MODIFICATION OF INTERFACIAL ADHESION WITH A FUNCTIONALIZED POLYMER IN PLA/WOOD COMPOSITES

Áron Csikós\textsuperscript{1,2}, Gábor Faludi\textsuperscript{1,2}, Attila Domján\textsuperscript{3}, Károly Renner\textsuperscript{1,2,*}, János Móczó\textsuperscript{1,2} and Béla Pukánszky\textsuperscript{1,2}

\textsuperscript{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

\textsuperscript{2}Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

\textsuperscript{3}Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

*Corresponding author: Phone: +36-1-463-2479, Fax: +36-1-463-3474, Email: krenner@mail.bme.hu
ABSTRACT

Maleic anhydride (MA) grafted poly(lactic acid) (PLA) coupling agents (MAPLA) were prepared by reactive processing. The amount of peroxide initiator and MA was changed in a relatively wide range. Coupling efficiency was checked in PLA/wood composites as a function of grafting degree, coupling agent and wood content. The analysis of the results showed that chain scission takes place in PLA during reactive modification. The occurrence of grafting could not be proved by FTIR spectroscopy, but a detailed NMR analysis showed that the degree of grafting depends on the amount of both reactants; a maximum of 2.5 MA groups/PLA chain could be grafted under the conditions used in the study. The functionalized polymer proved to be an efficient coupling agent in PLA/wood composites. Efficiency increased with increasing number of functionality and coupling agent amount. Coupling resulted in increased strength and reinforcement. Acoustic emission analysis of deformation processes supported by microscopy proved that the dominating local deformation process is the fracture of the fibers, but small extent of debonding also occurs in neat, uncoupled composites. The prevention of debonding by coupling resulted in the improved performance of the composites. Local processes initiate the immediate failure of the composite irrespectively of their mechanism.

KEYWORDS: poly(lactic acid) (PLA), wood reinforcement, maleated PLA, coupling, local deformations, failure mechanism

1. INTRODUCTION

The application of natural fiber reinforced composites increases with a very high rate all over the world. Most of these materials are based on commodity polymers and used in the building and automotive industry [1]. However, the application of biopolymers
increases even faster due to the increasing environmental awareness of the public [2]. Poly(lactic acid) is one of the polymers which penetrated the market very rapidly 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 recently [3]. Besides its advantages PLA has also some drawbacks thus it is modified by a variety of methods including reinforcement with natural fibers [4,5]. The preparation of PLA/wood fiber composites offer the possibility of achieving an advantageous property profile at a reasonable price.

The wood flour used for the reinforcement of thermoplastics usually consists of relatively large particles with dimensions exceeding those of traditional fillers by orders of magnitude. An average size of several 100 μm is not uncommon for these materials. The dominating deformation mechanism is often debonding in particulate filled and short fiber reinforced composites. Debonding stress depends on particle size interfacial adhesion determined by the surface energy of the components [6]. As a consequence, large wood particles with small surface energy [7] easily debond from the matrix polymer under the effect of external load, which results in the formation of voids and premature failure [8,9]. Debonding was shown to be the dominating micromechanical deformation process in PP/wood composites not containing a coupling agent [8,9]. Interfacial adhesion is claimed to be weak also in PLA/wood composites by a number of authors [10-17], but the question is contradictory, since the detailed analysis of interfacial interactions indicated relatively strong adhesion between PLA and wood [18]. The study of micromechanical deformation processes proved that the dominating deformation mechanism is the fracture of the fibers, confirming further the existence of strong interfacial adhesion, but other mechanisms, like debonding or fiber pull-out also occurred simultaneously. Coupling does not improve composite properties further if adhesion is strong and the fracture of the fibers is the
dominating failure process, but eliminating the other two processes could lead to improved composite strength.

Interfacial interactions are modified in numerous ways in polymer/wood composites. Although physical methods like mercerization [19,20] or plasma and high energy radiation [21,22] were claimed to be beneficial, chemical coupling is the most frequent method to improve composite properties. Functionalized polymers, mainly maleated PP and PE, are frequently used in polyolefin composites [20,23-25], but other compounds are also applied quite often to achieve coupling. Silanes are claimed to improve interfacial adhesion, but the results published are often questionable and the chemistry is unclear [26,27]. Much more successful are isocyanates [28,29] and triazines in PVC and PS composites [30,31], while N,N-(1,3-phenylene dimaleimide) (BMI) proved to be successful coupling agent not only in several polymer/filler micro and nanocomposites [32,33], but also in PLA/wood composites [34].

In spite of the successful application of various compounds as coupling agents, one of the most obvious routes to improve interfacial adhesion in PLA/wood composites seems to be the preparation and use of maleic anhydride modified PLA (MAPLA). As mentioned above, the approach proved to be very efficient in polyolefin composites [23,35-39]. The preparation of MAPLA has been done in two different ways. Carlson et al. [40] as well as Zhu et al. [41] grafted maleic anhydride to PLA with peroxide initiation in the melt, in an extruder. Plackett [42], on the other hand, modified the polymer in solution with a different peroxide and the same approach was followed by Wu [43] as well. All four groups reported the successful modification of PLA with MA, various amounts, between 0.6 and 1.0 wt%, of MA was attached to the PLA chains. However, the effect and efficiency of the functionalized polymer proved to be different and the results contradictory. The modulus of PLA/natural fiber composites containing MAPLA
increased with fiber content in all cases that is not very surprising. Strength, on the other hand, was often smaller than that of the uncoupled composite indicating poor interfacial adhesion \([42,44]\). Quero \([45]\) and Avella \([46]\), however, observed the increase of composite strength upon the application of the functionalized polymer.

Considering the contradictory reports on the effect of functionalized PLA on the properties of PLA/natural fiber composites, the goal of our study was to prepare MAPLA with different degree of functionalization and investigate its effect on the mechanical properties and failure mechanism of PLA/wood composites. The effect of various parameters on the mechanical properties of the composites and on deformation and failure processes was followed by various methods and the relevance of changing failure mechanism for practice is also discussed briefly in the final section of the paper.

2. EXPERIMENTAL

2.1. Preparation of the functionalized polymer

The polymer used in the grafting experiments was the Ingeo 3251 D grade of NatureWorks (USA). It is offered for injection molding purposes and has an MFI of 35 g/10 min measured at 190 °C and 2.16 kg load. The polymer contains less than 2 % D isomer and its density is 1.24 g/cm³. Maleic anhydride (furane-2,5-dion) was purchased from Aldrich and it was used without further purification. 2,5-di(t-butylperoxy)-2,5-dimethylhexane (Luperox 101, Arkema, France) was applied as initiator in the grafting experiments. MAPLA was prepared by reactive extrusion using a Rheomex 3/4" singe screw extruder attached to a Haake Rheocord EU 10 V driving unit. Zone temperatures were set to 160-170-180-190 °C, while screw speed was 30 rpm. PLA was dried before
extrusion in a vacuum oven at 120 °C for 4 hours. Maleic acid and the initiator were dissolved in 20 ml acetone and added to the dry granules. The homogenized material was placed into an oven at 80 °C for 5 min to evaporate acetone. Strands of 2 mm thickness were extruded, pelletized and dried in a vacuum oven to remove unreacted maleic anhydride. The functionalized polymer produced was characterized by FTIR and NMR spectroscopy and its MFI was also measured. FTIR spectra were recorded on a Bruker Tensor 27 apparatus in the wavelength range of 4000-400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\) and 16 scans. Varian NMR system operating at 400 MHz of \(^1\)H resonance with a 5 mm Z-gradient double resonance probe was used to record NMR spectra. Deuterated chloroform was used as solvent to prepare solutions from 15-20 mg solid material in 0.6 ml solvent. All samples dissolved without residue. The signals of the solvent was used as reference (7.27 ppm on the \(^1\)H and 77.40 ppm on the \(^{13}\)C scale). A relaxation delay of 16 s and 4 s acquisition time with detection of 256 transients were used for the single pulse \(^1\)H measurements because of the large dilution used. Standard parameters and 2 s relaxation time were applied for two dimensional(\(^1\)H-\(^{13}\)C) heteronuclear single quantum correlation (HSQC) and heteronuclear multiple quantum correlation (HMQC) analysis. All measurements were carried out at 25 °C.

2.2. Materials

The PLA used for composite preparation was the Ingeo 4032D 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\(^3\), 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 \(\mu\)m and an aspect ratio of 6.8. Particle characteristics were
determined quantitatively by laser light scattering, but also by image analysis from SEM micrographs.

2.3. Compounding

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 and the coupling agent was added first into the internal mixer and melted, then after a few seconds of homogenization the wood flour was introduced and mixing was continued for 10 min. Two series of experiments were carried out to check the effect of the functionalized polymer (MAPLA) on properties. In the first, the amount of coupling agent with various grafting degree was changed from 0 to 20 wt% at 30 vol% wood fiber loading. In the second wood content was varied from 0 to 60 vol% at different, constant MAPLA contents changing from 0 to 20 vol% in 5 vol% steps. 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.

2.4. Characterization

Mechanical properties were characterized by the tensile testing of specimens cut from the 1 mm thick plates. The measurements were done at 5 mm/min cross-head speed and 115 mm gauge length 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. Compression molded films of about 150 μm thickness were used for the polarization optical microscopy (POM) study. Films containing 5 vol% wood flour were broken in tensile and then micrographs were recorded on the broken surfaces.

3. RESULTS AND DISCUSSION

The results are discussed in several sections. Grafting experiments and the resulting structure are presented in the first section followed by the evaluation of the efficiency of the obtained material next. The effect of coupling on mechanical properties and local deformations is presented in the following section, while fracture mechanism and consequences for practice are discussed in the last.

3.1. Grafting

Attempts were made to functionalize PLA with maleic anhydride before. Modification was done under various conditions, both in the melt and in solution. We decided to use reactive processing because of its simplicity and the absence of solvents. We used the concentrations of the reactants reported before as optimal for grafting, i.e. 0.5 wt% peroxide and 2 wt% MA, as reference, and changed their amount in a wider range around these values. Grafting is a chemical reaction which modifies chain structure, but side reactions may also take place in the melt. Besides attaching functional groups to PLA, molecular weight may be also changed by scission or cross-linking. Viscosity is proportional to molecular weight, thus such chemical changes can be followed by rheology. The MFR of the polymer is plotted against the amount of maleic anhydride at 0.5 wt% peroxide content in Fig. 1. The peroxide itself decreases MFR slightly indicating
cross-linking or at least branching. The presence of MA results in considerable decrease in viscosity indicating the occurrence of chain scission reactions. The non-linear correlation indicates that MFR reaches a saturation value, but it is far beyond the range of MA concentrations used, if it exists at all. A very similar correlation is obtained if MFR is plotted against peroxide content which was changed in the range of 0 and 1.5 wt% at 2 wt% MA content (not shown). The results confirm the degrading effect of MA and chain extension in the presence of the peroxide. The existence of a saturation value is indicated here as well. The results of the two series indicate that chemical reactions take place in the melt indeed, but they do not prove in any way that grafting occurs.

We expected to prove grafting by chemical analysis. FTIR and NMR spectroscopy were used by others to analyze reaction products. Zhou [41] and Avella [46] observed a shoulder at 1850 cm\(^{-1}\) on the FTIR spectra of modified PLA and assigned it to the anhydride group of MA. Based on their results they claimed successful grafting. The FTIR spectra of neat PLA and two of the grafted products prepared with the largest amount of the reactants are shown in Fig. 2. The spectra are completely identical indicating the lack of grafting. However, the bands identified by the two groups are present also in MA thus the observed shoulder might result from improper purification.

The NMR spectrum of the product prepared with 2 wt% MA and 1.5 wt% peroxide is presented in Fig. 3. The assignment of the signals was done by two dimensional homo and hetero nuclear correlation measurements supported by literature references [47,48]. The number of hydroxyl groups can be determined by the integration of signal \(c\) and from the value obtained we can determine the molecular weight of the sample. The number of attached MA groups was calculated from the integral of signals \(d\) and \(e\), since neat PLA does not have signals in this region. Our assignment of signals and the calculation of attached MA groups differs from that of Orozco [47] and Quero [41], the first group
included chain end hydroxyls appearing at 4.28 ppm into the integral, while the second calculated the number of attached MA groups from signals appearing at 2.25 ppm belonging to free MA molecules.

The recorded NMR spectra and the calculations indicated that we succeeded in grafting MA groups onto the PLA chain. The number of MA groups attached to PLA increased with increasing amount of MA in the reaction mixture. However, at 0.5 wt% peroxide content grafting degree is very small and it reaches saturation at about 0.6 chain/PLA molecule around 2.0 wt% MA content (not shown), and the spectra indicate also the presence of free MA in the product. On the other hand, as Fig. 4 shows, grafting degree increases continuously with increasing amount of peroxide at 2 wt% MA content. The maximum number of MA groups is 2.5/PLA chain under the conditions used; further experiments are needed to check if grafting degree can be increased even further by adding more peroxide to the reaction mixture. We hoped, however, that the degree of grafting achieved is sufficient for effective coupling.

3.2. Coupling efficiency

After establishing the fact that grafting occurred indeed, we wanted to check the efficiency of the obtained functionalized polymer as coupling agent. MAPLA was prepared with 2 wt% MA and the proper amount of peroxide to obtain polymers with various degree of grafting from 0.2 to 2.4 MA/PLA chain in sufficient amounts for the coupling experiments. Composites were prepared at 30 vol% wood content with different amounts of MAPLA and mechanical properties were determined. The modulus of the composites remained practically unchanged or decreased slightly (not shown), thus we present the composition dependence of tensile strength instead which is known to show changes in the strength of interfacial adhesion rather sensitively [39]. In Fig. 5 tensile
strength is plotted against the amount of MAPLA added to the composites. The figure clearly shows that strength increases with increasing amount and functionality of the coupling agent confirming that grafting was successful.

Fig. 5 also shows that the increase in strength with functionality is not linear and a larger step can be observed when we go from grafting degree 1.6 to 2.4 MA group/chain. The number of MAPLA samples is not sufficiently large to claim that 2.4 MA groups/molecule is so much more beneficial than the rest; further experiments are under way to determine the effect of grafting degree on coupling efficiency more accurately. However, the fact of coupling is proved unambiguously. One might consider the effect of coupling on composite strength small, but we must call the attention here to the fact that interfacial interactions were proved to be strong already in the neat PLA/wood composites without any modification. Coupling can prevent only the debonding and/or pull-out of very large wood particles, but MAPLA seems to do this quite efficiently.

3.3. Properties and reinforcement

Testing the effect of interfacial interactions at a single composition may lead to false conclusions, thus we measured mechanical properties as a function of wood content. This approach allows us to determine the reinforcing effect of the fibers quantitatively and analyze deformation mechanism. The uncertainty related to the effect of the degree of grafting on coupling efficiency led us to select the functionalized polymer with 1.6 MA groups/PLA chain for further experiments. The amount of coupling agent was changed between 0 and 20 wt% in 5 wt% steps in this series of experiments. The modulus of all composites increased with increasing wood content as expected and in accordance with previous experience stiffness did not change much with increasing amount of coupling agent (not shown).
The tensile strength of PLA/wood composites is plotted against wood content in Fig. 6. The effect of coupling is clearly seen in the figure. Strength decreases quite steeply in the neat polymer, while it changes much slower as the amount of coupling agent increases in the composite. The largest strength is achieved with the largest amount of functionalized polymer. The results also show that the effect approaches saturation, further increase in the amount of MAPLA would not result in larger strength.

The effect of reinforcement can be expressed quantitatively with the help of an appropriate model. Such a model was developed earlier to describe the composition dependence of the tensile yield stress [49], tensile strength [50] and fracture properties [51] of particulate filled and short fiber reinforced polymers. The model for strength simplified for small deformations can be expressed as

\[
\sigma = \sigma_0 \frac{1 - \phi}{1 + 2.5\phi} \exp(B\phi)
\]  

where \(\sigma\) and \(\sigma_0\) are composite and matrix strength, respectively, \(\phi\) the volume fraction of wood in the composite and \(B\) is a parameter expressing reinforcement; parameter \(B\) is related to interfacial adhesion. The model takes into account the effect of matrix properties \((\sigma_0)\), that of decreasing effective load-bearing cross-section with increasing wood content \((1-\phi)/(1+2.5\phi)\) and interactions \([\exp(B\phi)]\). Parameter \(B\) shows the extent of reinforcement, the load carried by the dispersed component. Parameter \(B\) can be determined relatively easily from the linearized form of the equation. Rearrangement and plotting reduced composite strength against filler content gives a straight line with the slope of \(B\).

Parameter \(B\) is plotted against the amount of the functionalized polymer in Fig. 7. The values range from 2.2 to 2.5, a range which seems to be small, but the value of \(B\) depends also on matrix stiffness. It is reasonably large for the relatively stiff PLA already in the neat polymer and increases even further upon coupling. The figure also shows that
reinforcement approaches a saturation value indeed, as concluded by the visual observation of Fig. 6.

The composition dependence of modulus or strength does not offer any information about the local deformation processes taking place around the particles during deformation and the interpretation of SEM micrographs is usually difficult, the conclusions drawn are often doubtful. Acoustic emission measurements, on the other hand, detect signals resulting from local processes and their analysis at least indicate the dominating process taking place in the material. The dominating process usually determines the final performance of the material. Cumulative number of signal traces [8,9,52] are presented in Fig. 8 for composites containing 20 vol% wood at different MAPLA contents. The shape of the traces indicate strong interaction (see initiation strain) and fiber fracture as the dominating local deformation process [9,18,52-54]. Initiation strain and thus also initiation stress increases[39] with increasing MAPLA content indicating better stress transfer at larger amount of coupling agent. Initiation stress determined from plots like those presented in Fig. 8 is plotted against wood content in Fig. 9. The figure clearly shows that initiation deformation and stress increases with increasing MAPLA content proving that the synthesized functional polymers are efficient coupling agents indeed.

3.4. Fracture mechanism, consequences

Earlier studies have shown that various local deformation processes take place during the deformation of PLA/wood composites. Debonding, fiber pull out and the fracture of the fibers were observed to occur simultaneously. Depending on their aspect ratio, the fibers may fracture parallel or perpendicular to their axis. Only good interfacial adhesion can result in fiber fracture as the dominating local deformation process.
However, in this case composite strength is determined by the inherent strength of the fiber and cannot be improved by coupling. On the other hand, the results presented in previous sections showed an increase in strength with coupling which was even larger than in our previous effort to improve interfacial adhesion by coupling [BMI]. The only reasonable explanation for the effect is that several local deformation processes take place during the loading of the material indeed. Debonding stress is inversely proportional to particle size and depends on interfacial adhesion as well. Debonding is initiated at small stresses for large particles and week interaction and it leads to immediate failure because of the small deformability of PLA. We can assume safely that we prevented the debonding of large particles by using the functionalized polymer and thus increased composite strength.

Although never conclusive, microscopy might support our assumption further. A polarization optical and a SEM micrograph are shown in Fig. 10 for a composite containing 30 vol% wood and 15 wt% MAPLA. The micrographs are representative, most of the others recorded send a very similar message. The fracture of a particle is clearly seen in the POM (indicated by the circle) and broken fibers appear on the SEM micrograph. No trace of debonding or pull-out can be observed in the composites containing any of the coupling agents, at least on the micrographs recorded. Based on microscopy we can safely state that in the composites containing MAPLA fiber fracture is the dominating failure process indeed.

We claimed above that local deformation processes lead to immediate failure after their initiation. In order to substantiate this statement, we plotted composite strength against the initiation stress determined by acoustic emission (Fig. 11). A very close correlation is obtained which is independent of the amount of filler or coupling agent in the composite. However, the actual values are not, more MAPLA leads to larger initiation
stress and larger composite strength (see points at the upper right corner of the figure). The correlation proves very strongly that controlling local deformation process is the only way to improve composite strength. The figure also confirms indirectly that debonding must take place in the neat, uncoupled composite and in those containing small amount of MAPLA, otherwise composite strength could not be increased at all. Besides modifying interfacial adhesion, composite properties can be changed also by the proper selection of the reinforcing component (particle characteristics, inherent strength).

4. CONCLUSIONS

The analysis of the results obtained in experiments to produce poly(lactic acid) functionalized with maleic anhydride showed that chain scission of PLA takes place during reactive modification. The occurrence of grafting could not be proved by FTIR spectroscopy, but a detailed NMR analysis showed that the degree of grafting depends on the amount of both reactants; a maximum number of 2.5 MA groups/PLA chain could be grafted under the conditions used in the study. The functionalized polymer proved to be an efficient coupling agent in PLA/wood composites. Efficiency increased with increasing number of functionality and coupling agent amount. Coupling resulted in increased strength and reinforcement. Acoustic emission analysis of deformation processes supported by microscopy proved that the dominating local deformation process is the fracture of the fibers, but small extent of debonding also occurs in neat, uncoupled composites. The prevention of debonding by coupling resulted in the improved performance of the composites. Local processes initiate the immediate failure of the composite irrespectively of their mechanism.

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6. REFERENCES


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7. CAPTIONS

Fig. 1  Effect of the maleic anhydride concentration of the reaction mixture during reactive processing on the melt flow rate of the resulting functionalized polymer. Peroxide content: 0.5 wt%.

Fig. 2  FTIR spectra of the neat PLA polymer and two reaction products. a) neat polymer, b) 4 wt% MA and 0.5 wt% peroxide, c) 2 wt% MA and 1.5 wt% peroxide.

Fig. 3  $^1$H NMR spectrum of the graft copolymer produced with 2 wt% MA and 1.5 wt% peroxide and the assignment of the peaks.

Fig. 4  Effect of peroxide content on the degree of grafting at 2 wt% MA content of the reaction mixture.

Fig. 5  Dependence of composite strength on the amount and functionality of MAPLA at 30 vol% wood content. Symbols: (○) 0.2, (▽) 0.7, (□) 1.6, (◇) 2.5 MA group/PLA chain.

Fig. 6  Tensile strength of PLA wood composites plotted against wood content at various coupling agent concentrations. MAPLA functionality: 1.6 MA group/chain. Symbols: (□) 0, (△) 5, (▽) 10, (◇) 15, (○) 20 wt% MAPLA.

Fig. 7  Effect of MAPLA content of PLA/wood composites on the reinforcing effect of wood (parameter $B$, see Eq. 1).

Fig. 8  Influence of MAPLA content on the cumulative number of signal traces of PLA/wood composites containing 20 vol% wood. MAPLA functionality: 1.6 MA groups/chain.

Fig. 9  Dependence of the initiation stress of local deformations on wood and MAPLA content. MAPLA functionality: 1.6 MA group/chain. Symbols: (□)
0, (△) 5, (▽) 10, (◇) 15, (○) 20 wt% MAPLA.

**Fig. 10** Microscopic evidence of fiber fracture in PLA/wood composites at 15 wt% MAPLA content. a) POM, 5 vol% wood, b) 20 vol% wood.

**Fig. 11** Correlation between composite strength and the initiation stress of the dominating local deformation process. Symbols: (□) 0, (△) 5, (▽) 10, (◇) 15, (○) 20 wt% MAPLA.
Csikós, Fig. 1

The diagram illustrates the relationship between MFR (in g/10 min) and MA content (in wt%) for different MA content levels. The graph shows a trend where the MFR increases as the MA content increases. The point labeled '0 wt% peroxide' indicates the MFR at 0 wt% MA content with error bars showing the variability at each data point.
Csikós, Fig. 2
Csikós, Fig. 3
Csikós, Fig. 5

![Graph showing the relationship between Weight fraction of MAPLA and Tensile strength (MPa). The graph displays multiple curves representing different data sets, each with error bars indicating variability. The x-axis represents the weight fraction of MAPLA ranging from 0.00 to 0.25, while the y-axis shows the tensile strength in MPa ranging from 40 to 60.]
Csikós, Fig. 6

![Graph showing the relationship between tensile strength (MPa) and volume fraction of wood. The graph displays a downward trend indicating a decrease in tensile strength as the volume fraction of wood increases.](image-url)
Csikós, Fig. 7

![Graph showing Parameter B vs. MAPLA content (wt%)](image-url)
Csikós, Fig. 8
Initiation stress, $\sigma_{AE}$ (MPa) vs Volume fraction of wood for 0 wt% and 20 wt% MAPLA.
Csikós, Fig. 10

a)

b)
Csikós, Fig. 11

![Graph showing the relationship between tensile strength (MPa) and initiation stress, $\sigma_{AE}$ (MPa). The graph includes data points and a trend line.]