PLA/WOOD BIOCOMPOSITES: IMPROVING COMPOSITE STRENGTH BY CHEMICAL TREATMENT OF THE FIBERS

R. Csizmadia[1,2], G. Faludi[1,2], K. Renner[1,2], J. Móczó[1,2,*] and

B. 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-1525 Budapest, P.O. Box 17, Hungary

*Corresponding author: Phone: +36-1-463-3477, Fax: +36-1-463-3474, E-mail: jmoczo@mail.bme.hu

ABSTRACT

A resol type phenolic resin was prepared for the impregnation of wood particles used for the reinforcement of PLA. A preliminary study showed that the resin penetrates wood with rates depending on the concentration of the solution and on temperature. Treatment with a solution of 1 wt% resin resulted in a considerable increase of composite strength and decrease of water absorption. Composite strength improved as a result of increased inherent strength of the wood, but interfacial adhesion might be modified as well. When wood was treated with resin solutions of larger concentrations, the strength of the composites decreased, first slightly, then drastically to a very small value. A larger amount of resin results in a thick coating on wood with inferior mechanical properties. At large resin contents the mechanism of deformation changes; the thick coating breaks very easily leading to the catastrophic failure of the composites at very small loads.

1. INTRODUCTION

In recent years the interest in poly(lactic acid) (PLA) increased quite considerably for several reasons including the growing environmental awareness of the public, decreasing price with growing capacity, and acceptable processability [1]. A further advantage is that PLA does not degrade biologically under usual service conditions thus parts can be designed and produced from it with long lifetime, while, on the other hand, it is compostable that makes disposal easy and environmentally friendly [1]. However, PLA has some disadvantages as well including sensitivity to water, fast physical ageing, limited impact resistance and large stiffness in some applications [2,3]. As a consequence, PLA is modified in many ways to develop materials with appropriate property profiles, among others by plasticization [4-6], impact modification [1,7-10] and by the introduction of fillers [11-16] or fibers [17-24], especially for structural applications.

The combination of PLA with lignocellulosic fibers results in decreased price and increased stiffness, while maintaining the environmental advantage, compostability [25]. However, similarly to PLA, natural fibers also have some disadvantages like heat and water sensitivity, poor adhesion to a number of polymers and poor transverse strength [26]. The majority of thermoplastic/natural fiber composites are produced from commodity polymers and wood (WPC) [26], and interfacial adhesion is weak in most of them indeed. Weak interactions were claimed to develop between the components also in PLA/wood composites by many authors [18-20,23,27-31], but our previous study and the estimation of the strength of adhesion by three independent methods indicated rather strong adhesion between wood and poly(lactic acid) [32]. The results of the study also showed that PLA/wood composites usually fail by the fracture of large wood particles that leads to crack initiation and catastrophic failure. The attempt to improve interfacial interaction by coupling proved to be successful. However, the improvement achieved was small, since it prevented only the debonding of a few very large wood particles, but not the fracture of the others. Since the failure of the composites is caused mainly by the fracture of the fibers and their inherent strength seems to be the limiting factor in increasing composite strength, a new strategy was necessary to improve composite properties.

The elementary fibers in wood are attached by lignin acting as an adhesive. Attempts were made to improve the properties of PP/wood composites by the addition of lignin [33-36]. Although the results were not very convincing, the general idea may hold and the inherent strength of wood might be improved by chemical treatment. As a consequence, the general idea and goal of this work was to impregnate wood with a phenolic resin to increase the strength of the wood particles and thus composite strength. An additional benefit could be decreased water absorption, since extensive water uptake may limit application in certain areas.

2. EXPERIMENTAL

The phenolic resin used in the experiments was prepared in a three neck flask fitted

with a reflux condenser, thermometer and magnetic stirrer. 16 g (0.4 mol) NaOH was added gradually to the mixture of 94.11 g (1 mol) phenol and 145.86 g (1.7 mol) formaldehyde placed previously in the flask, which was immersed into an oil bath of 120 °C. First the reaction mixture started to boil then its temperature decreased gradually. 30 min after boiling, temperature was set to 80 °C and the mixture was heated for 2 more hours. Subsequently the reaction mixture with a solid content of 56 wt% was let to cool to room temperature. Water content was decreased by evaporation to obtain a solid content of about 80 wt% and then it was diluted with ethanol to prepare a resin solution with a solid content of 46 wt% for impregnation. Before the impregnation of a larger amount of wood for composite preparation, we determined the rate of resin penetration by immersing wood blocks of 25 x 25 x 4 mm dimensions into resin solutions of different concentrations and following the propagation of the diffusion front by light microscopy as a function of time by cutting slices from the blocks. Larger amounts of wood flour were impregnated for composite preparation. The necessary amount of wood (e.g. 25 g) was placed into an aluminum tray and the resin solution (e.g. 250 ml) was poured on it. The slurry was homogenized thoroughly then the resulting material was slowly dried at 40 °C for 100-150 hours. Subsequently the dry, impregnated wood flour was ground in a mortar and then passed through a sieve with hole size of 500 μm. Larger particles were ground and sieved repeatedly until all passed through the sieve. Adhesion forces were relatively weak thus large particles could be crushed easily. The resulting powder was used in the extraction/dissolution and water absorption experiments. Impregnated wood powder was dried in an air circulation oven for 4 hours at 105 °C before composite preparation. The efficiency of the impregnation process and the location of the resin on or in wood particles were determined by extraction/dissolution experiments. 25 g impregnated wood flour was put into 500 ml distilled water and stirred at room temperature for different times. After the elapse of extraction time wood was filtered out of the slurry, dried at 50 °C and weighed. The difference between the initial and final weight was regarded as the extracted amount of resin.

The PLA used in the experiments was the Ingeo 4032 D grade (M_n = 88500 g/mol

and $M_w/M_n = 1.8$) purchased from NatureWorks (USA). The grade is recommended for extrusion by the producer. The polymer (<2% D isomer) has a density of 1.24 g/cm^3 and its MFR is 3.9 g/10 min at 190 °C and 2.16 kg load. The Filtracel EFC 1000 (Rettenmaier and Söhne GmbH) wood fiber was used as reinforcement. The fiber has an average particle size of 210 μm and an aspect ratio of 6.8. Wood particles were impregnated with 0.5, 1, 3, 5 and 10 wt% solutions then dried for 100 hours at 40 °C.

Poly(lactic acid) was dried in a vacuum oven before composite preparation (110 °C for 4 hours), while wood in an air circulation oven at 105 °C for 4 hours. The components were homogenized using a Brabender W 50 EHT internal mixer at 180 °C, 50 rpm for 10 min. Fiber content changed from 0 to 60 vol% in 9 steps. The homogenized material was compression molded to 1 mm thick plates at 190 °C using a Fontijne SRA 100 machine. All specimens were kept in a room with controlled temperature and humidity (23 °C and 50 %) for at least one week prior further testing. Mechanical properties were characterized by the tensile testing of specimens cut from the 1 mm thick plates. Measurements were carried out at a cross-head speed of 5 mm/min and gauge length of 115 mm using an Instron 5566 apparatus. Micromechanical deformation processes were followed by acoustic emission (AE) measurements. A Sensophone AED 40/4 apparatus was used to record and analyze acoustic signals generated during tensile testing. The particle characteristics of wood and the structure, as well as the deformation mechanism of the composites were studied by scanning electron microscopy, SEM (JEOL JSM-6380 LA). Micrographs were recorded on tensile fracture surfaces. The water absorption of impregnated wood flour was determined by keeping samples in a desiccator at 100 % relative humidity and 23 °C.

3. RESULTS AND DISCUSSION

The results are reported in three sections. First we discuss the diffusion experiments which formed the basis for the preparation of impregnated wood. Composite properties are described next, followed by the interpretation of the results. Consequences for practice will be mentioned briefly in this section.

3.1. Impregnation

Before the preparation of impregnated wood we had to see if the resin penetrates the particles indeed. We designed model experiments and impregnated wood blocks prepared for the purpose. Slices were cut at increasing intervals from the blocks and studied by microscopy. The penetration of the resin into the wood specimen is demonstrated by a series of micrographs in **Fig. 1.** The propagation of the front could be followed with acceptable accuracy. **Fig. 2** presents some of the results of the impregnation model experiments. The rate of penetration increased with the concentration of the solution and diffusion path approached saturation indicating Fickian diffusion.

Diffusion coefficient could be determined from the absorption isotherms by fitting **Eq. 1** to the experimental points

$$L = 3\sqrt{2\,D\,t} \qquad\qquad (1)$$

where L is the depth of penetration, D is diffusion coefficient and t the time of diffusion. The validity of the approach was checked by plotting the depth of penetration against the time of diffusion. Two correlations obtained at 50 wt% resin concentration are presented in **Fig. 3** for two temperatures, 25 and 40 °C. In spite of some deviations, the correlations are straight lines indeed, as predicted by **Eq. 1** and the rate of diffusion increased with temperature as expected. Diffusion rates derived from the results were used to calculate the time of impregnation for the wood fibers used in the composites.

As mentioned in the experimental part, wood flour was impregnated with resin solutions of different concentrations for further experiments. Wood particles treated with 10 wt% resin solution stuck together and formed large lumps, which were quite difficult to separate, thus this wood could not be used for composite preparation (**Fig. 4**). As a consequence, in further experiments we used wood flour treated with 1, 3 and 5 wt% resin solutions.

Finally, before composite preparation we also checked the location of the resin. Since we prepared the impregnated wood by evaporating ethanol and water from the slur-

ry, the resin could have been inside the wood particles but also on their surface. The location of the resin was checked by dissolution experiments. The results are presented in **Fig. 5,** in which the extracted amount of resin is plotted against the time of dissolution for samples impregnated with different amounts of resin. Extracted amounts are related to the total amount of resin used for treatment. Dissolution is very fast initially, and then slows down at longer times. We assume that resin covering the surface of the particles dissolves first, followed by slow diffusion at longer times. A considerable amount of resin is located on the surface of the particles and this amount is very large for the sample treated with a solution of 5 wt% resin.

3.2. Composites

Stiffness increases quite steeply approaching 8 GPa at the largest wood content (**Fig. 6**). The effect of resin treatment is small, practically negligible at small wood content, but the results clearly show that it is beneficial. The modulus of composites prepared with the impregnated particles is always larger than that of materials containing the neat wood. This is slightly surprising, since modulus is determined at very small deformations and interfacial adhesion or small changes in the inherent properties of the wood are not expected to influence it significantly. However, the use of stiffer particles, due to resin penetration, for reinforcement should result in composites with larger modulus.

The effect of impregnation on composite strength is much more drastic than on modulus (**Fig. 7**). The strength of the composite prepared with the neat fiber decreases continuously, but not very steeply. This composition dependence indicates the absence of structural effects and is in accordance with earlier conclusions about reasonably strong interfacial adhesion between the components [32]. Treatment with 1 wt% resin solution increases the strength of the composites and changes the slope of the strength vs. wood content correlation. Larger composite strength may result from improved adhesion and/or increased inherent strength of the wood, as was our original assumption. At larger resin contents, however, strength decreases significantly and the effect is especially pronounced for

the treatment with 5 wt% resin solution. Based on the composition dependence of composite strength, we can only speculate about the reason for the drastic decrease of strength and definitely further evaluation and results are needed to explain it reasonably. Possible reasons could be changing structure or deformation mechanism or both.

The dependence of composite strength on fiber content can be described quantitatively by a simple model developed earlier [37,38]. For cases when deformation is small and strain hardening can be neglected, the correlation can be written in the simplified form of **Eq. 2**

$$\sigma = \sigma_0 \frac{1-\varphi}{1+2.5\,\varphi} \exp(B\,\varphi) \tag{2}$$

where σ and σ_0 are composite and matrix strength, respectively, φ is the volume fraction of the fiber in the composite and B is a parameter related to the load carried by the fiber. B expresses reinforcement quantitatively and it depends also on interfacial adhesion. **Eq. 2** can be written in linear form (**Eq. 3**)

$$\ln \sigma_{red} = \ln \frac{\sigma\,(1+2.5\,\varphi)}{1-\varphi} = \ln \sigma_0 + B\,\varphi \tag{3}$$

and if we plot reduced strength as a function of fiber content, we must obtain a straight line, the slope of which is parameter B. The strength of the four series of composites is plotted in the form of **Eq. 3** in **Fig. 8**. We obtain straight lines for the neat fiber and the one treated with 1 wt% resin solution, but the other two series offer a completely different picture. Although the strength of the composites containing the fibers impregnated with 3 wt% solution also fall on a straight line at small fiber content, it deviates from this line at large wood loadings; in fact the points are scattered all over the plot. No correlation whatsoever can be established for the last series, for composites which contain the wood treated with 5 wt% resin solution. Any deviation from the linear correlation indicates structural effects, usually aggregation, or changing deformation mechanism. Although we do not

have any reason to suspect that the dispersion of wood will be different for the neat and the treated fibers, particles may touch each other for purely geometrical reasons [39,40]. As a consequence, decreased strength may result from this effect, or treatment modifies deformation and failure mechanism.

Acoustic emission measurements may offer additional information about local deformation processes related to the particles. The different elastic properties of the components induce inhomogeneous stress distribution around the particles during deformation. Local stress maxima result in a variety of local deformation processes. In particulate filled polymers the most frequent micromechanical deformation process is debonding, especially when adhesion between the components is poor, but shear yielding and a number of fiber related processes can also be observed in wood fiber reinforced composites. Most of these processes release an elastic wave, which can be detected by appropriate sensors. In PLA/wood composites the fracture of the fibers was found to be the dominating deformation process [**32**].

The result of an acoustic emission experiment carried out on the composite containing 15 vol% of the fiber treated with 1 wt% resin solution is presented in **Fig. 9**. The small circles indicate individual signals (events, hits). The stress vs. strain trace is also plotted as reference. It is obvious that considerable acoustic activity starts only above a certain deformation and lasts until the end of the measurement, up to failure. Further conclusions are difficult to draw from the individual signals, but the cumulative number of signal trace offers additional information. The shape of the trace was shown to be related to the mechanism of deformation. An S shaped saturation curve was assigned to debonding [40,41], while exponentially increasing traces like the one shown in **Fig. 9** usually indicate fiber fracture as the dominating process [39,40]. Acoustic emission testing of the composite containing the same amount of fiber, but impregnated with 5 wt% resin solution yield a completely different result (**Fig. 10**). Ultimate deformation is very small as well as the number of individual signals. These latter are scattered all over the plot, but most of them evolve during the fracture of the specimen. Obviously, the failure of the

composite occurs by a different process than in the previous case, at treatment with a solution of 1 wt% resin. This mechanism is initiated at a much smaller load than the other and is not accompanied by acoustic emission signals. The cumulative number of signal traces allows the determination of a characteristic deformation (ε_{AE}) and stress (σ_{AE}) value as shown in **Fig. 9**. The initiation stress of the dominating micromechanical deformation process is plotted against fiber content in **Fig. 11**. Changing mechanism and small initiation stress are clearly demonstrated by the figure. However, we still cannot identify the new mechanism resulting from the impregnation of wood with excess resin.

3.3. Discussion, consequences

Previous studies proved that the strength of the composite is determined by micromechanical deformations both in PP and PLA composites. Fiber fracture was identified as the dominating mechanism in the latter. Increasing fiber strength was assumed to lead to stronger composites and the assumption proved to be true for compositions containing the fibers treated with 1 wt% resin soltution. Based on the preliminary impregnation study we can state with fairly good certainty that the resin penetrates the wood particles and changes their properties. Increased composite strength must result from this change, but the modification of interfacial interactions cannot be excluded either. However, the large decrease in initiation and composite strength at large resin and wood content cannot be explained in this way.

SEM micrographs recorded on impregnated wood particles are presented in **Fig. 12**. The wood treated with 1 wt% resin solution (**Fig. 12a**) does not look very different from the non-treated, neat fiber. On the other hand, when wood is treated with a solution of 5 wt% resin, a thick resin layer covers the wood particles clearly visible in **Fig. 12b**. Even small individual droplets of the resin can also be distinguished in the micrograph. We may assume that the thick resin layer breaks very easily, because phenolic resins are usually quite brittle.

SEM micrographs taken from the fracture surface of composites created during

tensile testing are shown in **Fig. 13** to support the assumption presented above. **Fig. 13a** was recorded on a PLA composite containing neat wood. The micrograph confirms our earlier conclusion about the fracture of the fibers. A wood particle fractured along its axis occupies the center of the micrograph. On the other hand, according to **Fig. 13b** the failure of the resin layer covering the particle is the dominating process in the composite containing the wood flour impregnated with a solution of 5 wt% resin. We could not detect the aggregation of wood particles in any of the micrographs recorded. However, the fracture of the resin layer is evident in many SEM micrographs. Obviously, the new mechanism, which is initiated at a very small stress, is the failure of the resin layer.

The consequence of this mechanism is very evident in **Fig. 14**, in which we plotted composite strength against the initiation stress of the dominating micromechanical deformation process. The correlation is extremely close indicating that local deformation processes determine composite strength and the specimens fail catastrophically almost immediately after the initiation of the actual process. It is also evident from the figure that the correlation is independent of the mechanism of the deformation. On the other hand, the points are divided into two groups. Some of the composites are quite strong and fail with the fracture of the fibers (see **Fig. 13a**). Mostly the composites prepared with the neat fiber and that treated with 1 wt% resin belong to this group (see upper right section of the figure), but a few points from the other two series are also included. At large resin and wood content the mechanism of deformation changes resulting in quite weak composites, the strength of which does not exceed 30 MPa, about half that of the best material. As mentioned above, the new mechanism is the failure of the resin coating; the thick layer around a single particle can fail very easily.

Obviously, excessive amount of resin cannot be used for the impregnation or coating of wood particles, but a small quantity is definitely beneficial. At the beginning of the project we also hoped for an improvement in the water sensitivity of the composites. Decreased sensitivity, i.e. water uptake, would lead to better dimensional stability and an extended range of applications for the PLA/wood composites studied. The water absorption

of impregnated wood is plotted against time in **Fig. 15**. We can see that water absorption decreases already at the smallest amount of resin used for treatment compared to neat wood. In fact water absorption is more than **17 %** for this latter, not even reaching saturation in the time interval of the test, but it decreases to around **6 %** already at 1 wt% resin treatment. As a consequence, improved strength is combined with decreased water absorption as a result of the treatment.

4. CONCLUSIONS

The impregnation of wood with a resol type phenolic resin proved to be a successful approach to improve the properties of PLA/wood composites. Treatment with a solution of 1 wt% resin resulted in a considerable increase of composite strength and decrease of water absorption. Composite strength improved as a result of increased inherent strength of wood, but interfacial adhesion might be modified as well. When wood was treated with resin solutions of larger concentrations, the strength of the composites decreased, first slightly, then drastically to a very small value, below 10 MPa. Larger amount of resin results in a thick coating on the wood particles. The study of micromechanical deformation processes by acoustic emission measurements proved that the mechanism of deformation changes at large resin contents. The thick coating breaks very easily leading to the catastrophic failure of the composites at very small loads. Although the approach proved to be successful and the treatment beneficial, further experiments are needed to optimize the properties of the resin, its amount and the technology of the treatment to arrive to maximum effect.

6. REFERENCES

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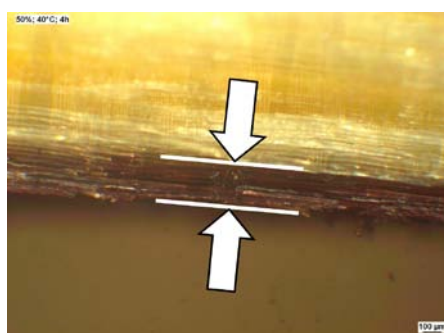
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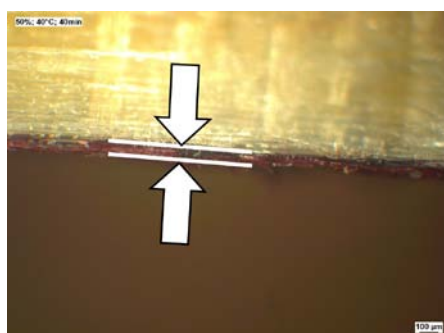
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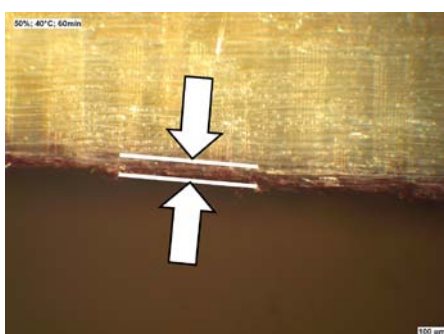
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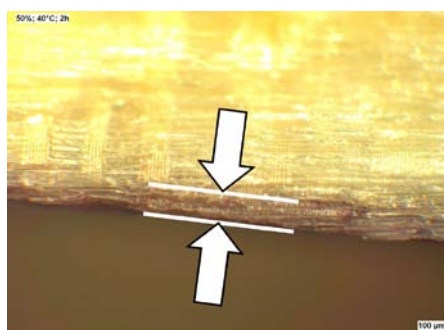
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Fig. 1   Penetration of a phenolic resin solution of 50 wt% solid content into a
              model wood block at 25 °C. a) 40 min, b) 60 min, c) 2 h, d) 4 h.
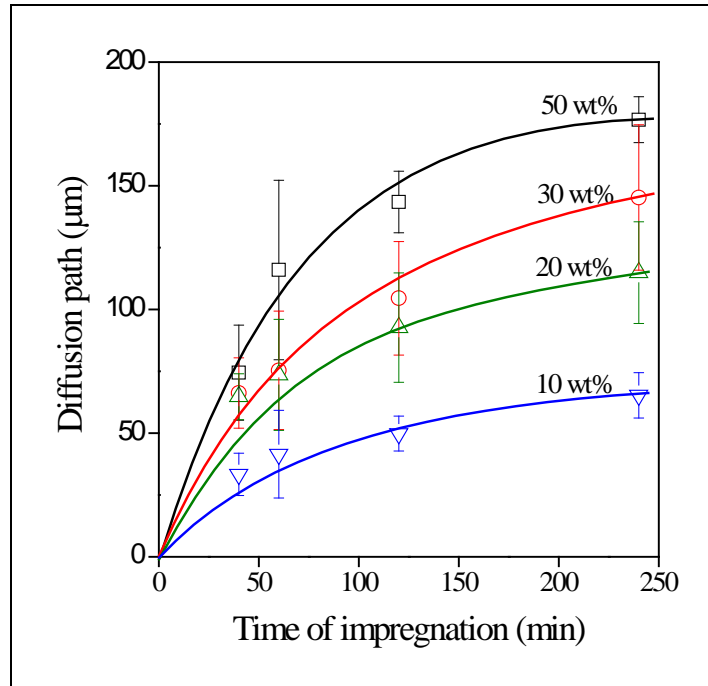
Fig. 2   Time and concentration dependence of the diffusion path of phenolic resin solutions into a wood block at 25 °C. Symbols: (∇) 10, (Δ) 20, ($\bigcirc$) 30 and ($\square$) wt% solid content.
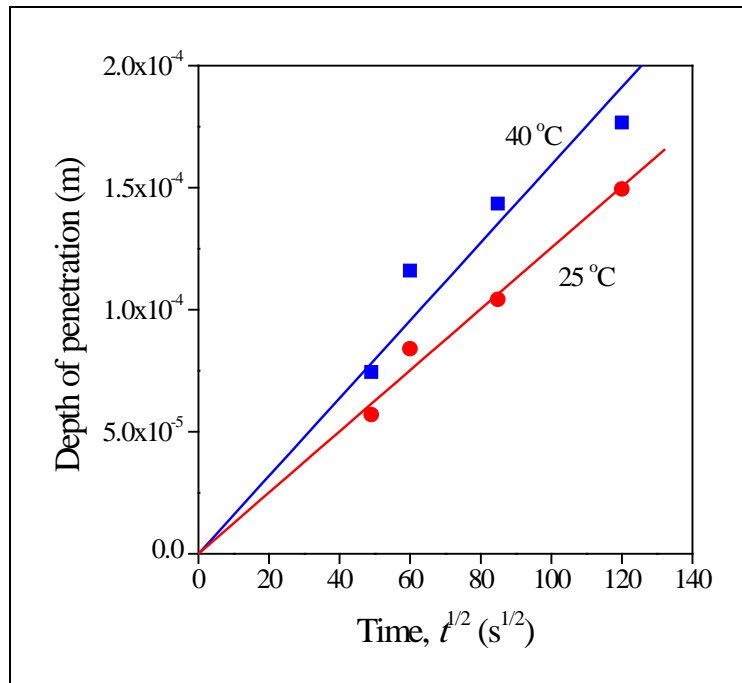
Fig. 3   Time dependence of the depth of penetration for a phenolic resin solution of 50 wt% solid content plotted according to **Eq. 1**. Symbols: ($\bullet$) 25, ($\blacksquare$) 40 °C.

Fig. 4   Wood particles impregnated with phenolic resin solutions of different solid content; concentration is 0.5, 1, 3, 5, and 10 wt%, respectively, and increases from left to right.
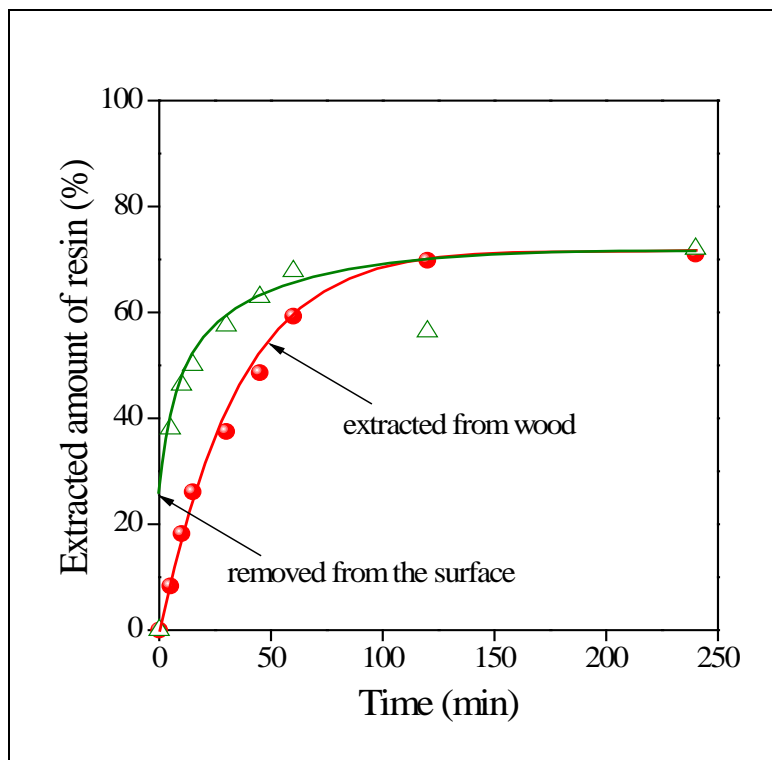
Fig. 5   Time dependence of the extraction of phenolic resin from impregnated wood particles. Removal of resin from the surface and the bulk. Symbols: (●) 1, (Δ) 5 wt% resin solution used for impregnation.
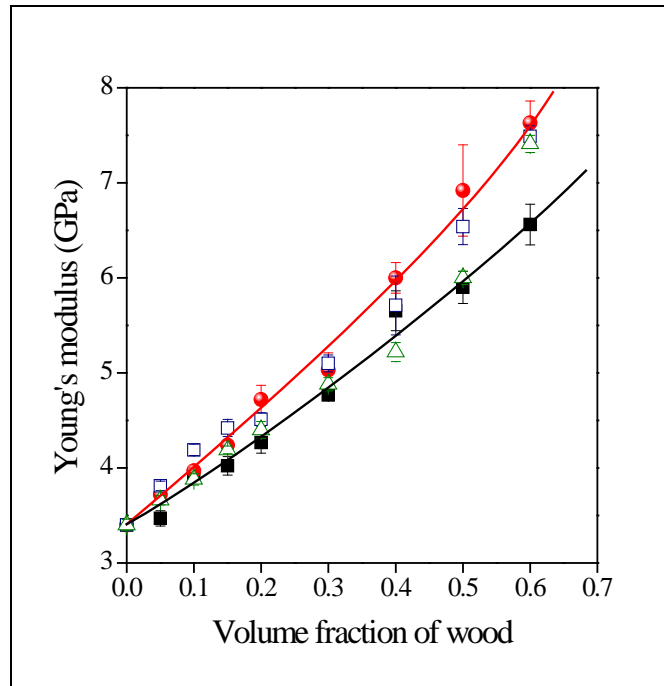
Fig. 6   Effect of wood content and resin treatment on the stiffness of PLA/wood composites. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.
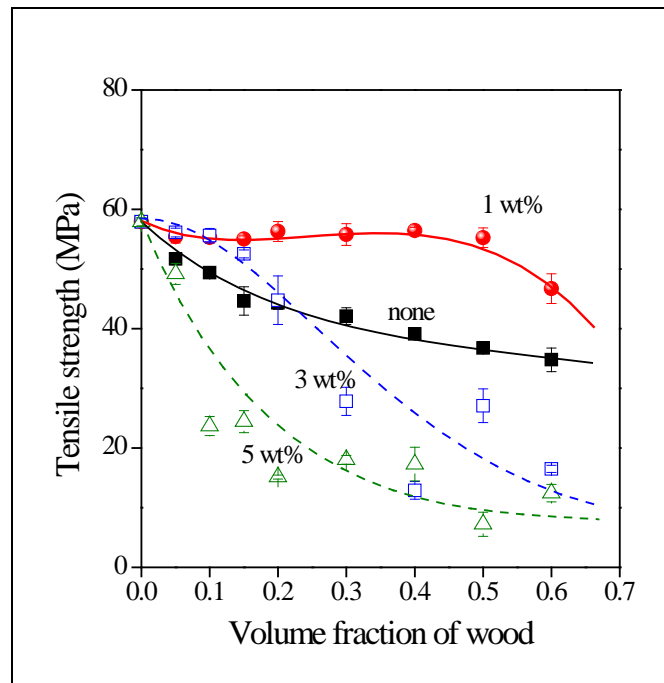
Fig. 7   Dependence of the tensile strength of PLA/wood composites on wood content and on the concentration of the resin solution used for impregnation. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.
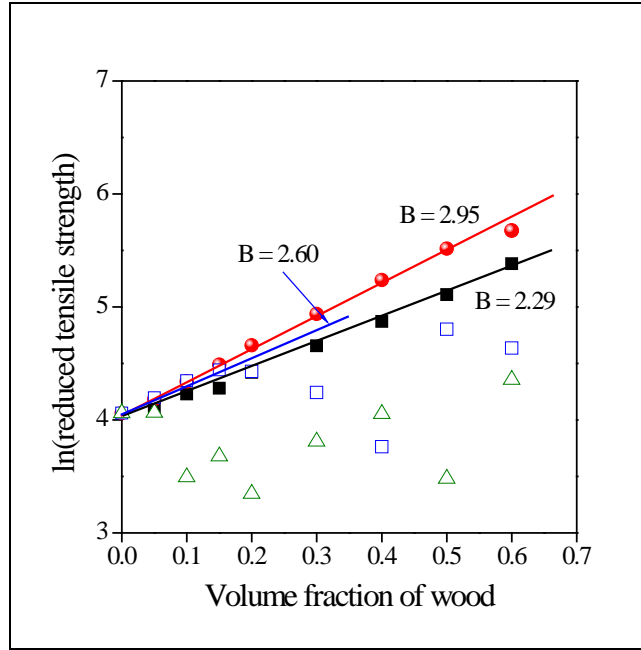
Fig. 8 Reduced tensile strength of PLA/wood composites plotted against filler content in the representation of **Eq. 3**. Deviation from linearity indicates structural effects or change of deformation mechanism. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.
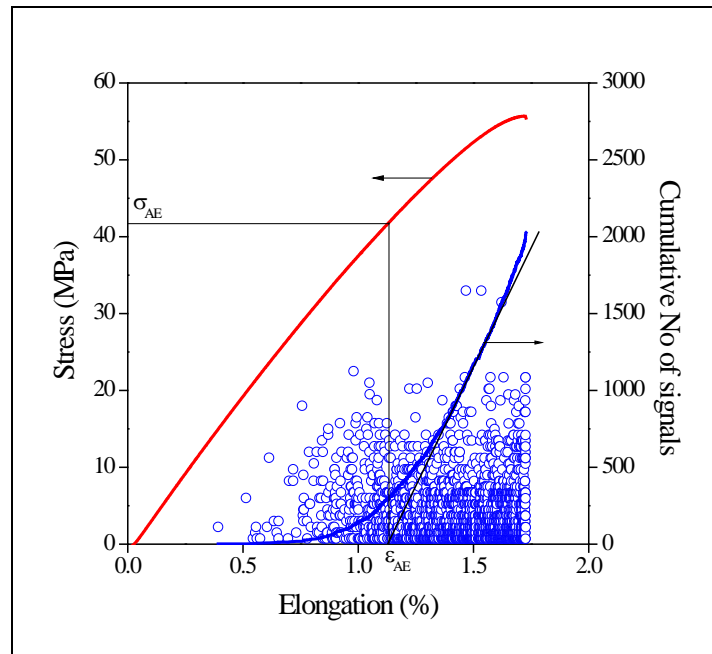
Fig. 9 Acoustic emission testing of a PLA/wood composite containing 15 vol% wood treated with 1 wt% solution of the phenolic resin used. The circles indicate individual signals. The stress vs. strain and the cumulative No. of signal traces are also included.
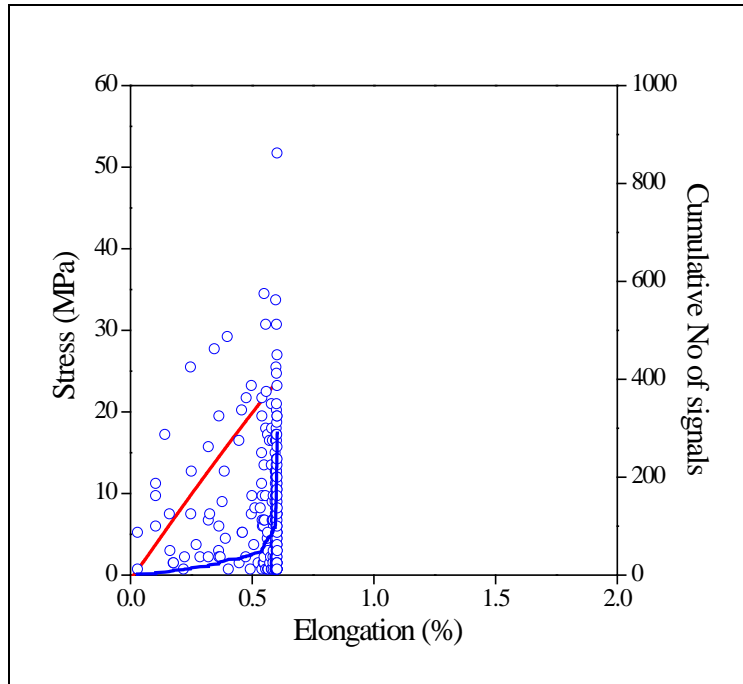
Fig. 10   Effect of resin content on the acoustic activity of a PLA/wood composite containing 15 vol% wood treated with a resin solution of 5 wt%. Compare results to **Fig. 9**.
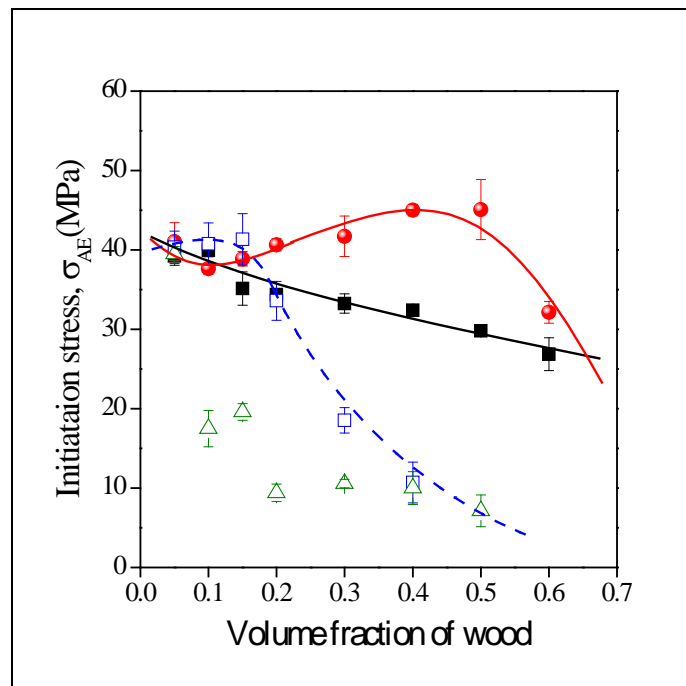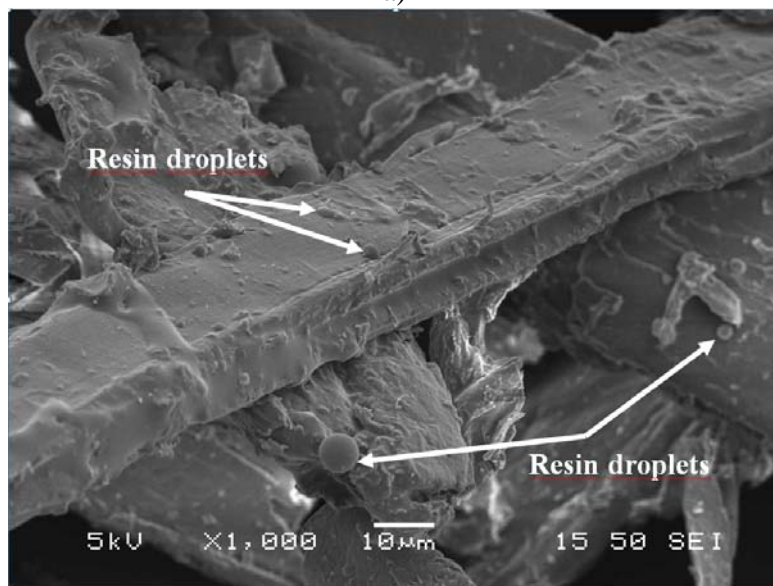

Fig. 11 Effect of wood content on the initiation stress of the dominating micromechanical deformation process in PLA/wood composites. Effect of the concentration of the resin solution used for treatment. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.
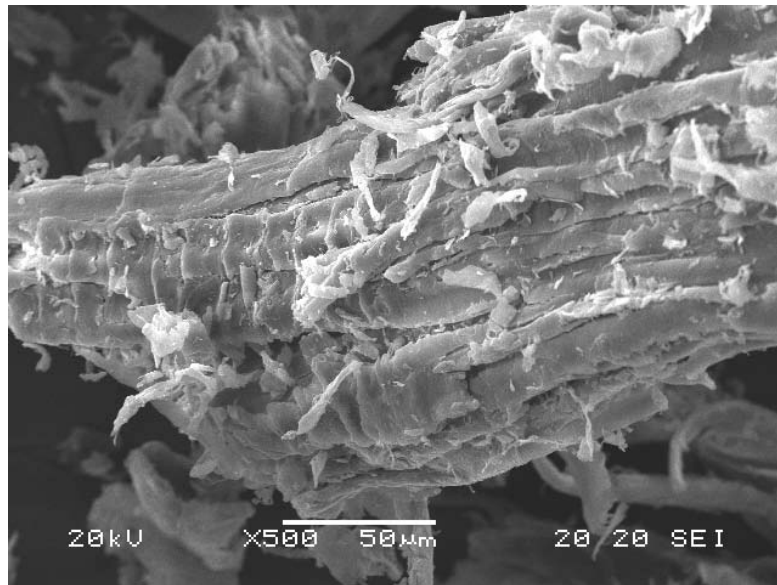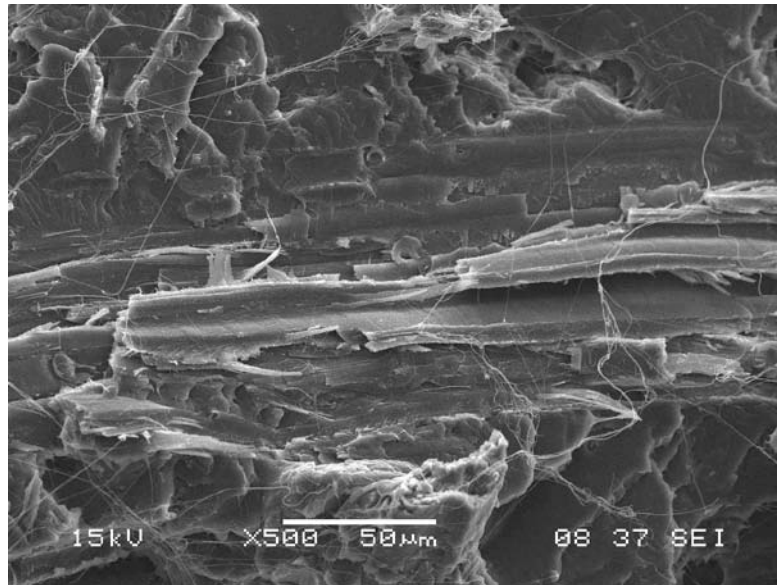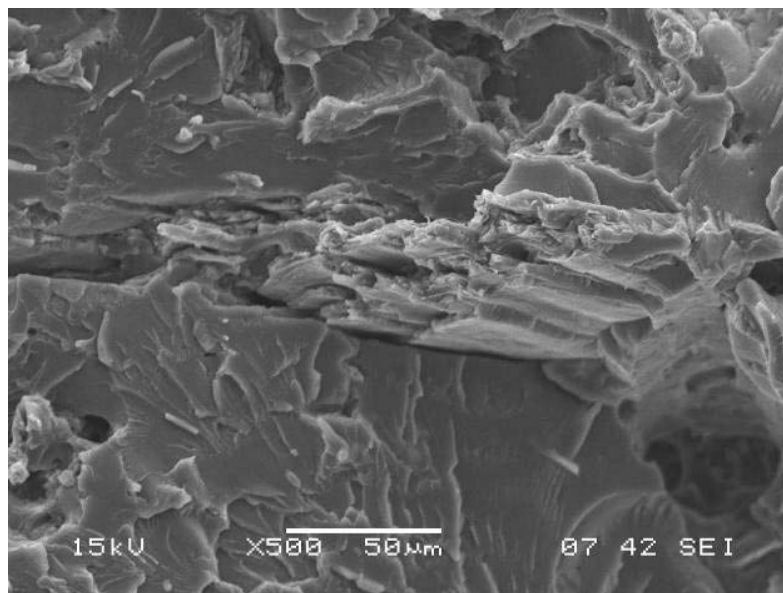
a)

b)

Fig. 12   SEM micrographs taken from wood impregnated with phenolic resin. a) 1 wt%,

   b) 5 wt% resin solution.

a)

b)

Fig. 13   Failure of PLA/wood composites in tensile testing; effect of resin treatment. Wood content: 20 vol%. a) neat wood, b) 5 wt% resin.
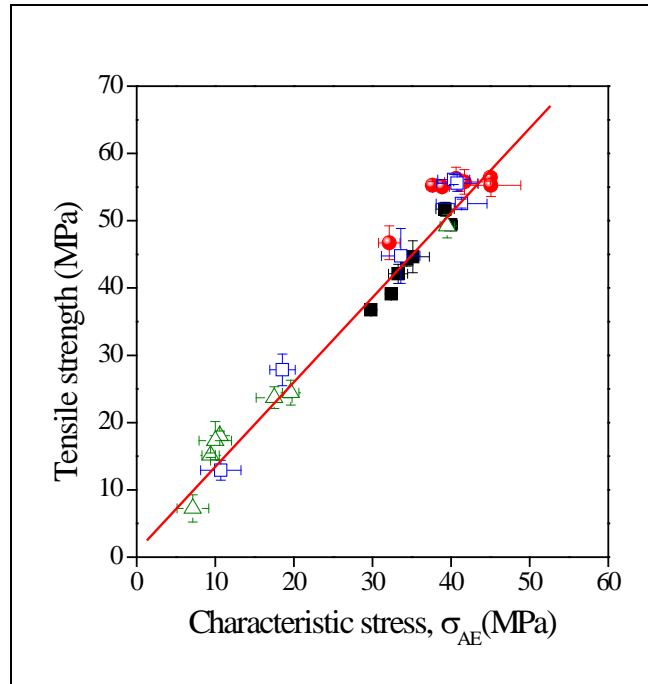
Fig. 14 Correlation between the strength of PLA/wood composites and the initiation stress of the dominating micromechanical deformation process occurring during deformation. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.
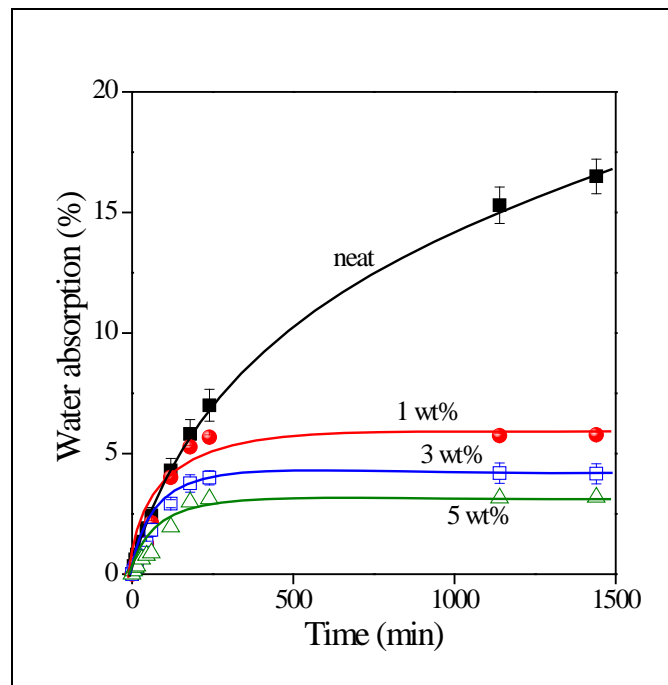

Fig. 15 Effect of phenolic resin treatment on the water absorption of wood flour. Symbols: (■) neat, (●) 1, (□) 3, (Δ) 5 wt% resin solution.