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Correlations among interactions, structure and properties in lignin-based polymer blends and hybrid systems

Thesis book

by

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1. Introduction

Lignin is a biopolymer with great potential because it is widely available and has a versatile structure with many functional groups. These features make it suitable for use in many different industries, and intensive research has been going on for decades to facilitate the use of lignin also in the plastics industry. Despite a few notable examples in other sectors, a true breakthrough in the large-scale application of lignin in plastics has yet to be achieved. While research in this area is active, the unique, variable, and complex properties of lignin continue to pose substantial challenges in developing robust solutions. In many cases, lignin is incorporated into polymer systems only in small amounts, and it is often difficult to draw meaningful conclusions from studies that lack systematic sample preparation and comprehensive characterisation across a range of compositions. As a result, numerous questions remain open in each research project, and contradictory findings are common.

Understanding the relationships between the structure, properties, and interfacial interactions in polymer blends and composites is crucial for the advancement of lignin-based systems. Our research group has previously conducted detailed investigations into the specific dispersion, π–π, hydrogen bonding, and ionic interactions between the components of polymer/lignin blends. Nevertheless, even with systematic studies, fully elucidating the behaviour of lignin-based systems remains a formidable challenge. Many open questions persist, particularly regarding the analysis and competitive nature of hydrogen bonding and ionic interactions. Additionally, we sought to explore the behaviour of lignin in hybrid polymer systems. Therefore, the Thesis focused on a more in-depth understanding of polymer/lignin blends as well as their hybrid polymer systems, aiming to clarify the complex relationships that govern their structure and properties.

2. Background

Lignin is a complex organic polymer that is a major component of plant cell walls, serving as a chemical and physical link between the two primary matrix components, cellulose and hemicellulose. This compound is found in varying concentrations in different types of plants, with wood being one of the richest sources. The structural diversity of lignin arises from the various ways the three monomer units [p-hydroxyphenyl (H),

guaiacyl (G), and syringyl (S)] interconnect to produce its complex architecture. Lignin also has various functional groups, such as phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, carbonyl groups, and methoxyl groups. The amount of these functional groups may differ depending on the type of plant and the extraction method used[1].

Technical lignins are derived as byproducts from various pretreatment or separation processes in which lignocellulosic biomasses are used as raw materials, like in the paper industry or in second-generation bioethanol production. These technical or commercial lignins can be divided into two major categories depending on the pulping procedure. Sulfur-containing lignins include kraft lignin and lignosulfonates, which are produced using sulfur-based pulping processes. Sulfur-free lignins include soda lignins, organosolv lignins, steam-explosion lignins, and others derived from processes that do not involve sulfur compounds. Of the total commercial technical lignin produced each year (excluding that used for energy), lignosulfonates account for approximately 80%, kraft lignin for about 15%, and hydrolysis and soda lignin together make up around 5%. Kraft lignin is a chemically modified, sulfur-containing by-product of kraft pulping. It is characterised by significant phenolic hydroxyl content and limited direct applicability due to residual carbohydrates and sulfur. Lignosulfonates are water-soluble, sulfonated lignin derivatives produced as by-products of sulfite pulping, notable for their higher molecular weight, larger sulfur and ash content, and their branched, functionalised polymer structure[2].

Out of the total amount of lignin produced, approximately 98–99% is either directly or indirectly burned to generate heat and power. Conversely, only a small fraction, around 1–2% of the produced lignin, undergoes chemical conversion to yield speciality chemicals and products[3]. Despite its potential for creating high-value products, widespread availability, and substantial research efforts, lignin has not yet been employed commercially. Several factors hinder the industrial utilisation of lignin, including its non-uniform structure, unique chemical reactivity, and the presence of various organic and inorganic

1. Calvo-Flores, F.G., Dobado, J.A., Isac-García, J., Martín-Martínez, F.J., Lignin and Lignans as Renewable Raw Materials, John Wiley & Sons, Inc., Chichester, **2015**.
2. Chung, H., Washburn, N.R., in: Faruk, O. (Ed.), Lignin Polym. Compos., Elsevier, Oxford, **2016**, pp. 13–25.
3. Patel, R., Dhar, P., Babaei-Ghazvini, A., Nikkhah Dafchahi, M., Acharya, B., *Bioresour. Technol. Reports*, 22, **2023**, 101463.

impurities[4]. Additionally, challenges are encountered in the recovery of lignins from product streams.

In the past decades, numerous publications and reviews discussed the utilisation of lignin in the field of plastics as antioxidant, or fire-retardant additive, or raw material for thermosetting and thermoplastic materials. Blending is a common and effective approach for developing materials with novel and improved properties. Lignin has been incorporated into various natural and synthetic polymers[5]. The thermoplastic materials based on lignin offer cost-effective and partially carbon-neutral options. However, similarly to blends of commodity and engineering polymers, most polymer/lignin blends are only partially miscible, resulting in a heterogeneous structure. In most cases, the incorporation of lignin into thermoplastics has also led to deteoriated mechanical strength[6].

The properties of such heterogeneous polymer systems are determined by four main factors: component characteristics, their ratio (composition), the resulting structure, and interfacial interactions[7]. The interactions are particularly critical in blends, as they influence the mutual solubility of the phases, the thickness and properties of the interphase formed, and ultimately overall blend morphology. Moreover, the structure and properties of partially miscible blends are affected by processing conditions, which can affect conclusions about compatibility when drawn from macroscopic properties or morphology[8]. The strong self-interactions among lignin molecules, resulting from their numerous polar functional groups, also play a crucial role in determining the structure and properties of polymer/lignin blends. Unfortunately, only a few studies address the correlation between miscibility, structure, and properties, and even fewer do so quantitatively, despite the importance of these relationships.

The required property combination often cannot be achieved by simple blending of the two components. Introducing the concept of hybrid materials for lignin-based polymers offers a promising route to overcome the limitations arising from the polarity and complex functionality of lignin, hindering its uniform dispersion and strong interfacial

4. Vishtal, A., Kraslawski, A., *BioResources*, 6, **2011**, 3547–3568.
5. Bajwa, D.S., Pourhashem, G., Ullah, A.H., Bajwa, S.G., *Ind. Crops Prod.*, 139, **2019**, 111526.
6. Kun, D., Pukánszky, B., *Eur. Polym. J.*, 93, **2017**, 618–641.
7. Imre, B., Pukánszky, B., *Eur. Polym. J.*, 49, **2013**, 1215–1233.
8. Fekete, E., Pukánszky, B., Peredy, Z., *Angew. Makromol. Chemie*, 199, **1992**, 87–101.

adhesion within most polymer matrices. Hybrid polymer materials are systems where either a single polymer matrix is reinforced with two or more different types of fillers or fibers, a single type of reinforcement is incorporated into a blend of various polymers, or the combination of these strategies is applied[9]. The original aim of developing such hybrids is to achieve significant improvements in targeted mechanical properties by exploiting the potential synergistic effects of the individual components. However, such a synergy does not always exist in practice, and hybrid composites often show only moderate performance. Essentially, hybridisation means mixing different components to tailor the final properties of the material. Combining lignin with additional reinforcing or toughening agents – such as fibres, fillers, or elastomers – makes it possible to tailor the morphology and properties of the material more efficiently and broaden its application potential.

3. Materials and methods

Two-component blends were prepared from ethylene-vinyl alcohol (EVOH) copolymers and Bretax SRO2 grade lignosulfonate from to study the factors influencing blend morphology. The vinyl alcohol (VOH) content of the copolymers varied from 52 to 76 mol%, resulting in changing interactions. Low-density polyethylene (PE-LD) with zero VOH content was used as reference. Ionomers were prepared from ethylene-acrylic acid (EAA) copolymer neutralised with anhydrous sodium carbonate (Na_2CO_3). EAA copolymers with the degree of neutralisation of 0, 17, 33, 50, and 67% were blended with the Bretax CRO2 grade lignosulfonate. The amount of lignin in these blends changed from 0 to 50 or 60 vol% in 10 vol% steps. Two- and three-component blends were prepared from polylactic acid (PLA), the Indulin AT kraft lignin and poly(butylene adipate-co-terephthalate) (PBAT). The lignin content of the PLA/lignin blends varied between 0 and 50 vol%, and that of the PBAT/lignin blends between 0 and 70 vol%, respectively, in 10 vol% increments in both cases. Two-component blends were prepared from PLA and PBAT in the entire composition range; composition changed in 10 vol% steps in this case, too.

Hybrid blends contained 10, 20 and 30 vol% lignin, and their PBAT content changed between 0 and 80 vol%, respectively, in 10 vol% steps. A maleic anhydride grafted PLA

9. Czigány, T., in: Polym. Compos., Springer, Boston, **2005**, pp. 309–328.

coupling agent (MAPLA) was added to improve the interaction between PLA and the other two components at 10 wt%, which was calculated for the amount of the dispersed component. The components were homogenised in an internal mixer. Torque and temperature were recorded during mixing and used in further analysis. Plates of 1 mm thickness were compression molded from the homogenised blends. Subsequently, tensile bars were machined from the plates for further testing.

The heterophase ethylene-propylene copolymer (rPP) was homogenised in an extruder with the SRO2 grade lignosulfonate and flax fiber. The lignin content of the hybrid composites changed from 10 to 50 vol%, while their flax content changed from 10 to 30 vol%, both in 10 vol% steps. Two-component rPP/flax composites and rPP/lignin blends were used as reference. The amount of maleic anhydride-functionalized polypropylene (MAPP) was always 10 wt% calculated for the total amount of natural reinforcements. After extrusion, standard tensile test specimens were injection molded.

Before homogenisation, the components were dried to remove their moisture content, and the prepared specimens were stored at ambient temperature (23 °C, 50% RH) for a week before testing.

To determine the relaxation transitions and glass transition temperature (T_g) of the PLA/lignin/PBAT blends, dynamic mechanical thermal analysis (DMTA) was carried out in tensile mode. Transitions were also studied by differential scanning calorimetry (DSC) in two heating and one cooling runs. Melt flow rate measurements characterised the rheological characteristics of fiber-containing hybrid composites. Mechanical properties were analysed by tensile testing, while local deformation processes were followed by acoustic emission testing. Impact resistance was characterised by the notched Charpy impact strength, and instrumented impact tests were also carried out. The structure of the blends was also analysed by scanning electron microscopy (SEM). Thin slices were cut from the 1 mm thick plates followed by the complete dissolution of lignosulfonate from the slices by soaking them in distilled water. The kraft lignin was dissolved from the slices by soaking them in a 70:30 mixture of acetone and distilled water. 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, and the

structure of the materials was also studied through digital optical microscopy (DOM). The interactions within EAA/lignin and ionomer/lignin blends were analysed using classical molecular dynamics simulations.

4. Results

4.1 Structure evolution in EVOH/lignin blends

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 worth paying more attention to this question. Accordingly, we prepared EVOH/lignin blends in a wide range of lignin contents (**Publication 1**). In spite of the hydrogen bonds developing between the components, lignin and EVOH 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%. 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 interfacial interactions and a large amount of the dispersed component lead to coalescence. We observed that the original lignin particles of around 80 μm size break up to much smaller ones; particle sizes below 1 μm form at large VOH content (**Fig. 1**). We proved that thermodynamic factors are stronger than kinetic ones in the studied system because changing shear stresses do not influence particle size much. The coalescence of particles is determined by composition

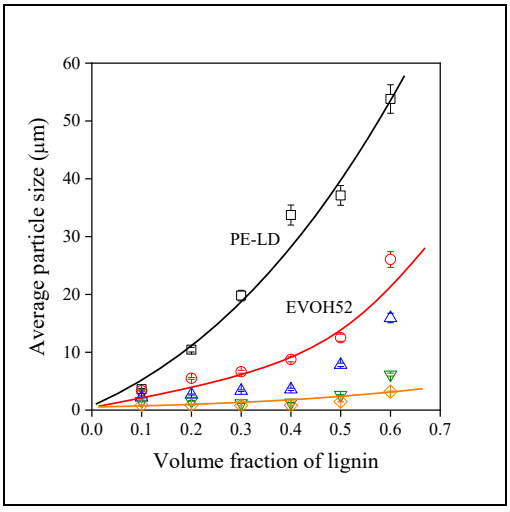

Fig. 1 *Composition dependence of the number average particle size of lignin in polymer/lignin blends. Effect of VOH content. Symbols:* (□) *PE-LD,* (○) *EVOH52,* (△) *EVOH62,* (▽) *EVOH68,* (◇) *EVOH76.*

and component interactions, and we proposed a simple semi-empirical model to describe the correlation of these variables:

$$d = k_3 \chi^{1/2} + k_4 \chi \varphi^2 \quad (4.1)$$

where d is the diameter of the dispersed phase, χ is the Flory-Huggins interaction parameter, φ is the volume fraction of the dispersed phase, and k_3 and k_4 are constants. Parameter $k_3\chi^{1/2}$ corresponds to a critical particle size, while the combined parameter $k_4\chi$ contains the coalescence probability. We found good agreement between the prediction of the model and experimental data. Because the size of dispersed lignin particles strongly affects the properties of the blends, we concluded that the control of thermodynamic factors will result in blends with better properties.

4.2 Competitive interactions in ionomer/lignin blends

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 neutralised, 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, which is a common feature of lignosulfonates as well. Recently, our group produced blends from a lignosulfonate and commercially available ionomers for the first time[10]. The functional groups of ionomers and lignosulfonate can form hydrogen and ionic bonds; thus, in their blends, strong interactions form at the interface between the components. In commercially available ionomers, several variables (type of monomers, molecular weight, carboxylate counter-ion, concentration of carboxyl and carboxylate groups) changed simultaneously, thus preventing the accurate quantitative analysis of the competition between ionic and hydrogen bonding. For this reason, we prepared ionomers from an ethylene-acrylic acid copolymer (EAA) by neutralising the acid groups with sodium carbonate in different ratios (**Publication 2**). Consequently, the concentrations of carboxyl and carboxylate groups were systematically varied in the copolymers to study the competition of hydrogen and ionic bonds forming between lignin and ionomers. The

10. Szabó, G., Kun, D., Renner, K., Pukánszky, B., *Mater. Des.*, 152, **2018**, 129–139.

effect of this competition was studied through the correlation of local deformation processes, structure (**Fig. 2**), and the composition dependence of tensile strength in blends. We also analysed the results quantitatively using appropriate models. Contrary to our expectations, if the acid groups in the ionomer matrix are neutralised to a larger extent, i.e., the number of carboxylate groups increases, the interactions are weaker than in the EAA 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 fewer hydrogen bonds between the ionomer and lignin. Additionally, the carboxylate groups of the ionomer are present in larger numbers in the clusters than at the interface between the components. As a result, optimising the degree of neutralisation – and thus the balance of interactions – enables the production of structural materials from ionomer/lignin blends containing approximately 30 vol% lignin, with an acceptable combination of modulus, tensile strength, and elongation at break.

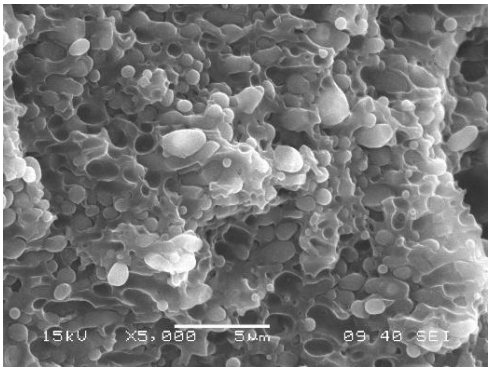

Fig. 2 *SEM micrograph of an ionomer/lignin blend demonstrating debonding. Magnification: 5000x. Lignin content: 30 vol%. Degree of neutralisation: 50%.*

4.3 Properties of PLA/lignin/PBAT hybrid blends

Previously, many attempts have been made to apply lignin in PLA/lignin blends, to decrease the price, possibly improve the mechanical properties and reduce the carbon footprint of the final product. However, the large stiffness but small strength, deformability and impact resistance of PLA/lignin blends hinder their future practical application. Hybridisation is thought to be an approach that solves all problems related to the structure and properties of heterogeneous blends and composites. In accordance, we aimed to

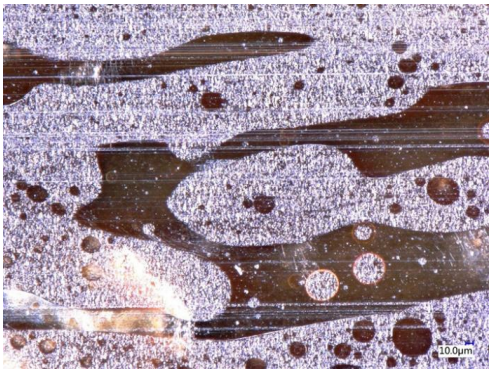

Fig. 3 *DOM micrograph of a PLA/lignin/PBAT blend at 30 vol% lignin and 30 vol% PBAT content. The blend also contained MAPLA.*

explore the possibility of improving the mechanical properties, especially the brittleness, of PLA/lignin blends by adding PBAT as a third component (**Publication 3**). Theoretical considerations and thermal analysis showed that the interactions among all components are weak; they are immiscible with each other. The interactions between PBAT and lignin are somewhat stronger than those between PLA and the other two components. The maleic anhydride grafted PLA added as a coupling agent proved completely ineffective; it does not modify the interactions. The structural analysis confirmed the immiscibility of the components; the structure of the blends was heterogeneous at each composition. A dispersed structure formed when the concentration of one of the components was small, while, depending on lignin content, an interpenetrating network-like structure developed, and phase inversion took place. The width of the IPN-like structure (**Fig. 3**) is relatively narrow, proving the formation of weak interactions among the components again. Lignin was located mainly in the PBAT phase. We proved that the properties are determined by the relative amount of PBAT and PLA (**Fig. 4**), and the addition of lignin deteriorates properties, mainly the deformability of the blends. The expected improvement in properties has not been achieved. However, these results contribute to a better

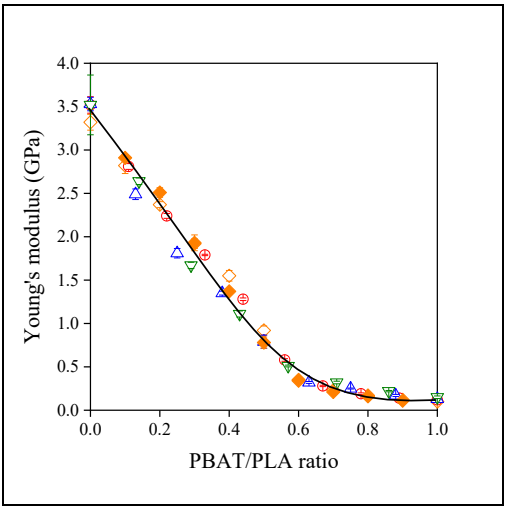

Fig. 4 *Effect of the PBAT/PLA ratio on the Young's modulus of the studied two- and three-component blends. Symbols: (◆) PLA/PBAT; lignin content in three-component blends: (○) 10, (△) 20, (▽) 30 vol%. Empty symbols with and full symbols without MAPLA.*

understanding of structure–property correlations in lignin-based hybrid blends and help the design of multicomponent polymer systems

4.4 PP/lignin/flax composites for structural applications

PP is a commodity polymer used in large quantities in all areas of life. In recent years, polymers, and thus also PP, have been often modified with natural materials like wood flour, lignin, or natural fibers like flax and hemp. Modifying PP with natural components increases stiffness and dimensional stability but often leads to decreased impact resistance. The use of such natural additives has the advantage of reducing the amount of fossil fuel content, improving the carbon footprint of the material, and decreasing its price. The required property combination often cannot be achieved using a single additive. Recently, more and more attempts have been made to prepare hybrid PP materials containing two polymers and a reinforcement, filler or fiber or a polymer matrix with two different fibers. In accordance with these considerations, our goal was to prepare a PP composite containing the largest possible amount of the natural additives while offering a good combination of properties (**Publication 4**). Therefore, hybrid composites were prepared from a PP reactor blend (rPP), lignin and flax fibers. Interfacial adhesion was improved using a functionalized PP (MAPP) coupling agent. The processability of the composites was characterised by the measurement of melt flow rate, while the mechanical properties were determined by tensile and impact testing. We found that combining lignin and flax fibers yields materials with an advantageous property profile, considerably decreased carbon footprint and acceptable price. We proved that the application of flax compensates for the deteriorating effect of lignin on deformability and especially

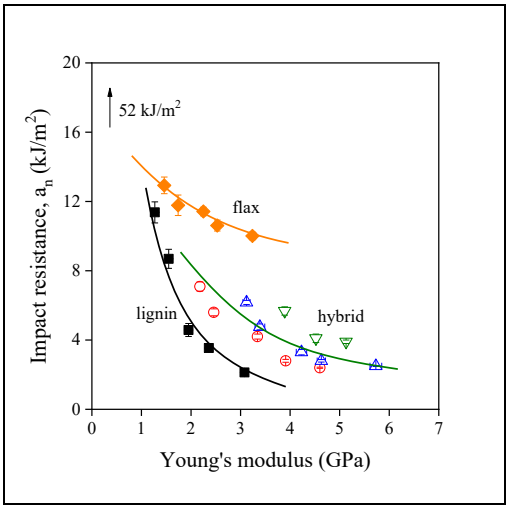

Fig. 5 *Correlation between the stiffness and impact resistance of two and three-component rPP composites containing MAPP. Advantageous effect of hybridisation. Symbols:* (■) *lignin,* (◆) *flax, hybrid composites at* (○) *10,* (△) *20, and* (▽) *30 vol% flax.*

on impact resistance. Significant improvement was also achieved in stiffness and strength (**Fig. 5**). A coupling agent must be applied to obtain this property combination because of the poor interaction between PP and natural reinforcements. We demonstrated that the developed compounds may successfully compete with materials offered on the market.

4.5 Modelling the properties of PP/lignin/flax hybrid composites

Numerous reports in the literature claim the successful use of multiple components to achieve an advantageous property profile for polymeric materials. The authors reporting their experiments on these hybrid materials almost invariably claim the presence of synergism, a beneficial combination of two or more components resulting in materials with properties exceeding additivity. However, almost all of these claims are based merely on visual observations of primary experimental results and rarely on quantitative analysis. Hybridisation raises many questions; without addressing them, the claimed property improvement might not occur. Considering the increasing importance of natural additives and reinforcements and the uncertainties and contradictions mentioned above, we decided to analyse quantitatively the potential synergism in rPP/lignin/flax hybrid composites and look for the possible coupling effect of lignin (**Publication 5**). We extended the models developed for composites with a single additive to hybrid materials, in order to describe the compositional dependence of tensile strength and impact resistance. The composition dependence of the tensile strength in a composite containing two reinforcing additives can be expressed as

$$\sigma_T = \sigma_{Tm}\,\lambda^n \frac{1-(\varphi_1+\varphi_2)}{1+2.5\,(\varphi_1+\varphi_2)} \exp(B_1\,\varphi_1 + B_2\,\varphi_2 + B_{12}\,\varphi_1\,\varphi_2) \qquad (4.2)$$

where σ_T is the true tensile strength of hybrid systems, σ_{Tm} is the true tensile strength of the matrix, λ is the relative elongation of the material, n is the strain-hardening factor defined for the matrix, φ_1 and φ_2 are the volume fraction of components, B_1 and B_2 express the load-bearing capacities of the two components, and B_{12} considers interactions, i.e., structural effects such as embedding, preferential adsorption, or coupling. The agreement between the measured data and the model predictions was excellent. The addition of flax to rPP/lignin blends proved to be advantageous, as flax reinforces the polymer more efficiently than lignin (**Fig. 6**) and also enhances impact strength. We showed that the two

reinforcements acted independently, with their effects being additive; synergism was not detected. The extended models enable the identification and verification of synergistic or antagonistic effects, and we also successfully applied them to data published in the literature. Overall, we demonstrated that the effects of individual components in hybrid materials can be reliably assessed only through quantitative analysis and modelling.

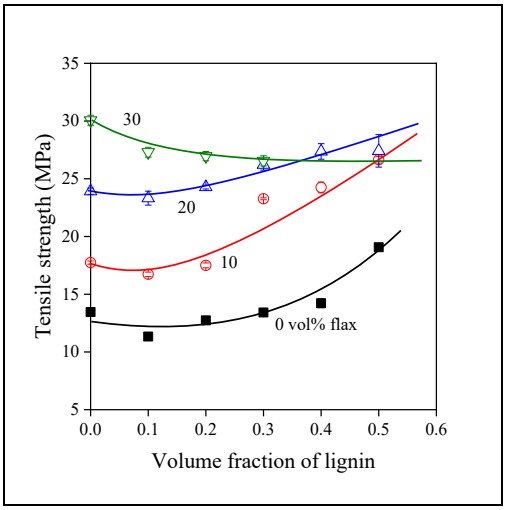

Fig. 6 *Dependence of the tensile strength of rPP/MAPP/lignin/flax hybrid composites on lignin and flax content. Symbols:* (■) *0,* (○) *10,* (△) *20, and* (▽) *30 vol% flax.*

5. Possible applications

In this thesis, we demonstrated the potential applications of our results in developing sustainable, lignin-based polymer blends and hybrid systems with tailored properties. By systematically controlling interactions and composition, we can achieve materials with enhanced stiffness, acceptable strength, and reduced carbon footprint; characteristics desirable for structural uses in fields such as automotive, construction, packaging, and various consumer products. Our quantitative modelling and empirical equations provide a reliable basis to predict structure-property relationships, enabling us to design optimal material formulations for specific target applications.

6. New scientific results

1. We showed that EVOH copolymers form heterogeneous blends with lignin. We proved that thermodynamic factors have a greater influence on the size of dispersed lignin particles than kinetics in these blends; thus, controlling thermodynamic factors is the key to develope lignin-based blends with improved properties. We created a simple semi-empirical model and described for the first time the particle coalescence in EVOH/lignin blends and proved that it depends mainly on blend composition and the interaction of the components (**Thesis chapter 3**, **Publication 1**).

2. With a novel combination of experiments, modelling, and simulation, we proved that although strong ionic interactions develop within the phases as well as on the interface in ionomer/lignin blends, the role of hydrogen bonds is more critical than ionic interactions in the determination of blend properties (**Thesis chapter 4**, **Publication 2**).

3. We systematically analysed the interactions among the components of PLA/lignin/PBAT blends and found that these interactions are weak. Weak interactions lead to immiscibility and a heterogeneous structure. Because of thermodynamic reasons, lignin is located mainly in the PBAT phase, and thus it influences properties only to a limited extent. The properties of such blends are determined by the relative amount of PBAT and PLA (**Thesis chapter 5**, **Publication 3**).

4. We prepared PP/flax/lignin hybrid composites with exceptionally large natural reinforcement content, and with a systematic analysis we showed that the application of flax compensates for the deteriorating effect of lignin on deformability and impact resistance. Significant improvement was achieved also in stiffness and strength (**Thesis chapter 6**, **Publication 4**).

5. We showed that hybridisation, i.e., the combination of the natural fiber and lignin in PP composites, is an advantageous concept. The combination of lignin and flax fibers yields materials with an advantageous property profile, considerably decreased carbon footprint and acceptable price. The composites developed can successfully compete with fiber reinforced materials offered on the market (**Thesis chapter 6**, **Publication 4**).

6. Unlike the general approach abundant in the literature to predict synergism in hybrid composites by the visual observation of primary data, we analysed the simultaneous effect of lignin and flax in PP quantitatively using appropriate models. We proved that the two reinforcements act independently. For the first time, we extended the models developed for two-component materials to hybrids containing at least three components and successfully used them for the identification and verification of synergism or antagonism in hybrid materials. By analysing results published in the literature, we proved that most claims about synergism are incorrect and contrary to expectations component effects are often antagonistic (**Thesis chapter 7**, **Publication 5**).

7. Publications

6.1 Publications used for the preparation of the Thesis

1. Pregi, E., Kun, D., Vu, V., Pukánszky, B., Structure Evolution in Poly(Ethylene-Co-Vinyl Alcohol)/Lignin Blends: Effect of Interactions and Composition, *Eur. Polym. J.,* 111*,* **2019**, 74–81, DOI: 10.1016/j.eurpolymj.2018.11.040 (IF: 3.862, IC: 4)
2. Pregi, E., Blasius, J., Kun, D., Hollóczki, O., Pukánszky, B., Effect of Competitive Interactions on the Structure and Properties of Blends Prepared from an Industrial Lignosulfonate Polymer, *Int. J. Biol. Macromol.*, 254, **2024**, 127694., DOI: 10.1016/j.ijbiomac.2023.127694 (IF: 7.7, IC: 1)
3. Pregi, E., Romsics, I., Várdai, R., Pukánszky, B., Interactions, Structure and Properties of PLA/Lignin/PBAT Hybrid Blends, *Polymers (Basel)*, 15, **2023**, 3237, DOI: 10.3390/polym15153237 (IF: 4.7, IC: 15)
4. Pregi, E., Faludi, G., Kun, D., Móczó, J., Pukánszky, B., Three-Component Polypropylene/Lignin/Flax Composites with High Natural Additive Content for Structural Applications, *Ind. Crops Prod.*, 182, **2022**, 114890, DOI: 10.1016/j.indcrop.2022.114890 (IF: 5.9, IC: 15)
5. Pregi, E., Kun, D., Faludi, G., Móczó, J., Pukánszky, B., Modeling the Mechanical Properties of Polypropylene/Lignin/Flax Hybrid Composites, *Mater. Des.*, 220, **2022**, 110833, DOI: 10.1016/j.matdes.2022.110833 (IF: 8.4, IC: 12)

6.2 Other publications related to the Thesis

1. Pregi, E., Kun, D., Wacha, A., Pukánszky, B., The Role of Ionic Clusters in the Determination of the Properties of Partially Neutralized Ethylene-Acrylic Acid Ionomers, *Eur. Polym. J.,* 142*,* **2021**, 110110, DOI: 10.1016/j.eurpolymj.2020.110110 (IF: 5.546, IC: 19)

6.3 Other publications not related to the Thesis

1. Tátraaljai, D., Tang, Y., Pregi, E., Vági, E., Pukánszky, B., Pomegranate Extract for the Processing Stabilization of Polyethylene, *J. Vinyl Addit. Technol.*, **2021**, 1–10, DOI: 10.1002/vnl.21874 (IF: 2.229, IC: 6)
2. Horváth, F., Bodrogi, D., Hilt, B., Pregi, E., Menyhárd, A., Organogelators with Dual β- and α-Nucleating Ability in Isotactic Polypropylene, *J. Therm. Anal. Calorim.*, 147, **2022**, 9451–9468, DOI: 10.1007/s10973-022-11203-z (IF: 4.4, IC: 8)
3. Tátraaljai, D., Tang, Y., Pregi, E., Vági, E., Horváth, V., Pukánszky, B., Stabilization of PE with Pomegranate Extract: Contradictions and Possible Mechanisms, *Antioxidants*, 11, **2022**, 418, DOI: 10.3390/antiox11020418 (IF: 6.6, IC: 2)
4. Takács, K., Tátraaljai, D., Pregi, E., Huszthy, P., Pukánszky, B., Synthesis and Evaluation of a Novel Natural-Based Phosphine Antioxidant for the Thermal Stabilization of Polyethylene, *J. Therm. Anal. Calorim.*, 147, **2022**, 12513–12522, DOI: 10.1007/s10973-022-11421-5 (IF: 4.4, IC: 5)

5. Takács, K., Pregi, E., Vági, E., Renkecz, T., Tátraaljai, D., Pukánszky, B., Processing Stabilization of Polyethylene with Grape Peel Extract: Effect of Extraction Technology and Composition, *Molecules*, 28, **2023**, 1011, DOI: 10.3390/molecules28031011 (IF: 4.2, IC: 6)
6. Ferdinánd, M., Jerabek, M., Várdai, R., Pregi, E., Lummerstorfer, T., Gahleitner, M., Faludi, G., Móczó, J., Pukánszky, B., Factors and Processes Determining the Impact Resistance of PP Impact Copolymers with Multi-Phase Structure, *Express Polym. Lett.*, 18, **2024**, 406–419, DOI: 10.3144/expresspolymlett.2024.30 (IF: 2.7, IC: 0)
7. Takács, K., Slezák, E., Pregi, E., Plachi, D., Vági, E., Tátraaljai, D., Pukánszky, B., Stabilization of Polyethylene with Grape Pomace Extract: Effect of Natural Oil Content, *Polym. Degrad. Stab.*, 221, **2024**, 110678, DOI: 10.1016/j.polymdegradstab.2024.110678 (IF: 6.3, IC: 4)
8. Várdai, R., Romsics, I., Pregi, E., Faludi, G., Móczó, J., Pukánszky, B., Engineering Material from Flexible Food Packaging Waste: Property Profile and Feasibility, *Polym. Compos.*, 45, **2024**, 16796–16805, DOI: 10.1002/pc.28931 (IF: 4.8, IC: 3)
9. Romsics, I., Várdai, R., Pregi, E., Faludi, G., Hegyesi, N., Móczó, J., Pukánszky, B., Fiber Reinforced Structural Material from the Waste of a Multilayer Food Packaging Film: Interactions, Structure, Properties, *Compos. Part A Appl. Sci. Manuf.*, 193, **2025**, 108821, DOI: 10.1016/j.compositesa.2025.108821 (IF: 8.9, IC: 1)

6.4 Conference presentations

1. Pregi, E., Horváth, E., Faludi, G., Pukánszky, B., Development of hybrid PP composites containing lignin and flax, 4th International Conference on Bio-based Polymers and Composites, September 2–6, 2018, Balatonfüred, Hungary
2. Pregi, E., Faludi, G., Pukánszky, B., Lignint és lent tartalmazó hibrid polipropilén kompozitok fejlesztése, Fiatal Diplomások Fóruma, December 4, 2018, Budapest, Hungary
3. Pregi, E., Faludi, G., Pukánszky, B., Lignin és lent tartalmazó hibrid polipropilén kompozitok fejlesztése, XXXIV. Országos Tudományos Diákköri Konferencia Kémiai és Vegyipari szekció, March 21–22, 2019, Budapest, Hungary
4. Pregi, E., Faludi, G., Pukánszky, B., Development of hybrid PP composites containing lignin and flax, 8th Bratislava Young Polymer Scientist Conference, March 25–28, 2019, Oščadnica, Slovakia
5. Pregi, E., Faludi, G., Pukánszky, B., Lignint és lent tartalmazó hibrid polipropilén kompozitok fejlesztése, MTA TTK AKI Polimerfizikai Olsztályának Szemináriuma, April 9, 2019, Budapest, Hungary
6. Pregi, E., Faludi, G., Pukánszky, B., Effect of fiber content on the properties of hybrid PP composites containing lignin and flax, 1st Olah George Conference, September 23, 2019 Budapest, Hungary
7. Pregi, E., Kovács, N., Faludi, G., Pukánszky, B., Structure and properties of multicomponent films based on lignin, The 10th Conference on Green Chemistry and Nanotechnologies in Polymeric Materials, October 9–11, 2019, Riga, Latvia

8. Pregi, E., Gottschall, R, Pukánszky, B., A lignin típusának hatása a polimer/lignin keverékek szerkezetére és tulajdonságaira, XXV. Nemzetközi Vegyészkonferencia, October 24–26, 2019, Kolozsvár, Romania
9. Tátraaljai, D., Pregi, E., Vági, E, Renkecz, T., Székely, E., Pukánszky, B., Processing stabilization of polyethylene with natural extracts from grape pomace, 1st Greenering International Conference, February 15–16, 2021, Costa da Caparica, Portugal (online)
10. Vági, E, Szentirmai, A., Khasawneh, B., Amanor, R., Molnár, M., Tátraaljai, D., Pregi, E., Pukánszky, B., Székely, E., A biorefinery concept for valorisation of pomegranate peel and seed using green technologies, 29th European Biomass Conference & Exhibition, April 26–29, 2021, Marseille, France (online)
11. Kanyar, B., Pregi, E., Várdai, R., Bartos, A., Faludi, G., Pukánszky, B., Kinetic study of polyurethane formation using cycloaliphatic isocyanate, 33rd International Symposium on Polymer Analysis and Characterization, June 5–8, 2022, Milan, Italy
12. Pregi, E., Romsics, I., Kanyar, B., Várdai, R., Faludi, G., Pukánszky, B., Structure-property correlations in three-component PLA/PBAT/lignin blends, 33rd International Symposium on Polymer Analysis and Characterization, June 5–8, 2022, Milan, Italy
13. Pregi, E., Romsics, I., Ferdinánd, M. L., Imre, B., Pukánszky, B., Structure and properties of three component PLA/PBAT/lignin blends, 19th International Conference on Renewable Resources and Biorefineries, May 31–June 2, 2023, Riga, Latvia
14. Ferdinánd, M. L., Pregi, E., Imre, B., Pukánszky, B., Poly(lactic acid) reinforced with synthetic polymer fibers: Interactions, structure and properties, 19th International Conference on Renewable Resources and Biorefineries, May 31–June 2, 2023, Riga, Latvia
15. Pregi, E., Bartos, A., Várdai, R., Bolgár, J., Pukánszky, B., Effect of fibre attrition and interfacial adhesion on the properties of natural fiber-reinforced polypropylene composites, 3rd International Conference on Materials and Nanomaterials, July 29–31, 2024, Lisbon, Portugal
16. Várdai, R., Romsics, I., Schäffer, Á., Ferdinánd, M. L., Faludi, G., Pregi, E., Bartos, A., Móczó, J., Pukánszky, B., Structure and Property Correlations in Natural Fiber Reinforced Composites, 3rd International Conference on Materials and Nanomaterials, July 29–31, 2024, Lisbon, Portugal
17. Pregi, E., Budai, J. E., Bridge H. E., Tofani, G., Imre, B., Pukánszky, B., Synthesis and properties of lignin-based polyurethane elastomers: The effect of lignin type, 5th Conference on Bio-based Polymers and Composites, September 1–5, 2024, Esztergom, Hungary
18. Várdai, R., Romsics, I., Schäffer, Á., Ferdinánd, M. L., Faludi, G., Pregi, E., Bartos, A., Móczó, J., Pukánszky, B., Structure and property correlations in natural fiber reinforced composites, 5th Conference on Bio-based Polymers and Composites, September 1–5, 2024, Esztergom, Hungary
19. Fehér, A., Zarbali, A., Pregi, E., Imre, B., BOOST4BIOEAST – Enhancing national bioeconomy through BIOEAST HUBs, 5th Conference on Bio-based Polymers and Composites, September 1–5, 2024, Esztergom, Hungary

20. Modrovics, J., Kota, I., Cserta, L., Rácz, L. R., Várdai. R., Romsics, I., Pregi, E., Faludi, G., Development of outdoor fitness park elements using advanced composite materials and functional coatings (2019-1.1.1-PIACI-KFI-2019-00205), 5th Conference on Bio-based Polymers and Composites, September 1–5, 2024, Esztergom, Hungary
21. Budai, J. E., Pregi, E., Imre, B., ROBUST – Valorisation of recycled polyurethane foam components, 5th Conference on Bio-based Polymers and Composites, September 1–5, 2024, Esztergom, Hungary
22. Budai, J. E., György Pregi, E., Imre, B., Chemical Recycling of Flexible Polyurethane Foams by Glycolysis: Toward a More Sustainable Polyol Recovery, 3rd Conference on Green Chemistry and Sustainable Coatings, June 16–18, 2025, Pisa, Italy