

# $\beta$ -Polypropylene/Wood Flour Composites: Effects of Specific $\beta$ -Nucleation and Coupling Agent on Mechanical Behavior

Jiří Kotek, Ivan Kelnar, Hana Synková, Zdeněk Starý, Josef Baldrian

*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

Received 17 April 2006; accepted 5 July 2006

DOI 10.1002/app.25134

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polypropylene/wood flour composites were prepared by melt compounding. To improve their mechanical performance, the matrix polypropylene was modified with a specific nucleation agent based on an amide of dicarboxylic acid, which promotes crystallization predominantly in the  $\beta$ -phase. The resulting material was used as a matrix for composites containing 10%, 20%, and 30% of wood flour. Uniform dispersion of the filler and improved interfacial adhesion was ensured by

compatibilization with a small amount of maleic anhydride-grafted polypropylene. A beneficial effect of application of the nucleation agent together with a compatibilizer on the resulting mechanical behavior was shown. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 506–511, 2007

**Key words:**  $\beta$ -polypropylene; wood flour; mechanical behavior

## INTRODUCTION

Polypropylene filled with natural cellulosic fibers has gained importance as a result of many advantages. Natural fibers have mechanical properties comparable to those of synthetic fibers such as glass, but they are lighter, less expensive, and biodegradable, and they release energy when incinerated. Moreover, the carbon dioxide formed in the process is a “giving back” of that consumed during plant growth. In contrast, combination of cellulosic fibers with a polymer often leads to poor mechanical properties, except for stiffness.<sup>1</sup> This is because of the incompatibility of a polar hydrophilic filler and a hydrophobic matrix leading to weak interfacial adhesion. Moreover, strong fiber–fiber interactions resulting from intermolecular hydrogen bonding lead to poor dispersion in polypropylene matrix. To overcome these difficulties, both physical and chemical methods are applied to optimize the interface. Physical treatments, such as plasma treatment,<sup>2,3</sup> corona treatment,<sup>4</sup> and thermotreatment,<sup>5</sup> change the structural and surface properties of the fiber, affecting its mechanical bonding to polymers. Chemical methods consist of surface modification and/or addition of a coupling agent. The fibers are usually treated with

stearic acid,<sup>6,7</sup> silanes,<sup>8,9</sup> esterification with acetic anhydride,<sup>7,8,10,11</sup> propionic anhydride,<sup>11</sup> or maleic anhydride.<sup>12</sup> Maleic anhydride-grafted polypropylenes are often added as compatibilizers.<sup>1,13–16</sup> Although higher interfacial adhesion improves the strength, the toughness of the composites tends to exhibit opposite behavior. Low toughness of polypropylene reinforced by cellulosic fibers is usually improved by adding an impact modifier, such as styrene/butadiene rubber,<sup>17</sup> ethylene-methyl acrylate,<sup>15</sup> ethylene-propylene-diene terpolymer,<sup>13,14</sup> or maleated styrene-ethylene/butenes-styrene triblock copolymer.<sup>13</sup>

Recently we have shown that the ductility of polypropylene/calcium carbonate particulate composites can be successfully enhanced by the nucleation of the  $\beta$ -phase in the matrix using a specific nucleating agent.<sup>18</sup> The aim of this work was to check whether the higher ductility of  $\beta$ -polypropylene could compensate for the detrimental effect of filler on the failure behavior of polypropylene/wood flour composites. To facilitate dispersion of wood flour and improve the interfacial adhesion between filler and the matrix, a small amount of maleic anhydride-grafted polypropylene was used.

## EXPERIMENTAL

### Materials and specimens

A commercial-grade isotactic polypropylene homopolymer Mosten 58.412 (Chemopetrol, Litvínov, Czech Republic) with basic stabilization was used as a

Correspondence to: J. Kotek (kotek@imc.cas.cz).

Contract grant sponsor: Czech Science Foundation; contract grant number: 106/02/P027.

starting material throughout this study. The material is characterized by a melt flow index of 3 g/10 min (230°C, 21.2 N) and a weight-average molecular weight  $M_w$  of ~ 320,000. In this work, the starting material is labeled as PP. To obtain a material rich in the β-phase, the polymer was modified with a selective β-nucleator NJ-Star NU-100 (RIKA, UK), *N,N'*-dicyclohexyl-naphthalene-2,6-dicarboxamide. Based on our previous studies,<sup>18,19</sup> the concentration 0.03 wt % of the nucleator was chosen to obtain polypropylene rich in the β-phase. The nucleant was premixed with a polypropylene powder and compounded with neat polypropylene pellets, using a corotative twin screw extruder. The extrudates were then pelletized. The β-nucleated material is labeled as PPB. Aspen wood flour (mesh 60) was used as a filler. Maleic anhydride-grafted polypropylene (MAPP) Tabond PH 5007 (Silon, Czech Republic) was used as a coupling agent. The maleic group content of this modifier is of 0.7 wt %. The matrix polypropylene/MAPP weight ratio was fixed at 95/5.

The composites were prepared by subsequent mixing the starting (PP) and β-nucleated (PPB) polypropylenes with wood flour (WF) and maleated polypropylene (MAPP) in the chamber of a Brabender Plasti-Corder at 190°C and 60 rpm for 10 min. Prior to mixing, the wood flour was dried under vacuum in an oven at 80°C for 24 h. The composition of the studied materials is summarized in Table I. The material removed from the chamber was compression-molded immediately in three steps: 2 min at 190°C at 50 kN, 2 min at the same temperature at 100 kN, and cooling at a pressure of 50 kN at 45°C. From 2-mm-thick compression-molded sheets, the dumbbell specimens with a gauge length of 25 mm and width of 5 mm (type 1BA according to the ISO 527 standard) were milled.

**Sample characterization and testing**

The structure was assessed by scanning electron microscopy and X-ray diffraction (XRD). Wide-angle X-ray scattering (WAXS) was performed in transmission mode. A powder diffractometer HZG (Präzisionsmechanik Freiberg, Germany) using  $\text{CuK}_\alpha$  radiation monochromatized with a β-filter was used for the measurements. The relative amount of the β-form in the crystalline phase was characterized by the ratio *K*. Its value was obtained from intensities of crystalline reflections of α- and β-phase using the following relation:<sup>9</sup>

$$K = I_\beta / (I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3} + I_\beta), \quad (1)$$

where  $I_\beta$  is the integral intensity of 300 reflection of the β-phase, and  $I_{\alpha 1}$ ,  $I_{\alpha 2}$ , and  $I_{\alpha 3}$  are the integral intensities of the 110, 040, and 130 reflections of the α-phase, respectively.

**TABLE I**  
**Composition of Prepared Polypropylene/Wood Flour Composites**

	PP (wt %)	PPB (wt %)	WF (wt %)	MAPP (wt %)
1	100	—	—	—
2	—	100	—	—
3	95	—	—	5
4	—	95	—	5
5	90	—	10	—
6	80	—	20	—
7	70	—	30	—
8	85.5	—	10	4.5
9	76	—	20	4
10	66.5	—	30	3.5
11	—	90	10	—
12	—	80	20	—
13	—	70	30	—
14	—	85.5	10	4.5
15	—	76	20	4
16	—	66.5	30	3.5

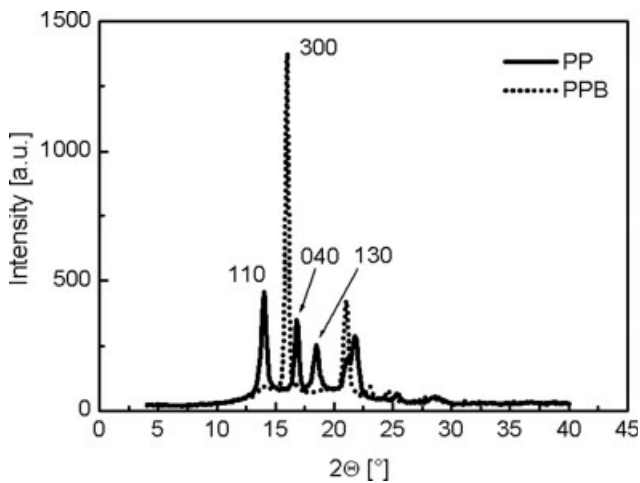
Tensile tests were performed using an Instron 5800 tensile tester at room temperature and a cross-head speed of 5 mm/min except for the Young modulus determination, which was carried out at a lower cross-head speed of 1 mm/min. The following mechanical characteristics were derived from the stress-strain curves: Young modulus, *E*, yield stress,  $\sigma_y$  or tensile strength,  $\sigma_M$  and strain at break,  $\epsilon_b$ . The reported values are averages of 10 individual measurements.

The room temperature tensile impact strength,  $a_t$ , was measured using a Zwick hammer with an energy of 4 J and one-side notched specimens. The cross-section of the specimens was 2 × 10 mm<sup>2</sup> and the notch depth was 2 mm. The fracture surfaces were examined by scanning electron microscopy (SEM; Vega, Tescan Brno, Czech Republic).

**RESULTS AND DISCUSSION**

**β-Phase content**

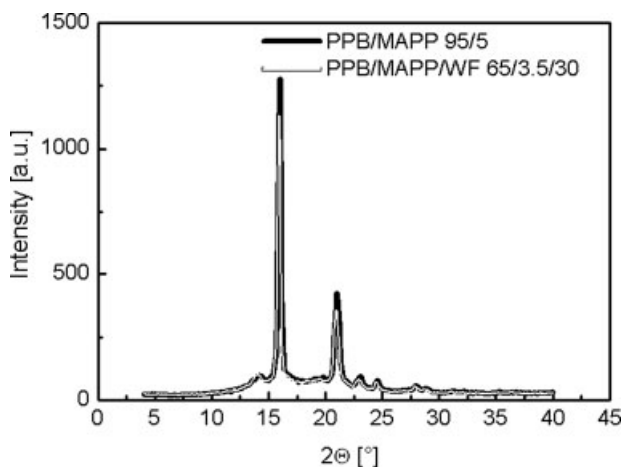
Figure 1 shows typical wide-angle X-ray scattering (WAXS) patterns of non-nucleated (PP) and β-nucleated (PPB) polypropylenes. Non-nucleated polypropylene exhibits three main reflections at diffraction angle  $2\theta = 14.1^\circ$ ,  $16.9^\circ$ , and  $18.8^\circ$ , which correspond to the primary reflection of the (110), (040), and (130) planes of the α-PP crystals, respectively. No such reflections can be identified in the WAXS pattern of the nucleated PPB; only an insignificant small reflection remains at  $2\theta = 14.1^\circ$  and the other two reflections disappear completely. On the other hand, a pronounced peak at  $2\theta = 16.0^\circ$  corresponding to the reflection of the (300) plane of the β-PP crystals appears. This clearly demonstrates that the addition of



**Figure 1** Wide-angle X-ray diffraction curves of non-nucleated (PP) and  $\beta$ -nucleated (PPB) polypropylenes.

0.03 wt % of the  $\beta$ -nucleator together with the used compression molding process leads to the material containing high-purity  $\beta$ -crystals. The corresponding ratio  $K$ , which determines the relative amount of the  $\beta$ -form in the crystalline phase, is higher than 98%. As can be seen in Figure 2, the addition of 5 wt % of MAPP to PPB polypropylene does not change the WAXS pattern and therefore does not affect the  $\beta$ -phase content. The effect of the presence of wood flour on crystallization of  $\beta$ -nucleated PPB is also negligible; see the pattern of PP/MAPP/WF (65/3.5/30) in Figure 2. It is important to note that the patterns of all the materials with PPB matrix are virtually identical.

The effects of the  $\beta$ -nucleating agent and the presence of MAPP and wood flour on the  $\beta$ -phase content can be summarized as follows: (1) in contrast to injection-molded specimens,<sup>18</sup> compression-molded



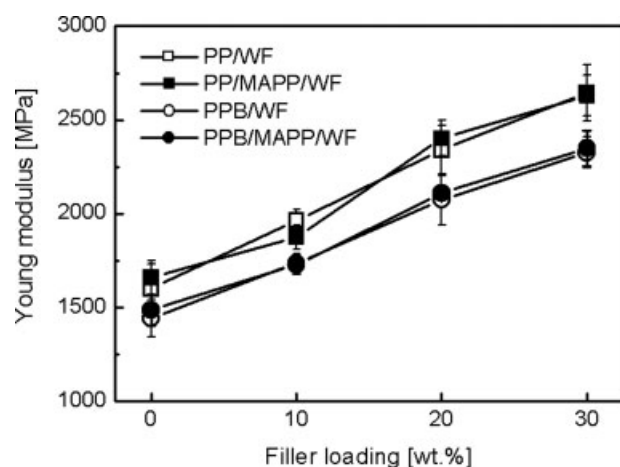
**Figure 2** Wide-angle X-ray diffraction curves of PPB/MAPP (95/5) blend and PPB/MAPP/WF (65/35/30) composite.

sheets from nucleated polypropylene contain high-purity  $\beta$ -modification; and (2) the addition of maleated polypropylene and/or the wood flour does not affect the  $\beta$ -phase content.

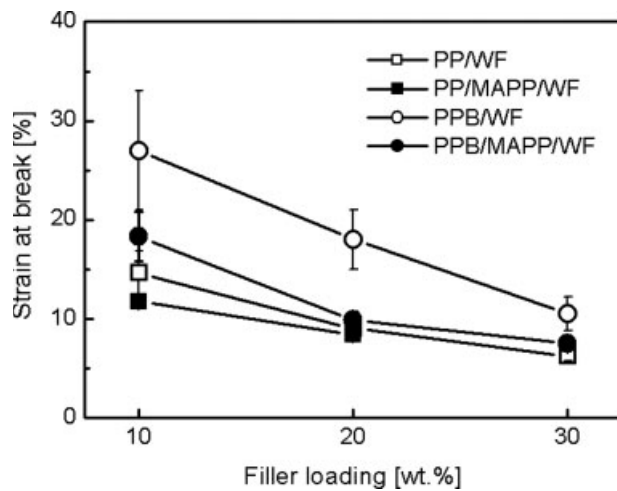
### Mechanical behavior

The presence of  $\beta$ -phase crystals is imprinted in a particular way in all mechanical characteristics. Both stiffness and yield stress are decreased in comparison with polypropylene containing solely the  $\alpha$ -crystals. The yield stress drops from 35.2 MPa for the nonmodified material to 28.3 MPa for the  $\beta$ -nucleated polypropylene. The Young modulus also drops from 1600 MPa (PP) to 1420 MPa (PPB). In contrast, the drawability expressed by strain-at-break value is significantly higher for the nucleated PPB. While neat PP fails (at given test conditions and specimen geometry) at the strain about 110%, the PPB exhibits the strain at break of 270%. The compounding of these two polypropylenes with MAPP in the weight ratio of 95/5 does not affect markedly the tensile behavior and the evaluated mechanical characteristics remain unchanged within experimental error.

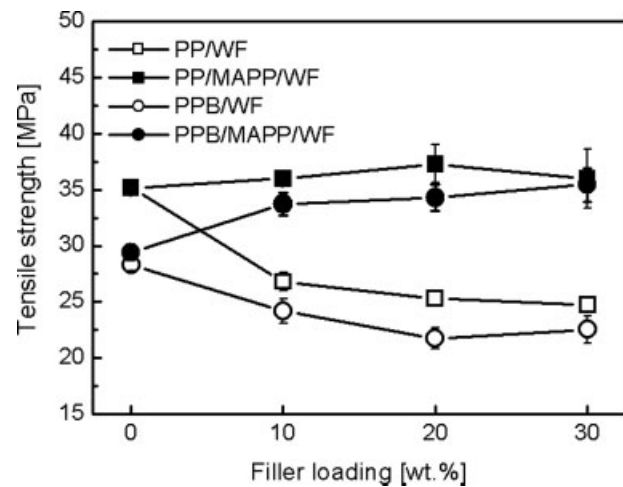
Mechanical behavior of composites reflects both the properties of the polypropylene matrix and the presence of the filler and coupling agent. A variation of tensile moduli of the composites is shown in Figure 3. Thus, the tensile moduli of composites with PP matrix are systematically higher than those of composites with nucleated matrix. In all cases, the moduli increase with increasing filler content. As in the case of unfilled matrices, the presence of MAPP does not affect markedly the stiffness of the composites. While all unreinforced matrices (PP, PPB, PP/MAPP, and PPB/MAPP) exhibit typical ductile be-



**Figure 3** Young modulus as a function of wood flour content.



**Figure 4** Strain-at-break as a function of wood flour content.



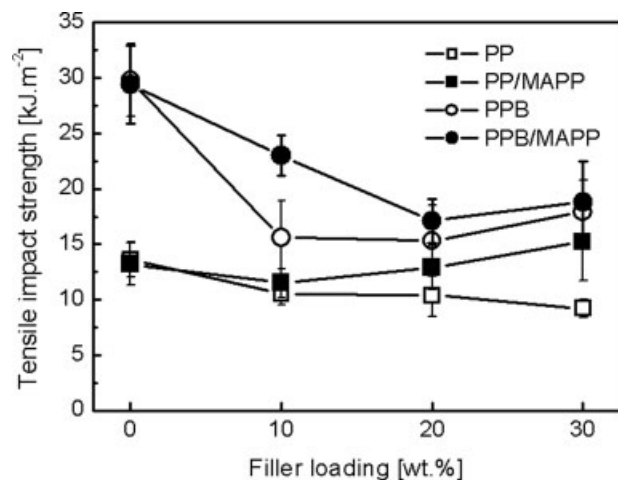
**Figure 5** Tensile strength as a function of wood flour content.

havior with heterogeneous deformation that is concentrated in a shoulder of a growing neck, addition of the wood flour changes the behavior to semibrittle: the composites break down immediately after reaching the yield point. This manifests itself in the dependence of the strain-at-break on the wood flour content (Fig. 4). It can be seen that the strain-at-break of neat polypropylene steeply decreases from 110% to 15% by addition of 10 wt % of WF and then decreases again with increasing filler content. The presence of the  $\beta$ -phase in the PPB matrix improves the ductility of the composites. Indeed, the composites with PPB matrix exhibit systematically higher strain-at-break values than those with PP matrix. However, the addition of MAPP, which improves interfacial adhesion, decreases the elongation at the break and almost diminishes the positive effect of the  $\beta$ -phase. Similarly, the strain-at-break of composites with PP matrix also slightly decreases on addition of the coupling agent.

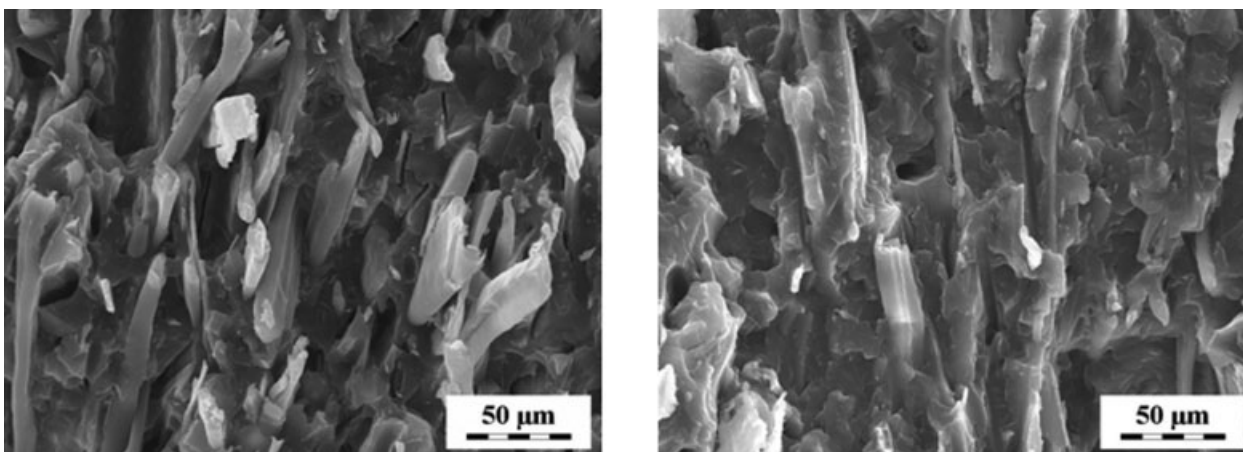
The improved filler/matrix interfacial adhesion, which shows a detrimental effect on the resulting ductility of the composites, positively affects the tensile strength (Fig. 5). The sole addition of wood flour into PP or PPB matrices leads to a decrease in tensile strength, which tends to decrease with increasing filler loading. This behavior can be ascribed to poor adhesion between the polymer matrix and the filler, which allows debonding and pulling out of fibers at the onset of plastic deformation. At the same time, the intrinsic properties of the matrices are imprinted in the final strength of the composites. Thus, the tensile strength of the composites with PPB matrix is systematically lower than corresponding values for PP/WF composites. The decisive effect of the interfacial adhesion on the tensile strength is demonstrated in Figure 5. The addition of a small amount of

the coupling agent (MAPP) leads to significantly enhanced tensile strength. The values of tensile strength of composites with non-nucleated PP matrix are comparable or even slightly higher than the yield-stress value of the matrix. In the case of the  $\beta$ -polypropylene matrix (PPB), the tensile strength of composites is markedly improved than the corresponding matrix value.

The evolution of toughness expressed by notched tensile impact strength as a function of wood flour content is shown in Figure 6. It can be seen that  $\beta$ -polypropylene (PPB) exhibits a significantly higher tensile impact strength than the neat PP. In both cases, addition of 10 wt% of wood flour decreases toughness. A further increase in the filler content in PP matrix leads to a slight decrease in impact strength. The addition of MAPP and the resulting improved filler/matrix strength increases the energy



**Figure 6** Tensile impact strength as a function of wood flour content.



**Figure 7** SEMs of fracture surfaces. Noncompatibilized PP/WF (left) and compatibilized PP/MAPP/WF (right) composites containing 30 wt % of wood flour.

consumption during impact leading to higher values of tensile impact strength, which increases with increasing wood flour loading. To explain this behavior, SEM examination of fracture surfaces was done. Figure 7(a) shows the impact fracture surface of PP/WF 70/30 composite, where numerous pull-out fibers can be seen. In contrast, the fiber pull-out in corresponding composite with maleated PP as a coupling agent [PP/MAPP/WF 66.5/3.5/30; Fig. 7(b)] was significantly suppressed. At the same time, the pull-out length is also markedly reduced and the fibers are coated with the matrix. This suggests that the energy absorption mechanisms in composites containing the coupling agent consists mainly of matrix and fiber fracture. The obtained results indicate that this mechanism absorbs more energy during tensile impact than the matrix/fiber debonding and fiber pull-out, which dominate in PP/WF composites. The high toughness of  $\beta$ -nucleated polypropylene PPB results in enhanced impact strength of its composites. Indeed, the composites with PPB matrix exhibit a systematically higher tensile impact strength than the composites with PP matrix. Again, the improved interface in composites containing MAPP leads to a higher energy absorption during tensile impact.

## CONCLUSIONS

The objective of this study was to investigate the effects of a combination of specific nucleation of the  $\beta$ -phase in polypropylene matrix and addition of a coupling agent on mechanical behavior of polypropylene/wood flour composites. Following conclusions can be drawn from the results:

1. Addition of a small amount of a specific  $\beta$ -nucleant (*N,N'*-dicyclohexyl-naphthalene-2,6-

dicarboxamide) to isotactic polypropylene induces predominant formation of the crystalline  $\beta$ -phase in compression-molded specimens. The presence of coupling agent (maleated polypropylene) or of the wood flour does not affect the  $\beta$ -phase content.

2. The gain in polypropylene ductility imparted by the presence of the crystalline  $\beta$ -phase is accompanied by a small reduction in stiffness and yield stress. On the other hand, the addition of 5 wt % of the MAPP does not change the tensile behavior of unfilled samples.
3. Tensile testing showed an increase in stiffness with increasing amount of wood flour and an accompanying decrease in strain-at-break and tensile strength. Both stiffness and strength of the composites with  $\beta$ -nucleated matrices are lower than those of the materials with non-nucleated matrices. In contrast, the positive effect of the presence of the  $\beta$ -phase on ductility is obvious: the values of strain-at-break and of tensile impact strength are systematically higher. Addition of MAPP, resulting in better interfacial adhesion, shows almost a positive effect on mechanical behavior of the composites: it significantly increases tensile strength, improves tensile impact strength and does not deteriorate the stiffness. The strain-at-break values, however, are reduced.

Even if the favorable effect of the  $\beta$ -phase on plasticity is suppressed by the presence of filler, the compatibilized composite with  $\beta$ -nucleated matrix containing 30 wt % of wood flour exhibits 1.4 times higher modulus and also higher tensile impact strength than neat polypropylene. At the same time, its tensile strength reaches a comparable value with that of neat polypropylene.

**References**

1. Bledzki, A. K.; Gassan J. *Prog Polym Sci* 1999, 24, 221.
2. Couto, E.; Tan, I. H.; Demarquette, N.; Caraschi, J. C.; Leao, A. *Polym Eng Sci* 2002, 42, 790.
3. Yuan, X.; Jayaraman, K.; Bhattacharyya, D. *Composites: Part A* 2004, 35, 1363.
4. Belgacem, M. N.; Bataille, P.; Sapeiha S. *J Appl Polym Sci* 1994, 53, 379.
5. Sapeiha, S.; Pupo, J. F.; Schreiber, H. *J Appl Polym Sci* 1989, 37, 233.
6. Raj, R. G.; Kokta, B. V.; Dembele, F.; Sanschagrain, B. *J Appl Polym Sci* 1989, 38, 1987.
7. Zafeiropoulos, N. E.; Williams, D. R.; Baillie, C. A.; Matthews, F. L. *Composites: Part A* 2002, 33, 1083.
8. Sreekala, M. S.; Kumaran, M. G.; Thomas, S. *J Appl Polym Sci* 1997, 66, 821.
9. Coutinho, F. M. B.; Costa, T. H. S. *Polym Test* 1999, 18, 58.
10. Rana, A. K.; Basak, R. K.; Mitra, B. C.; Lawther, M.; Banerjee, A. N. *J Appl Polym Sci* 1997, 64, 1517.
11. Tserki, V.; Zafeiropoulos, N. E.; Simon, F.; Panayiotou, C. *Composites: Part A* 2005, 36, 1110.
12. Nunez, A. J.; Sturm, P. C.; Kenny, J. M.; Aranguren, M. I.; Marcovich, N. E.; Reboredo, M. M. *J Appl Polym Sci* 2003, 88, 1420.
13. Oksman, K.; Clemons, C. *J Appl Polym Sci* 1998, 67, 1503.
14. Park, B. D.; Balatinecz J. J. *Polym Compos* 1997, 18, 79.
15. Sombatsompop, N.; Yotinwattanakumtorn, C.; Rhongpin, C. *J Appl Polym Sci* 2005, 97, 475.
16. Tajvidi, M. *J Appl Polym Sci* 2005, 98, 665.
17. Hristov, V. N.; Vasileva, S. T.; Krumova, M.; Lach, R.; Michler, G. H. *Polym Compos* 2004, 25, 521.
18. Kotek, J.; Kelnar, I.; Baldrian, J.; Raab, M. *Eur Polym J* 2004, 40, 679.
19. Kotek, J.; Raab, M.; Baldrian, J.; Grellmann, W. *J Appl Polym Sci* 2002, 85, 1174.