Modified Polypropylene Wood Flour Composites. II. Fracture, Deformation, and Mechanical Properties

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ABSTRACT: The effect of grafting level of maleic anhydride (MA) in the maleated polypropylene (PPMA) on the fracture, deformation mechanisms, and mechanical properties of polypropylene (PP) wood flour composites was studied. Tensile strength, elongation at break, and impact strength are noticeably improved with addition of interfacial modifiers as maximum values of the examined mechanical properties were detected when concentration of MA in the compatibilizer was 1 wt %. To explore the microstructure and deformation mechanisms, scanning electron microscopy was employed. It was found that low concentrations of MA up to 1 wt % led to the creation of a thin and irregular polymer layer assisted formation of fibrillated plastic deformation zone around the wood particles, while the bulk PP matrix experienced voiding and brittle fracture. Higher concentrations of MA fetch to stronger interaction between PP and wood flour, the reason for brittle fracture and reduced ductility of the matrix. The impact fracture behavior of the composites during Instrumented impact tests is also discussed with respect to the interfacial bond strength. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1286–1292, 2004

Key words: polypropylene wood flour composites; maleated polypropylene; structure; mechanical properties; deformation

INTRODUCTION

In recent years, thermoplastics reinforced with different natural fillers have received considerable attention because of many advantages. These composites have light weight, reasonable strength and stiffness, and low cost and can be readily processed by conventional plastics processing techniques such as extrusion and injection molding. The problem with the compatibilization of the nonpolar polypropylene (PP) and hydrophilic wood fillers is of great importance and there are many reports in the literature investigating interfacial interactions between polymer matrices and wood fillers.[1–5] The stress transfer efficiency plays a dominant role in determining the mechanical properties of the composite and it is of crucial importance to maintain good stiffness to impact strength balance to expand the applicability of these composite materials. In most cases of composites containing untreated fillers, tensile strength and elongation are lower than those of unfilled polymers.[6–8]

One product widely used for modifying both polymers and wood fillers is maleic anhydride (MA). MA grafted on the backbone of synthetic polymers such as polyethylene and PP has been proved to form either covalent ester or hydrogen bonds when reacting with hydroxyl groups at the cellulose surface.[9–12] Maleated polypropylene (PPMA) copolymers grafted to the wood surface allow production of composites with good adhesion between the two phases and satisfactory mechanical properties.[13–17]

Despite much evidence of the positive role of PPMA, the structural details of interfacial interactions are less understood. In addition, little work has been done to ascertain and account for the morphological changes, deformation, and fracture mechanisms associated with improvement of mechanical properties of PP wood-filled composites. Wu et al.[18] extensively investigated the effect of wood fiber surface pretreatment on the interfacial strength and mechanical properties of wood fiber/PP composites and demonstrated that fiber surface significantly influenced the fiber–matrix interfacial bond strength and mechanical properties of the composites. The authors reported a synergistic toughening effect between the wood fiber and maleated styrene-(ethylene-*co*-butylene)-styrene (SEBS-*g*-MA) copolymer in the impact test of PP/wood fiber composites and discussed in detail the deformation mechanisms with respect to the interfacial bond strength. The influence of the concentration of MA in the maleated polypropylene seems to be of great importance, but insufficiently explored, for attaining superior mechanical properties. Differences in MA con-

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tent and distribution onto the polymer chains can lead to formation of miscellaneous physical or chemical linkages between the matrix and wood filler, which would result in different microstructure, and hence, mechanical response of the composites. Le Thi and Gauthier[19] investigated the influence of different parameters during reactive extrusion, among them the concentration of MA in PP-*g*-MA and the content of PP-*g*-MA in the PP/sisal fiber composites. They reported that the rate of PP-*g*-MA and the maleic anhydride content in PP-*g*-MA led to an increase in the impact strength and breaking stress. Bledzki et al.[20] studied the influence of the content of maleated polypropylene on the physicomechanical properties of hard and soft wood fiber reinforced PP and concluded that PPMA was more effective at a lower percentage; however, an explanation of the observed phenomena had not been given. Oksman and Lindberg[21] explored the mechanical properties of recycled low-density polyethylene/wood flour composites and optimized the content of SEBS-*g*-MA compatibilizer in the composites. They ascertained that the composites' tensile strength, elongation at break, and impact strength were improved with addition of SEBS-*g*-MA and reached maximum levels with 4 wt % SEBS-*g*-MA content. Further addition of the compatibilizer did not improve the tensile strength because of the fact that higher loadings of the elastomeric compatibilizer would affect the matrix properties. The large increase of elongation at break between 0 and 4 wt % compatibilizer content was attributed to interfacial effects, but with increasing elastomer content, soft rubber inclusions in the matrix were expected to dominate. Xie and colleagues[22] reported that the impact fracture energy, total impact duration, crack initiation, and propagation time of PP/sisal fiber composites tended to increase with increasing content of the SEBS-*g*-MA compatibilizer. Karnani et al.[23] found that the increase of PPMA content from 2 to 5% in PP/kenaf fiber composites resulted in some modest property improvements compared to improvements on addition of PPMA to the unmodified PP. The authors concluded that this could be attributed to the excess peroxide and free radicals not removed after the maleation reaction, which would initiate further chain scission of the PP during subsequent processing.

Another important factor that could influence the structure and properties of the PP wood-filled composites is the degree of maleation of the initial compatibilizer. It was demonstrated by Duvall and colleagues[24,25] that the low-anhydride compatibilizer (LAC) with 0.2 wt % grafted MA imparted much higher fracture strain and toughness to PP/PA 6 blends than did high-anhydride compatibilizer (HAC) with 2.7 wt % grafted MA at similar content of the compatibilizer maleated polypropylene. The authors concluded that during compression molding intimate content in the melt state allowed the interdiffusion and subsequent cocrystallization of PP with LAC. Under the same conditions, it appeared that PP and HAC did not interdiffuse. The phase segregation of HAC and PP near the interface resulted in an adhesion strength that appeared to be lower than the draw stress of PP. Therefore, interfacial failure occurred as the PP matrix began to draw, which produced voids and sites for crack initiation.

TABLE I
Basic Characteristics of Neat Polypropylene and Maleated Polypropylenes

Property	PP	PPMA05	PPMA10	PPMA15
Density (g/cm^3)	0.91	0.90	0.89	0.88
Melt flow index (g/10 min) (2.16 kg, 230°C)	6.0	10.0	12.4	16.6
MA concentration (wt %)	—	0.5	1.0	1.5

Keeping in mind the obvious discrepancies in the experimental results obtained by different research groups, it should be pointed out that more detailed investigations are needed to elucidate the complicated deformation and fracture mechanisms in the multicomponent polymer systems. The aim of this study was to investigate the effect of low-concentration grafted levels of maleic anhydride in the maleated polypropylene on the fracture, deformation mechanisms, and mechanical properties of PP wood flour composites.

EXPERIMENTAL

Materials and composite preparation

The PP used in this work was polypropylene–ethylene copolymer (2 mol % ethylene) grade Buplen 7523, supplied by Luck Oil Bulgaria. Wood flour (WFI) from pine tree with an average particle size within 15–50 μm was used as filler without any treatment prior to processing (TPK Masiv Ltd., V. Tarnovo, Bulgaria). Three different types of noncommercial maleated polypropylenes were used as coupling agents. These products, designated PPMA05, PPMA10, and PPMA15, containing 0.5, 1.0 and 1.5 wt % grafted maleic anhydride, respectively, were prepared by reactive extrusion in a single-screw extruder. The concentration of the maleic anhydride units attached to the PP backbone was estimated after removing the unreacted anhydride and poly(maleic anhydride) by vacuum drying at 120°C for 100 h, by FTIR spectroscopy according to the method of Sclavons described in ref. 26. Table I summarizes the physical properties of the polymers used in this study. Compositions of various PP composites are outlined in Table II.

The untreated wood flour, PP, and PPMA pellets were preblended in a mixer, and then the mixtures

TABLE II
Composites Composition

Sample code	PP (wt %)	WF1 (wt %)	PPMA05 (wt %)	PPMA10 (wt %)	PPMA15 (wt %)
PP	100	—	—	—	—
PPWF1	95	5	—	—	—
PPWF105	80	5	15	—	—
PPWF110	80	5	—	15	—
PPWF115	80	5	—	—	15

were extruded twice in a single-screw extruder with a length-to-diameter ratio *L/D* of 32. The temperature of feeding, mixing, and compression extruder processing zones I, II, and III and the die were 150, 170, 180°C, respectively, and the screw speed was 40 rpm. The extruded materials were air quenched and granulated. The granules were annealed in an oven for 3 h at 105°C and compression molded at 180°C into 2- and 4-mm-thick plates according to ISO 293 standard procedure.

Tensile testing

Tensile testing of dumbbell-shaped 2-mm-thick test pieces was performed on a Zwick 1425 testing machine at a crosshead speed of 50 mm/min. The tensile strength (σ_b) and elongation at break (ε_b) were calculated from the tensile test data. At least 15 specimens of each composite were tested.

Impact testing

Charpy impact test of 80 × 10 × 4 mm test pieces was employed to characterize the impact properties of the composites by using a IKBV-4 instrumented impact pendulum tester at a velocity of 1 m/s. A V-notch having a notch tip radius of 0.1 mm was introduced on the narrow side of the test bars by means of a Ceast notch cutter. At least 10 specimens of each composite were tested and the Charpy notched impact strength (a_{cN}) was evaluated according to ISO 179 standard procedure.

Morphological observations

The fracture surfaces of the specimens from tensile testing were sputtered coated with gold and observed by using a JEOL JSM-6300 scanning electron microscope (SEM) at an accelerating voltage of 8 kV.

RESULTS AND DISCUSSION

Mechanical properties and deformation mechanisms

The microstructure of the polymer composites affected its mechanical properties to a large extent. The results from tensile testing are shown in Figure 1.

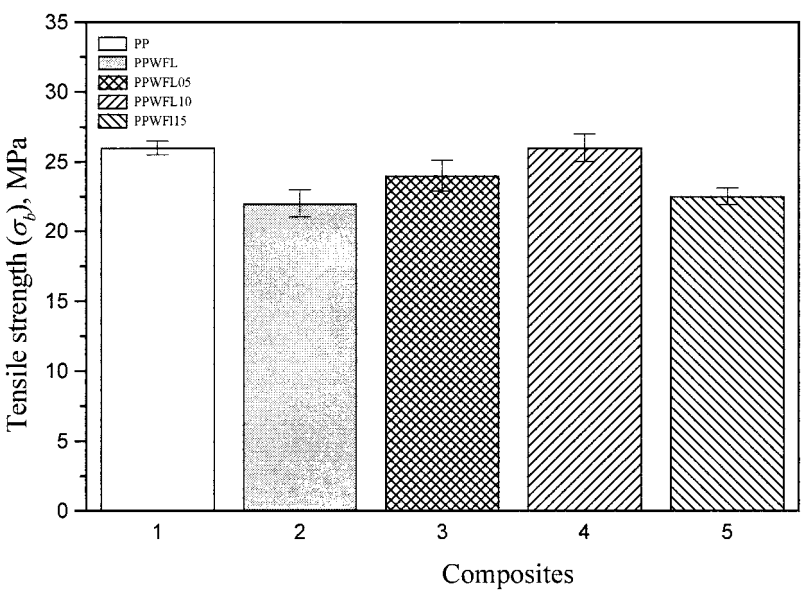

Figure 1 Tensile strength (σ_b) of PP wood flour composites.

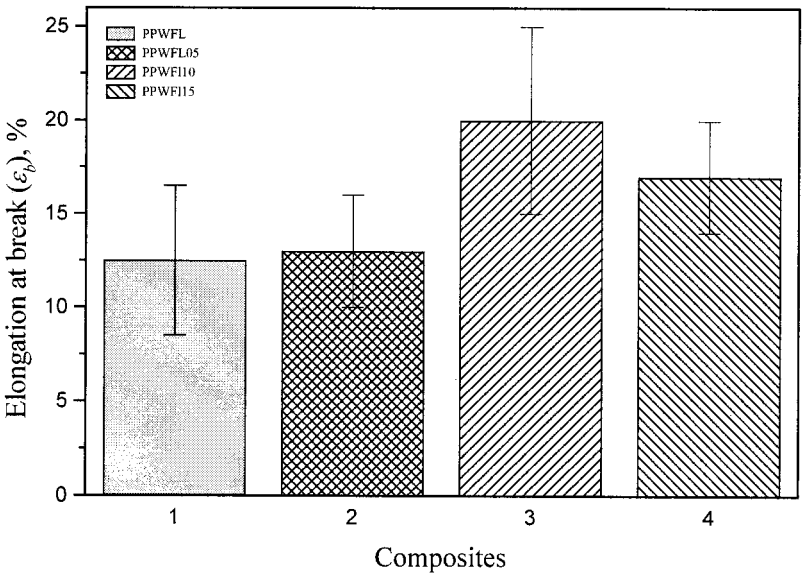

Figure 2 Elongation at break (ε_b) of PP wood flour composites.

Generally, the tensile strength of the PP/wood-filled composites decreases with increasing the percentage of the wood flour, mainly because of worse transfer of the applied load through the interface.

It is well known that addition of maleated polypropylene to the PP wood flour composites increases the tensile properties of the composites and our results comply with those obtained by other authors.[20–22] It is interesting to note, however, that there is an optimal level of grafted MA in the compatibilizer giving maximum tensile strength, which in this investigation turned out to be approximately 1 wt %. Increasing MA-grafted level in the compatibilizer above this concentration (composite PPWF115) reduces the tensile strength almost to that of the unmodified PP wood flour composite (composite PPWF1). These results are in accordance with the morphological observations, and it could be inferred that the concentration of MA in the compatibilizer plays an important role in the processes occurring at the interface. Therefore, the deformation, fracture, and mechanical properties of the composites could be predicted and designed by appropriate usage of fillers and suitable coupling agents. Low concentration of MA in the compatibilizer conduces to formation of a thinner interfacial layer from which polymer fibrils capable of absorbing more energy may be readily stretched out during deformation. The higher concentration of MA groups attached onto the PP chains gives rise to strong interaction, probably by formation of chemical bonds between MA groups from PPMA and cellulose hydroxyl groups. For that reason, the fracture mode is predominantly brittle, characterized by cohesive failure in both PP matrix and wood particle.

The effect of the various compatibilizers on the elongation at break is shown in Figure 2. As a rule, fillers with higher stiffness than the matrix cause a dramatic decrease in the elongation at break.[27] The obtained results for the unmodified PP wood flour composite are in accordance with the abovementioned rule. Adding maleated polypropylene, however, increases the elongation at break as the most pronounced effect was detected again in the case of the composite PPWF110 containing 1 wt % MA in the compatibilizer.

Increasing concentration of MA in the compatibilizer up to 1.5 wt % contributes to decreased elongation at break and ductility of the PP matrix. It should be also emphasized that the composites with low MA concentration deform plastically during the test with intensive stress whitening, while the composite PPWF115 deforms and fractures predominantly in brittle mode without significant plastic deformation before fracture.

For better understanding of the deformation behavior of modified PP wood flour composites, the tensile fractured surfaces were investigated by SEM. The interfacial regions between PP matrix and wood flour particles were preferably observed in more detail.

Figure 3 shows the tensile fractured surface of the unmodified PP wood flour composite. A wood particle (a) is embedded in the cavitated PP matrix and there is a gap (b) around the particle, indicating poor adhesion between the matrix and wood particle. On the fractured surface, many wood particles pulled out of the matrix can be seen. The fracture occurs concomitantly within the PP matrix and wood particles without plastic deformation. It seems that intensive voids formation in the bulk matrix and their subsequent coalescence in larger voids and cracks leads to premature brittle fracture at low stress level and elongation.

Figure 4 represents the tensile fractured surface of PPWF105 composite. There is no significant difference

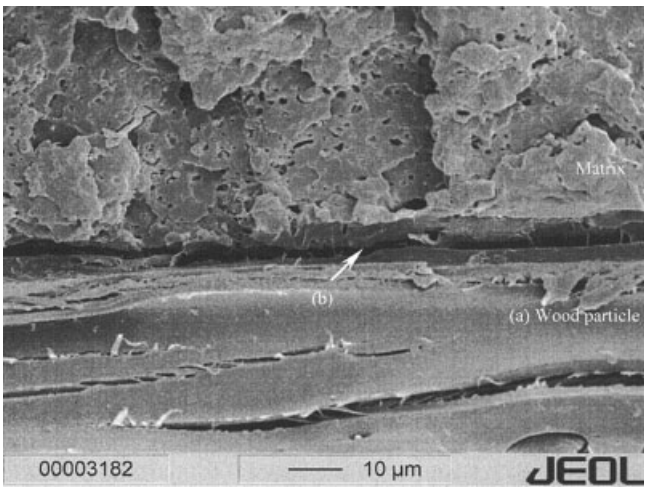

Figure 3 SEM micrograph of the tensile fractured surface of PPWF1 composite.

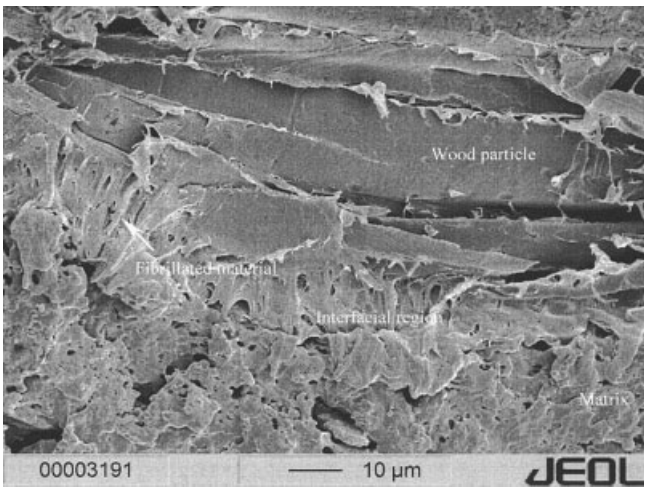

Figure 5 SEM micrograph of the tensile fractured surface of PPWF110 composite.

in the fracture mode in comparison to that of the unmodified composite; however, the fracture occurs selectively at the interfacial regions. Little plastic deformation and the very small gap between the cavitated PP matrix and wood particle indicate improved adhesion, likely due to some kind of physical interaction between the compatibilizer and the wood flour.

Figure 5 reveals the fracture mode of the PP wood flour composite containing compatibilizer with 1 wt % grafted MA. There is an obvious difference in the deformation mechanism compared to that of the unmodified PP wood flour composite. The wood particles are probably coated with a thin and irregular polymer layer capable of deforming plastically, and fibrils are stretched between wood particles and PP matrix. It seems that these fibrils had been formed at some stage of the deformation process, and the tendency to get orientated during the tensile testing created a plastic deformation zone with thickness of about 5–20 μm around the wood particles. In this case, the failure occurs most commonly at the interfacial regions rather than within the PP matrix or wood particles. However, it is worth noting that the plastic deformation zone predominantly develops around the wood particles, while the bulk matrix experiences void formation and brittle fracture. It could be implied that the deformation mechanisms of compatibilized PP wood flour composites will depend largely upon and could be governed by the interparticle distance. In addition, it might be speculated that, by increasing the wood filler loading and by using suitable interfacial modifiers, significant improvement of the mechanical properties could be attained, although the stress state will be altered and other deformation mechanisms could have taken place in such a case. Further work should then be focused on blends with higher filler content to establish whether the same or some other phenomena will be observed.

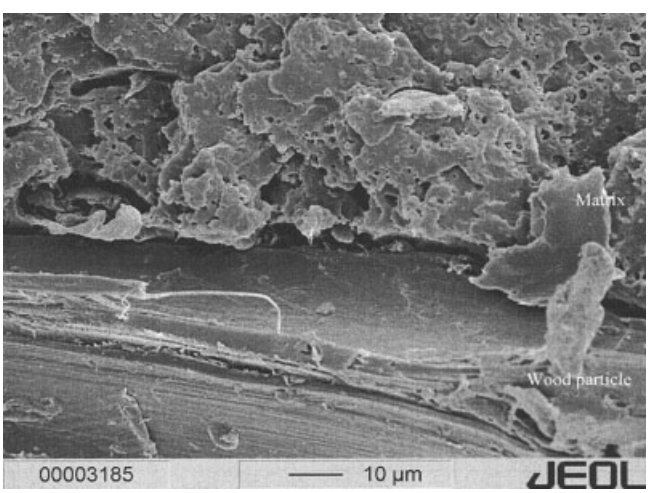

Figure 4 SEM micrograph of the tensile fractured surface of PPWF105 composite.

The main deformation mechanism in the case of PPWF115 is voids formation and brittle fracture of the matrix. However, some plastic deformation develops at certain regions on the wood surface (a), as seen in Figure 6. The interfacial bond between the matrix and wood particles is very strong, causing fracture of the wood particles rather than being debonded or pulled out of the matrix.

Impact properties

Figure 7 illustrates the force-deflection (*F-d*) curves of PP wood flour composites obtained by means of an Instrumented impact device. The overall fracture process may be divided into crack initiation and crack propagation stages. During crack initiation, stress builds up at the notch tip but it is too low to enable crack propagation.[28] Unmodified PP wood flour com-

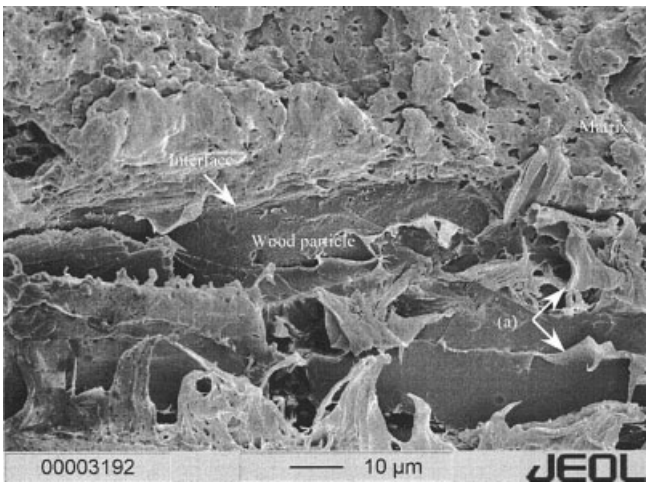

Figure 6 SEM micrograph of the tensile fractured surface of PPWF115 composite.

posite exhibits brittle fracture characterized by an approximately linear loading curve, ending in a sharp drop after reaching the maximum load. Plastic deformation at the notch tip is limited and insufficient to cause significant deviation from linearity and the crack growth is unstable. The plateau at the maximum load seen on the *F-d* curves becomes broader with increasing concentration of MA in the compatibilizer, and it is due to plastic deformation at the notch tip visible as a circumferential stress whitened zone on the specimen surface. However, in the case of PPWF115, the plateau at the maximum load shortens, which is a result of the reduced ductility of the composite.

The Charpy notched impact strength of the composites is presented in Figure 8. Generally, the impact strength of filled PP decreases in comparison to that of virgin PP mainly because of altering the local stress distribution and also because of decreasing the part of the impact energy dissipated by the matrix.[29] Maleated polypropylene provides better adhesion between the matrix and wood flour, leading to enhanced impact strength, as can be seen in Figure 8.

Unambiguously, the maximum impact strength was determined for the composite containing 1 wt % MA in the compatibilizer. The slightly reduced impact strength of PPWF115 composite is caused by very strong interfacial bond strength, as was observed by SEM. When this composite is subjected to impact loading, plastic deformation of PP matrix is depressed by the high strain rate as well as the constraint imposed by the rigid filler.[18] The material in front of the crack tip in this circumstance is subjected to plain–strain conditions and the crack propagates through the PP matrix with little plastic deformation.

CONCLUSION

The effect of maleic anhydride concentration in the compatibilizer on the fracture, deformation mechanisms, and mechanical properties of PP wood flour composites was studied. The poorer mechanical properties of the unmodified PP wood flour composite are due to poor adhesion between the PP matrix and wood flour. The tensile strength, elongation at break, and impact strength are noticeably improved with addition of maleated polypropylene as interfacial modifier.

The concentration of MA in the compatibilizer was found to have a significant effect on the microstruc-

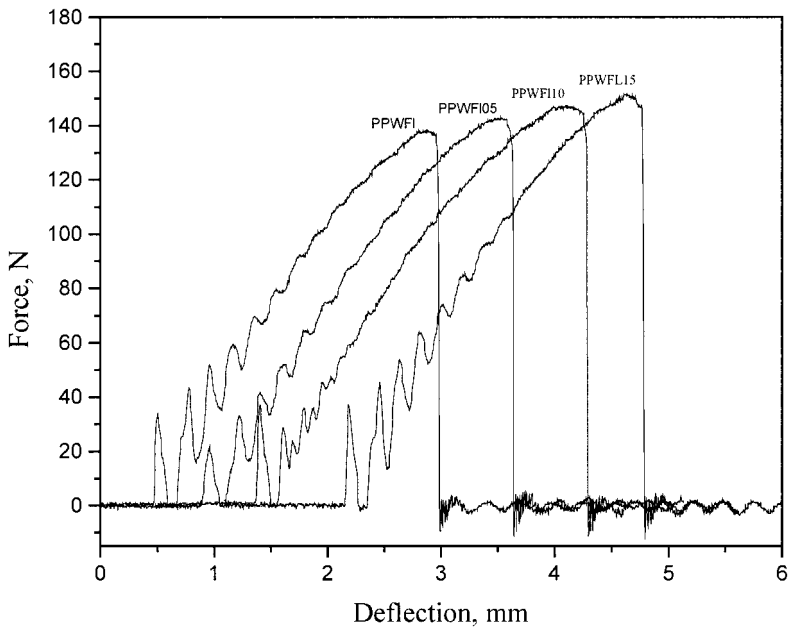

Figure 7 Force-deflection (*F-d*) curves of PP wood fiber composites.

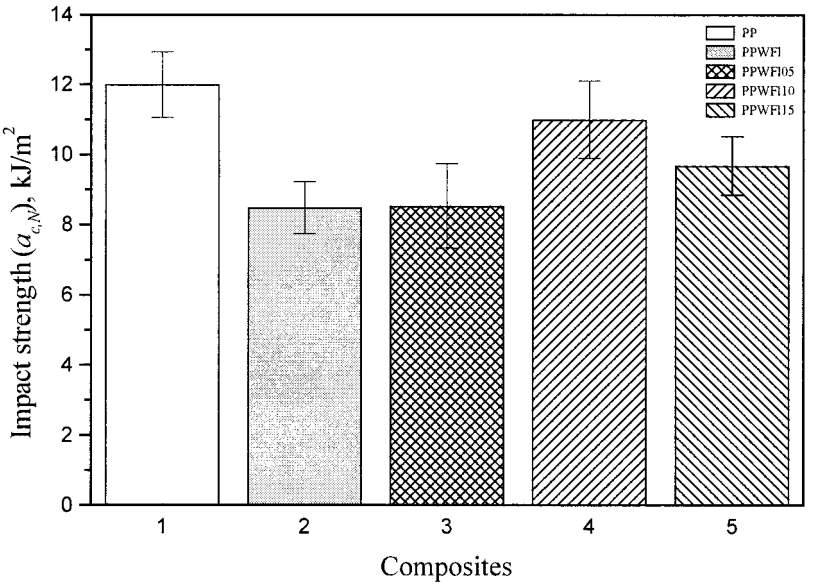

Figure 8 Charpy notched impact strength (a_{cN}) of PP wood flour composites.

ture, thus on the deformation mechanism and mechanical properties of the composites. It was established that, with addition of maleated polypropylene containing 1 wt % grafted maleic anhydride, a composite with optimal mechanical properties was obtained. The deformation mechanism of the unmodified PP wood flour composite characterizes with voids formation and brittle fracture of the matrix, wood particles debonding, and pulling out of the PP matrix. Low concentration of maleic anhydride in the compatibilizer leads to the creation of a thin and irregular polymer layer, which assists formation of plastic deformation zone around the wood particles during tensile testing. A higher concentration of MA in the compatibilizer results in stronger interaction between the PP matrix and wood filler, which causes brittle fracture and reduced ductility of the PP matrix.

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