COMPOSITES SCIENCE AND TECHNOLOGY

VOLUME 89, 13 DECEMBER 2013, PAGES 77–82

http://dx.doi.org/10.1016/j.compscitech.2013.09.009

http://www.sciencedirect.com/science/article/pii/S0266353813003710

IMPROVING INTERFACIAL ADHESION IN PLA/WOOD BIOCOMPOSITES

G. Faludi[1,2], G. Dora[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: +36-1-463-2967, Fax: +36-1-463-3474, Email: krenner@mail.bme.hu

ABSTRACT

Two reactive coupling agents, N,N-(1,3-phenylene dimaleiimide) (BMI) and 1,1-(methylenedi-4,1-phenylene)bismaleimide (DBMI) were used to improve interfacial adhesion in PLA/wood composites. First the effect of the coupling agents was established in a series of experiments in which the amount of coupling agent changed at constant wood content, and then the effect of coupling was determined at various wood loadings (0-60 vol%). Composites were homogenized in an internal mixer and compression molded to plates. Tensile properties were determined and micromechanical deformations were studied by acoustic emission measurements. The two compounds improved the properties of the composites. Stiffness, strength and deformability increased simultaneously supplying sufficient proof for coupling. Because of the flexibility of the molecule, DBMI is a more efficient coupling agent in the studied composites than BMI. However, the effect of coupling is small, because only a few very large particles debond under the effect of external load. Smaller particles adhere strongly to the matrix even without coupling proving that interfacial adhesion is strong in PLA/wood composites.

KEYWORDS: A. Polymer-matrix composites (PMCs), A. coupling agents, B. mechanical properties, C. deformations, B. fracture,

1. INTRODUCTION

The application of natural fiber reinforced composites increases with a very high rate in all areas of the economy. They are based mostly on commodity polymers and used mainly in the building and the automotive industry [1]. However, with increasing environmental awareness of the public, biopolymers are preferred in all possible areas [2]. Poly(lactic acid) is one of the polymers which may gain wider application because of its

advantageous properties. It is produced from natural feedstock, compostable, have good stiffness and strength, and increasing production capacities even decreased its price somewhat [3]. Besides its advantages PLA has also some drawbacks thus it is modified through different approaches including plasticization [4], blending [5,6] and reinforcing with fibers [7,8]. PLA/wood fiber composites offer the possibility to achieve an advantageous property profile at a reasonable price.

The wood used for the reinforcement of thermoplastics usually has a relatively large particle size, which exceeds the size of traditional fillers of a few microns. An average size of several 100 μm is not uncommon for these materials. Debonding stress depends on interfacial adhesion, which is determined by the surface energy of the components. As a consequence, the large particles of wood with small surface energy [9] easily debond from the matrix polymer under the effect of external load [10,11]. Debonding results in the formation of voids and often in the premature failure of the material. Debonding was shown to be the dominating micromechanical deformation process in PP/wood composites not containing a coupling agent [10,11]. Although interfacial adhesion is claimed to be weak also in PLA/wood composites [12-14], detailed investigations and the estimation of adhesion by three independent methods indicated relatively strong adhesion between PLA and wood [15]. The study of micromechanical deformation processes proved that the dominating deformation mechanism is the fracture of the fibers, but other mechanisms, like debonding or fiber pull-out could not be excluded either. Although coupling cannot improve composite properties if adhesion is strong and the fracture of the fibers is the dominating process indeed, preventing the occurrence of the other two processes could lead to improved composite strength.

Interfacial interactions are modified in numerous ways in polymer/wood composites. Sodium hydroxide was shown to improve composite strength [16,17], but

plasma and high energy radiation was also used with success [18,19]. However, chemical coupling is the most frequent method to improve composite properties. Funcionalized polymers, mainly maleinated PP and PE, are used the most frequently in polyolefin composites [17,20-22], but the application of other compounds is also attempted quite often. Silanes are claimed to improve interfacial adhesion, but the results published are often questionable and the chemistry is unclear [23,24]. Much more successful were isocyanates, like polymethylene-polyphenyl-isocyanate (PMPPI) [25,26], and triazines in PVC and PS composites [27,28]. N,N-(1,3-phenylene dimaleiimide) (BMI) is a very reactive compound which proved to be successful coupling agent in several polymer/filler micro and nanocomposites [29,30]. Although no attempt has been made to apply it in polymer/wood composites, it might improve interfacial interactions also in these materials.

As a consequence, the goal of our study was to improve interfacial adhesion in PLA/wood composites by the use of BMI. For the first time, we also tried a similar compound, 1,1-(methylenedi-4,1-phenylene)bismaleimide (DBMI), which was mentioned, but has not applied up to now, as coupling agent in the PLA/wood composites studied. We wanted to see if the conditions of coupling, i.e. improved adhesion on both sides of the interface, could be achieved through the use of these compounds. Successful coupling could also decide on the issue debated in the literature for some time, the strength of interfacial adhesion in PP/wood composites. If the general belief is true and adhesion is weak, successful coupling would improve composite properties considerably. On the other hand, if our earlier conclusion is correct and adhesion is inherently strong, only marginal improvement in strength is expected as an effect. The novelty of our work is in the use of new compounds as coupling agents, the verification of their coupling effect and answering the debated question of adhesion in PLA/wood composites.

2. EXPERIMENTAL

The PLA used in the experiments was the Ingeo 4032D grade (M_n = 88500 g/mol and M_w/M_n = 1.8) purchased from NatureWorks (USA) recommended for extrusion by the producer. The polymer (<2% D isomer) has a density of 1.24 g/cm^3, while its MFI 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. Particle characteristics were determined quantitatively by laser light scattering, but also by image analysis from SEM micrographs. BMI and DBMI were purchased from Aldrich and they were used as received.

Both poly(lactic acid) and the fibers were dried in vacuum oven before composite preparation (110°C for 4 hours and 105 °C for 4 hours, respectively). The components were homogenized using a Brabender W 50 EHT internal mixer at 180 °C, 50 rpm for 10 min. The polymer was melted in the internal mixer and then the coupling agents were added in powder form. After a few seconds of homogenization the wood flour was introduced into the mixer and mixing was continued for 10 min. Two series of experiments were carried out to check the possible effect of the two compounds. In the first, the amount of coupling agent changed from 0 to 10 wt% at 30 vol% wood fiber loading. Coupling agent content was kept constant at 5 wt% calculated for the amount of wood in the second and fiber loading changed from 0 to 60 vol%. The homogenized material was compression molded to 1 mm thick plates at 190 °C for 5 min 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 using an Instron 5566 apparatus. The measurements were done at 5 mm/min cross-head speed and 115 mm gauge length. 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.

3. RESULTS AND DISCUSSION

The results are discussed in several sections. First observations made in the first series will be presented briefly then the effect of wood content on properties is described more in detail. Deformation and failure, chemistry and consequences for practice are discussed in the last few sections.

3.1. Amount of coupling agent

As mentioned in the experimental section, the amount of coupling agent was changed from 0 to 10 wt% in 5 steps in the first series of experiments at constant wood content. Our goal was to check any changes in the strength and other characteristics of the composites determined by tensile testing. We expected the strength to increase in the case of successful coupling, and deformability to decrease at the same time. The modulus of composites depends only slightly on interfacial adhesion [31,32], thus we assumed that it would not change much; and our expectations proved true (not shown).

The effect of coupling agent content on tensile strength is presented in **Fig. 1** for composites containing the two potential coupling agents in different amounts. Although a slight, but clear increase can be observed in strength in the figure and apparently DBMI is a more efficient coupling agent than BMI. Strength increases continuously in the second

case, while a maximum seems to appear in strength when DBMI is used. Considering the standard deviation of the measurement, the existence of the maximum is questionable, but the effect cannot be denied, the two compounds act as coupling agents in PLA/wood composites. We can also conclude that it is superfluous to increase the amount of the coupling agents above 5 wt%; strength does not increase at larger coupling agent content.

Elongation-at-break, i.e. deformability, changed as well (not shown), but contrary to our expectations it increased slightly. The direction of this change also indicates successful coupling, since it shows that the micromechanical deformation process, which initiates failure, occurs at larger deformation, consequently at larger load. Although the effect of the coupling agent was small, we decided to go into the second phase of the project and carry out experiments at different wood contents.

3.2. Wood content

The dependence of the stiffness of the composites on wood content is shown in **Fig. 2** in the presence of the two coupling agents. Modulus increases with wood content as expected, but rather surprisingly that of the composites containing the coupling agents is significantly larger than the stiffness of the composites without coupling. We could not see this effect at the single wood content of the first series. It is quite difficult to explain the increase of modulus on coupling, since most of our experience shows that stiffness does not depend very much on the strength of interfacial interactions [32,33]. Modulus is measured at very small deformations thus small changes in the deformability of the matrix or that of the interphase do not influence it much, the volume fraction of the fiber dominates. However, since large particles debond very easily under the effect of very small loads [10], it is possible that debonding leads to the formation of voids and the resulting material has a smaller stiffness than at strong adhesion created by the coupling

agent.

Coupling is confirmed further by **Fig. 3** presenting the composition dependence of tensile strength. The effect is surprisingly large, but also the shape of the correlation changes slightly. The composition dependence shown by the PLA/wood composites without coupling is typical for particulate filled polymers, in which debonding is the dominating micromechanical deformation process. Coupling, on the other hand, increases strength significantly resulting in considerable reinforcement. If we accept our tentative explanation presented above about the role of large particles, the considerable effect indicates that even large particles are coupled to the polymer, debonding is limited even more than before, and the dominating deformation process is the fracture of the particles. Unfortunately, large particles do not only debond more easily than smaller ones, but the probability of their fracture is also larger.

Reinforcement can be expressed quantitatively by a simple model developed earlier to describe the composition dependence of tensile yield stress or tensile strength [34,35]. For strength the correlation takes the following form [35]

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

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$ and $\lambda = L/L_0$, where L_0 is the initial length of the specimen between the gauges and L the length at failure) of the composite and the matrix, respectively, n is a parameter expressing the strain hardening tendency of the matrix, φ is the volume fraction of the fiber and B is related to its relative load-bearing capacity, i.e. to the extent of reinforcement, which depends among other factors, also on interfacial interaction. If we plot the natural logarithm of reduced strength, i.e. tensile strength divided by the second and third terms on the right hand side of the equation, against fiber content, we should obtain straight lines, the slope of which corresponds to

parameter *B*, i.e. to the reinforcing effect of the fiber. Reduced tensile strength is plotted against wood content in **Fig. 4** in this form and we obtain linear correlations indeed. The slope of the two series of composites containing the two coupling agents is larger than that prepared with neat wood in complete accordance with previous results presented on stiffness and strength. Calculated *B* values are compiled in **Table 1** to express the effect of the coupling agents in quantitative terms. Although the effect is not very large it is significant and consequent, and the values of the table also show that DBMI is slightly more efficient than BMI. We must assume that changing interfacial interaction modifies also the micromechanical deformation processes occurring during deformation in the material.

3.3. Deformation and failure

Micromechanical deformations can be followed by acoustic emission measurements. In heterogeneous materials stress concentration develops around the heterogeneities under the effect of external load, which initiate local deformation processes. Some of these, like debonding and fiber fracture, generate elastic waves which can be detected by appropriate sensors. The result of such a measurement is shown in **Fig. 5**. The small circles are individual acoustic signals (events, hits), while the steeply increasing curve represents the cumulative number of signals detected during the test. The stress vs. strain trace is also plotted for reference.

Although it is difficult to draw far reaching conclusions from individual signals, the shape of the cumulative number of signal trace offers information about the mechanism of local deformations. Stepwise curves approaching a plateau indicate debonding [33,36], while the fracture of the fibers was assigned to such steeply increasing traces as the one shown in **Fig. 5** [15]. It is also obvious that acoustic events start to appear

above a certain deformation threshold, i.e. the mechanism is initiated by a critical load. We can determine this critical deformation (ε_{AE}) and the corresponding stress (σ_{AE}) value, which are characteristic for the dominating deformation process, in the way shown in the figure. Changes in this value might offer further information about the effect of the coupling agents on the behavior of the composite, and about the mechanism of deformation and failure.

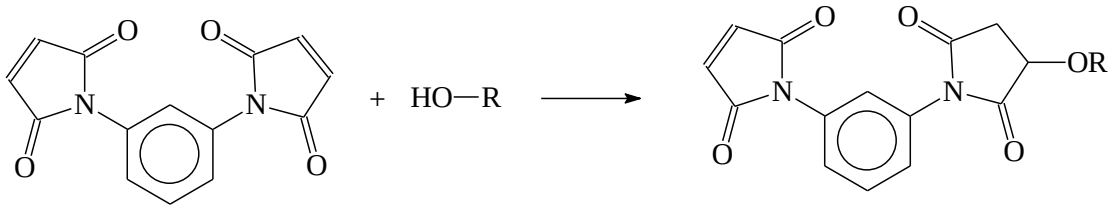
Cumulative number of signal traces are compared for three composites in Fig. 6, for the one prepared with the neat wood and for those containing the two coupling agents. The figure clearly shows that acoustic activity starts at larger deformation for the two composites prepared with the coupling agents and also the corresponding stress vs. strain traces prove the coupling effect. Larger deformation means that the dominating deformation starts later and it is initiated at larger load, a conclusion which agrees well with our earlier one about the suppression of the debonding of large particles.

Acoustic measurements were supported by SEM study. Micrographs were recorded on the fracture surface of samples created during the tensile test. A representative micrograph is presented in **Fig. 7**, which clearly demonstrates that debonding or fiber pull-out hardly occurs and the dominating deformation mechanism is the fracture of the fibers. Naturally, SEM micrographs cannot supply unassailable proof for the mechanism of deformation and failure, but their evidence is completely in line with other results.

3.4. Discussion, consequences

All the results presented in previous sections indicate quite unambiguously that the two coupling agents used in this study have positive effect on the strength of PLA/wood composites. Stiffness, strength and even deformability increase in their presence and the simultaneous increase of these properties clearly proves that coupling occurs indeed, even

if the effect is rather small. The mechanism of coupling is unclear at the moment, we can only speculate about the possible reactions taking place in the melt. Both compounds are very reactive and it was recognized earlier that nucleophilic agents such as amines and thiols could readily react with the double bonds of maleimides [37,38]. In our case, hydroxyl groups in cellulose and on end of PLA chains must be considered as less reactive species, nevertheless oxa-Michael reaction can take place under the severe conditions of processing [39]. The proposed reaction mechanism is shown in Scheme 1.



Scheme 1 Oxa-Michael reaction between the hydroxyl group of PLA or cellulose and BMI

Naturally further experiments are needed to prove the occurrence of the reaction, but if it occurs, it would definitely lead to coupling and prevent debonding leading to the effect shown in previous sections. Further, ring opening reactions may also occur, but no evidence could be found in the literature for them. Understandingly, organic chemists rarely carry out reactions under the conditions used by us (melt, high temperature, shear). The apparently larger efficiency of DBMI can be explained with the larger flexibility of the molecule, since otherwise the reactivity of the two compounds should be very similar.

Coupling and improved interfacial adhesion results in delayed initiation of the dominating micromechanical process which leads to the failure of the composite. Assuming such a close relationship between micromechanical processes and macroscopic properties might seem doubtful, but **Fig. 8** clearly proves the connection. Tensile strength is plotted against the characteristic stress determined in the way indicated in **Fig. 6**. The

close correlation proves that once the local process started, the composite fails. The smaller initiation stresses and strengths of the composites not containing the coupling agent (△) unambiguously prove the positive effect of the two coupling agents and the slight superiority of DBMI (○).

Finally, we must refer to the small effect of coupling on composite properties. Considerably larger increase was observed in PP composites upon the use of a functionalized polymer (MAPP); composite strength increased from 17 MPa to about 41 MPa in a composite containing 47 vol% fiber [33]. However, if we accept the fact that in PLA interfacial interaction is strong already in the uncoupled composite and only very large particles debond, the small effect can be understood and accepted. The prevention of the few debonding events occurring during deformation results in simultaneous improvement of stiffness, strength and deformability. However, further improvement in composite strength is possible only if we can increase the inherent strength of wood particles by the proper selection of their size or by their chemical modification.

4. CONCLUSIONS

The two compounds applied as coupling agents in PLA/wood composites proved to be effective; they improved the properties of the composites. Stiffness, strength and deformability increased simultaneously supplying further proof for coupling. Because of the flexibility of the molecule, DBMI is a more efficient coupling agent in the studied composites. However, the effect of coupling is small, because only a few very large particles debond under the effect of external load. Smaller particles seem to adhere strongly to the matrix proving our earlier conclusion that interfacial adhesion is inherently strong in PLA/wood composites. Accordingly, the effect must depend on the size of the particles, increasing with increasing particle size. However, this tentative explanation

needs further proof and the mechanism of coupling reactions must be also determined with additional experiments.

5. ACKNOWLEDGEMENT

The authors are indebted to Zsolt László for his help in the determination of the particle characteristics of wood. The research on heterogeneous polymer systems was financed by the National Scientific Research Fund of Hungary (OTKA Grant No. K 101124) and by the Forbioplast FP7 project of EU (212239); we appreciate the support very much. One of the authors (KR) is grateful also to the János Bolyai Research Scholarship of the Hungarian Academy of Sciences for its support.

6. REFERENCES

[1] Clemons C.: Raw materials for wood-polymer composites. in 'Wood-polymer composites' eds.: Oksman K. and Sain M.) CRC Press LLC, Boca Raton, 1-22 (2008)

[2] Markarian J.: Biopolymers present new market opportunities for additives in packaging. Plastics, Additives and Compounding, 10, 22-25 (2008).

[3] Sawyer D. J.: Bioprocessing - no longer a field of dreams. Macromolecular Symposia, 201, 271-282 (2003).

[4] Martin O., Averous L.: Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. Polymer, 42, 6209-6219 (2001).

[5] Li Y., Shimizu H.: Toughening of Polylactide by Melt Blending with a Biodegradable Poly(ether)urethane Elastomer. Macromolecular Bioscience, 7, 921-928 (2007).

[6] Yao M., Deng H., Mai F., Wang K., Zhang Q., Chen F., Fu Q.: Modification of poly(lactic acid)/poly(propylene carbonate) blends through melt compounding with

maleic anhydride. Express Polymer Letters, 5, 937-949 (2011).

[7] Huda M. S., Drzal L. T., Mohanty A. K., Misra M.: Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: A comparative study. Composites Science and Technology, 66, 1813-1824 (2006).

[8] Bledzki A. K., Jaszkiewicz A., Scherzer D.: Mechanical properties of PLA composites with man-made cellulose and abaca fibres. Composites Part A: Applied Science and Manufacturing, 40, 404-412 (2009).

[9] Maldas D., Kokta B. V.: Interfacial adhesion of lignocellulosic materials in polymer composites: an overview. Composite Interfaces, 1, 87-108 (1993).

[10] Dányádi L., Renner K., Móczó J., Pukánszky B.: Wood flour filled polypropylene composites: Interfacial adhesion and micromechanical deformations. Polymer Engineering and Science, 47, 1246-1255 (2007).

[11] Renner K., Kenyó C., Móczó J., Pukánszky B.: Micromechanical deformation processes in PP/wood composites: Particle characteristics, adhesion, mechanisms. Composites Part a-Applied Science and Manufacturing, 41, 1653-1661 (2010).

[12] Bax B., Müssig J.: Impact and tensile properties of PLA/Cordenka and PLA/flax composites. Composites Science and Technology, 68, 1601-1607 (2008).

[13] Huda M. S., Drzal L. T., Misra M., Mohanty A. K.: Wood-fiber-reinforced poly(lactic acid) composites: Evaluation of the physicomechanical and morphological properties. Journal of Applied Polymer Science, 102, 4856-4869 (2006).

[14] Oksman K., Skrifvars M., Selin J.-F.: Natural fibres as reinforcement in polylactic acid (PLA) composites. Composites Science and Technology, 63, 1317-1324 (2003).

[15] Dora G., Faludi G., Imre B., Renner K., Móczó J., Pukánszky B.: PLA/Lignocelulosic Fiber Composites: Interfacial Adhesion and Failure Mechanism. Journal of Applied

Polymer Science, submitted, (2013).

[16] Gassan J., Bledzki A. K.: Possibilities for improving the mechanical properties of jute epoxy composites by alkali treatment of fibres. Composites Science and Technology, 59, 1303-1309 (1999).

[17] Beg M. D. H., Pickering K. L.: Fiber pretreatment and its effects on wood fiber reinforced polypropylene composites. Materials and Manufacturing Processes, 21, 303-307 (2006).

[18] Yuan X. W., Jayaraman K., Bhattacharyya D.: Effects of plasma treatment in enhancing the performance of woodfibre-polypropylene composites. Composites Part a-Applied Science and Manufacturing, 35, 1363-1374 (2004).

[19] Gouanve F., Marais S., Bessadok A., Langevin D., Morvan C., Metayer M.: Study of water sorption in modified flax fibers. Journal of Applied Polymer Science, 101, 4281-4289 (2006).

[20] Bledzki A. K., Faruk O., Huque M.: Physico-mechanical studies of wood fiber reinforced composites. Polymer-Plastics Technology and Engineering, 41, 435-451 (2002).

[21] Felix J. M., Gatenholm P.: The Nature of Adhesion in Composites of Modified Cellulose Fibers and Polypropylene. Journal of Applied Polymer Science, 42, 609-620 (1991).

[22] Keledi G., Sudár A., Burgstaller C., Renner K., Móczó J., Pukánszky B.: Tensile and impact properties of three-component PP/wood/elastomer composites. Express Polymer Letters, 6, 224-236 (2012).

[23] Kokta B. V., Raj R. G., Daneault C.: Use of Wood Flour as Filler in Polypropylene - Studies on Mechanical-Properties. Polymer-Plastics Technology and Engineering, 28, 247-259 (1989).

[24] Valadez-Gonzalez A., Cervantes-Uc J. M., Olayo R., Herrera-Franco P. J.: Effect of fiber surface treatment on the fiber-matrix bond strength of natural fiber reinforced composites. Composites Part B-Engineering, 30, 309-320 (1999).

[25] Kokta B. V., Maldas D., Daneault C., Beland P.: Composites of Polyvinyl Chloride-Wood Fibers. I. Effect of Isocyanate as a Bonding Agent. Polymer-Plastics Technology and Engineering, 29, 87-118 (1990).

[26] Raj R. G., Kokta B. V., Daneault C.: Effect of chemical treatment of fibers on the mechanical properties of polyethylene-wood fiber composites. Journal of Adhesion Science and Technology, 3, 55-64 (1989).

[27] Joly C., Gauthier R., Escoubes M.: Partial masking of cellulosic fiber hydrophilicity for composite applications. Water sorption by chemically modified fibers. Journal of Applied Polymer Science, 61, 57-69 (1996).

[28] Bledzki A. K., Gassan J.: Composites reinforced with cellulose based fibres. Progress in Polymer Science, 24, 221-274 (1999).

[29] Liauw C. M., Khunová V., Lees G. C., Rothon R. N.: Interphase structure development in impact modified PP/$Mg(OH)_2$ composites reactively processed with 1,3-phenylene dimaleimide. Macromolecular Symposia, 170, 205-212 (2001).

[30] Khunová V., Hurst J., Liauw C.: Reactive processing of particulate filled polymers: m-phenylene bismaleimide modified polyethylene/magnesium hydroxide composites. Polymer Bulletin, 42, 457-463 LA - English (1999).

[31] Pukánszky B.: Effect of interfacial interactions on the deformation and failure properties of PP/$CaCO_3$ composites. New Polymeric Materials, 3, 205-217 (1992).

[32] Dányádi L., Renner K., Szabó Z., Nagy G., Móczó J., Pukánszky B.: Wood flour filled PP composites: adhesion, deformation, failure. Polymers for Advanced Technologies, 17, 967-974 (2006).

[33] Renner K., Móczó J., Pukánszky B.: Deformation and failure of PP composites reinforced with lignocellulosic fibers: Effect of inherent strength of the particles. Composites Science and Technology, 69, 1653-1659 (2009).

[34] Pukánszky B., Turcsányi B., Tüdős F.: Effect of interfacial interaction on the tensile yield stress of polymer composites. in 'Interfaces in polymer, ceramic, and metal matrix composites' (ed.: Ishida H.) Elsevier, New York, 467-477 (1988)

[35] Pukánszky B.: Influence of Interface Interaction on the Ultimate Tensile Properties of Polymer Composites. Composites, 21, 255-262 (1990).

[36] Renner K., Yang M. S., Móczó J., Choi H. J., Pukánszky B.: Analysis of the debonding process in polypropylene model composites. European Polymer Journal, 41, 2520-2529 (2005).

[37] Sharpless N. E., Flavin M.: The Reactions of Amines and Amino Acids with Maleimides. Structure of the Reaction Products Deduced from Infrared and Nuclear Magnetic Resonance Spectroscopy*. Biochemistry, 5, 2963-2971 (1966).

[38] Borges C. R., Watson J. T.: Recognition of cysteine-containing peptides through prompt fragmentation of the 4-dimethylaminophenylazophenyl-4'-maleimide derivative during analysis by MALDI-MS. Protein Science, 12, 1567-1572 (2003).

[39] Nising C. F., Brase S.: Recent developments in the field of oxa-Michael reactions. Chemical Society Reviews, 41, 988-999 (2012).

Table 1 Effect of coupling on the reinforcing effect of wood in PLA

Coupling	Matrix strength[a] (MPa)	Parameter *B*	R^{2b}
none	54.5	2.29	0.9968
BMI	61.0	2.54	0.9984
DBMI	61.2	2.62	0.9994

a) calculated from the intersection of the $\ln\sigma_{rel}$ vs. φ lines (measured value 56.1 MPa)
b) determination coefficient showing the goodness of the linear fit

7. CAPTIONS

Fig. 1 Effect of the amount of coupling agent on the tensile strength of PLA/wood composites at 30 vol% fiber content. Symbols: (□) BMI, (○) DBMI.

Fig. 2 Young's modulus of PLA/wood composites plotted against wood content; effect of coupling. Symbols: (□) BMI, (○) DBMI, (Δ) no coupling.

Fig. 3 Effect of wood content and coupling on the tensile strength of PLA/wood composites. Symbols: (□) BMI, (○) DBMI, (Δ) no coupling.

Fig. 4 Composition dependence of the reduced tensile strength of PLA/wood composites (linear form of **Eq. 1**); effect of coupling on reinforcement. Symbols: (□) BMI, (○) DBMI, (Δ) no coupling.

Fig. 5 Acoustic emission testing of a PLA/wood composite; volume fraction of wood is 0.1, no coupling. Small circles are individual acoustic events. Stress vs. strain trace is plotted for reference.

Fig. 6 Comparison of the effect of coupling on the cumulative number of signal traces of PLA/wood composites containing 30 vol% fiber; ——— BMI, ---------- DBMI, ···-···-··· no coupling.

Fig. 7 SEM micrograph taken from the fracture surface of a PLA/wood composite with DBMI coupling at 30 vol% fiber content. Fracture of wood particles.

Fig. 8 Correlation between the initiation stress of the dominating micromechanical deformation process (mostly fiber fracture) and the tensile strength of PLA/wood composites. Symbols: (□) BMI, (○) DBMI, (Δ) no coupling.

Faludi, Fig. 1

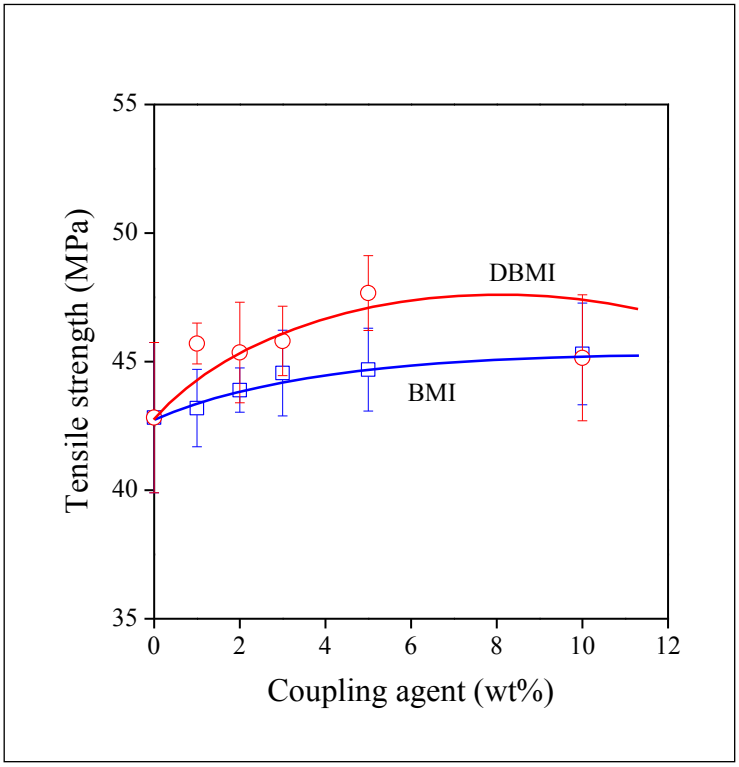


Fig. 1 Effect of the amount of coupling agent on the tensile strength of PLA/wood composites at 30 vol% fiber content. Symbols: (☐) BMI, (○) DBMI.

Faludi, Fig. 2

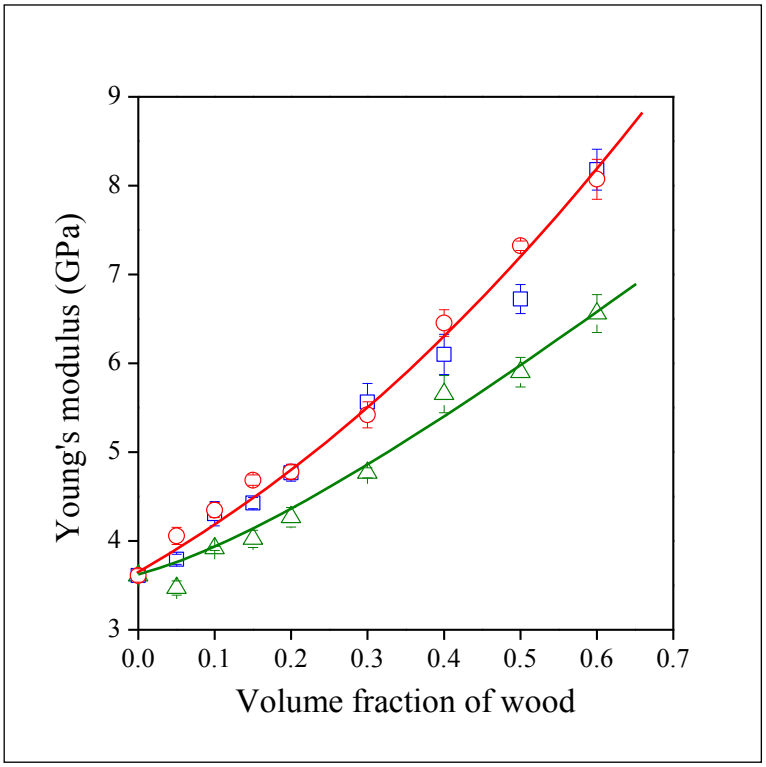


Fig. 2 Young's modulus of PLA/wood composites plotted against wood content; effect of coupling. Symbols: (☐) BMI, (○) DBMI, (Δ) no coupling.

Faludi, Fig. 3

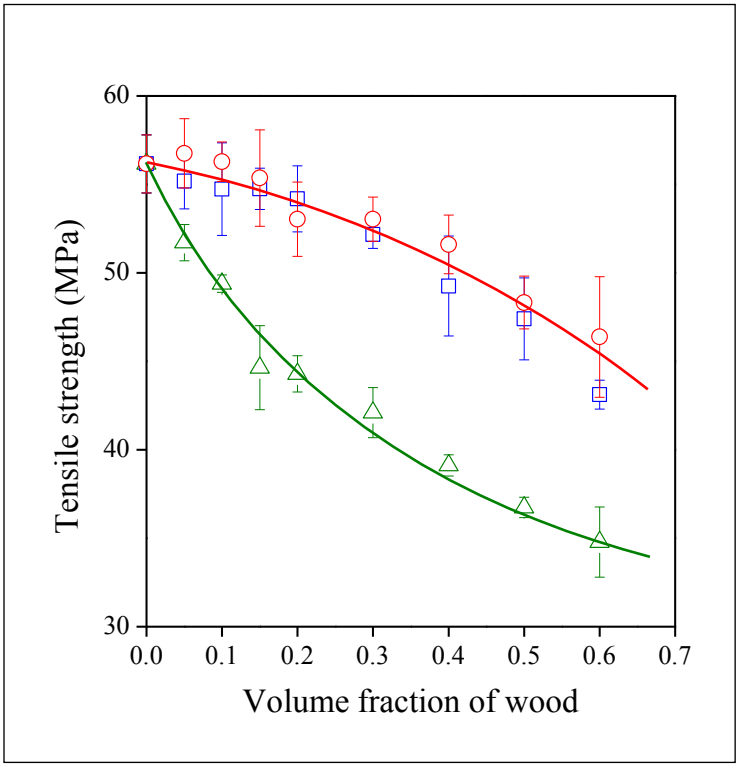


Fig. 3 Effect of wood content and coupling on the tensile strength of PLA/wood composites. Symbols: (☐) BMI, (○) DBMI, (Δ) no coupling.

Faludi, Fig. 4

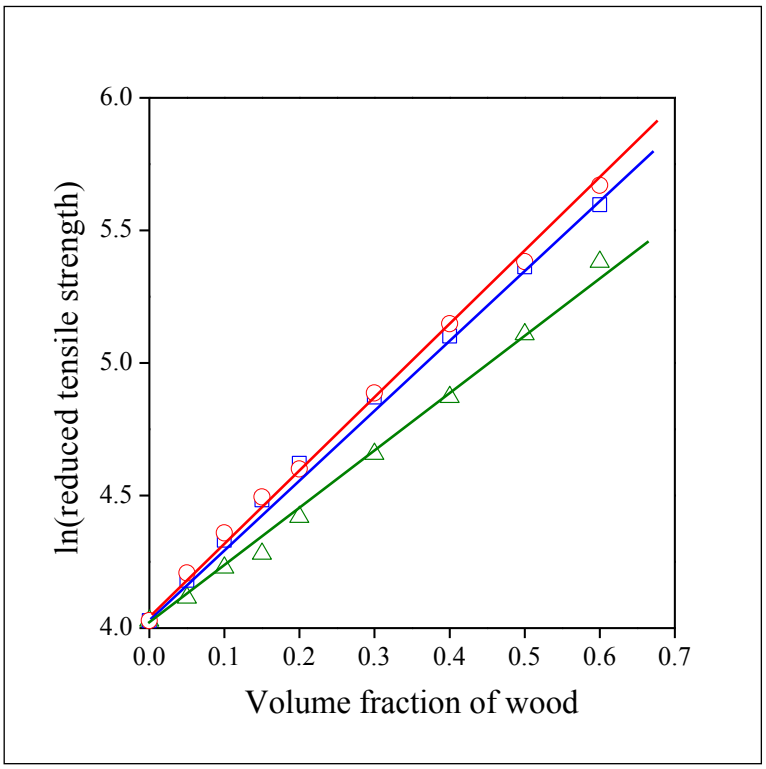


Fig. 4 Composition dependence of the reduced tensile strength of PLA/wood composites (linear form of **Eq. 1**); effect of coupling on reinforcement. Symbols: (☐) BMI, (○) DBMI, (Δ) no coupling.

Faludi, Fig. 5

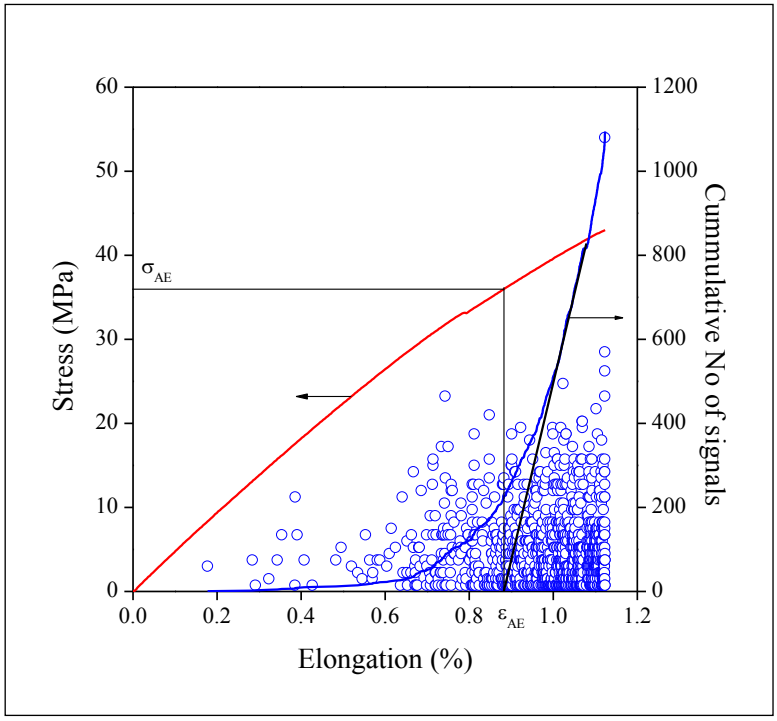


Fig. 5 Acoustic emission testing of a PLA/wood composite; volume fraction of wood is 0.1, no coupling. Small circles are individual acoustic events. Stress vs. strain trace is plotted for reference.

Faludi, Fig. 6

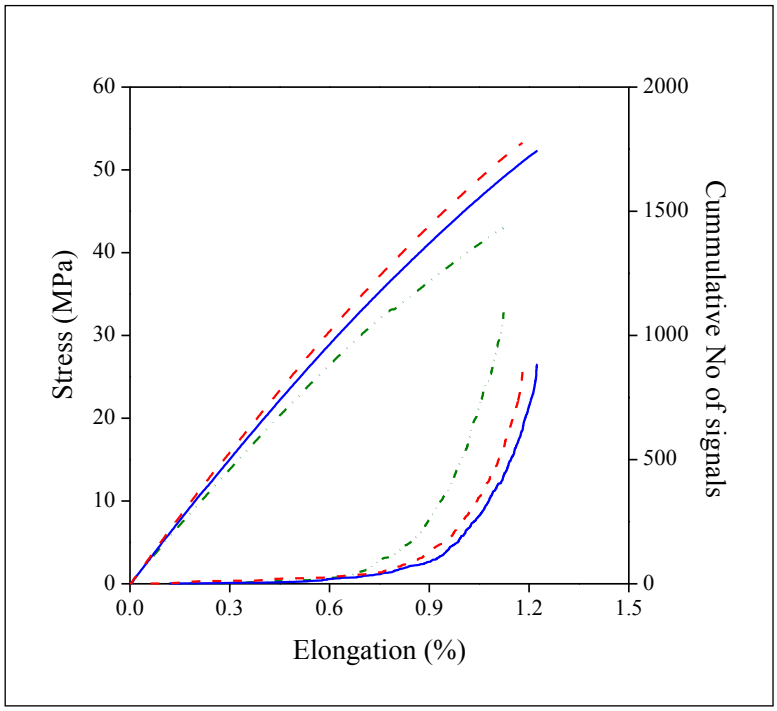


Fig. 6 Comparison of the effect of coupling on the cumulative number of signal traces of PLA/wood composites containing 30 vol% fiber; ——— BMI, ---------- DBMI, ···-···-··· no

coupling.

Faludi, Fig. 7

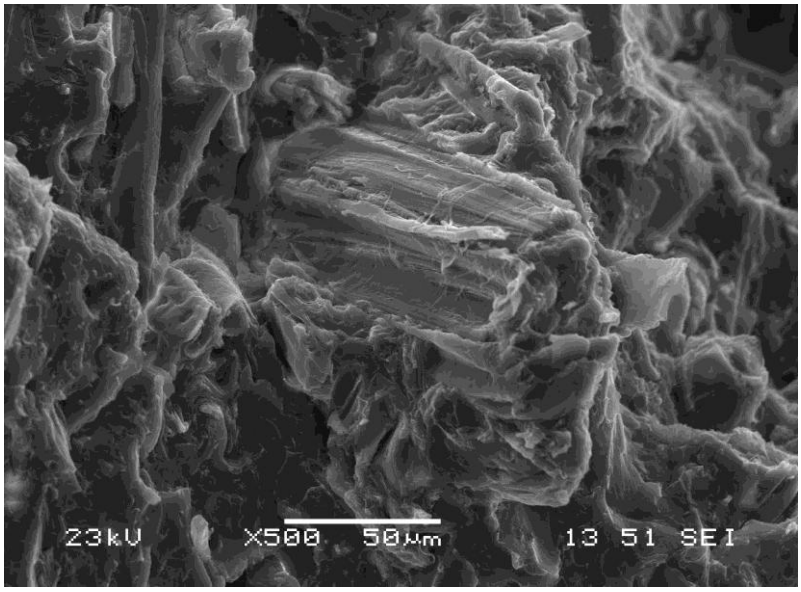


Fig. 7 SEM micrograph taken from the fracture surface of a PLA/wood composite with DBMI coupling at 30 vol% fiber content. Fracture of wood particles.

Faludi, Fig. 8

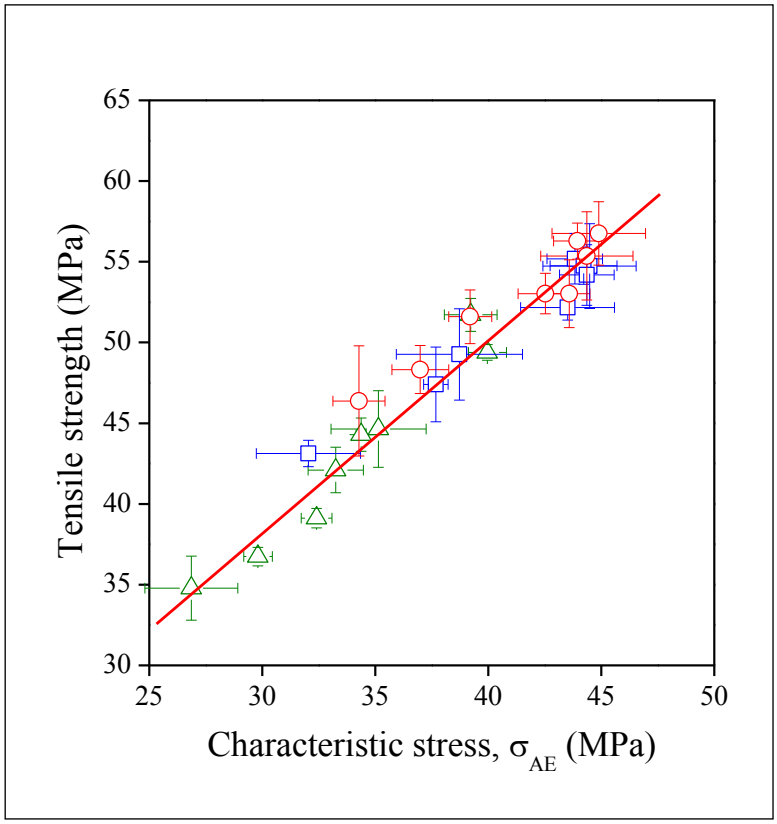


Fig. 8 Correlation between the initiation stress of the dominating micromechanical deformation process (mostly fiber fracture) and the tensile strength of PLA/wood composites. Symbols: (□) BMI, (○) DBMI, (Δ) no coupling.