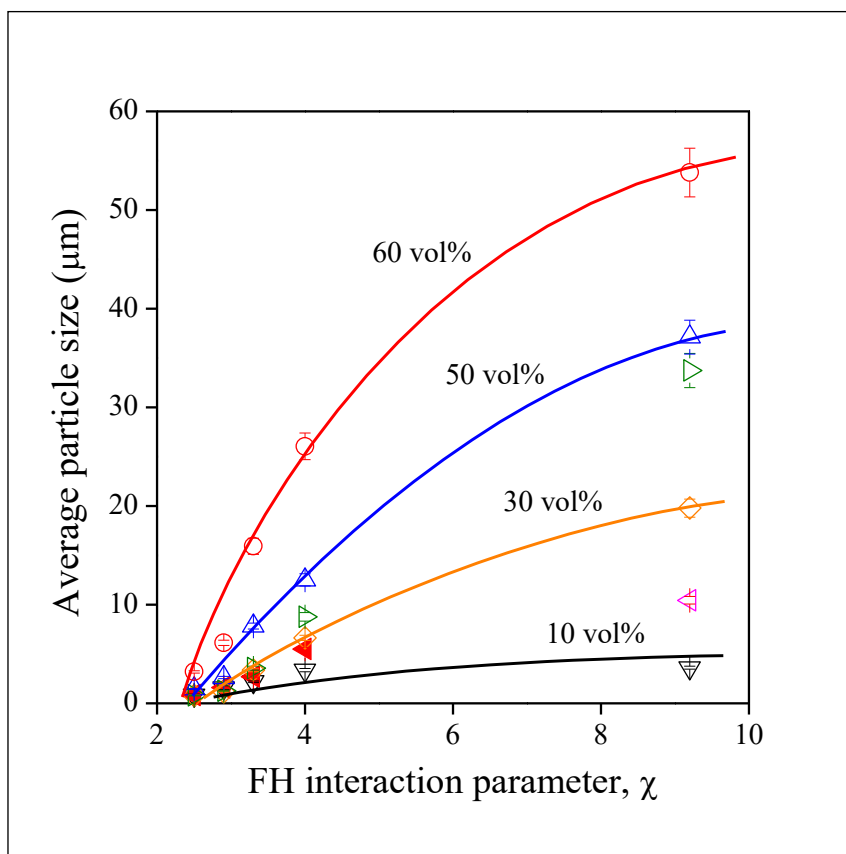
Fig. 4   Correlation between the number average particle size and the Flory-Huggins interaction parameter in polymer/lignin blends. Symbols: ($\triangledown$) 10, ($\triangleleft$) 20, ($\diamondsuit$) 30, ($\triangleright$) 40, ($\triangle$) 50, ($\bigcirc$) 60 vol% lignin.

The effect of this thermodynamic factor on structure is demonstrated well by **Fig. 4** in which the size of dispersed lignin particles is plotted against the Flory-Huggins interaction parameter. Particle size invariably increases with increasing χ, i.e. with decreasing interaction and miscibility. However, **Fig. 4** also emphasizes the role of composition, particle size increases considerably with increasing lignin content. Based on these results we can unambiguously identify two factors influencing particle size: interactions and lignin content.

However, the possible effect of kinetics must be also considered during the evaluation of the results. Shear stresses may change considerably with lignin content and also as a function of the chemical structure of the matrix polymer. The torque measured in the internal mixer during the homogenization of the components is proportional to shear stress and matrix viscosity, even if the absolute value of these latter is difficult to calculate. Equilibrium torque is plotted against lignin content in **Fig. 5** confirming the statement above. Torque increases from about 10 to 25 Nm in the polyethylene matrix, but it changes somewhat also for the other polymers. Accordingly, changing shear conditions might also influence the size of the dispersed lignin particles.
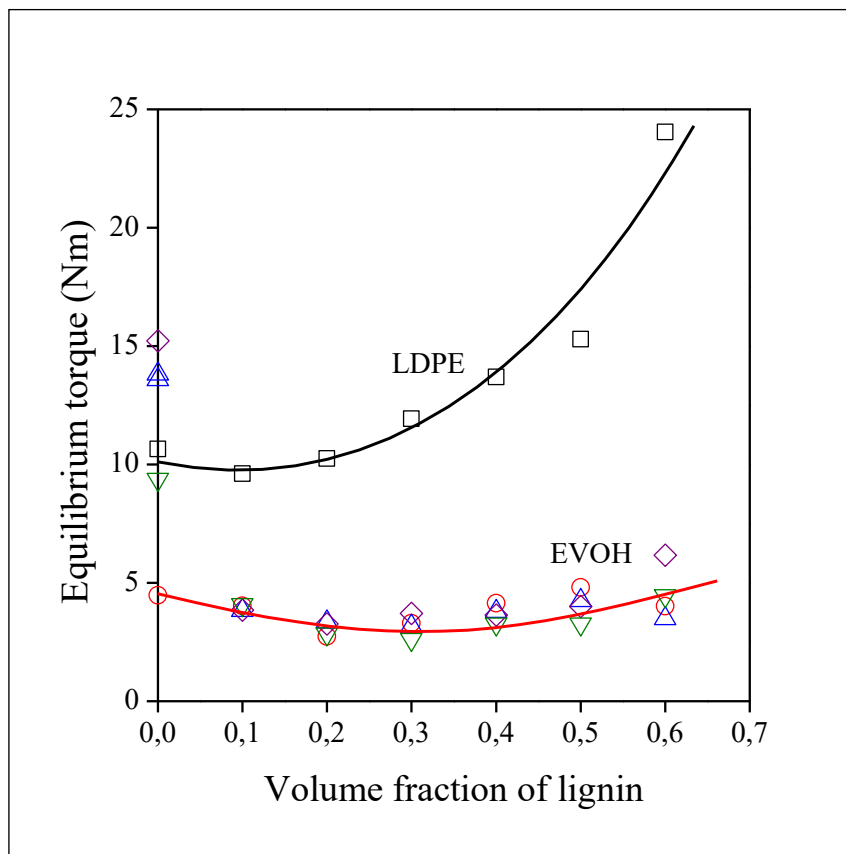

Fig. 5   Dependence of the equilibrium torque recorded during the homogenization of the polymer/lignin blends in the internal mixer on lignin content. Symbols are the same as in **Fig. 2**.

It is quite strange that torque, i.e. viscosity, decreases with increasing lignin content. A tentative explanation might be the change of the interactions developing in the blends. Self-interactions are very strong both in the EVOH polymer and in lignin resulting in very high viscosity for both components. However, unlike interactions also develop upon their blending, which might lead to the observed change of viscosity.

In order to check the possible effect of kinetics on structure, the number average particle size is plotted against equilibrium torque in **Fig. 6**. The size of the particles is completely independent of torque for the EVOH copolymers, at least under the shear conditions of our study. Particle size seems to change in LDPE, but it increases with increasing torque, i.e. shear stress, which does not agree with theories saying that particle size should decrease with increasing intensity of shear. The tendency observed in **Fig. 6** for LDPE is obviously the effect of another factor that also changes with increasing lignin content together with torque. The results presented in **Figs. 5** and **6** clearly indicate that the dominating factors in the determination of the particle size of lignin are interactions and lignin content, and kinetics plays a secondary role.
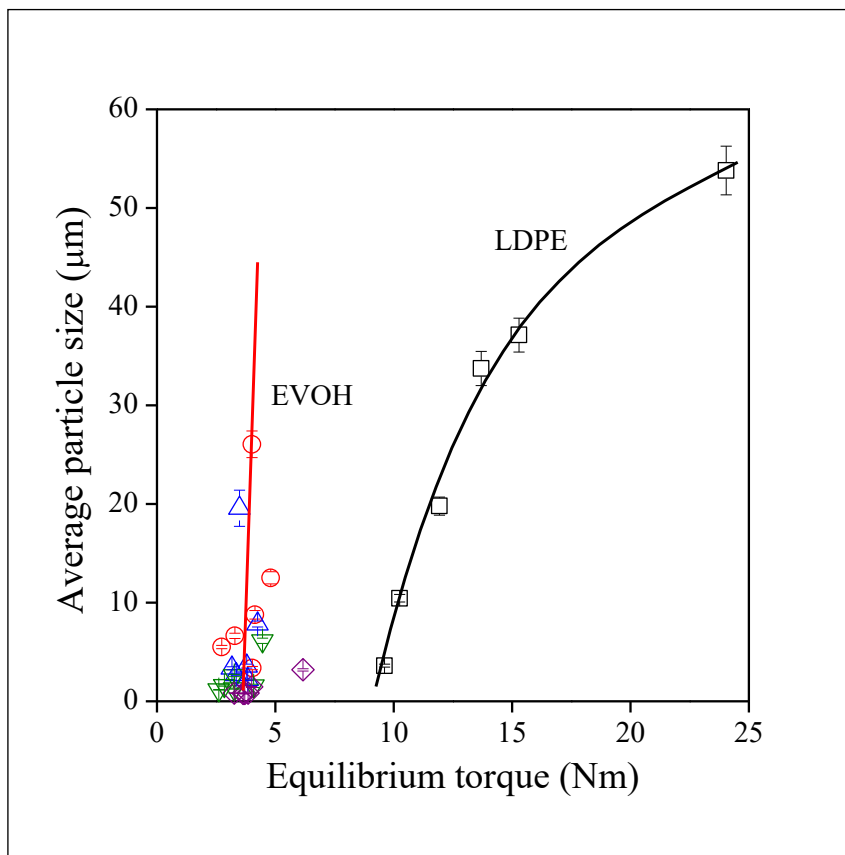
Fig. 6   Independence of blend structure of kinetic effects; number average particle size of lignin vs. equilibrium torque. Symbols are the same as in **Fig. 2**.

3.3. Modelling

Two processes take place during the blending of polymers, the break-up of large particles, as we have seen also in our case, and the coalescence of smaller ones. In equilibrium, the two proceed at the same rate and particle size reaches a constant value. Various models exist which describe the dependence of dispersed particle size on thermodynamic and kinetic factors, some of them are very complicated. In order to facilitate handling a simplified approach based on the models of Tokita [37] and Fortelný [43] was successfully used to predict the diameter (*d*) of the dispersed phase forming during the mixing of two

immiscible polymers [44]

$$d = \frac{8 \, \alpha \, f(\eta_{rel})}{\pi \, \eta_m} \gamma_{AB} \, \varphi \tag{2}$$

where γ_{AB} is interfacial tension, φ is the volume fraction of the dispersed phase, $f(\eta_{rel})$ is a function of the relative viscosity of the two components with a value close to 1 [45], α is the coalescence probability of colliding particles and η_m is the viscosity of the matrix polymer. Interfacial tension is related to the Flory-Huggins interaction parameter in the following way [46,47]

$$\gamma_{AB} = \frac{b \, R \, T}{V_r} \chi^{1/2} \tag{3}$$

where b is the effective length of a monomer unit. Introducing **Eq. 3** into **Eq. 2** results in

$$d = \frac{8 \, \alpha \, b \, R \, T}{\pi \, V_r \, \eta_m} \chi^{1/2} \varphi \tag{4}$$

which can be simplified into the following form by assuming some of the variables to be constant and combining them into a single parameter, k_1

$$d = k_1 \, \chi^{1/2} \varphi \tag{5}$$

Eq. 5 relates directly the structure of the blend (dispersed particle size, d) to the composition (volume fraction of lignin) and the parameter expressing the strength of interaction (Flory-Huggins interaction parameter, χ). We must mention here that most approaches assume that the effect volume fraction on droplet size is determined by the dependence of breakup frequency on size, but the correlation has not be established unambiguously so far [35].

The results obtained in the experiments were plotted in the way indicated by the model in **Fig. 7**. The model predicts linear correlation between the variables of **Eq. 5** and the model seems to be valid indeed, since straight lines were obtained as expected. The negative intersection of the lines and the changing slope indicate the role of some factor which influences particle size but was neglected during the simplified treatment.
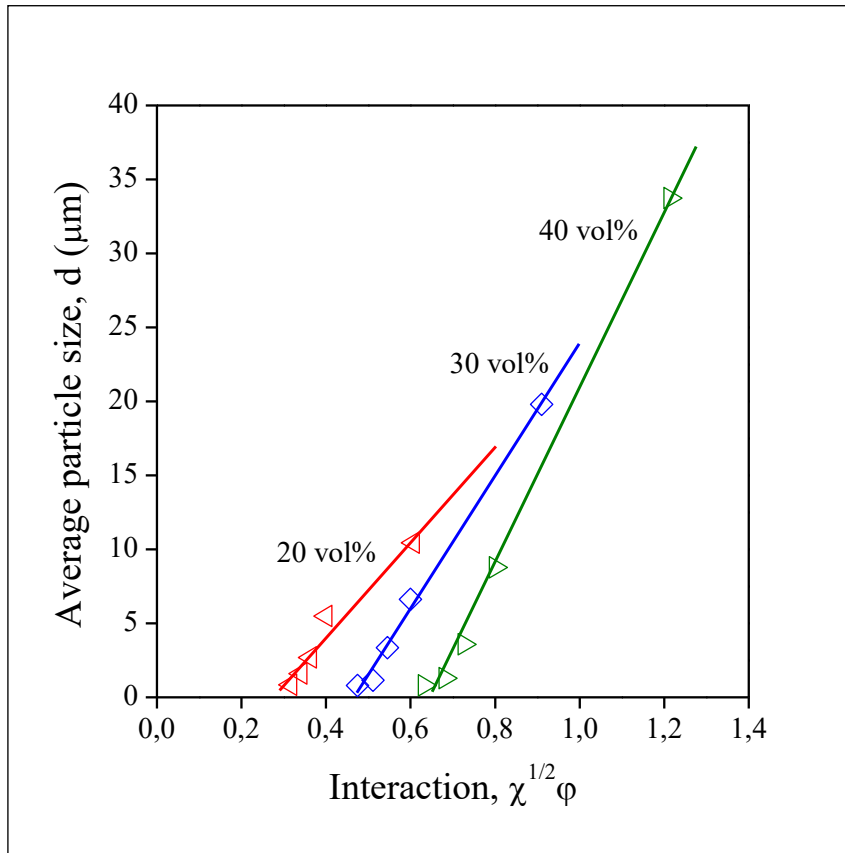
Fig. 7 Number average particle size of dispersed lignin particles plotted according to the correlation of **Eq. 5**. Symbols are the same as in **Fig. 4**.

Eq. 5 can be rearranged into another form by dividing both sides of the equation by $\chi^{1/2}$. Plotting the results in this form should lead to linear correlations with zero interception. The results are plotted in this form in **Fig. 8** for certain combinations of materials. In spite of the prediction of the simple approach, the relationship between the variables is far from linear and interceptions differ from zero. The correlations indicate that one or more of the parameters assumed constant and included in k_1 change with the chemical structure of the matrix polymer and the composition of the blend, respectively. In **Eq. 5** the constant contains several parameters

$$k_1 = \frac{8 \, \alpha \, b \, R \, T}{V_r \, \eta_m} \tag{6}$$

The effective length of a repeat unit (b), the reference volume (V_r), temperature (T) and the universal gas constant (R) can be regarded as constant indeed, and the viscosity of the matrix (η_m) does not influence particle size as shown by **Fig. 6**. As a consequence, the only parameter that can change is coalescence probability, thus we must consider its dependence on the chemical structure of the matrix polymer and the composition of the blend more thoroughly.
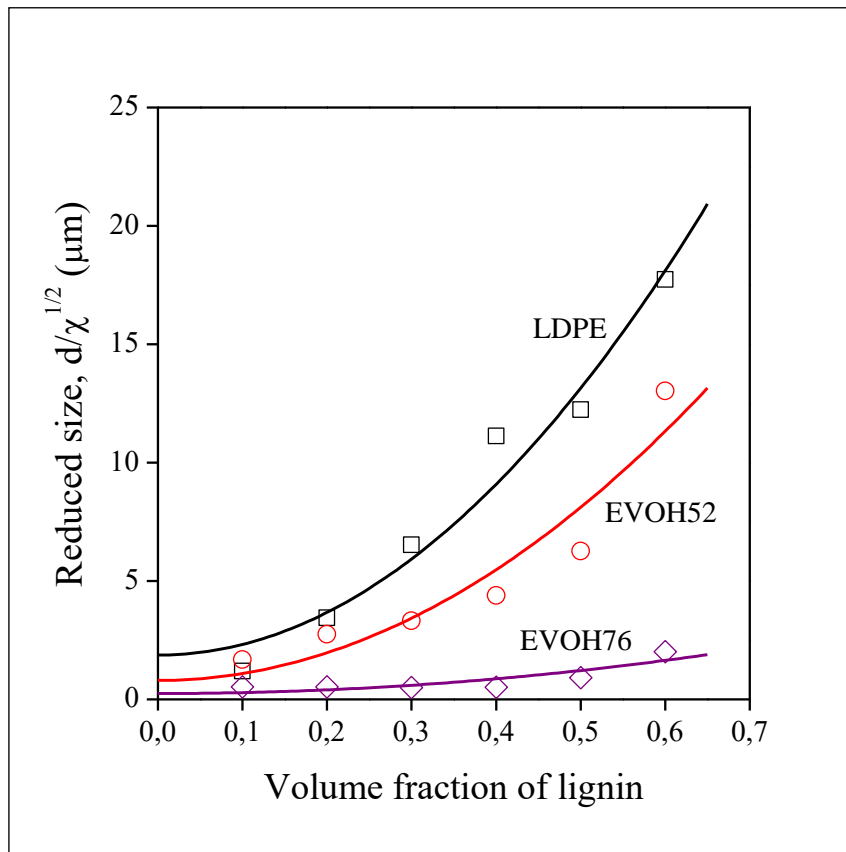

Fig. 8   Effect of lignin content on the reduced size ($d/\chi^{1/2}$) of the dispersed lignin particles. Symbols are the same as in **Fig. 2**.

3.4. Coalescence probability

In his excellent book chapter Fortelný [35] summarizes existing theories for the break-up and coalescence of particles and the evolution of structure during the preparation of polymer blends. Diverse and most complicated correlations were proposed for coalescence probability based on fluid dynamics. These formulae contain a large number of parameters including the viscosity of the components, particle size, shear rate, interfacial tension and some geometric constants [35,36,48,49]. Among the parameters listed only interfacial tension is related to the chemical structure of the polymers, and thus to interactions, and none of them contains the amount of the dispersed phase although one would assume that coalescence probability must increase with increasing amount of the dispersed particles. Based on the results presented in **Fig. 7**, we propose the following empirical correlation for coalescence probability

$$\alpha = k_2 \, \chi^{1/2} \, \varphi \tag{7}$$

in which interactions are represented by the Flory-Huggins interaction parameter and the amount of lignin by its volume fraction. Taking into account the fact that the intersection of the correlations in **Fig. 8** is not zero, we apply the more rigorous approach of Fortelný and Kovář [38] to describe the size of the dispersed particles, i.e.

$$d = d_c + \frac{\gamma_{AB} \, \alpha}{\eta_m \, f} \, \varphi \tag{8}$$

where f is the frequency of particle break-up which is regarded as constant, and d_c a critical particle size which forms upon phase separation and is proportional to the square root of Flory-Huggins interaction parameter [38,47]. Introducing **Eq. 7** into **Eq. 8** and combining the variables regarded as constant into parameters we obtain

$$d = k_3 \, \chi^{1/2} + k_4 \, \chi \, \varphi^2 \tag{9}$$

describing the dependence of particle size on composition and component interactions. We

must emphasize here, that all parameters related to the kinetics of particle break-up were regarded as constant under the more or less equilibrium conditions of our study, which might not be valid in other systems.

Eq. 9 was fitted to the experimental data and the resulting parameters are listed in **Table 2**. The determination coefficient of the fitting (R^2), i.e. the goodness of the fit is reasonable in most cases. The somewhat smaller values of R^2 obtained for the polymers with large VOH content can be explained with the relatively small changes in particle size as a function of composition for these polymers (see **Fig. 2**) and with the large uncertainty in the determination of particle size.

Table 2   Parameters determined by the fitting of the proposed model (**Eq. 9**) to the experimental data; coalescence probability and critical particle size

Matrix	$d_c = k_3\,\chi^{1/2}$	$k_4\,\chi$	R^{2a}
LDPE	5.67	136.8	0.9640
EVOH52	1.60	58.5	0.9004
EVOH62	0.33	36.9	0.8684
EVOH68	0.58	12.0	0.7094
EVOH76	0.39	6.1	0.7550

a) Determination coefficient indicating the goodness of the fit.

The intercept of the fitted function, i.e. critical particle size, should depend linearly on the square root of the Flory-Huggins interaction parameter. A linear correlation is predicted between the other fitting parameter and χ. The constants obtained are plotted against χ in **Figs. 9** and **10** in accordance with **Eq. 9**. Both correlations are straight lines indeed with very limited deviation from the general tendency, which strongly corroborates the approach.

According to the results coalescence probability decreases strongly with decreasing interaction of the components, i.e. with increasing interfacial tension in accordance with published theories. Parameter $k_3\chi^{1/2}$ corresponds to the critical particle size. The results confirm its existence, on the one hand, while indicate that this critical size strongly decreases with increasing strength of component interactions. The proposed approach describes the evolution of structure quite well in EVOH/lignin blends and it is strongly justified by the agreement with experimental results.
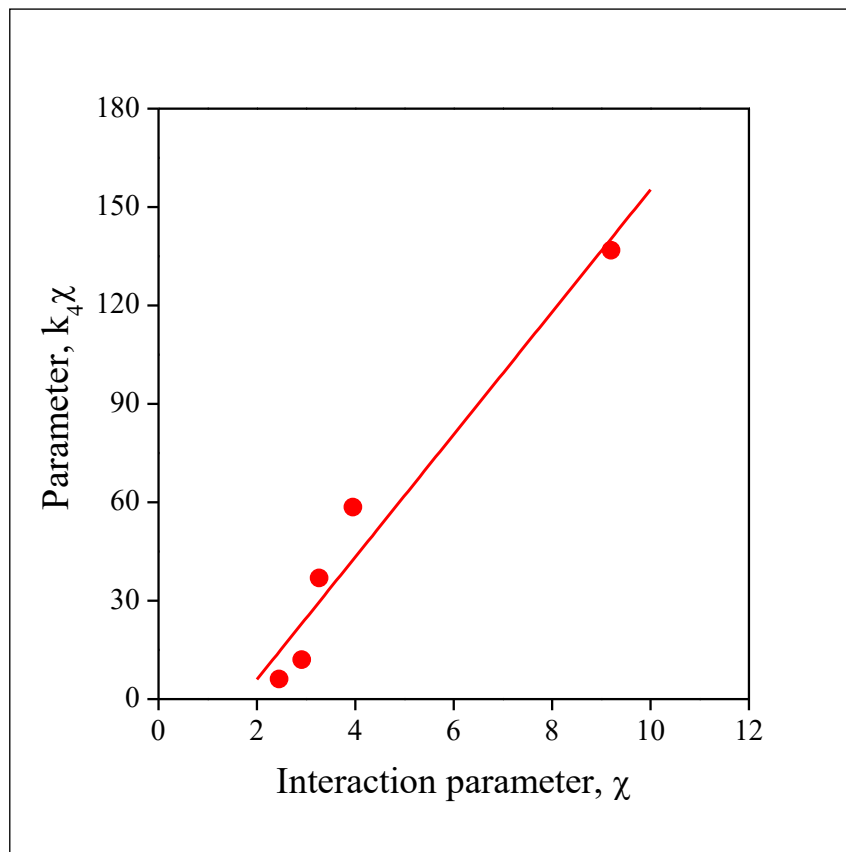

Fig. 9   Correlation between the combined parameter $k_4\chi$ containing coalescence probability and the Flory-Huggins interaction parameter, see **Eq. 9**.
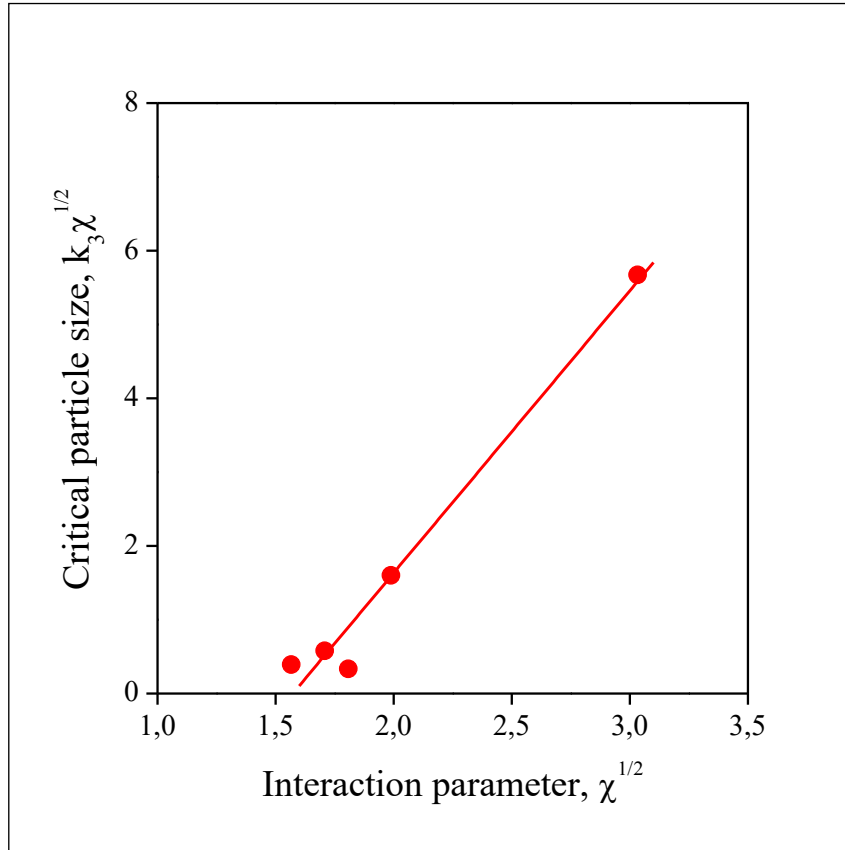
Fig. 10   Dependence of the critical particle size ($k_3\chi^{1/2}$) on component interactions, see
Eq. 9.

3.5. Comparison to existing theories, reliability

Several equations describing the composition dependence of particle size were pub-
lished already in the literature [35,36,38,39,44,50]. These formulae, including **Eq. 9**, are
derived from the direct analysis of the dynamic equilibrium between particle break-up and
coalescence, and they are mostly multiple power functions of the variables (composition).
The simplest formula is **Eq. 2**, which is actually a power function with the exponent of 1
[44]. This model neglects the existence of a critical particle size, thus it cannot be used for
the data presented in this paper. The formula proposed by Fortelný and Kovář [38], i.e. **Eq.
8** contains the critical particle size. The shape of the correlations presented in **Figs. 2** and **8**

indicates that the validity of the linear model is limited to smaller concentrations of the dispersed phase. The range of validity can be widened by increasing the exponent. Huneault et al. [50] proposed a formula with an exponent of 4/3

$$d = d_c + (6C_H Ca_c t_B)^{1/2} \varphi^{4/3} \tag{10}$$

where C_H is a coalescence constant, Ca_c the critical capillary number, and t_B a dimensionless breakup time of the droplets of the dispersed phase. The fit of the various approaches described by **Eqs. 8-10** is presented in **Fig. 11**, which indicates also their range of validity.
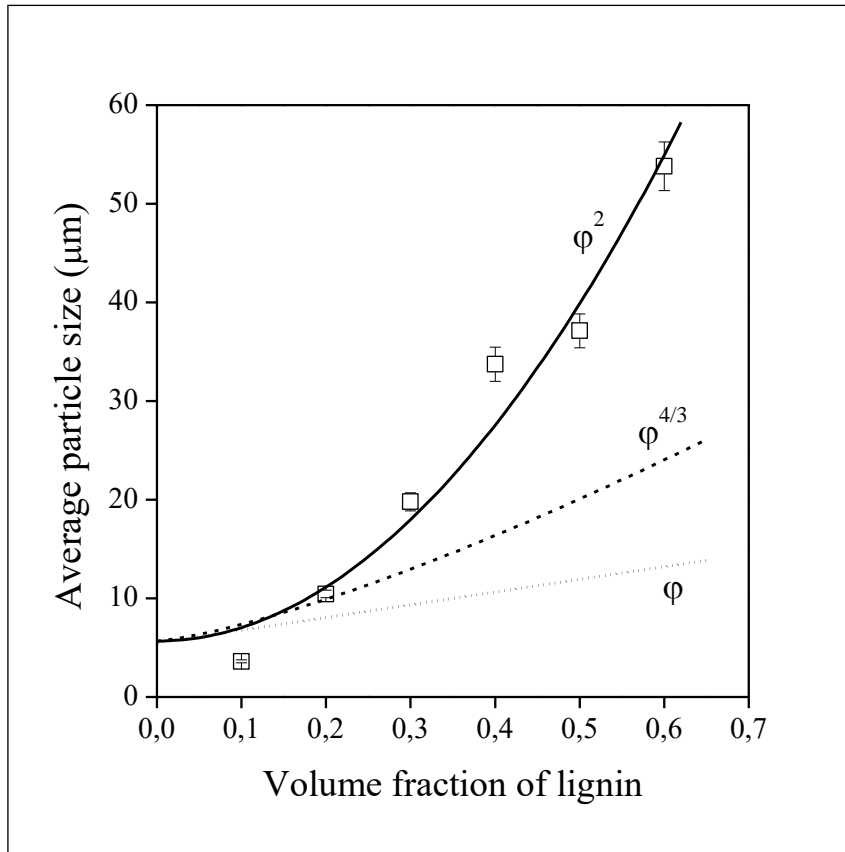

Fig. 11   Comparison of the reliability of published theories and their range of validity for LDPE/lignin blends (see **Eqs. 8-10**). Models: •••••••• **Eq. 8** Fortelný and Kovář [38]; ------ **Eq. 10** by Huneault et al. [50]; ——— **Eq. 9**, this work.

The data obtained for the LDPE/lignin blend are used for comparison, since particle size shows the largest dependence on composition in this blend. The relationships are practically the same for all the PVOH/lignin blends, but because of the smaller particle sizes, the differences are also smaller. Our model agrees with the experimental results quite well even at large concentrations of lignin, so we may assume that **Eq. 9** is valid in the studied concentration range. The model of Fortelný and Kovář [38] describes the data only up to 10-15 vol% of lignin content, while that of Huneault et al. [50] up to 20-25 vol% (see **Fig. 11**). Reliability is better also for these two latter models for the EVOH68/lignin blends because of smaller differences in particles size; therefore, we assume that the validity range of these models widens as the Flory-Huggins interaction parameter and thus particle size decreases. This assumption is corroborated also by the composition dependence of droplet size published for polypropylene (PP)/ethylene-propylene rubber (EPR) blends [36,43,49]. These blends have a small Flory-Huggins interaction parameter; EPR droplets smaller than 1.5 μm are dispersed in PP. The model proposed by Huneault et al. [50] is valid up to 30 vol% dispersed phase content, while the linear model [38] up to 20-30 vol% depending on the chemical structure of the components, i.e. their compatibility.

A formula with an exponent of 2, i.e. similar to ours was also proposed by Fortelný et al. [35,39]

$$d = d_c + \left(\frac{4}{\pi}\right)^2 f_c d_c \alpha^2 \varphi^2 \tag{11}$$

where f_c is a function containing the rheological properties of the two components. However, this model cannot not be used for our data because of the very different assumptions used during its development. Firstly, **Eq. 11** was developed for dilute systems in which particle break-up is the dominating process. Secondly, Fortelný et al. [35,39] analyzed the kinetics of particle break-up and coalescence and the model does not include any parameter which

is directly related to interactions. **Eq. 11** contains the coalescence probability, but does not define the factors determining it.

Fortelný et al. [36] created also a full quadratic formula

$$d = d_c + \frac{8\gamma_{AB}\alpha}{\pi f \eta_m}\varphi + \frac{2\gamma_{AB}K_2}{f \eta_m \gamma}\varphi^2 \qquad (12)$$

where K_2 is a fitting constant. The application of this model results in overfitting for blends with small Flory-Huggins interaction parameter, because of the relatively small changes in particle size as a function of composition and the large uncertainty of particle size determination. Overfitting, in this case, means that polynomials with a minimum can be fitted to the experimental results that cannot be explained reasonably, because of the negligible role of kinetic effects.

4. CONCLUSIONS

In spite of the hydrogen bonds developing between the components, lignin and ethylene-vinyl alcohol copolymers form heterogeneous blends, because of the strong self-interactions of lignin. Because of immiscibility, lignin is dispersed in the form of particles in the EVOH phase even at lignin contents as large as 60 vol%. The size of dispersed lignin particles is determined by particle break-up and coalescence, the original lignin particles of around 80 μm size break up to much smaller ones; particle sizes below one micrometer form at large vinyl alcohol content. Thermodynamic factors are stronger than kinetic ones in the studied system, changing shear stresses do not influence particle size much. The coalescence of particles is determined by composition and component interactions and a simple semi-empirical model was proposed to describe the correlations of these variables quantitatively. Good agreement was found between the prediction of the model and experimental data. The size of dispersed lignin particles affects strongly the properties of the blends and the control

of thermodynamic factors result in blends with better properties.

6. REFERENCES

[1]   D. Kun, B. Pukánszky, Polymer/lignin blends: Interactions, properties, applications, Eur. Polym. J. 93 (2017) 618–641. doi:10.1016/j.eurpolymj.2017.04.035.

[2]   B. Bozsódi, V. Romhányi, P. Pataki, D. Kun, K. Renner, B. Pukánszky, Modification of interactions in polypropylene/lignosulfonate blends, Mater. Des. 103 (2016) 32–39. doi:10.1016/j.matdes.2016.04.061.

[3]   P. Buono, A. Duval, P. Verge, L. Averous, Y. Habibi, New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation, ACS Sustain. Chem. Eng. 4 (2016) 5212–5222. doi:10.1021/acssuschemeng.6b00903.

[4]   M. Culebras, A. Beaucamp, Y. Wang, M.M. Clauss, E. Frank, M.N. Collins, Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors, ACS Sustain. Chem. Eng. 6 (2018) 8816–8825. doi:10.1021/acssuschemeng.8b01170.

[5]   S. Atifi, C. Miao, W.Y. Hamad, Surface modification of lignin for applications in polypropylene blends, J. Appl. Polym. Sci. 134 (2017) 45103. doi:10.1002/app.45103.

[6]   H. Ye, Y. Zhang, Z. Yu, Effect of Desulfonation of Lignosulfonate on the Properties of Poly(Lactic Acid)/Lignin Composites, BioResources. 12 (2017) 4810–4829. doi:10.15376/biores.12.3.4810-4829.

[7]   G. Szabó, V. Romhányi, D. Kun, K. Renner, B. Pukánszky, Competitive Interactions in Aromatic Polymer/Lignosulfonate Blends, ACS Sustain. Chem. Eng. 5 (2017) 410–419. doi:10.1021/acssuschemeng.6b01785.

[8]   J. Tomaszewska, L. Klapiszewski, K. Skorczewska, T.J. Szalaty, T. Jesionowski, Advanced organic-inorganic hybrid fillers as functional additives for poly(vinyl chloride), Polimery. 62 (2017) 19–26. doi:10.14314/polimery.2017.019.

[9]   A.T.R. Sugano-Segura, L.B. Tavares, J.G.F. Rizzi, D.S. Rosa, M.C. Salvadori, D.J. dos Santos, Mechanical and thermal properties of electron beam-irradiated polypropylene reinforced with Kraft lignin, Radiat. Phys. Chem. 139 (2017) 5–10. doi:10.1016/j.radphyschem.2017.05.016.

[10]   P.A. Victor, S.B. Gonçalves, F. Machado, Styrene/Lignin-Based Polymeric Composites Obtained Through a Sequential Mass-Suspension Polymerization Process, J. Polym. Environ. 26 (2018) 1755–1774. doi:10.1007/s10924-017-1078-2.

[11]   B. Podolyák, D. Kun, K. Renner, B. Pukánszky, Hydrogen bonding interactions in poly(ethylene-co-vinyl alcohol)/lignin blends, Int. J. Biol. Macromol. 107 (2018) 1203–1211. doi:10.1016/j.ijbiomac.2017.09.098.

[12]   D. Ye, J. Kong, S. Gu, Y. Zhou, C. Huang, W. Xu, X. Zhang, Selective aminolysis of acetylated lignin: Toward simultaneously improving thermal-oxidative stability and maintaining mechanical properties of polypropylene, Int. J. Biol. Macromol. 108 (2018) 775–781. doi:10.1016/j.ijbiomac.2017.10.168.

[13]   E.M. Zadeh, S.F. O'Keefe, Y.-T. Kim, Utilization of Lignin in Biopolymeric Packaging Films, ACS Omega. 3 (2018) 7388–7398.

doi:10.1021/acsomega.7b01341.

[14] B. Pang, S. Yang, W. Fang, T.-Q. Yuan, D.S. Argyropoulos, R.-C. Sun, Structure-property relationships for technical lignins for the production of lignin-phenol-formaldehyde resins, Ind. Crops Prod. 108 (2017) 316–326. doi:10.1016/j.indcrop.2017.07.009.

[15] F. Ferdosian, Z. Yuan, M. Anderson, C. (Charles) Xu, Synthesis and characterization of hydrolysis lignin-based epoxy resins, Ind. Crops Prod. 91 (2016) 295–301. doi:10.1016/j.indcrop.2016.07.020.

[16] Ł. Klapiszewski, A. Jamrozik, B. Strzemiecka, I. Koltsov, B. Borek, D. Matykiewicz, A. Voelkel, T. Jesionowski, Characteristics of Multifunctional, Eco-Friendly Lignin-Al2O3 Hybrid Fillers and Their Influence on the Properties of Composites for Abrasive Tools, Molecules. 22 (2017) 1920. doi:10.3390/molecules22111920.

[17] L.B. Tavares, C. V. Boas, G.R. Schleder, A.M. Nacas, D.S. Rosa, D.J. Santos, Bio-based polyurethane prepared from Kraft lignin and modified castor oil, Express Polym. Lett. 10 (2016) 927–940. doi:10.3144/expresspolymlett.2016.86.

[18] J. Wang, S. Li, R. Liang, B. Wu, Y. He, Synthesis and characterization of water-soluble PEGylated lignin-based polymers by macromolecular azo coupling reaction, Chinese Chem. Lett. 29 (2018) 143–146. doi:10.1016/j.cclet.2017.07.008.

[19] O.A.T. Dias, D.R. Negrão, D.F.C. Gonçalves, I. Cesarino, A.L. Leão, Recent approaches and future trends for lignin-based materials, Mol. Cryst. Liq. Cryst. 655 (2017) 204–223. doi:10.1080/15421406.2017.1360713.

[20] H. Jeong, J. Park, S. Kim, J. Lee, J.W. Cho, Use of acetylated softwood kraft lignin as filler in synthetic polymers, Fibers Polym. 13 (2012) 1310–1318. doi:10.1007/s12221-012-1310-6.

[21] C. Liu, C. Xiao, H. Liang, Properties and structure of PVP-lignin "blend films," J.

Appl. Polym. Sci. 95 (2005) 1405–1411. doi:10.1002/app.21367.

[22] G. Cunxiu, C. Donghua, T. Wanjun, L. Changhua, Properties and thermal degradation study of blend films with poly(4-vinylpyridine) and lignin, J. Appl. Polym. Sci. 97 (2005) 1875–1879. doi:10.1002/app.21465.

[23] P.C. Rodrigues, M.P. Cantão, P. Janissek, P.C.. Scarpa, A.L. Mathias, L.P. Ramos, M.A.. Gomes, Polyaniline/lignin blends: FTIR, MEV and electrochemical characterization, Eur. Polym. J. 38 (2002) 2213–2217. doi:10.1016/S0014-3057(02)00114-3.

[24] S. El Raghi, R.. Zahran, B.. Gebril, Effect of weathering on some properties of polyvinyl chloride/lignin blends, Mater. Lett. 46 (2000) 332–342. doi:10.1016/S0167-577X(00)00197-X.

[25] W. Ouyang, Y. Huang, H. Luo, D. Wang, Poly(Lactic Acid) Blended with Cellulolytic Enzyme Lignin: Mechanical and Thermal Properties and Morphology Evaluation, J. Polym. Environ. 20 (2012) 1–9. doi:10.1007/s10924-011-0359-4.

[26] P. Mousavioun, W.O.S. Doherty, G. George, Thermal stability and miscibility of poly(hydroxybutyrate) and soda lignin blends, Ind. Crops Prod. 32 (2010) 656–661. doi:10.1016/J.INDCROP.2010.08.001.

[27] P. Mousavioun, P.J. Halley, W.O.S. Doherty, Thermophysical properties and rheology of PHB/lignin blends, Ind. Crops Prod. 50 (2013) 270–275. doi:10.1016/J.INDCROP.2013.07.026.

[28] J.F. Kadla, S. Kubo, Lignin-based polymer blends: analysis of intermolecular interactions in lignin–synthetic polymer blends, Compos. Part A Appl. Sci. Manuf. 35 (2004) 395–400. doi:10.1016/j.compositesa.2003.09.019.

[29] K. Dobrovszky, F. Ronkay, Effects of SEBS-g-MA on Rheology, Morphology and Mechanical Properties of PET/HDPE Blends, Int. Polym. Process. 30 (2015) 91–99.

doi:10.3139/217.2970.

[30] B. Imre, D. Bedő, A. Domján, P. Schön, G.J. Vancso, B. Pukánszky, Structure, properties and interfacial interactions in poly(lactic acid)/polyurethane blends prepared by reactive processing, Eur. Polym. J. 49 (2013) 3104–3113. doi:10.1016/J.EURPOLYMJ.2013.07.007.

[31] C. Yu, D. Shi, J. Wang, H. Shi, T. Jiang, Y. Yang, G.-H. Hu, R.K.Y. Li, Effect of a dual compatibilizer on the formation of co-continuous morphology of immiscible polymer blends, Mater. Des. 107 (2016) 171–177. doi:10.1016/j.matdes.2016.06.044.

[32] K. Dobrovszky, F. Ronkay, Effects of Phase Inversion on Molding Shrinkage, Mechanical, and Burning Properties of Injection-molded PET/HDPE and PS/HDPE Polymer Blends, Polym. Plast. Technol. Eng. 56 (2017) 1147–1157. doi:10.1080/03602559.2016.1255752.

[33] S. Wu, Phase structure and adhesion in polymer blends: A criterion for rubber toughening, Polymer (Guildf). 26 (1985) 1855–1863. doi:10.1016/0032-3861(85)90015-1.

[34] B. Pukánszky, I. Fortelný, J. Kovář, F. Tüdős, Particle break-up and coalescence in heterogeneous PP/EPDM blends; effect of particle size on some mechanical properties, Plast. Rubber Compos. Process. Appl. 15 (1991) 31–38.

[35] I. Fortelný, Theoretical aspects of phase morphology development, in: S. Thomas, G. Groeninckx, C. Harrats (Eds.), Micro- Nanostructured Multiph. Polym. Blend Syst. Phase Morphol. Interfaces, CRC Press, Boca Raton, 2006: pp. 43–90. doi:10.1201/9781420026542.

[36] I. Fortelný, J. Kovář, M. Stephan, Analysis of the Phase Structure Development during the Melt Mixing of Polymer Blends, J. Elastomers Plast. 28 (1996) 106–139.

doi:10.1177/009524439602800202.

[37] N. Tokita, Analysis of Morphology Formation in Elastomer Blends, Rubber Chem. Technol. 50 (1977) 292–300. doi:10.5254/1.3535144.

[38] I. Fortelný, J. Kovář, Droplet size of the minor component in the mixing of melts of immiscible polymers, Eur. Polym. J. 25 (1989) 317–319. doi:10.1016/0014-3057(89)90239-5.

[39] I. Fortelný, Analysis of the effect of breakup frequency on the steady droplet size in flowing polymer blends, Rheol. Acta. 40 (2001) 485–489. doi:10.1007/s003970100174.

[40] S. Krause, Polymer Compatibility, J. Macromol. Sci. Part C Polym. Rev. 7 (1972) 251–314. doi:10.1080/15321797208068166.

[41] B.O. Myrvold, The Hansen Solubility Parameters of Some Lignosulfonates, World Acad. Sci. Eng. Technol. Int. J. Energy Power Eng. 1 (2014) 261.

[42] K.L. Hoy, New values of the solubility parameters from vapor pressure data, J. Paint Technol. 42 (1970) 76–118.

[43] I. Fortelný, D. Kamenická, J. Kovář, Effect of the viscosity of components on the phase structure and impact strength of polypropylene/ethylene-propylene elastomer blends, Angew. Makromol. Chemie. 164 (1988) 125–141. doi:10.1002/apmc.1988.051640110.

[44] E. Fekete, B. Pukánszky, Z. Peredy, Mutual correlations between parameters characterizing the miscibility, structure and mechanical properties of polymer blends, Angew. Makromol. Chemie. 199 (1992) 87–101. doi:10.1002/apmc.1992.051990108.

[45] G.I. Taylor, The Formation of Emulsions in Definable Fields of Flow, Proc. R. Soc. A Math. Phys. Eng. Sci. 146 (1934) 501–523. doi:10.1098/rspa.1934.0169.

[46] E. Helfand, Theory of inhomogeneous polymers: Lattice model for polymer–polymer interfaces, J. Chem. Phys. 63 (1975) 2192–2198. doi:10.1063/1.431599.

[47] H.-W. Kammer, Surface and Interfacial Tension of Polymer Melts — Thermodynamic Theory of the Interface between Immiscible Polymers, Zeitschrift Für Phys. Chemie. 258 (1977) 1149–1161. doi:10.1515/zpch-1977-258153.

[48] I. Fortelný, A. Živný, Extensional flow induced coalescence in polymer blends, Rheol. Acta. 42 (2003) 454–461. doi:10.1007/s00397-003-0300-4.

[49] I. Fortelný, B. Dimzoski, D. Michálková, J. Mikešová, L. Kaprálková, Dependence of the Average Size of Particles Formed during Steady Mixing on their Concentration in Immiscible Polymer Blends, J. Macromol. Sci. Part B. 52 (2013) 662–673. doi:10.1080/00222348.2012.720176.

[50] M.A. Huneault, Z.H. Shi, L.A. Utracki, Development of polymer blend morphology during compounding in a twin-screw extruder. Part IV: A new computational model with coalescence, Polym. Eng. Sci. 35 (1995) 115–127. doi:10.1002/pen.760350114.