

Wood flour filled PP composites: Compatibilization and adhesion

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Abstract

PP/wood flour composites were prepared in a wide range of compositions in an internal mixer at 180 °C, 50 rpm and 15 min. Interfacial adhesion was modified by the introduction of two maleinated polypropylenes (MAPP) with different molecular weights and functionality. Wood content was changed between 0 and 70 wt%, while MAPP/wood ratio between 0 and 0.25. Compression molded plates of 1 mm thickness were prepared for testing. Structure was characterized by X-ray diffraction and DSC measurements. Interfacial adhesion was estimated quantitatively with model calculations. The results showed that the morphology of the components and that of the composites does not change as a result of compounding and the wood flour used in these experiments does not nucleate PP. The most important structural phenomena determining properties are the orientation of the anisotropic wood flour particles and their aggregation. Both structural phenomena depend on processing conditions and on the dimensions of the product. Much larger improvement could be achieved by the addition of a functionalized polymer in thicker samples than in thin specimens. MAPP has a maximum efficiency at around 0.05–0.10 MAPP/wood ratio in the composites of this study due to the limited surface available for coupling. MAPP with larger molecular weight and smaller functionality proved to be more advantageous in the improvement of composite strength, because it can form larger number of entanglements per molecule than the small molecular weight compound. On the other hand, the smaller molecular weight coupling agent decreases viscosity and improves processability considerably, thus optimization of composition is essential to achieve maximum performance.

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1. Introduction

Recently the production and application of thermoplastic polymers reinforced with wood flour and natural fibers increased considerably [1,2]. Such materials offer significant advantages, which justify their use. Wood flour is obtained from natural resources, it is available in various forms in

large quantities, light, cheap, and it can be added to commodity matrices in considerable amounts thus offering economically advantageous solutions [1–4]. The main drawbacks of such composites are their water sensitivity and relatively poor dimensional stability, changing wood fiber characteristics with origin and the time of the harvest, and poor adhesion to basically all matrix polymers [4,5].

The main application area of wood flour filled composites is the building and automotive industry [1,3,6,7], but they are also applied for packaging, for the preparation of various household articles, furniture, office appliances and other items [3,6]. In most of these applications they are used as structural materials, where the load-bearing

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capacity of the dispersed component is crucial. This latter is determined by the particle characteristics of the reinforcement and by interfacial adhesion [8–10]. In particulate filled and short fiber reinforced composites the dominating micromechanical deformation process is usually debonding [11,12]. Voids are created under the effect of external load, which easily merge to large cracks leading to catastrophic failure. Debonding stress depends on particle size, on the stiffness of the matrix and on interfacial adhesion [13–15]. Wood flour particles are large, thus they debond easily, and the process can be hindered only by improved adhesion.

Interfacial interactions are very weak in wood flour filled composites, because the surface free energy of both the filler and the polymer is very small [16–18]. As a consequence adhesion must be improved practically always to achieve acceptable properties. Various techniques are used or at least tried for the improvement of interfacial adhesion including the treatment of the wood with sodium hydroxide [4,19,20], coupling with functional silanes [4], or the coating of wood flour with stearic acid [21,22]. However, polymers functionalized with maleic anhydride (MA) or acrylic acid (AA) are introduced the most often into polyolefin composites [2–4,17,19–30]. The functional groups of these polymers were shown to interact strongly or even react chemically with the surface of wood [17,24,26], while the long alkyl chains diffuse into the matrix making stress transfer possible. The stiffness of the composites is not influenced significantly by the presence of the functionalized polymer [3,17,27], but strength usually increases considerably [2,3,17,19,27,28]. The tensile and flexural strength of polymers usually decreases with increasing filler content in the absence of coupling [2,19,28,31], but the correlation can be turned around and considerable increase can be achieved with the help of functionalized polymers.

Contradictory information is available about the effect of the amount of functionalized polymer on composite properties. Some sources claim that tensile and flexural strength as well as impact resistance pass through a maximum as a function of the amount of functionalized polymer [32], but most research groups do not study this question, but apply the coupling compound in a fixed amount related to the mass of the wood [21,29]. Similarly, the effect of the characteristics, i.e. molecular weight and degree of functionalization, of the compatibilizer on composite properties is not completely clear. Several authors claim that larger molecular weight and smaller functional group content are more advantageous than the opposite [17,23]. Their conclusions are based on the measurement of tensile strength and interfacial shear strength, but the number of such studies is limited and most of them do not offer a satisfactory explanation for the effect of these factors on composite properties.

In previous papers we presented the effect of various factors on the deformation and failure of wood flour filled PP composites [31,33]. We found that the dominating micromechanical deformation mechanism is debonding in these

materials, indeed. A more detailed study revealed that besides debonding, other deformation processes, like the disintegration of aggregates and the fracture of wood particles also occur during the failure of the composites [31]. In accordance with literature information, interfacial adhesion plays a crucial role in the determination of composite properties and the introduction of functionalized polymer considerably influences strength. However, up to now we have not investigated the effect of the amount and properties of the functionalized polymer. As a consequence, the main goal of this study was to determine the strength of interfacial interaction quantitatively both in the presence and absence of functionalized polymers and to define the influence of MAPP characteristics on the properties of PP/wood composites.

2. Experimental

The polymer used as matrix in the experiments was the Tipplon K948 grade block copolymer (ethylene content: 8–11%, density: 0.9 g/cm³, MFR: 45 g/10 min at 230 °C and 21.6 N) produced by TVK, Hungary. The Filtracel EFC 1000 grade wood flour was obtained from J. Rettenmaier and Söhne GmbH, Germany. This particular grade is produced from soft wood and its average particle size is around 210 µm. Two maleinated polypropylenes with considerably different properties were added to the composites in order to improve properties. Licomont AR 504 (Clariant GmbH, Germany) is a low molecular weight ($M_n = 3500$ g/mol) polymer with high maleic anhydride content (3.5 wt%). On the other hand, the Orevac CA 100 polymer (Atofina, France) has a much lower functionality (1.0 wt%), but larger molecular weight ($M_n = 25,000$ g/mol). The wood flour content of the composites changed between 0 and 70 wt% and MAPP/wood ratio varied from 0 to 0.25 in 0.05 steps.

The components were homogenized in a Brabender W 350 E internal mixer of 350 cm³ nominal volume at 180 °C and 50 rpm for 15 min. The homogenized material was compression molded into 1 mm thick plates at 180 °C using a Wickert WLP 800/4/2.5 machine with 1 min preheating and 5 min molding time at 150 bar. Specimens cut from the plates were used for tensile testing and morphological characterization.

The average particle size and the size distribution of the filler were determined using a Malvern 2000 laser diffraction particle analyzer equipped with a Sirocco 2000 sampling unit. The crystalline structure of the components was characterized by X-ray diffraction (XRD) using a Philips PW 1830/PW 1050 equipment with Cu K α radiation at 40 kV and 35 mA anode excitation. Melting and crystallization characteristics of PP were determined by differential scanning calorimetry (DSC) using the DSC 30 cell of a Mettler TA 4000 instrument in the temperature range from 30 to 220 °C. Two heating and cooling runs were carried out in nitrogen atmosphere on about 10 mg samples with heating and cooling rates of 10 °C/min. Characteristic val-

ues derived from the second heating and cooling run were used for evaluation. Changes in the viscosity of the melt were followed by the determination of melt flow rate (MFR) using a Zwick 4105 instrument. The measurements were done at 190 °C with 5 kg weight. Mechanical properties were characterized by tensile testing using an Instron 5566 apparatus at 23 °C and 50% relative humidity. Samples were conditioned for 48 h in this atmosphere before testing. Stiffness (E) was determined at 0.5 mm/min cross-head speed and 60 mm gauge length. Tensile strength (σ), and elongation-at-break (ϵ) were calculated from force vs. deformation traces recorded on the same specimens at 5 mm/min cross-head speed. The structure of the composites was studied by scanning electron microscopy (SEM) on fracture surfaces created at liquid nitrogen temperature. Micrographs were taken from the broken surfaces using a JEOL 5500 LV equipment.

3. Results and discussion

A large number of factors influence the properties of wood flour filled polymers. The particle size and size distribution of the wood, its aspect ratio and attrition during processing, the molecular weight and functionality of the maleinated polymer all play an important role in the determination of composite properties. Composition is determined by wood flour and MAPP content. Wood was shown to modify the crystalline structure of PP and to induce transcrystallization [30]. The orientation, orientation distribution and possible aggregation of wood particles all add to the structural variety of such composites. Finally, interfacial adhesion is determined by the presence or absence of MAPP, but also by its functionality, since larger maleic anhydride content was claimed to lead to stronger interaction and decreased impact resistance [25]. It is impossible to consider all these factors in one paper, thus although we mention most of them, we focus our attention on composition, interaction and MAPP properties.

3.1. Structure

We can obtain some idea about the particle characteristics of the wood flour used in our composites from Fig. 1. According to the micrograph, the particles are anisotropic and their average aspect ratio is around 7. Their size covers a wide range from several microns to several millimeters. According to the results of particle size analysis, the average size of this particular wood flour is around 210 μm . This value must be treated with caution, because anisotropy biases somewhat the results of the laser diffraction measurements. However, the knowledge of the magnitude of particle size is of real importance for us, since large particles debond easily under the effect of external load [13–15]. Already very small loads induce the separation of the interfaces at 500–1000 μm size. Extensive debonding leads to the decrease of strength with increasing filler content [9,12].

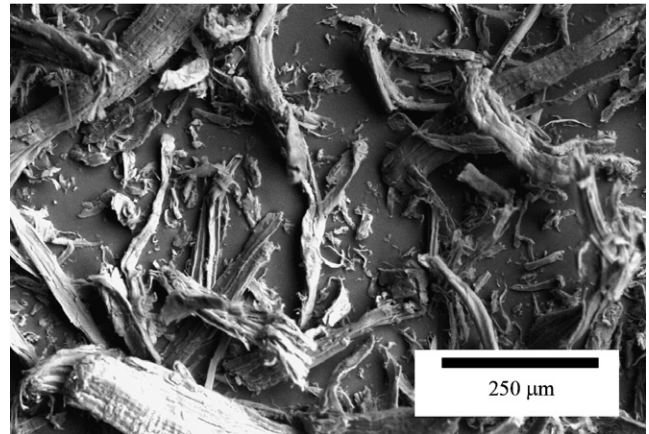


Fig. 1. SEM micrograph showing the particle characteristics of the wood flour used in the study.

Cellulose is a crystalline material. Processing at high temperatures may change its structure and properties. On the other hand, cellulose fibers, as well as processing conditions may also influence the crystalline structure of the matrix polymer [28,29]. Wide angle X-ray diffraction was used for the detection of changes in the crystalline structure of both the wood and the PP matrix. The XRD traces of the components and that of two composites containing different amounts of wood flour are presented in Fig. 2. The XRD trace recorded on the wood flour is characteristic for the cellulose I form [34,35] and it does not change during compounding. Our PP block copolymer crystallizes in the α -form. The possible presence of the β modification was checked by comparing the recorded pattern to that of a sample crystallized entirely in this form [36]; no trace of the β modification could be found either in the neat polymer or in the composites. Compounding did not change

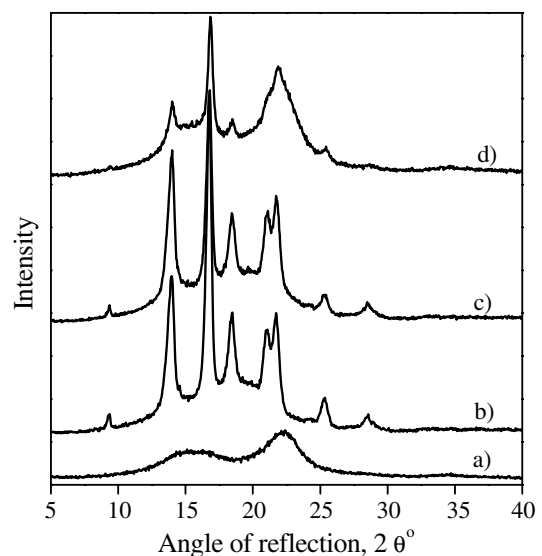


Fig. 2. XRD traces recorded on the components and on some composites: (a) wood flour, (b) PP, (c) composite with 10 wt% and (d) with 70 wt% wood; no MAPP was added.

the crystal modification of PP, and the addition of functionalized polymers did not have any effect on crystalline morphology either.

Cellulose was shown to nucleate PP and induce trans-crystallinity [28,30,37,38]. Nucleation results in decreased spherulite size, while increased crystallization temperature leads to higher crystallinity and thicker lamellae [39]. These changes lead to an increase in the stiffness of the polymer matrix [40]. The crystallization temperature of PP is presented in Fig. 3 as a function of wood flour content. Rather surprisingly, crystallization temperature decreases with increasing wood flour content and does not increase as some literature information predicts [28–30]. Obviously, wood flour does not nucleate the polymer used in the study, but some other factor leads to the decrease of crystallization temperature. We selected this grade of polymer to obtain good processability (MFI) and impact resistance (block copolymer) for the final product. However, the additive package contained talc as nucleating agent. Talc must interact with the wood flour, or the functionalized polymer may encapsulate it, thus it loses its nucleation effect. Interaction with the wood is surprising, but very probable, since crystallization temperature decreases also in the absence of a functionalized polymer. We may conclude from these results that the crystalline structure of either the polymer or that of the reinforcing wood flour is not influenced significantly by compounding or by the incorporation of a functionalized polymer.

3.2. Properties

Young's modulus of the PP/wood composites prepared is plotted as a function of composition in Fig. 4. MAPP/wood ratio was 0.1 in these composites. Stiffness increases from about 1.4 GPa to about 4.0 GPa, i.e. wood particles

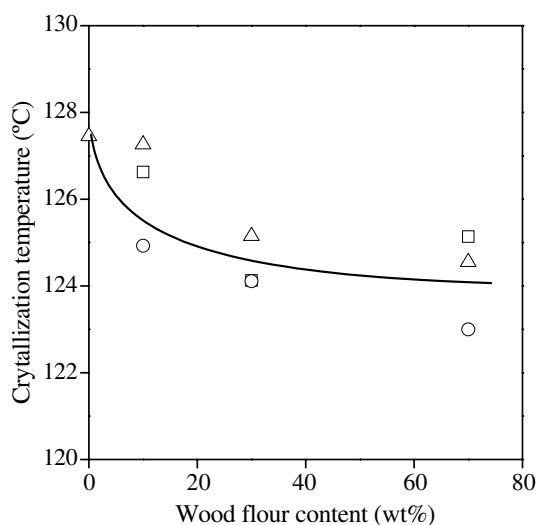


Fig. 3. Changing crystallization temperature of PP with increasing wood flour content. MAPP/wood ratio: 0.2. Symbols: (△) no MAPP, (□) Orevac CA 100, (○) Licomont AR 504.

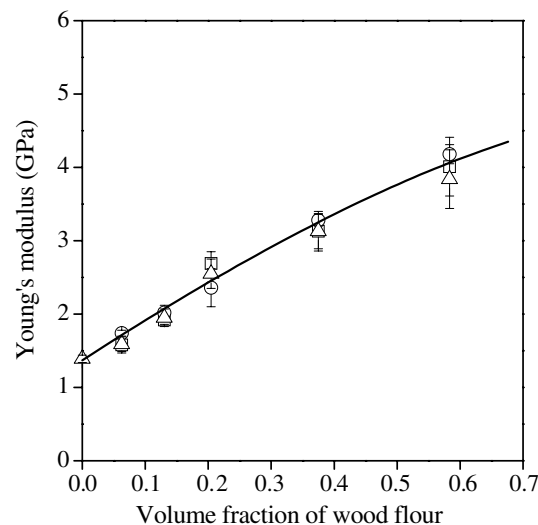


Fig. 4. Effect of wood content and the type of MAPP on the stiffness of PP/wood composites. MAPP/wood ratio: 0.1. Symbols: (△) no MAPP, (□) Orevac CA 100, (○) Licomont AR 504.

exerted the expected reinforcing effect. Stiffness is completely independent of the presence or absence and also of the amount of the functionalized polymer (not shown). This result agrees well with some literature sources claiming that the presence of maleinated PP does not influence stiffness [3,17,27], although others found some effect on flexural modulus [17,27]. Literature references and our previous experience also showed that stiffness is less sensitive to changes in interfacial interactions than properties measured at larger deformations [41]. We may safely conclude, though, that some of the wood fibers orientate parallel to the direction of load and orientation is very similar in all composites.

As expected, much larger differences are observed in the composition dependence of the tensile strength of the composites (Fig. 5) than in stiffness. Reinforcement is observed in all cases due to the proper orientation of the wood particles, but its extent differs considerably in the three sets of composites. Neat wood has the smallest reinforcing effect. The maleinated PP with the larger functionality and smaller molecular weight improves strength only slightly, while composites containing the Orevac CA 100 grade have considerably larger strength. The use of functionalized polymers with larger functionality was claimed to be more beneficial in PP/wood composites before, based on the reasoning that larger number of MA groups would result in stronger interaction and decreased impact resistance [2,25]. One may wonder here about the definition of the strength of interaction, though.

We can also observe a maximum in strength as a function of wood flour content, which is difficult to explain without further analysis and study. It may result from changes in the orientation of the wood flour fibers with increasing filler content. Orientation was shown to depend on composition in PP/talc composites [42]. Decreased orientation was observed at larger filler content due to the

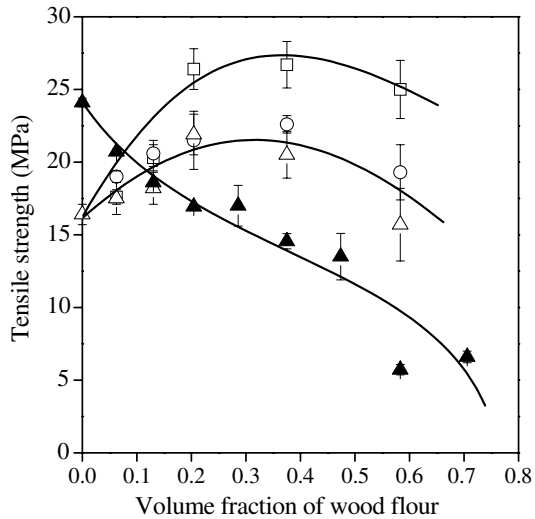


Fig. 5. Tensile strength of PP/wood composites plotted as a function of wood flour content. Effect of MAPP characteristics. MAPP/wood ratio: 0.1. Symbols: (Δ) no MAPP, (\square) Orevac CA 100, (\circ) Licomont AR 504, 1 mm thickness; (\blacktriangle) no MAPP, 4 mm thick sample.

physical interaction of the particles, what may occur also in our wood composites. However, the practically linear correlation between Young's modulus and wood content contradicts this explanation (see Fig. 4); stiffness should also exhibit a maximum if orientation changes considerably. The aggregation of wood flour particles was observed at high filler content [31,32]. The probability of the formation of aggregates increases with increasing wood flour content and strength decreases with increasing number and size of the aggregates. The maximum appears at the same composition, thus aggregation depends on composition, while the value of the maximum is determined by adhesion and the load carried by the wood flour particles. The tensile strength of composite samples with 4 mm thickness and not containing any MAPP is also plotted in the figure for comparison. Strength decreases continuously with increasing wood content in this case indicating strong differences in the average orientation of the particles. A sharper decrease is observed in strength at the largest wood content showing considerable aggregation. Although these composites were prepared with a different matrix polymer, we believe that processing conditions and part dimensions determine the structure and properties of the composites.

The elongation-at-break values of the composites are plotted against wood flour content in Fig. 6 at the same MAPP/wood ratio as before. The two functionalized polymers have different effect on this property as well, i.e. they influence the deformation and failure of the composites slightly differently. This difference may result from the dissimilar strength of interaction as claimed by some sources [25] or some other factors influencing stress transfer between the polymer and the reinforcing fibers. It is interesting to note that the deformability of composites containing the neat wood flour and of those prepared with the small molecular weight coupling agent is very similar,

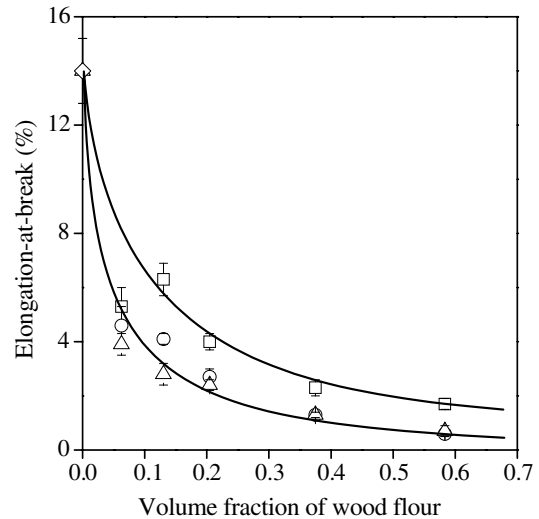


Fig. 6. Influence of filler content and the properties of MAPP on the deformability of PP/wood composites. MAPP/wood ratio and symbols are the same as in Fig. 5.

although interfacial adhesion must be different in the two cases.

All mechanical properties presented above were determined at the same MAPP/wood ratio of 0.1; we have not discussed the effect of this variable practically at all. One of the reasons was that the dependence of mechanical properties on wood flour content is very similar at all MAPP/wood ratios, i.e. continuous increase of stiffness, maximum in strength and decreasing deformability with increasing wood content. This statement is confirmed by Fig. 7, in which the tensile strength of PP/wood composites is presented as a function of MAPP/wood ratio at 70 wt% wood content. The MAPP with the larger molecular weight increases strength already at 0.05 MAPP/wood ratio, and

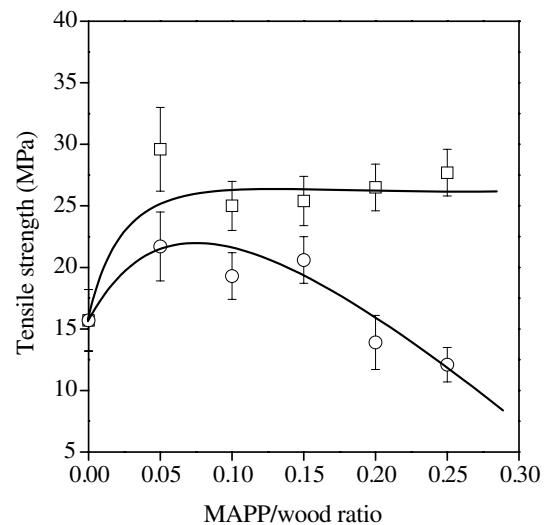


Fig. 7. Effect of MAPP type and content on the tensile strength of PP/wood composites at 70 wt% wood flour loading. Symbols: (\square) Orevac CA 100, (\circ) Licomont AR 504.

further addition of the functionalized polymer does not change strength. The small molecular weight coupling agent also increases strength, but the correlation exhibits a maximum in agreement with published results [23]. The maximum is reached at 0.05–0.10 MAPP/wood ratio also in this case; this is the optimum amount of coupling agent in the combination of polymer, wood flour and processing conditions used in our experiments.

3.3. Interfacial adhesion, reinforcement

The strength of interfacial adhesion can be expressed quantitatively by a simple model developed earlier for the description of the composition dependence of the tensile yield stress and tensile strength of particulate filled composites [8,9,43]. According to the model, tensile strength is determined by several factors, i.e.

$$\sigma_T = \sigma_{T0} \lambda^n \frac{1 - \varphi}{1 + 2.5\varphi} \exp(B\varphi) \quad (1)$$

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$, and $\lambda = L/L_0$) of the composite and the matrix, respectively, λ is relative elongation, n accounts for to the strain hardening of the matrix, φ is the volume fraction of wood in the composite, while B is a parameter expressing the load-bearing capacity of the filler. The term σ_T takes into account changing specimen dimensions during deformation, while λ^n the increase of strength due to strain hardening. The term $(1 - \varphi)/(1 + 2.5\varphi)$ expresses the effective load-bearing cross-section of the matrix and $\exp(B\varphi)$ is related to interfacial adhesion. In the case of PP/wood flour composites the effect of elongation, i.e. λ^n , can be neglected because of the small, far less than 100% elongation of the composites. Eq. (1) can be rearranged and expressed in linear form [8,9]:

$$\ln \sigma_{Tred} = \ln \frac{\sigma_T}{\lambda^n} \frac{1 + 2.5\varphi}{1 - \varphi} = \ln \sigma_{T0} + B\varphi \quad (2)$$

i.e. the plot of $\ln \sigma_{Tred}$ against filler content should result in a straight line with a slope of B , which is a measure of the load carried by the filler and depends on interfacial adhesion.

The composition dependence of tensile strength is plotted in the linear form of Eq. (2) in Fig. 8 for composites with 0.10 MAPP/wood ratio. We obtain straight lines in all three cases with different slopes indicating different relative load carried by the filler. The fit of the lines is relatively good considering the standard deviation of the measurement. The smallest B value is determined for the composites containing the neat wood, which agrees well with the expectations. Both MAPP coupling agents improve adhesion, but in a different extent. The smaller value obtained for Licomont AR 504 contradicts the explanation that larger maleic anhydride content results in stronger interaction [25]. The largest B value of 3.67 was obtained for the composites containing the larger molecular weight coupling agent, it is the most efficient in transferring stress and improving strength.

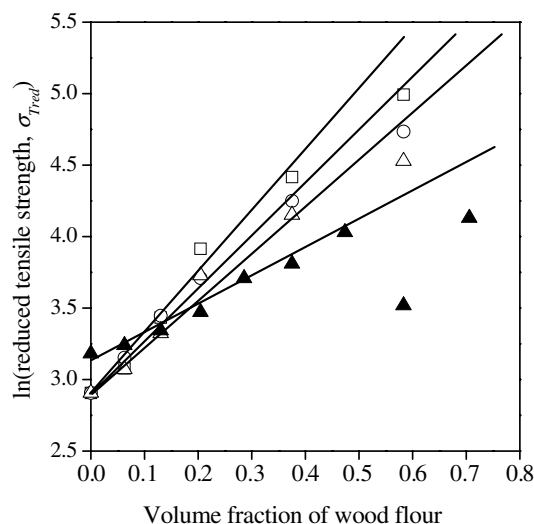


Fig. 8. Tensile strength of PP/wood flour composites plotted against filler content in the linear form of Eq. (2). Effect of MAPP type and specimen thickness. MAPP/wood ratio and symbols are the same as in Fig. 5.

The strength of the composites with the largest wood content deviates slightly from the straight line. Such deviations usually indicate the influence of structural effects. In the present case we may assume the occurrence of aggregation. At large wood flour content particles touch each other, form larger bundles, which fall apart relatively easily under the effect of external load. The strength of the 4 mm thick plates mentioned earlier is significantly smaller and the deviation from the straight line is larger indicating the strong effect of processing conditions and structure. In the 1 mm thick plates fibers align much more in the plane of the plate than in the thicker sample and larger shear stresses developing during compression molding result in less aggregation. The presence of aggregates was also confirmed by SEM micrographs taken from the fracture surface of composites with the largest filler content (Fig. 9). Although large wood content complicates analysis, the presence of aggregates is clear in the micrograph.

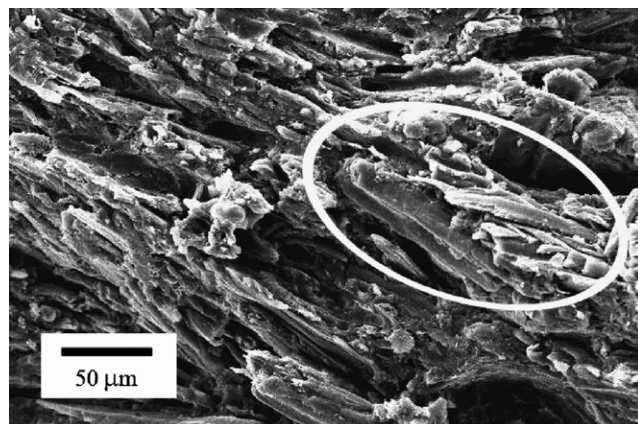


Fig. 9. Aggregation of wood particles at high wood content (70 wt%) in PP/wood composites; no MAPP.

The extent of reinforcement, i.e. parameter B , was determined at each MAPP/wood ratio studied. We obtain basically the same correlation as in the case of strength (see Fig. 10), which supports our earlier statement that the composition dependence of all properties is very similar independently of the amount of functionalized polymer added. The relative load carried by the wood flour increases up to 0.05 or 0.10 MAPP/wood ratio, levels off for Orevac CA 100, and shows a maximum for Licomont AR 504. These results prove again that interfacial adhesion is an important factor in the determination of composite properties, the amount of functionalized polymer has an optimum and that processing conditions and the resulting structure also affects strongly the performance of the composites.

3.4. Deformation and failure mechanism; other aspects

The results presented in the previous sections proved that an optimum exists in MAPP/wood ratio. We also saw that the characteristics of MAPP influence the mechanical properties of the composites. The evaluation of primary results did not offer an unambiguous explanation for these observations, thus we need further analysis in order to resolve these questions. Papers published in the literature showed that strong interaction, in most cases chemical bonds form between the active $-OH$ groups of cellulose and the functionalized polymer [24,26]. However, the number of available groups depends on the size of the wood particles, which is relatively large compared to usual mineral fillers. The specific surface area of the wood flour used in these experiments is only $1.3 \text{ m}^2/\text{g}$. The limited surface area of the filler explains the fact that all properties approach a constant value as a function of MAPP content.

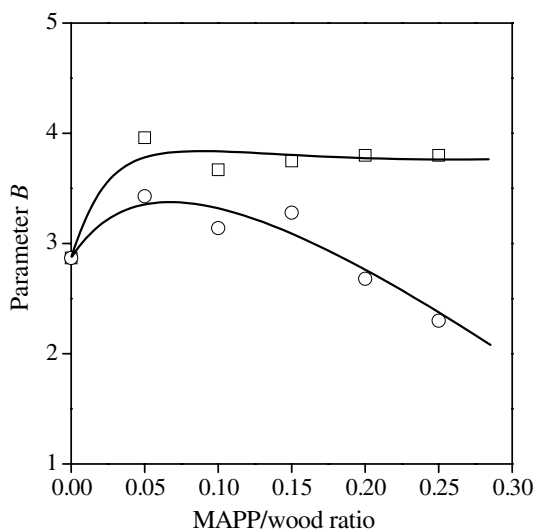


Fig. 10. Effect of MAPP properties on stress transfer and on the load-bearing capacity of the filler in PP/wood composites. Symbols: (□) Orevac CA 100, (○) Licomont AR 504.

The larger molecular weight functionalized polymer proved to be more efficient in improving stress transfer than its smaller molecular mass counterpart in spite of its lower functionality. Decreased impact strength of PP/wood composites was explained with the stronger interfacial adhesion and rigidity created by the larger functionality of MAPP used [25]. If we define the strength of adhesion by the strength of the covalent bonds formed, it must be the same for all MAPP coupling agents. A larger number of bonds may form on a unit surface of the wood in the case of larger functionality and this could lead to better stress transfer, but this was contradicted by our results. However, the filler/coupling agent interaction is only one side of the interphase forming in these composites and we must consider also the coupling agent/polymer interface. Large functionality leads to more reactions with the wood and shorter free chains, which cannot entangle with the polymer as efficiently as longer molecules. This leads to smaller deformability of the interphase, and of the entire composite. This effect is demonstrated well by Fig. 11 presenting the stress vs. elongation traces of three composites containing 50 wt% wood flour at 0.1 MAPP/wood ratio. The composite containing the high molecular weight coupling agent deforms more than twice as much as the other two composites. The smaller strength of the neat composite is caused by the easy debonding of the fibers leading to the free deformation of the matrix afterwards, until the voids merge to catastrophic cracks. The small molecular weight MAPP creates the same interfacial adhesion as the other compound, but it results in the lowest deformability. At high MAPP content, the smaller number of entanglements per molecule decreases also the deformability of the matrix and not only that of the interphase, which leads to premature failure and smaller strength.

Although the larger molecular weight MAPP with smaller functionality improves interfacial adhesion more effi-

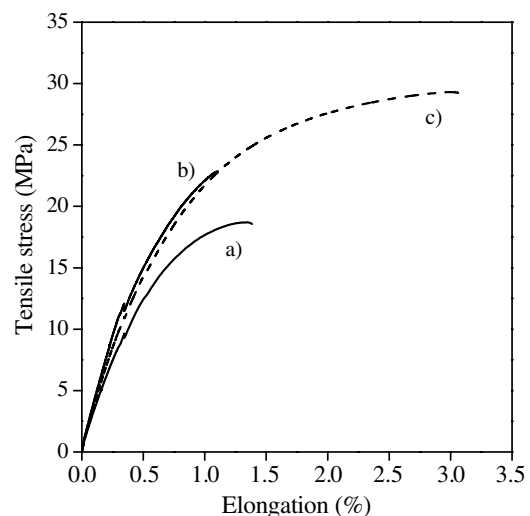


Fig. 11. Stress vs. elongation traces of PP/wood composites containing 50 wt% wood flour at 0.10 MAPP/wood ratio: (a) no MAPP, (b) Licomont AR 504, (c) Orevac CA 100.

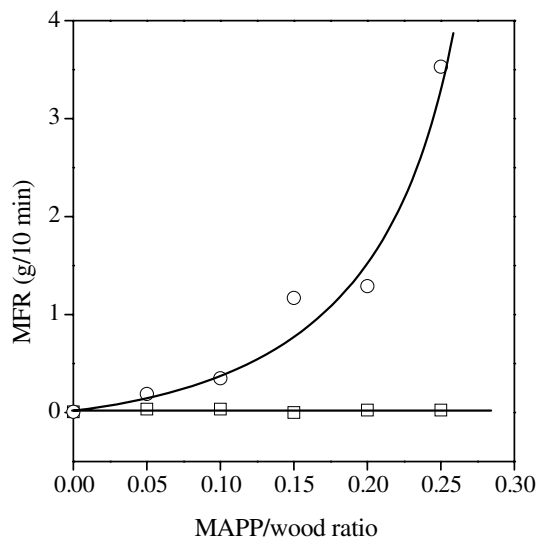


Fig. 12. Effect of the properties and the amount of the functionalized polymer on the viscosity of PP/wood composites at 70 wt% wood content. Symbols: (□) Orevac CA 100, (○) Licomont AR 504.

ciently than the other compound used, there are other aspects of composite preparation which merit some considerations. The viscosity of PP/wood composites increases dramatically at large wood contents. As a consequence, processability deteriorates leading to low productivity and bad surface quality. The molecular weight of the functional polymer can influence the rheological properties of the composites considerably. This is demonstrated clearly by Fig. 12 presenting the melt flow rate of PP/wood composites with 70 wt% filler content plotted as a function of MAPP/wood ratio. MFR remains practically the same at a very low value when the high molecular weight coupling agent is used, but increases very rapidly with MAPP content when Licomont is added. The effect becomes stronger with increasing wood flour content. Obviously, optimization of properties is needed to achieve simultaneously good load-bearing capacity of the reinforcement and acceptable processability of the composite.

4. Conclusions

The study of PP/wood flour composites in a wide range of wood content and relative amount of MAPP used as coupling agent showed that the morphology of the components and that of the composites does not change as a result of compounding. The wood flour used in these experiments does not nucleate PP. The most important structural phenomena determining properties are the orientation of the anisotropic wood flour particles and their aggregation. Results obtained on specimens with various thicknesses proved that both phenomena depend on processing conditions and on the dimensions of the product. Much larger improvement could be achieved by the addition of functionalized polymer in thicker samples than for thinner specimens. The amount of MAPP has a maximum efficiency at

around 0.05–0.10 MAPP/wood ratio in the composites of this study. The introduction of further amount of functionalized polymer is superfluous because of the limited surface available for coupling. MAPP with larger molecular weight and smaller functionality proved to be more advantageous in the improvement of composite strength, because it can form larger number of entanglements per molecule than the small molecular weight coupling agent. The quantitative determination of reinforcement proved that more entanglements lead to increased deformability and to larger load-bearing capacity of the wood fibers. On the other hand, the smaller molecular weight coupling agent decreases viscosity and improves processability considerably, thus optimization of composition is essential to achieve maximum performance.

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References

- [1] Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. *Prog Polym Sci* 1999;24(2):221–74.
- [2] Bledzki AK, Faruk O, Huque M. Physico-mechanical studies of wood fiber reinforced composites. *Polym Plast Technol Eng* 2002;41(3):435–51.
- [3] Bledzki AK, Letman M, Viksne A, Rence L. A comparison of compounding processes and wood type for wood fibre-PP composites. *Composites* 2005;A36(6):789–97.
- [4] Ichazo MN, Albano C, Gonzalez J, Perera R, Candal MV. Polypropylene/wood flour composites: treatments and properties. *Compos Struct* 2001;54(2-3):207–14.
- [5] Bledzki AK, Reihmane S, Gassan J. Thermoplastics reinforced with wood fillers: a literature review. *Polym Plast Technol Eng* 1998;37(4):451–68.
- [6] Jacob A. WPC industry focuses on performance and cost. *Reinf Plast* 2006;50:32–3.
- [7] Bledzki AK, Faruk O, Sperber VE. Cars from bio-fibres. *Macromol Mater Eng* 2006;291(5):449–57.
- [8] Pukánszky B, Turcsányi B, Tüdös F. Effect of interfacial interaction on the tensile yield stress of polymer composites. In: Ishida H, editor. *Interfaces in polymer ceramic and metal matrix composites*. New York: Elsevier; 1988. p. 467–77.
- [9] Pukánszky B. Influence of interface interaction on the ultimate tensile properties of polymer composites. *Composites* 1990;21(3):255–62.
- [10] Pukánszky B. Particulate filled polypropylene: structure and properties. In: Karger-Kocsis J, editor. *Polypropylene: structure blends and composites*, vol. 3. London: Chapman & Hall; 1995. p. 1–70.
- [11] Farris RJ. The influence of vacuole formation on the response and failure of filled elastomers. *Trans Soc Rheol* 1968;12(2):315–34.
- [12] Pukánszky B, van Es M, Maurer FHJ, Vörös G. Micromechanical deformations in particulate filled thermoplastics: volume strain measurements. *J Mater Sci* 1994;29(9):2350–8.

- [13] Vollenberg P, Heikens D, Ladan HCB. Experimental determination of thermal and adhesion stress in particle filled thermoplasts. *Polym Compos* 1988;9(6):382–8.
- [14] Vollenberg P. The mechanical behaviour of particle filled thermoplastics. PhD thesis, Eindhoven University of Technology; 1987.
- [15] Pukánszky B, Vörös G. Mechanism of interfacial interactions in particulate filled composites. *Compos Interfaces* 1993;1(5):411–27.
- [16] Maldas D, Kokta BV. Interfacial adhesion of lignocellulosic materials in polymer composites: an overview. *Compos Interfaces* 1993;1(1):87–108.
- [17] Kazayawoko M, Balatinecz JJ, Matuana LM. Surface modification and adhesion mechanism in woodfiber-polypropylene composites. *J Mater Sci* 1999;34(24):6189–99.
- [18] Dominkovics Z, Dányádi L, Pukánszky B. Surface modification of wood flour and its effect on the properties of PP/wood composites. *Composites* [submitted for publication].
- [19] Cantero G, Arbeláiz A, Mugika F, Valea A, Mondragon I. Mechanical behaviour of wood/polypropylene composites: Effects of fibre treatments and ageing processes. *J Reinf Plast Compos* 2003;22(1):37–50.
- [20] Beg MDH, Pickering KL. Fiber pretreatment and its effects on wood fiber reinforced polypropylene composites. *Mater Manuf Process* 2006;21(3):303–7.
- [21] Stark NM. Wood fiber derived from scrap pallets used in polypropylene composites. *Forest Prod J* 1999;49(6):39–46.
- [22] Raj RG, Kokta BV. Reinforcing high density polyethylene with cellulosic fibers I: The effect of additives on fiber dispersion and mechanical properties. *Polym Eng Sci* 1991;31(18):1358–62.
- [23] Sombatsomporn N, Yotinwattanakumtorn C, Thongpin C. Influence of type and concentration of maleic anhydride grafted polypropylene and impact modifiers on mechanical properties of PP/wood sawdust composites. *J Appl Polym Sci* 2005;97(2):475–84.
- [24] Lu JZ, Negulescu II, Wu Q. Maleated wood-fiber/high density-polyethylene composites: coupling mechanisms and interfacial characterization. *Compos Interfaces* 2005;12(1-2):125–40.
- [25] Hristov VN, Krumova M, Vasileva St, Michler GH. Modified polypropylene wood flour composites II. Fracture deformation and mechanical properties. *J Appl Polym Sci* 2004;92(2):1286–92.
- [26] Kazayawoko M, Balatinecz JJ, Woodhams RT. Diffuse reflectance Fourier transform infrared spectra of wood fibers treated with maleated polypropylenes. *J Appl Polym Sci* 1997;66(6):1163–73.
- [27] Li Q, Matuana LM. Effectiveness of maleated and acrylic acid-functionalized polyolefin coupling agents for HDPE-wood-flour composites. *J Thermoplast Compos Mater* 2003;16:551–64.
- [28] Qiu W, Zhang F, Endo T, Hirotsu T. Preparation and characteristics of composites of high-crystalline cellulose with polypropylene: effects of maleated polypropylene and cellulose content. *J Appl Polym Sci* 2003;87(2):337–45.
- [29] Hristov V, Vasileva S. Dynamic mechanical and thermal properties of modified poly(propylene) wood fiber composites. *Macromol Mater Eng* 2003;288(10):798–806.
- [30] Amash A, Zugenmaier P. Morphology and properties of isotropic and oriented samples of cellulose fibre-polypropylene composites. *Polymer* 2000;41(4):1589–96.
- [31] Dányádi L, Renner K, Móczó J, Pukánszky B. Wood flour filled PP composites: Interfacial adhesion and micromechanical deformations. *Polym Eng Sci* [in press].
- [32] Sain M, Suhara P, Law S, Bouilloux A. Interface modification and mechanical properties of natural fiber-polyolefin composite products. *J Reinf Plast Comp* 2005;24(2):121–30.
- [33] Dányádi L, Renner K, Szabó Z, Nagy G, Móczó J, Pukánszky B. Wood flour filled PP composites: adhesion, deformation, failure. *Polym Adv Technol* 2006;17(11-12):967–74.
- [34] Tasker S, Badyal JPS, Backson SCE, Richards RW. Hydroxyl accessibility in celluloses. *Polymer* 1994;35(22):4717–21.
- [35] Oh SY, Yoo DI, Shin Y, Kim HC, Kim HY, Chung YS, et al. Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydr Res* 2005;340(15):2376–91.
- [36] Menyhárd A, Varga J, Molnár G. Comparison of different β -nucleators for isotactic polypropylene by characterisation by DSC and temperature-modulated DSC (TMDSC) measurements. *J Therm Anal Calorim* 2006;83(3):625–30.
- [37] Varga J, Karger-Kocsis J. Rules of supermolecular structure formation in sheared isotactic polypropylene melts. *J Polym Sci* 1996;B34(4):657–70.
- [38] Karger-Kocsis J, Varga J. Interfacial morphology in PP-composites. In: Karger-Kocsis J, editor. *Polypropylene: an A–Z reference*. Dordrecht/Boston/London: Kluwer Academic Publishers; 1999. p. 348–56.
- [39] Varga J. Supermolecular structure of isotactic polypropylene. *J Mater Sci* 1992;27(10):2557–79.
- [40] Pukánszky B, Mudra I, Staniek P. Relation of crystalline structure and mechanical properties of nucleated polypropylene. *J Vinyl Additive Technol* 1997;3(1):53–7.
- [41] Pukánszky B. Effect of interfacial interactions on the deformation and failure properties of PP/CaCO₃ composites. *New Polym Mater* 1992;3:205–17.
- [42] Pukánszky B, Belina K, Rockenbauer A, Maurer FHJ. Effect of nucleation filler anisotropy and orientation on the properties of PP composites. *Composites* 1994;25:205–14.
- [43] Turcsányi B, Pukánszky B, Tüdös F. Composition dependence of tensile yield stress in filled polymers. *J Mater Sci Lett* 1988;7(2):160–2.