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BIODETERIORATION AND ECOTOXICITY OF PP/WOOD COMPOSITES: EFFECT OF WOOD CONTENT AND COUPLING

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ABSTRACT

Polypropylene (PP)/wood composites were produced by homogenization in a twin-screw extruder and injection molding of tensile bars. Their mechanical properties were determined before and after exposure to biological treatment, and the effect of the treatment was assessed by various ways including visual inspection and the measurement of weight loss. The ecotoxicity of the materials was also evaluated by using the bioluminescent bacteria *Vibrio fischeri*. The results proved that wood facilitates biodeterioration (colonization) under the conditions used. The coupling agents do not have inhibitory effect, but seems to stimulate fungal growth (biodeterioration) at large loads of wood flour. PP/wood composites can be considered quite durable, but the influence of wood content on environmental resistance must be taken into account for materials intended for applications requiring long-term outdoor exposure as the time of exposure to microbial colonization increases. Direct ecotoxic effect on aquatic ecosystems cannot be expected from PP/wood composites.

KEYWORDS: rPP/wood composites, coupling, colonization, biodeterioration, ecotoxicity

1. INTRODUCTION

Polymer/wood composites are used in increasing amounts all over the world, since they offer an environmentally friendly and economically viable alternative as structural materials (Bledzki et al., 2002a; Bledzki & Gassan, 1999; Bledzki et al., 2002b). They are prepared mostly from commodity polymers and a wide range of natural fibers and wood flour (Bledzki et al., 2002b; Clemons, 2008; Clemons & Caulfield, 2005; Sreekumar & Thomas, 2008). The main application areas of such materials are the automotive and the construction industry. Economical viability would be further increased if the matrix polymer of wood composites were waste recovered from the same industries (Clemons, 2002). The bumper of a number of small and medium sized cars is prepared from polypropylene (PP), which are recovered after the useful lifetime of the car yielding recycled PP (rPP). The composition of these materials varies in a wide range, they may contain fillers for increasing stiffness, elastomers to improve impact resistance, and the polymer itself can be a random or heterophase polymer with complicated structure and widely varying properties (Stamhuis, 1984; Stamhuis, 1988).

The reinforcement used in wood composites usually contains large particles, which are several 100 μm in size (Clemons & Caulfield, 2005). Since the surface energy of wood is relatively small, such particles easily debond from the surface under the effect of external force (Móczó & Pukánszky, 2008; Pukánszky & Vörös, 1993; Renner et al., 2009). To prevent debonding and achieve sufficient reinforcement, the fibers are usually coupled to the matrix polymer by functionalized polymers, mostly by maleated PP (MAPP) in polypropylene (Albano et al., 2001; Bledzki et al., 2002a; Dányádi et al., 2007a; Dányádi et al., 2010; Dányádi et al., 2007b; Ichazo et al., 2001). A different structure, the embedding of the filler or reinforcement into the elastomer can be achieved, if a functionalized elastomer, maleated ethylene-propylene-diene

(MAEPDM) polymer is used as impact modifier (Oksman, 1996; Oksman & Clemons, 1998). Such coupling agents may influence structure, properties and the behavior of the composites considerably.

The fact that a large number of wood plastics composite (WPC) products find outdoor applications has generated an urgent need to evaluate their susceptibility to environmental factors.

Biodeterioration refers to the gradual loss of the technical function and/or the deterioration of the aesthetic appearance of materials due to microorganisms (Flemming, 2010). Synthetic polymers are generally recalcitrant against microbial degradation, most of them are difficult to degrade or not biodegradable at all. Consequently, they have extended lifetime, but their functionality can be impaired much earlier because of biodeterioration. We also have to consider that even if the polymer itself is resistant to biodegradation, it may contain additives as plasticizers, antioxidants, colorants, flame retardants or wood, which can biodegrade and may influence the properties of the material (Lugauskas et al., 2004). Biodeterioration is usually a complex process for polymers starting with the consumption of accessible additives and progressing through the decomposition of the matrix (Flemming, 2010). Surface colonization and biofilm formation by microorganisms are common for most polymeric materials used outdoors. They change surface properties such as hydrophobicity, color or aesthetics and also may be a source to spread microbial contamination to the surroundings (Flemming, 2010). Once the surface is colonized the microorganisms use compounds from the polymeric material for their growth. At the same time, the polymer hydrolyses and the microorganism, as well as the products they release (e.g. pigments, enzymes) may diffuse into the bulk of the polymer. This results in the penetration of the biodegradation process below the surface of the material. The degradation of additives

and the polymer lead to embrittlement and loss of stability, as well as to fragmentation. Hydration and penetration into the polymer lead to swelling, the loss of insulation characteristics and to aesthetic deterioration, because of the diffusion of pigments, among others. Since wood fillers used in composite preparation are more susceptible to microbial attack than the polymeric matrix, they may affect the resistance of the composite to environmental effects. Consequently, it is important to evaluate the behavior of wood reinforced polymeric composites under environmental conditions.

For the environmentally safe application of newly designed polymers and biocomposites, it is important to prove that they and their degradation products do not have any ecotoxicological effect. The large size of polymer molecules limit transport across biological membranes and they are not very reactive, so they are supposed to be inert and not hazardous from a toxicity point of view (Anastas et al., 2000; Sheftel, 2000). However, in polymeric materials low molecular mass oligomers, additives (catalyst residues, plasticizers, flame retardants, etc.), and residual monomers may be weakly or not bound at all to the macromolecules and could be easily released during use (OECD, 2009). Some of these compounds are known to be hazardous to human health and the environment (e.g. formaldehyde, acrylonitrile, toluene diisocyanate, benzene, phthalates). There are many studies on ecotoxicity of degradation products, which form from biodegradable polymers after composting (Iovino et al., 2008; Witt et al., 2001). Nevertheless, potential ecotoxicological hazards during the production and service life of biopolymers have been studied only in a limited extent. The potential release of hazardous chemicals from polymers may be tested by measuring acute toxicity of aqueous extracts obtained from the sample materials (De Vetter et al., 2008; Lithner et al., 2009; Pilgard et al., 2010). Lithner et al. (Lithner et al., 2009) tested the acute toxic effect of aqueous extracts obtained from 32 plastic products made of

polycarbonate, polyvinyl chloride, polyurethane, polyethylene, polystyrene or polypropylene. They found nine materials displaying ecotoxic effect, among others a compact disc (recordable), the toxicity of which was traced back to the silver layer; plasticised PVC (artificial leather, bath tub toy, inflatable bathing ring and table cloth); or polyurethane (artificial leather, floor coating and children's handbag). Ecotoxicity of leachates has also been tested in wood (De Vetter et al., 2008) and furfurylated wood (Pilgard et al., 2010). To date, apart from the contributions mentioned above little information is available on the direct ecological impact of biocomposites.

Since biodeterioration of plastic/wood composites may limit the lifetime of the products prepared from them, the objective of the present work was to study the biodeterioration of polypropylene composites reinforced with wood flour. Recycled PP (rPP) was recovered from an industrial shredder and composites were prepared with a relatively wide range of wood content and with two coupling agents, a functionalized PP (MAPP) and a functionalized elastomer (MAEPDM) to study the effect of these factors on biodeterioration. Besides biodeterioration we wanted to check if PP/wood composites emitted hazardous chemical substances to water in concentrations causing acute toxic effects (ecotoxicity).

2. EXPERIMENTAL

The recycled PP was recovered from a shredder operated by Auto Mandy Car Kft., Hungary. The milled scrap contained exclusively bumper material, but the type and manufacturer of the cars is not known. The milled scrap contained ethylene-propylene phase identified by dynamic mechanical analysis (DMA) and about 10 wt% fillers (talc, glass fibers). The melt flow rate (MFR) of the granulate was 10.6 g/10 min (230 °C, 2.16 kg) and its stiffness 1.3 GPa. The maleated PP (MFR = 150-200 g/10 min

at 190 °C, 2.16 kg, maleic anhydride (MA) content 1 wt%) was the Orevac CA 100 product of Arkema, France, while the functionalized MAEPDM used was the Exxelor VA 1803 grade (MFR = 3 g/10 min at 190 °C, 2.16 kg, MA content 1.14 wt%, ethylene content 43 %) of Exxon Mobile, USA. The Filtracel EFC 1000 grade of Rettenmaier and Söhne GmbH, Germany was used as reinforcement. The average particle size of the wood flour was about 210 μm and its aspect ratio 6.8. The wood content of the composites changed from 0 to 60 wt% in 10 wt% steps, while the amount of functionalized polymer was always 10 % calculated for the amount of wood used.

The composites were homogenized in a ThermoPrism TSE 24 (Thermo Fisher Sci. Inc., USA) twin screw extruder with a screw diameter of 24 mm and length of 28 D at 220-220-220-220-220-210-40 °C barrel and 220 °C die temperature, and 400 rpm screw speed. After granulation the compounds were dried at 105 °C for 4 hours then injection molded to 4 mm thick standard tensile bars (170 x 10 x 4 mm) using a Demag Intelect 50/330-100 machine at 200-190-180-40 °C barrel, 210 °C nozzle and 50 °C mold temperatures. Injection pressure was 1000 bar, holding pressure 800 bar and holding time 20 sec. Specimens were conditioned for one week at 25 °C and 50 % RH before testing.

Apart from the thorough characterization of the components (MFR, DMA, differential scanning calorimetry (DSC), particle analysis), the specimens were subjected to tensile and impact testing. An Instron 5566 universal testing apparatus was used for tensile measurements at 5 mm/min cross-head speed and 115 mm gauge length. Impact testing was carried out using a Ceast Resil 5,5 impact tester with a 4 J hammer at 2.9 m/s speed. The deformation behavior of the specimens was also characterized by micromechanical testing (volume strain, acoustic emission), but these results have no relevance here and will be reported elsewhere. The tensile properties of the composites

were determined before and after biological treatment.

A modification of the standard test method was used to estimate the biodeterioration of PP/wood materials by the colonization of microorganisms in Petri dishes (ASTM G 21-90 and ISO 846). The specimens were exposed to a mixture of the fungi *Aspergillus niger* CECT 2807, *Penicillium funiculosum* CECT 2911, *Paecilomyces variotti* CECT 202130, *Gliocladium virens* CECT 2460, *Chaetomium globosum* CECT 2701 for 12 weeks at 30 ºC. The fungi were supplied by the Spanish Type Culture Collection (CECT). The specimens were placed under aseptic conditions in glass Steriplan Petri dish (200 x 45 mm) filled with minimal salt agar medium (composition reported in ISO 846) with (Method B) or without (Method A) added glucose (30 g/L). Samples were then inoculated by thoroughly spraying a suspension of equal parts of each fungus at a concentration of 10^6 spore/ml (in minimal salt liquid medium). Method A (medium without glucose) allowed to measure whether or not the fungi were able to grow from the materials as the sole nutrient source. Method B (medium with glucose) was used to evaluate possible inhibitory effect on microbial growth. The neat polymer (non-inoculated) was exposed simultaneously to the same environment for comparison. Each material was inspected visually and under the microscope to evaluate fungal growth after 12 weeks exposure. Specimens were then rinsed with ethanol (70%) and water to eliminate fungal biomass. After drying at 40 ºC for 5 days, samples were weighed to determine weight loss. Scanning electron micrographs (SEM) were taken from some of the samples. Dried specimens were coated with gold (Dányádi et al., 2007a) before recording the micrographs (Hitachi S-3500, Tokyo, Japan). Specimens subjected to the same treatment, but without either fungi or glucose, were used as one reference (R1), while a set of specimens were stored at 30 °C under dry conditions for another (R2). The results obtained on these latter were used to

calculate relative stiffness values presented in Fig. 5.

One stage batch leaching test based on EN 12457-4:2002 was used to obtain the aqueous extracts from samples for the ecotoxicity tests (Lithner et al., 2009). Materials in granule form (20 g) were placed in a 250 mL glass bottle and 200 mL of water was added resulting in a concentration of 10 L/kg liquid to solid ratio. All bottles were shaken at 150 rpm for 24 h at room temperature. Three replicates were made for each product and three bottles with deionised water were used as controls. After 24 h extraction, samples were left to settle for 15 min, the leachates were strained through a fine nylon fabric and the aqueous phase was tested for acute toxicity using the bioluminescent bacteria *Vibrio fischeri* (Biotox, Aboatox, Finland). Bioluminiscence of *V. fischeri* was measured in a Luminoskan Ascent microplate luminometer (Thermo-Electron Co., Vantaa, Finland) at 20 ºC. The testing was performed in a 96 well microplate. An aliquot of 100 µl of the sample was transferred to each well, after which 100 µl of the bacterial suspension was automatically dispensed into the sample. The light signal was recorded initially and after 30 min exposure to *V. fischeri* of different concentrations (from 1:2 to 1:64) of the leachates. The luminescence intensity after the incubation was compared to that of pure bacteria. Reduction in light intensity is regarded as toxicity. The results were normalized and the EC_{50} values (concentration producing a 50 % reduction in luminescence) were calculated. The EC_{50} was estimated on the basis of the dose-response traces. The linear correlation coefficient reached values between 0.89 and 0.99. The EC_{50} values were subsequently transformed into toxic units (TUs) with the formula of Sprague and Ramsay (Sprague and Ramsay, 1965) as cited by De Vetter et al. (De Vetter et al., 2008), i.e $TU = 100/EC_{50}$. Following ecotoxicity evaluation scale proposed by DeVetter et al. (De Vetter et al., 2008) leachates with less than 2 TUs were considered not toxic, hardly toxic (2–4 TUs),

slightly toxic (4–8 TUs), toxic (8–16 TUs) and quite toxic (> 16 TUs).

3. RESULTS AND DISCUSSION

The results are reported in several sections. Selected mechanical properties are presented first to show the effect of fiber content and coupling on structure and properties. The influence of these factors on colonization, biodeterioration and ecotoxicity are discussed in subsequent sections.

3.1. Properties

Two boundary structures may form in PP containing both an elastomeric phase (either copolymer or separately added) and a reinforcement. The additional components may be distributed separately from each other or the reinforcement can be embedded into the elastomer phase. The properties change accordingly, modulus increases continuously with filler content in the first case, while a smaller increase, constant value or even a decrease can occur in the second (Kolarik et al., 1987). The incorporation of the MAPP coupling agent results in separate distribution, while that of MAEPDM may promote encapsulation. However, the development of the latter structure depends also on kinetic effects, on the relative magnitude of adhesion and shear forces (Pukánszky et al., 1990); the presence of the functionalized polymer alone does not guarantee embedding.

The stiffness of the specimens is plotted against wood content in Fig. 1 a). Wood fibers reinforce PP considerably, stiffness increases from the initial value of 1.3 GPa to around 4 GPa. Composites without coupling agent and with MAPP have practically the same modulus proving that the strength of interfacial adhesion does not influence stiffness much (Dányádi et al., 2007a; Dányádi et al., 2007b; Renner et al., 2009). On

the other hand, the correlation obtained for the composites containing MAEPDM deviates from that of the other two sets of materials indicating a slight degree of embedding in this case. We may conclude that the type of coupling agent slightly influences the structure of the composites. However, the composition dependence of stiffness does not offer information about the strength of interfacial adhesion in our composites.

On the other hand, properties measured at larger deformations, i.e. yield stress and tensile strength, depend very much on interfacial adhesion (Dányádi et al., 2007a; Dányádi et al., 2007b; Dányádi et al., 2006; Renner et al., 2009). This is demonstrated well by Fig. 1 b) presenting the composition dependence of tensile strength for the three series of composites. The strength of the composite containing the MAPP coupling agent increases steeply with wood content indicating strong reinforcing effect of the wood flour used. Strength is almost constant in the other two cases showing poor adhesion and/or the effect of embedding. We may conclude that the selection of the coupling agent changes structure only slightly, but interfacial adhesion quite drastically. The question remains if these factors influence biodeterioration; the results of Ibach et al. (Ibach et al., 2002) indicated that the presence of MAPP promotes biodeterioration.

3.2. Colonization

The standard test method used allows to determine if a material has inhibitory effect on microbial growth (Method B) or if it is a nutrient for microorganism that biodegrade it (Method A). None of the materials tested inhibited fungal growth as shown by the growth of microorganisms around materials in glucose amended medium. Noticeable surface colonization was observed on all materials, irrespectively of the test method used. Colonization is shown in Fig. 2 for the three conditions used for testing

and compared with the non-inoculated specimen (R1). Fungal growth on the surface of materials is observed in both media, i.e. without (Method A) and with glucose (Method B). Obviously, materials contain nutritive substances that permit the growth of fungi. Studying the surface of the specimens by SEM revealed that fungi grow on them. Evident signs of material penetration were not observed (Fig. 3).

Visual evaluation of fungal growth offers more information about the effect of wood content and the type of coupling on the biological susceptibility of the composites tested. Visual growth was evaluated on a five grade semi-quantitative scale with the following classes: 0 no growth, 1 traces of growth with less than 10 % of the surface colonized, 2 visible growth covering the surface up to 25 %, 3 growth covering the surface up to 50 %, 4 growth larger than 50 % surface coverage, 5 heavy growth, complete coverage. The results of the evaluation are presented in Fig. 4 a). We can see that colonization occurs even without wood, but wood promotes the growth of fungi, since colonization increases detectably and significantly with increasing wood content. The presence of coupling agent does not seem to influence fungal growth much, although slight differences might be observed on closer scrutiny. At large wood content MAPP seems to help fungal growth, while MAEPDM apparently slightly inhibits it. The first observation is in line with those of Ibach (Ibach et al., 2002) and could be explained with the presence of the maleic anhydride groups increasing water adsorption and possible interaction with fungi. However, many arguments, including the effect of MAEPDM, can be brought against this reasoning like the chemical reaction of MAPP and wood, the acidic conditions created by hydrolyzed MA groups, etc. We are inclined to conclude that the coupling agent has none or only a slight effect on fungal growth and that the differences are caused by standard deviation and the uncertainty of the evaluation method.

3.3. Biodeterioration

The biodeterioration of polymers and their composites is usually evaluated by several means, the most frequently by water uptake, dimensional changes, mass loss, change in color and/or appearance, and in the possible modification of mechanical properties due to biological treatment. We measured mass loss, changes in tensile properties and evaluated the visual appearance of the specimens as described above (see Section 3.2). The mass loss of the specimens detected after 12 weeks of incubation is plotted against wood content in Fig. 4 b). The same trend and effects can be seen here as in colonization; larger weight reductions were measured in composites with large wood contents (50-60%). However, mass loss was smaller than 3% in all cases showing low degradability according to the CEN/TS 15083-1 standard.

The mechanical properties of the specimens were related to those of the reference series, the samples stored at 30 °C under dry conditions (R2). Since the standard deviation of the various characteristics is relatively large and the changes are small, this resulted in a considerable scatter of the values, but general tendencies can be established this way. However, the comparison of the effect of various factors (treatment, coupling) would have been much more difficult in any other way. The relative stiffness of the composites determined after 12 week biological treatment is plotted against wood content in Fig. 5. The various symbols of the same shape refer to different treatments, i.e. full symbol Method A (without glucose), symbol filled partially Method B (with glucose) and empty symbol is reference 1 without both glucose and fungi. The figure clearly shows that the effect of treatment is negligible, if any. We may conclude from this result that the changes are caused mainly by the presence of water. This conclusion agrees well with the observation of Dawson-Andoh et al. (Dawson-

Andoh et al., 2004), who found that those parts of their PVC/wood specimens deteriorated most, which were in constant contact with water and fungi. However, contrary to their result that wood content does not influence deterioration, Fig. 4 a) clearly shows that in our case biodeterioration increases with the amount of reinforcement. Decreasing stiffness might result from the swelling of wood modifying stress distribution around the inclusions as well as from the decrease of interfacial adhesion with treatment. The presence of MA groups is obviously beneficial and only slight changes can be observed in properties even after the 12 week long treatment in the case of the composites containing MAPP. The effect of treatment has practically the same effect on tensile strength (not shown), the influence of the various factors and even the magnitude of changes is practically the same for that property. We may conclude here that the type of coupling agent does not have a significant impact on biodeterioration at wood filler contents smaller than 50 vol%. Apart from local changes in color at certain spots (Fig. 2), no evident signs of material damage were observed on the surface of the specimens because of microbial colonization. On the other hand, MAPP seems to be beneficial in the retention of mechanical properties during biological attack.

3.4. Ecotoxicity

The ecotoxicity results obtained for the samples tested are shown in Fig. 6. Although there were significant differences in ecotoxic levels among samples depending on their composition, none of the analyzed samples reached values of TU (Toxic Units) larger than 2 (EC_{50}>100%), consequently no direct ecotoxic effect can be expected from these samples on aquatic ecosystems. This result is in agreement with those found by Lithner et al. (Lithner et al., 2009) in several PP based materials

(foldable water container and ground pipes), the leachates of which lacked toxic effect to *Daphnia magna*. It is remarkable that larger toxic values were observed in leachates from MAPP composites in comparison to MAEPDM or composites not containing any coupling agent. Pilgård et al. (Pilgård et al., 2010) suggested that the stronger toxicity to *V. fischeri* found for furfurylated wood than in non-treated wood cannot be attributed to maleic acid used in the furfurylation. Moreover, no information is available about the biocidal effect of maleic anhydride. Hence, the effect of MAPP on acute toxic values requires further study keeping in mind the fact that toxicity levels do not reach limits considered toxic even for these materials.

4. CONCLUSIONS

As a result of the biodeterioration studies carried out on rPP/wood composites with varying wood content and different coupling we found that wood facilitates biodeterioration (colonization) under the conditions used. The coupling agent does not have inhibitory effect but seems to stimulate fungal growth (biodeterioration) at large loads of wood flour. PP/wood composites can be considered quite durable, but the influence of wood content on environmental resistance must be taken into account for materials intended for applications requiring long-term outdoor exposure as the time of exposure to microbial colonization increases. Direct ecotoxic effect on aquatic ecosystems cannot be expected from rPP/wood composites.

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7. CAPTIONS

Fig. 1 Effect of wood content and coupling; a) on the stiffness of rPP/wood composites, b) on tensile strength. Symbols: (○) no coupling, (□) MAPP, (Δ) MAEPDM.

Fig. 2 Surface colonization of materials after 12 weeks incubation. On top from left to right: non-inoculated materials (control), Method A (without glucose), Method B; below: details of heavy or highly colonized surfaces showing spots of fungal growth.

Fig. 3 SEM images of fungi growing on the surface of materials; a) magnification: 500x, b) magnification: 7000x.

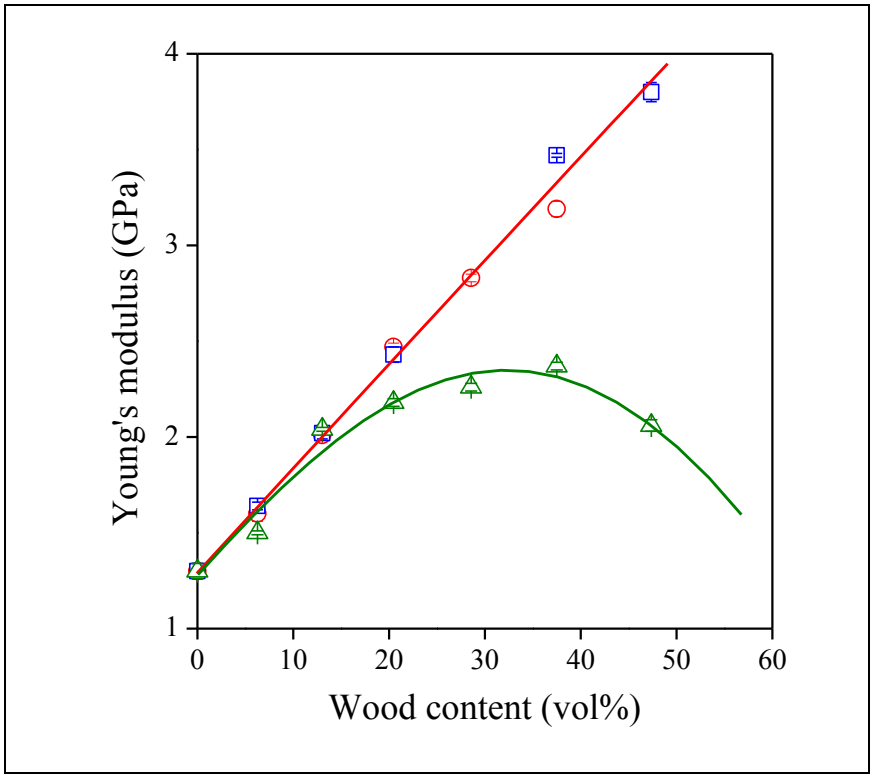
Fig. 4 Effect of wood content and coupling on a) fungal colonization (visual growth), b) on the mass loss of PP/wood composites after exposure to fungi for 12 weeks. Symbols: (○) no coupling, (□) MAPP, (Δ) MAEPDM.

Fig. 5 Influence of the variables on the relative stiffness of composites measured after biological treatment. Symbols: (○,⊖,●) no coupling, (□,⊟,■) MAPP, (Δ,⧋,▲) MAEPDM; (●,■,▲) Method A, (⊖,⊟,⧋) Method B, (○,□,Δ) reference 1 (no sugar and fungi).

Fig. 6 Ecotoxicity to *Vibrio fischeri* of aqueous leachates obtained from specimens after 24 h. Ecotoxicity is expressed in toxic units, TU < 2 is considered non-toxic. Symbols: (○) no coupling, (□) MAPP, (Δ) MAEPDM.

Figures

Sudár, Fig. 1



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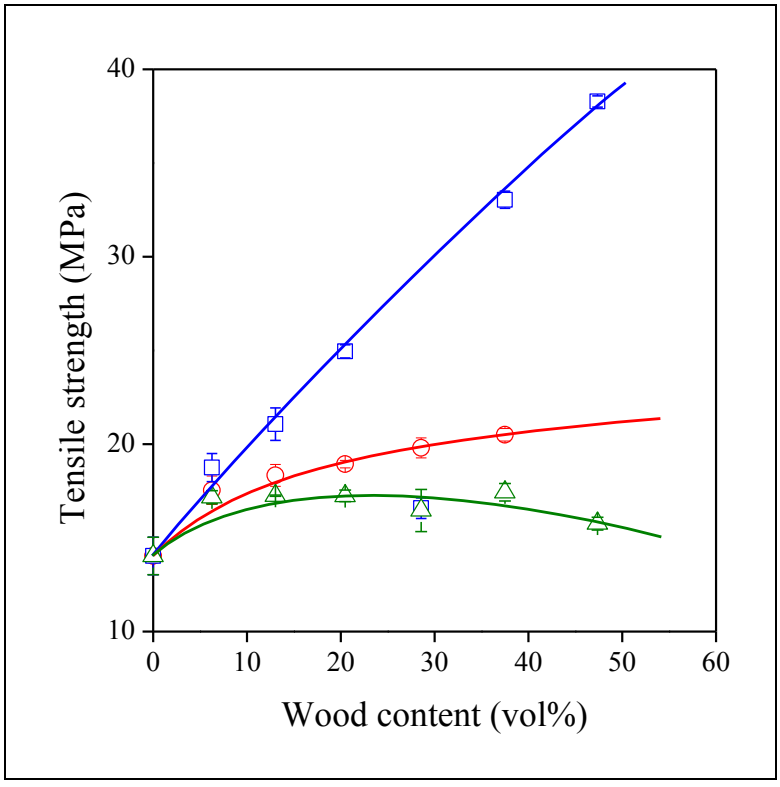
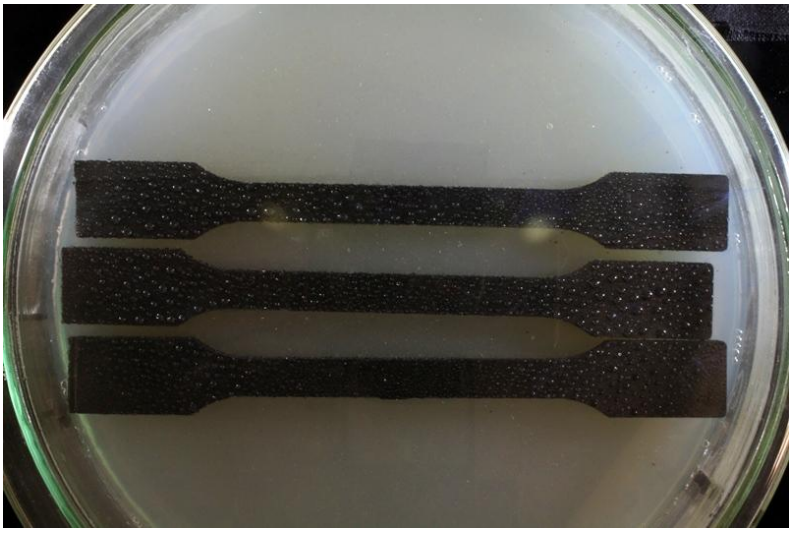


b)

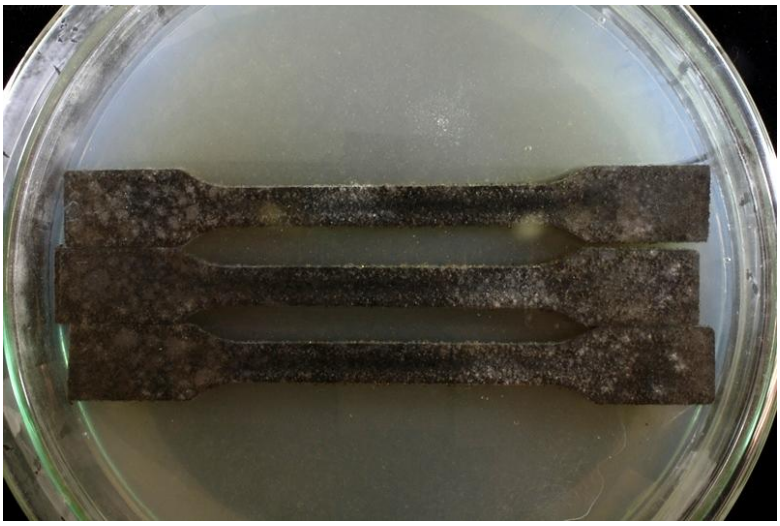
Sudár, Fig. 2



a)

b)

Sudár, Fig 2



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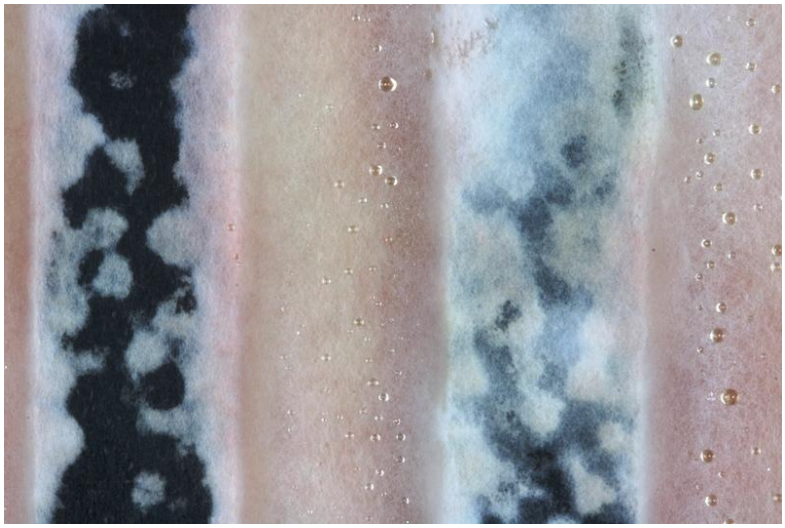
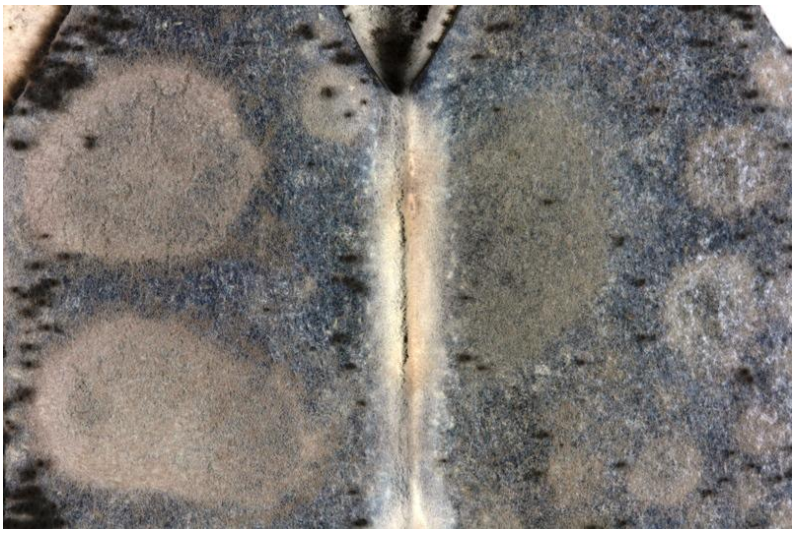


d)

Sudár, Fig. 2



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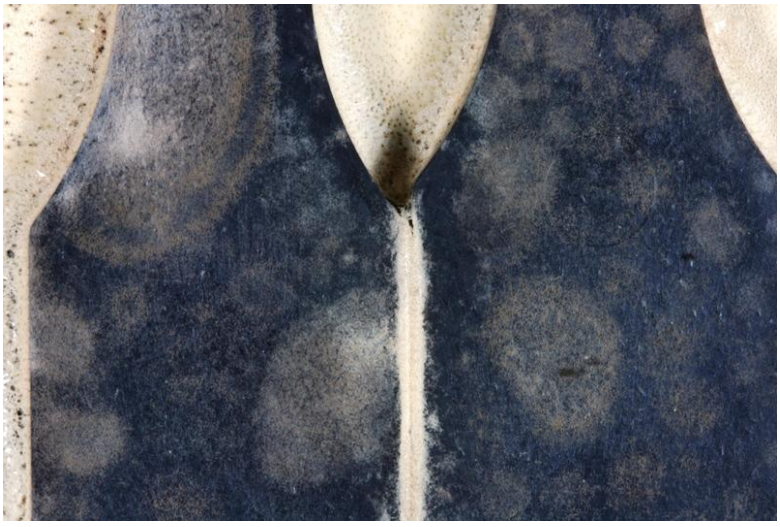
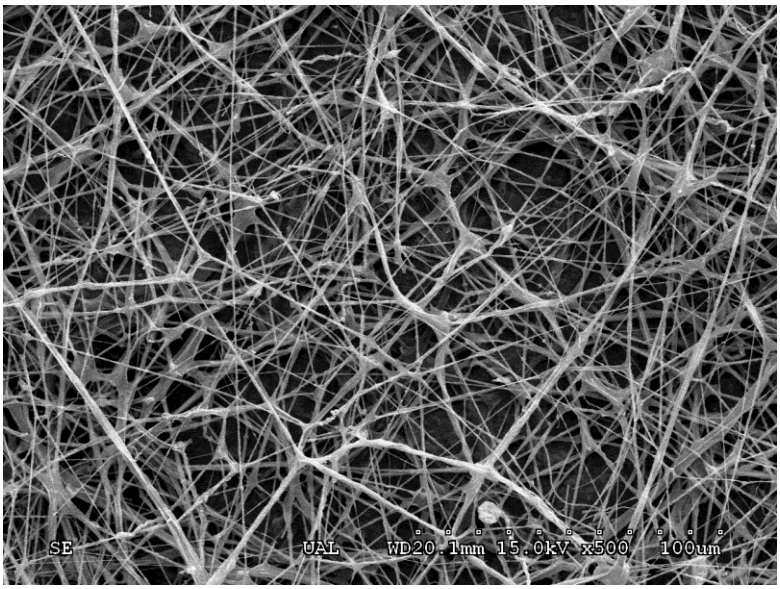


f)

Sudár, Fig. 3



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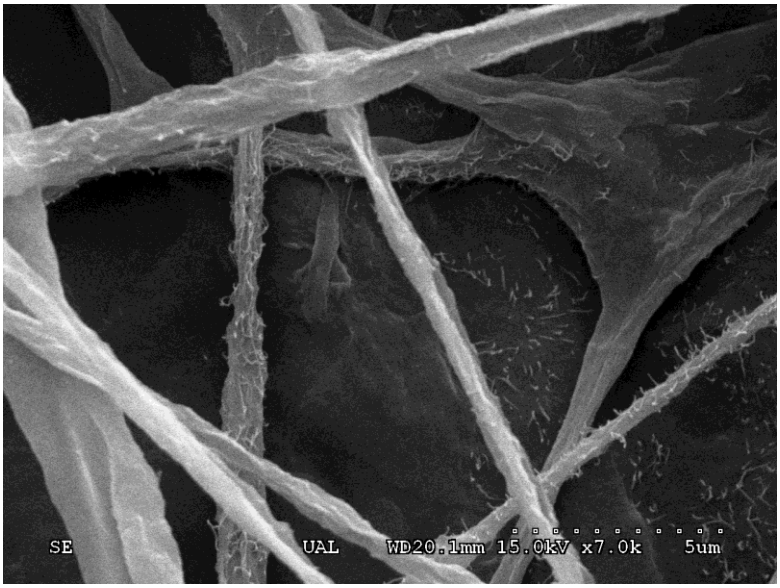
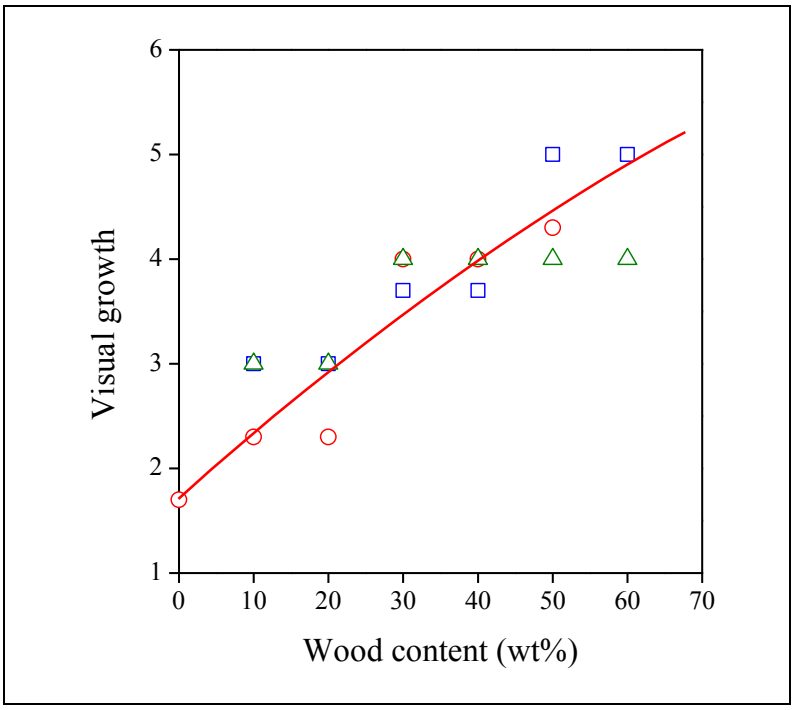


b)

Sudár, Fig. 4



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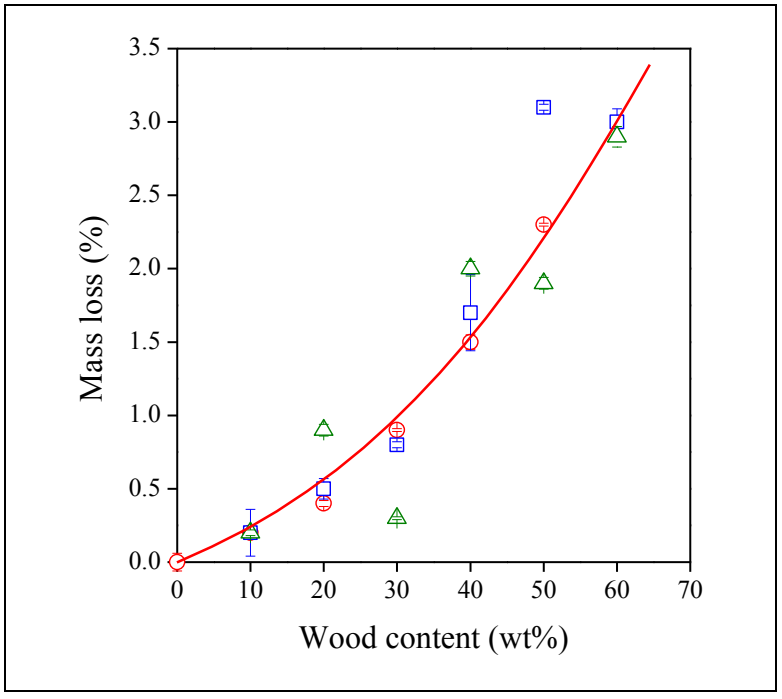
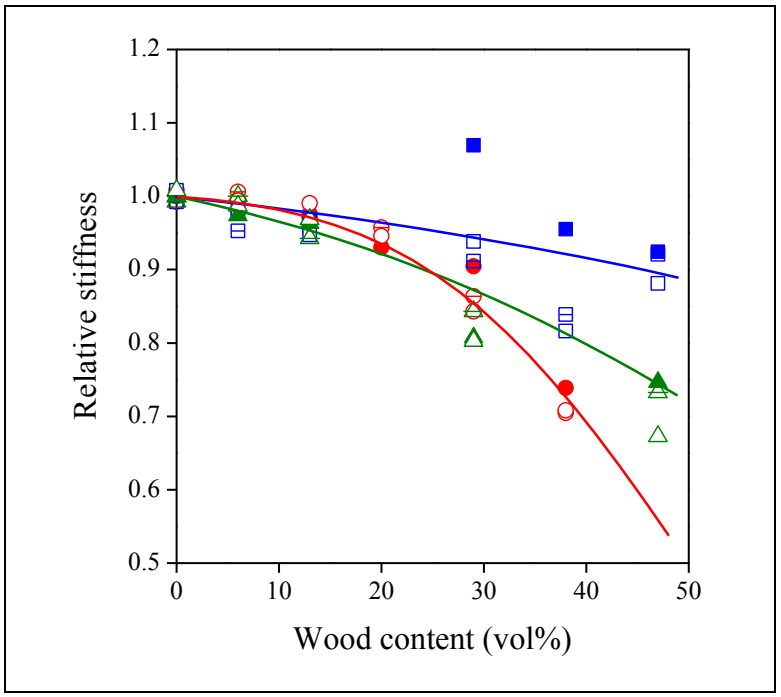
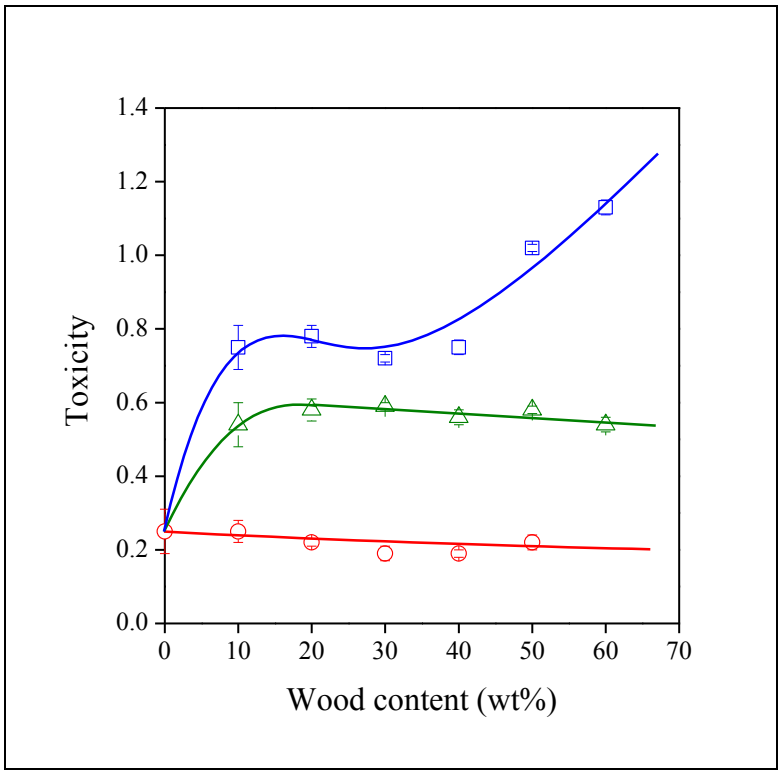


b)

Sudár, Fig. 5


Relative stiffness
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0
10
20
30
40
50
Wood content (vol%)

Sudár, Fig.6


Toxicity
Wood content (wt%)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
10
20
30
40
50
60
70