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Resistance of polypropylene-wood composites to fungi

Summary — In the present study, the composites of polypropylene and wood were prepared. The experimental material comprised two most common Polish timber species pine wood (*Pinus sylvestris* L.) as a softwood species and oak wood (*Quercus sp.*) as a hardwood species. The size of wood sawdust ranged from 0.5 to 1.0 mm. Two types of lignocellulosic materials were used in the experiments described: wood without any previous chemical treatment and wood after its mercerization (*i.e.* activated with NaOH). In addition the polypropylene-wood composite containing a block copolymer, *i.e.* styrene—ethylene—butylene—styrene (SEBS) was also obtained. The objective of this study was to evaluate the resistance of different kinds of polypropylene-wood composites to fungal decay. Weight losses and temporary tensile strength of composite samples after the mycological test were determined.

Key words: polypropylene-wood composites, biodegradation, mycological test, weight loss, tensile strength.

ODPORNOŚĆ KOMPOZYTÓW POLIPROPYLEN–DREWNO NA ROZKŁAD POWODOWANY PRZEZ GRZYBY

Streszczenie — Metodą wytłaczania i prasowania wytworzono kompozyty izotaktyczne polipropylen–drewno. W badaniach wykorzystano dwa gatunki drewna: sosnowe (*Pinus sylvestris* L.) i dębowe (*Quercus sp.*). W pracy stosowano drewno surowe oraz drewno po procesie merceryzacji, tj. po aktywowaniu wodnym roztworem NaOH. Wytworzono również kompozyty polipropylen–drewno z dodatkiem kopolimeru blokowego styren—etylen—butylen—styren (SEBS). Badano odporność uzyskanych kompozytów na rozkład powodowany przez grzyby degradujące tkankę drzewną (*Coniophora puteana* i *Coriolus versicolor*). W celu oceny stopnia biorozkładu po upływie 16 tygodni wyznaczano ubytki masy próbek kompozytów oraz badano ich wytrzymałość na rozciąganie. Stwierdzono, że ubytki masy (rys. 1) wszystkich wariantów kompozytów wynosiły poniżej 1,8 %. Uzyskane wartości mieszczą się w granicach błędu pomiaru. Stwierdzono, że wytrzymałość na rozciąganie (rys. 2) jest bardziej dokładnym kryterium biorozkładu. Obniżenie wytrzymałości na rozciąganie od 12 do 20 % stwierdzono w przypadku kompozytów na bazie drewna sosnowego, a niewielkie zmiany (do 5 %) w przypadku kompozytów z drewna dębowego. Natomiast najmniejszą wytrzymałość na zerwanie wykazywały kompozyty z dodatkiem środka kompatibilizującego (SEBS). Badania dowiodły, że możliwa jest biodegradacja drewna w matrycy polipropylenowej, pod warunkiem zapewniania dostępu strzępek grzybni do materiału lignocelulozowego w kompozycie.

Słowa kluczowe: kompozyty polipropylen-drewno, biodegradacja, grzyby degradujące tkankę drzewną, ubytek masy, wytrzymałość na rozciąganie.

In recent years, increasing interest has been observed in wood-polymer composites which can be attributed to their low prices, good mechanical properties, low density and the possibility to manufacture them employing almost all known technologies. Such lignocellulosic materials as: wood, flax, jute, sisal etc. have been used as fillers for such polymers as polyethylene [1, 2], polypropylene [3—5], polystyrene [6] and poly(vinyl chloride) [7].

The most difficult problem encountered when attempting to combine any lignocellulosic material with a thermoplastic matrix is their interfacial incompatibility. One of the major obstacles limiting the use of the wood fibers for reinforcing purposes is low compatibility between the hydrophilic wood fibers and the hydrophobic polymer matrix. Various methods are available which can improve the compatibility between the lignocellulosic reinforcement (or filler) and the matrix: the use of compatibilizers [8], grafting of polymers onto the lignocellulosic material [9], chemical modification of the lignocellulosic material [10].

Most of the scientific investigations of material design have largely focused on the improving of mechanical properties. Despite the claims of rot resistance, few

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scientific studies address the biodegradation of wood—polymer composites. Morris and Cooper [11] present only anecdotal evidence suggesting that a wood—plastic composite is susceptible to fungal decay.

In the present study, the composites of wood (pine or oak) and polypropylene were prepared. Moreover, to improve the interfacial adhesion between the wood fiber and the polypropylene matrix, the styrene—ethylene—butylene—styrene copolymer (SEBS) as a compatibilizer was used. In addition the authors employed wood mercerization with sodium hydroxide to remove the residual substances from lignocellulosic material.

The objective of this study was to evaluate the resistance of different kinds of wood-polypropylene composites to fungal decay. Weight losses and temporary tensile strength of composite samples after the mycological test were determined.

EXPERIMENTAL

Materials

Isotactic polypropylene (iPP) Malen P F-401 (Orlen Płock S.A.) was used as a matrix of the composite system.

The experimental material comprised two most common Polish timber species pine wood (*Pinus sylvestris* L.) as a softwood species and oak wood (*Quercus sp.*) as a hardwood species. The size of wood sawdust ranged from 0.5 to 1.0 mm. Two types of lignocellulosic materials were used in the experiments described: wood without any previous chemical treatment and wood after its mercerization (*i.e.* activated with NaOH). The mercerization process involved the treatment of wood with 16 % NaOH solution for 15 min [12].

In addition the polymer-wood composite containing block copolymer, *i.e.* styrene—ethylene—butylene—styrene (SEBS-1901X) made by Shell Chemical Co. was also obtained. The function of SEBS was to increase the interactions between the hydrophobic polymer matrix and the hydrophilic lignocellulose material. The proportion of SEBS copolymer in the composite was 10 % by weight.

Preparation of composites

The iPP-wood composites were obtained by the extrusion method and press molding. The mixture of 60 wt. % of polypropylene, 30 wt. % of wood and 10 % wt. of SEBS was mixed in a drum blender for 30 min. This mixture was then conveyed to the feed hopper of a single-screw extruder (Fairex, France). A die measuring 4 mm in diameter was attached to the extruder. During the extrusion, the temperatures in the four processing zones were chosen as: 140, 180, 190, and 195 ^{o}C and the die temperature was 190 ^{o}C. The screw's rotational speed was ranged from 25 to 30 rpm. Mixing temperature was controlled at less than 200 ^{o}C to avoid decomposition and degradation of wood fibers. The extrudate was cooled in water (20 ^{o}C) after exiting the die, and then pelletized into granules. Next, the granules were dried in an oven for 24 h at 60 ^{o}C.

Sample preparation

The granulated product was compounded using press molding (press-type P2) in order to obtain shaped samples for biological testing. The samples were prepared using the following parameters of the press: pressure 1 MPa, temperature 190 ^{o}C and cooling under pressure until solidification. The desired board measurements were achieved by pressing the materials into a metal form 4 × 100 × 100 mm from which the samples for fungal testing (100 × 8 × 4 mm) were cut. Each of the obtained strips had two sides exposed (to which fungi had easy access) and two sides intact covered with iPP.

Methods of testing

Biodegradation investigations

The tests were compatible with the standard PN-EN 113 ("Wood Preservatives — Test Method for Determining the Protective Effectiveness Wood Destroing Basidiomycetes—Determination of the Toxic Values"). To investigate fungal resistance of plastic-wood composites, the standard procedure was modified by changing sample size from 25 × 15 × 50 mm to 100 × 4 × 8 mm. Brown rot fungus (*C. puteana)* was used to investigate the bioresistance of composites made of pine wood, while white rot fungus (*C. versicolor)* was employed to test the bioresistance of oak wood. Prior to analyses, the composites were dried at the temperature of 103 ^{o}C for 18 hours and sterilized by a stream of water steam at the temperature of 110 ^{o}C for 20 min. Wood composite samples prepared in this way were placed onto the developed mycelium of the test fungus. Next they were put into Kolle flasks and placed in a room ensuring the temperature of 21±1 ^{o}C and 75±5 % air relative humidity. The mycological test lasted 16 weeks. After the termination of the test, samples were carefully cleaned and mycelium removed and they were dried at 103 ^{o}C until reaching of the constant weight. Composite weight losses were calculated from the weight differences of samples before and after the test.

Mechanical tests

Tensile testing of the composites was carried out at room temperature using an Instron machine Model 4481 at a constant speed of 5 mm/min. The mechanical tests were conducted according to the PN-81/C-89034 standard. Ten samples were tested to obtain average values. The tensile strength at break was determined for the composite samples before and after biological tests.

RESULTS AND DISCUSSION

Figure 1 presents the results of the mycological tests performed for 16 weeks using of *C. puteana* and *C. versicolor* as mentioned above.

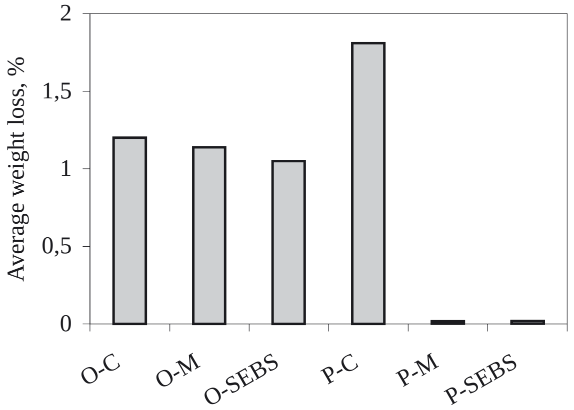

Fig. 1. Average weight loss of polypropylene-wood composites after mycological tests: O-C — polypropylene-untreated oak wood, O-M — polypropylene-mercerized oak wood, O-SEBS — polypropylene-oak wood-SEBS copolymer, P-C — polypropylene-untreated pine wood, P-M — polypropylene-mercerized pine wood, P-SEBS — polypropylene-pine wood--SEBS copolymer

Weight losses after the biological tests for all the examined composite treatments did not exceed 1.8 %, and can be considered as in the range of measurement error which is 3 % according to PN-EN 113. Therefore, it can be concluded that the examined composites were resistant to the decay caused by *C. puteana* and *C. versicolor* fungi.

Wood mechanical performance is commonly believed to be a more sensitive indicator of the incipient fungal attack [13, 14]. That is why tensile strength tests of the samples after fungal attack were carried out. The influence of the basidomecetes fungi on the tensile strength at break of the composites is shown in Figure 2.

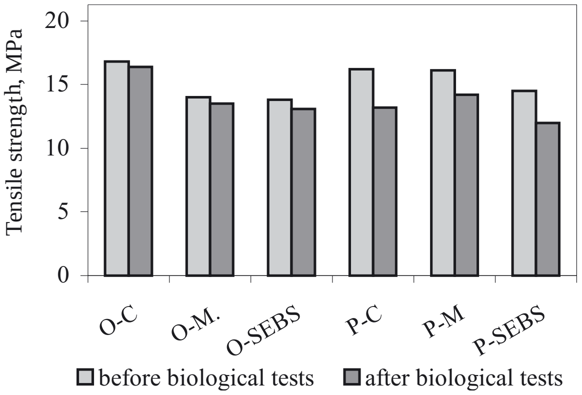

Fig. 2. Tensile strength of wood-polypropylene composites; denotations as in Fig. 1

The mechanical investigations revealed that the value of the decrease in tensile strength at break depended on the species of the wood applied. The tensile strength at break of iPP-wood composites obtained from iPP and untreated as well as mercerized pine wood decreased from 12 to 20 % after 16 weeks of the mycological test. This may indicate the beginning of the biodegradation process of the composites. In the case of composites made of iPP and untreated as well as mercerized oak wood, only small changes of the tensile strength at break (up to 5 %) were found.

It turned out that the tested fungi infested only those areas where wood was exposed, as a result of sample cutting. Following the wood-fungus interaction, the composite surface in this area became porous and this could have caused reduced tensile strength at break. In the cases of areas where the surface layers were made up of "pure polymer", the surface remained intact with no signs of fungal infestation. Biotic or abiotic factors such as fungi or water interact with a lignocellulosic material sealed in a polypropylene matrix only if they can have a direct access to wood.

Our observations are in keeping with studies of Wool *et al.* [15] and Pendleton *et al.* [16] who demonstrated that only the biodegradable components of composites, such as starch or wood meal with which fungi come in contact, undergo decomposition. They also found that hyphae failed to biodegrade polyethylene constituting part of the composite. Identical mechanisms of biodegradation probably occurred also in this study. In addition, it is well known that wood tissue degrading fungi can cause up to 90 % loss of its bulk [17]. Therefore, it can be assumed that it was the degraded wood that contributed most to the deterioration of composite mechanical properties after the mycological tests performed.

The observed smaller values of the decrease in strength of iPP-oak wood composites as a result of the fungal treatment could be attributed to the high natural oak wood resistance to decay caused by the fungi from the *Basidiomycitina* subclass [18].

Another area of our studies focused on investigating the impact of the addition of the coupling agent on the biodegradability of composite systems. It turned out that the composites containing a compatibilizer which had not been tested biologically were characterized by a worse resistance in comparison with the systems containing untreated or mercerized wood. One of the possible interpretations of this phenomenon can be that the compatibilizing agent caused improved processability and dispersion of wood in iPP and it was also responsible for its increased flexible properties. Since SEBS has smaller tensile strength in comparison with the polypropylene matrix, it is responsible for the reduction in the tensile strength of the composite system.

Moreover, it is also very interesting that composites with the compatibilizer exposed to the action of fungi were characterized by the worst tensile strength at break which was particularly noticeable in the case of the polypropylene-pine wood system. It appears then that the inclusion of the compatibilizing agent increased wood susceptibility to biodegradation. The explanation of this can probably be found in the change of the supramolecular structure of the composite material, which consisted of semicrystalline polypropylene and amorphous copolymer. It can be assumed that cellulose biodegradation will occur easier in the amorphous phase but in order to check this hypothesis it will be necessary to carry out biological tests of composites differing in the content of the stabilizing agent incorporated. It should also be added here that the incorporation of the SEBS copolymer increases the homogeneity of the wood filler in the polypropylene matrix and this, in turn, has a significant influence on the fungal accessibility to the lignocellulosic material. Improved wood distribution in the polymer will increase the probability of the fungal attack and biodegradability of the lignocellulosic material.

CONCLUSION

The experiments showed that wood biodegradation in the polypropylene matrix is possible provided mycelium hyphae gain access to the lignocellulosic material. The process of biodegradation of a composite system requires a complex approach taking into account the species of the wood applied as well as the type of the compatibilizing agents which are indispensable in the course of processing.

The results of investigations confirmed the literature information that the tensile strength test can be used as a criterion for the determination of the early stage of biodegradation [13].

The present study shows preliminary results of the investigations on the resistance of iPP—wood composites against fungi from *Basidiomycitina* subclass. The investigations will be continued using other species of fungi causing wood decay.

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REFERENCES

1. Marcovich N. E., Villar M. A.: *J. Appl. Polym. Sci.* 2003, **90**, 2775.
2. Kuciel S., Liber A.: *Polimery* 2005, **50**, 436.
3. Maiti S. N., Subbarao R., Ibrahim M. N.: *J. Appl. Polym. Sci.* 2004, **91**, 644.
4. Garbarczyk J., Borysiak S.: *Polimery* 2004, **49**, 541.
5. Bledzki A. K., Letman M., Viksne A., Rence L.: *Composites: Part A* 2005, **36**, 789.
6. Mishra S., Naik J. B.: *J. Appl. Polymer Sci.* 1998, **68**, 681.
7. Kokta B. V., Maldas D., Deneault C., Beland C.: *Polym. Compos.* 1990, **11**, 84.
8. Hill C. A. S.: *J. Institute Wood Sci.* 2000, **15**, 140.
9. Wu J., Yu D., Chan C. -M., May Y. -W.: *J. Appl. Polymer. Sci.* 2000, **76**, 1000.
10. Bledzki A. K., Reihmane S., Gassan J.: *J. Appl. Polymer. Sci.* 1996, **59**, 1326.
11. Morris P. I., Cooper P.: *Forest Prod. J.* 1998, **48**, 86.
12. Garbarczyk J., Borysiak S.: *Fibres Textiles East Eur.* 2003, **11**, 104.
13. Wilcox W.: *Wood and Fiber* 1978, **9**, 252.
14. Clemons C. M., Ibach R. E.: *Forest Prod. J.* 2004, **54**, No 4, 50.
15. Wool R. P., Raghavan D., Wagner G. C., Billieux S.: *J. Appl. Polymer Sci.* 2000, **77**, 1643.
16. Pendleton D. E., Hoffard T., Adcock T., Woodward B., Wolcott M. P.: *Forest Prod. J.* 2002, **52**, No 6, 21.
17. Unger A., Schniewind A. P., Unger W.: "Conservation of Wood Artifacts", Springer-Verlag, Berlin-Heidelberg-New York 2001.
18. PN-EN 350-2 "Trwałość drewna i materiałów drewnopochodnych — Naturalna trwałość drewna litego — Wytyczne dotyczące naturalnej trwałości i podatności na nasycenie wybranych gatunków drewna mających znaczenie w Europie".

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