Polypropylene Cellulose-Based Composites: The Effect of Bagasse Reinforcement and Polybutadiene Isocyanate Treatment on the Mechanical Properties

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Received 30 May 2008; accepted 24 June 2008
DOI 10.1002/app.29189
Published online 30 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Using bagasse fiber as the reinforcing filler and polypropylene as the thermoplastic matrix polymer, a reinforced composite was prepared, and its mechanical properties examined as a function of the amount of compatibilizing agents used. In the sample preparation, four levels of fiber loading (10, 20, 30, and 40 wt %), three levels of polybutadiene isocyanate (PBNCO) content (0, 2, and 4 wt %) and two levels of maleated polypropylenes (MAPP) content (0 and 3 wt %) as compatibilizing agents were used. The tensile properties of the composites improved as the fiber loading and the compatibilizing agents increased, but the impact strength was significantly decreased. The mechanical study revealed that the positive effect of compatibilizing agents on interfacial bonding. The composites treated with PBNCO showed superior tensile and impact properties than those without treatment. The findings indicated that bagasse as agro-waste material is a valuable renewable natural resource for composite production and could be utilized as a substitute for wood in composite industries. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1684–1689, 2009

Key words: compression; fibers; mechanical properties; polypropylene; reinforcement; filler

INTRODUCTION

In recent years, cellulosic fibers have gained significant interest as reinforcing filler for commercial thermoplastics. They are now fast evolving as a potential alternative to inorganic or synthetic materials for various applications.[1,2] The technical studies suggest that cellulosic fiber composites have the potential to compete with composites reinforced with inorganic fibers.[3] Studies are ongoing to find ways to use cellulosic fibers in place of synthetic materials as reinforcing fillers.[4–8]

The mechanical properties of cellulosic fibers and its application as reinforcing filler for thermoplastic materials have being largely studied.[9–13] However, the mechanical properties of composites reinforced with high performance inorganic fibers have still not been reached.[14] This situation can be explained by the noneffective bonding between polar-hydrophilic cellulosic fibers and nonpolar-hydrophobic plastics at fiber-matrix interface that causes the mechanical properties of the composites to be lowered. A number of investigators have explored the ability of additives to enhance adhesion and thereby improve properties such as tensile and impact strength of these composite materials.[15,16] The interfacial adhesion problem can be alleviated by the use of compatibilizing agents. These compatibilizing agents become chemically linked with the hydrophilic lignocellulosic filler on one side, while facilitating the wetting of the hydrophobic polymer chain on the other side. In other words, they have dual characteristics in that they possess both the hydrophilic and hydrophobic properties needed for them to adhere well with the cellulosic filler and matrix polymer. The improvement in mechanical properties is believed to be due to a better dispersion of fibers in the matrix, a more effective wetting of fibers by matrix resin and a better adhesion between the two phases.[17]

Faced with serious shortage of wood resources in developing countries, including Iran, creates interest to explore the potential application of agro-waste based composites for the wood industries.[18] Thus, several studies on the development of composites prepared using various agro-waste materials is being actively pursued.[16,19] Among the possible alternatives, the development of composites using bagasse fibers (BFs), as reinforcing fillers, and thermoplastic polymers, as matrices, is currently at the center of attention in Iran. Bagasse is one of the renewable agro-waste materials, which is a by-product from the sugar cane industry. About 32% of bagasse is produced from every tone of sugar cane been

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processed. In Iran, the production of bagasse is estimated to be around 2.5 million tones per year. Many studies have been carried out on the utilization of bagasse, such as in particleboards,[20,21] medium density fiberboard,[22,23] pulp,[18,24] and composites.[25–27]

In this study, the thermoplastic polymer, polypropylene was used as the matrix polymer and the agro-waste, bagasse fiber was used as the reinforcing filler to prepare a reinforced composite. Recent work[1,28–35] suggests that the use of maleated polypropylene (MAPP) significantly improves the fiber-matrix bonding. Maldas and Kokta,[36] and Nourbakhsh et al.[19] have also reported improved mechanical properties by using polybutadiene isocyanate (PBNCO) as compatibilizing or bonding agent. The purpose of the current research was to examine the effect of the compatibilizing agents (MAPP and PBNCO) on the interfacial bonding between hydrophilic filler and hydrophobic matrix polymer. The mechanical properties of the composite were examined at different fiber loading and the amount of compatibilizing agents used.

EXPERIMENTAL

Materials

Depithed sugarcane bagasse used as reinforcing filler was supplied by local sugar cane mill. The BFs were morphologically and chemically characterized (Table I). The fibers were produced by refiner mechanical pulp (RMP) process. The wood chips were steamed for 15 min at 7 MPa and 175°C, disc refined and then dried in a laboratory-made hot air tube dryer. The BF was screened, and the particles that passed through 60 mesh (250 μm) sieve screens were used. BF was oven-dried at 95°C for 24 h to maintain less than 4 wt % moisture content and then stored in sealed plastic bags.

TABLE I
Properties of Bagasse Fiber

Chemical components	
Cellulose (%)	55.3
Lignin (%)	21.0
Extractive (%)	2.9
Ash (%)	1.9
Fiber morphology	
Length (mm)	1.7
Diameter (μm)	19.6
Aspect ratio (L/D)*	84.6

* The ratio of fiber length to its diameter.

The matrix polymer, polypropylene (PP) (Poliran P10800), having a melt flow index of 7–10 g/10 min at 190°C under 2.16 Kg load was procured from Bandar Imam Petrochemical Company, Iran. PP was in the form of pellets with a density of 0.90 g/cm^3. The compatibilizing agent, MAPP was obtained from Eastman Chemical Products; Epolene G-3003™ has an acid number of 8 and a molecular weight of 103,500. PBNCO supplied by Kaucuk, Krasol® LBD3000, prepolymer based on liquid low-molecular weight polybutadiene. This product has free toluene diisocyanate (TDI) of 1.1 wt %, NCO group content of 3 wt %, and viscosity of 120 Pa s at 25°C.

Sample preparation

Four levels of fiber loading (10, 20, 30, and 40 wt %), three levels of PBNCO content (0, 2, and 4 wt %), and two levels of MAPP content (0 and 3 wt %) were used in the sample preparation. The composites were compounded with a laboratory mixer (Brabender) and then compression-molded into plates. The PP and MAPP mixtures were first introduced into the mixer soaked at 190°C for melting. The BFs were then added into the melted resin mixture with the rotor speed of 60 rpm. The PBNCO was subsequently added and mixed for 3 min. About 7 min of mixing was required for complete dispersion of materials. The resulted mixtures (compounds) were chopped and then plates were prepared by compression molding. Compression-molded was chosen since only small quantities of material were available and to reduce the formation of voids and to improve the fiber distribution. The fibers in the plates were randomly oriented. Typical molding conditions were: press temperature 190°C, pressure during heating and cooling 3.8-4 MPa, press time 3 min and cooling time 15 min.

Mechanical properties evaluation

The tensile properties, such as tensile strength and tensile modulus were determined with an Instron Universal Testing Machine (Model 1186) using dumbbell-like shaped specimens with a thickness of 3.2 mm as per the ASTM D 638[37] test method. The tests were performed at crosshead speed of 1.5 mm/min. The Charpy impact strength was measured with Instron Impact Pendulum Tester (Model PW5) according to ASTM D 256[38] with notched samples at room temperature. Each value obtained represented the average of five samples. Mechanical properties at each experimental condition were determined and the mean value of the property is plotted against BF content in Figures 1–5.

RESULTS AND DISCUSSION

Effect of fiber loading and MAPP content on the mechanical properties

According to the previous researches, the tensile strengths of the composites increased with increasing fiber loading and compatibilizing agents.[1,19,39–42]

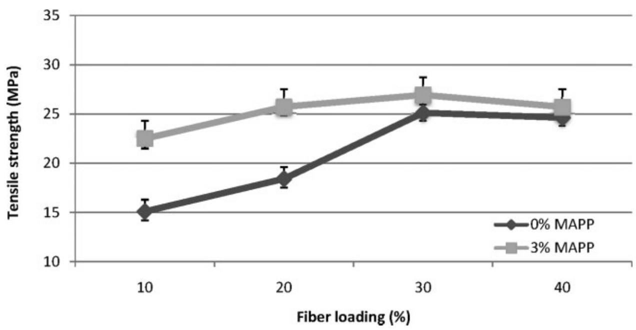

Figure 1 The effect of the BF loading and MAPP content on the tensile strength.

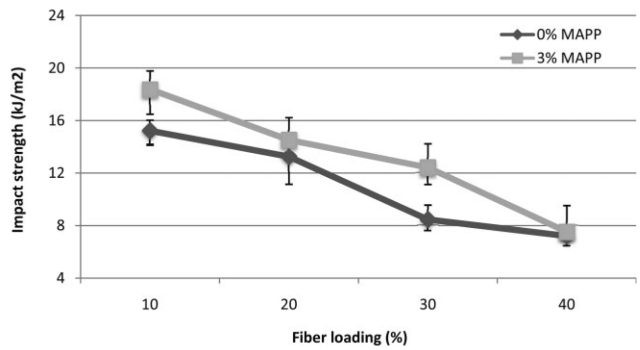

Figure 3 The effect of the BF loading and MAPP content on the notched impact strength.

It can be seen from Figure 1 that the tensile strength increases linearly with fiber content from 22.5 to 26.9 MPa. Whereas, without compatibilizer, the tensile strengths of the composites are in the range of 15 to 25 MPa at fiber loading from 10 to 40%, suggesting that, there is little stress transfer from the matrix to the fibers irrespective of the amount of fiber present. The use of MAPP improves interaction and adhesion between the fibers and matrix leading to better matrix to fiber stress transfer. Similar observations were reported by Felix and Gatenholm[17] where tensile strength of the composites increased linearly with fiber content when MAPP treated fibers were used instead of untreated fibers. Meyrs et al.[43] reported 21% increase in tensile strength for a 50 : 50 wood flour PP composites when MAPP was used as a compatibilizer. Stark and Rowlands[44] also reported a 27% increase in tensile strength of composite prepared with 40% wood fiber and 3% MAPP.

The tensile modulus (Fig. 2) increased with the fiber content of composites both with and without compatibilizers. It is obvious that the trend of the results is almost similar to those of tensile strength. To improve the bonding strength between the fiber and the matrix polymer, compatibilizing agents were used. At lower fiber content the tensile modulus does not seem to be affected by improved adhesion. However, at higher fiber loading the tensile modulus of the composites with compatibilizer was superior to that of the composites without compatibilizer. This is expected because compatibilizers can change the molecular morphology of the polymer chains near the fiber-polymer interphase. Yin et al.[45] reported that the addition of compatibilizing agent (MAPP) even at low levels (1–2%) increases the nucleation capacity of wood fibers for PP, and dramatically alters the crystal morphology of PP around the fiber. When MAPP is added, surface crystallization dominates over bulk crystallization and a transcrystalline layer can be formed around the wood fibers. Crystallites have much higher moduli as compared to the amorphous regions and can increase the modulus contribution of the polymer matrix to the composite modulus.[46]

Izod impact strength

Figure 3 shows the notched Izod impact strengths of the composites at different fiber loading and compatibilizing agent contents. Unlike tensile properties, the Izod impact strengths of the composites decreased drastically as the fiber content increased. This result is in agreement with other studies.[1,41] The presence of wood fibers in the PP matrix provides points of stress concentrations, thus providing sites for crack initiation. Another reason for decrease in impact strength may be the stiffening of polymer

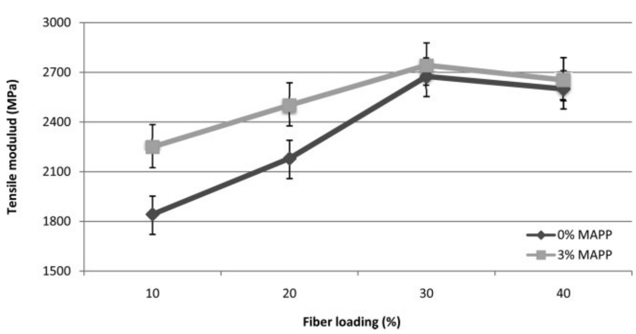

Figure 2 The effect of the BF loading and MAPP content on the tensile modulus.

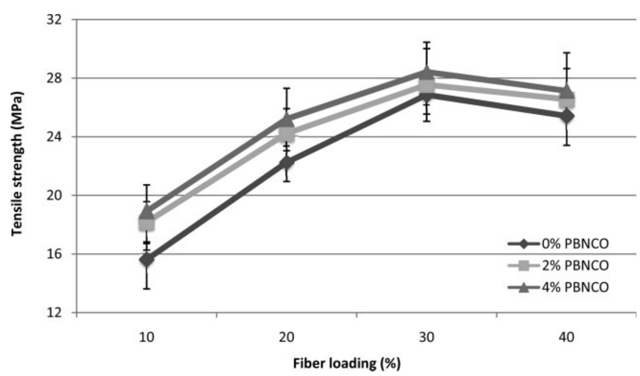

Figure 4 The effect of the BF loading and PBNCO content on the tensile strength.

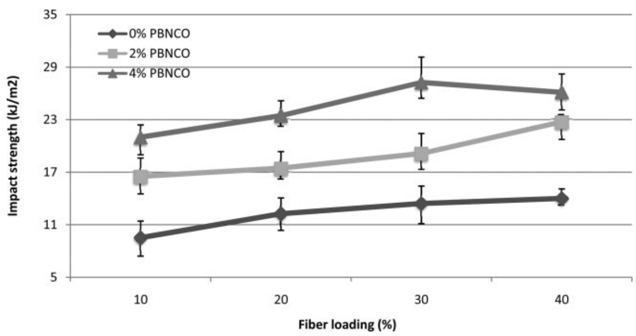

Figure 5 The effect of the BF loading and PBNCO content on the notched impact strength.

chains due to bonding between wood fibers and matrix. For high impact properties, in fact, a slightly weaker adhesion between fiber and polymer is desirable, as it would result in a higher degradation of impact energy, supporting the so-called fiber pull-out. Good adhesion on the contrary results in abrupt fiber fracture with a minor energy degradation.[40] Results as shown in Figure 3 are in agreement with this hypothesis.

Although, the compatibilizing agent had no significant effect on the impact strength, the specimen made with 3 wt % of MAPP exhibited slightly higher impact strength than the specimen made without compatibilizing agent. With the addition of the compatibilizing agent, the interfacial bonding between the fiber and the matrix polymer was improved, thus the crack was not initiated at the interface.

Poor impact strength may also be partly attributed to some thermal degradation of fiber due to high shear forces in the kneading section during compounding. However, for specific applications, the impact strength can be increased by using impact modifiers[47] or by using natural fibers having higher microfibril angle.[48]

Effect of fiber loading and PBNCO content on mechanical properties

Figure 4 shows the effect of fiber loading and the effect of PBNCO treatment on the tensile strength of the composites. Clearly, the strength increases as the BF loading is increased up to 30%. Exceeding this threshold value, the strength decreases. This indicates that the mat which is formed from BF is able to absorb stress transferred from the PP matrix. As the weight of BF in the composite sample is kept constant, an increase in the percentage of PBNCO would result in the reduction of matrix material in the composite. This study indicates that in addition to the ability of the mat to absorb stress transfer, the OH groups of BF contribute to the strength of the composites. This contribution might be in the form of OH-NCO reactions, producing urethane bonds.[49] It is a proven fact that NCO groups of PBNCO is reactive enough to react with OH from lignocellulosic materials. However, the enhancement of the properties is mostly observed for composites with up to 10–30% BF by weight or its equivalent OH groups; exceeding that the strength decreases as the % BF OH groups are increased. By comparing the strength of the untreated and isocyanate treated composites, there is an indication that the isocyanate treated samples fare better than the untreated. The reaction of BF with functional isocyanate may result in the reaction where one end would react with an OH group of BF and the other free to react with PP. This would create additional bonding to those of OH groups of EFB with isocyanate from the matrix component. This may explain why the isocyanate treated samples display better strength than those without treatment.

By looking at Figure 5, it can be seen that the notched impact strengths of the composites with isocyanate treated fibers are higher than those with the untreated fibers. This again shows that composites with treated fibers are able to absorb more energy from the matrix and distribute it more efficiently in the composite. This may be contributed to by the same factors mentioned earlier in the case of tensile properties. Overall, the results show that the impact strength increases as the percentage of BF is increased. This indicates that at high speed stress generation, as in the impact test, the linkages formed between the matrix and BF are not able to transfer the stress as well as when it is subjected to lower speed stress generation, as in tensile stress. However, those with 4% PBNCO treated fibers display the highest impact strength which may be due to the more flexible chains which could absorb and distribute energy efficiently.

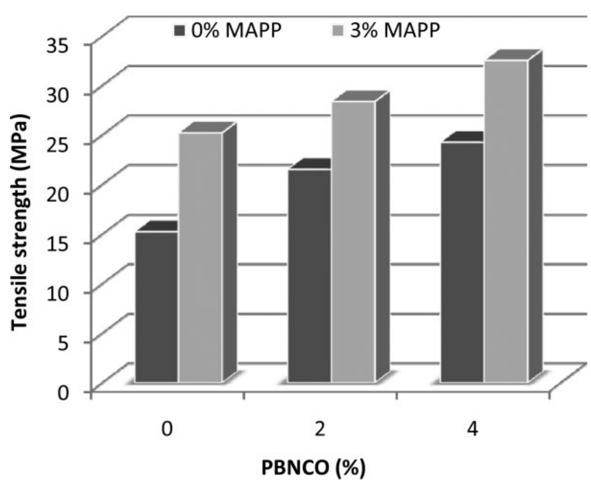

Figure 6 The effect of MAPP and PBNCO content on the notched impact strength.

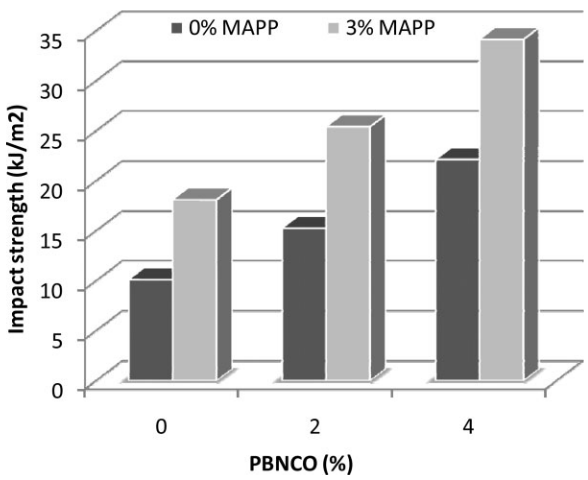

Figure 7 The effect of MAPP and PBNCO content on the notched impact strength.

Effect of PBNCO and MAPP content on the mechanical properties

Figure 6 shows the variation of tensile strength with PBNCO and MAPP concentrations. Tensile strength reveals an improvement with increase in PBNCO with a 3% MAPP concentration. A similar trend is seen in impact strength (Fig. 7). The improvement in tensile strength can be attributed to a better interfacial bonding, in the presence of PBNCO. It is worth noting that the improved interfacial bonding facilitates better load transfer to the reinforcing member and hence better tensile strength.[50,51]

CONCLUSIONS

A major issue in achieving true reinforcement from the incorporation of natural fibers is the inherent incompatibility between the hydrophilic fibers and the hydrophobic polymers, which results in poor adhesion and therefore in poor ability to transfer stress from the matrix to the reinforcing fiber. The effects of the incorporation of BF both with and without compatibilizing agents (MAPP and PBNCO) on the mechanical properties of PP composites were investigated. Mechanical properties, measured in tensile and impact tests, demonstrated that the fibers used in this work act as effective reinforcing agents for PP. The tensile strength increases linearly with fiber content from 22.5 to 26.9 MPa. Whereas, without compatibilizer, the tensile strengths of the composites are in the range of 15 to 25 MPa at fiber loading from 10 to 40%, suggesting that, there is little stress transfer from the matrix to the fibers irrespective of the amount of fiber present. From the study, it can be summarized that the utilization of BF in mat form has produced composites with acceptable properties. The properties displayed by the composites are believed to be predominantly influenced by the types of bonding produced. In general, the composites with isocyanate treated fibers show higher tensile and impact properties than those without treatment.

References

1. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. Compos Part A 2007, 38, 227.
2. Ashori, A. Bioresour Technol 2008, 99, 4661.
3. Gironès, J.; Pimenta, M. T. B.; Vilaseca, F.; de Carvalho, A. J. F.; Mutjé, P.; Curvelo, A. A. S. Carbohydrate Polym 2007, 68, 537.
4. Mishra, S.; Tripathy, S. S.; Misra, M.; Mohanty, A. K.; Nayak, S. K. Reinforced Plast Compos 2002, 21, 55.
5. Oksman, K.; Skrifvars, M.; Selin, J. F. Compos Sci Technol 2003, 63, 1317.
6. Gindl, W.; Jeronimidis, G. J Mater Sci 2004, 39, 3245.
7. Bartus, S. D.; Vaidya, U. K. Compos Structures 2005, 67, 263.
8. Sreekumar, P. A.; Kuruvilla, J.; Unnikrishnan, G.; Sabu, T. Compos Sci Technol 2007, 67, 453.
9. Lu, J. Z.; Wu, Q.; McNabb, H. S. Wood Fiber Sci 2000, 32, 88.
10. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276, 1.
11. Eichhorn, S. J.; Baillie, C. A.; Zafereiropoulos, N.; Mwaikambo, L. Y.; Ansell, M. P.; Dufresne, A.; Entwistle, K. M.; Herrera-Franco, P. J.; Escamilla, G. C.; Groom, L.; Hughes, M.; Hill, C.; Rials, T. G.; Wild, P. M. J Mater Sci 2001, 36, 2107.
12. Ashori, A.; Nourbakhsh, A. J Appl Polym Sci, to appear.
13. Cao, Y.; Goda, K.; Wu, Y. Acta Materia Compositae Sinica 2007, 24, 1.
14. Hornsby, P. R.; Hinrichsen, E.; Trivedi, K. J Mater Sci 1997, 32, 443.
15. Selke, S. E.; Wichman, I. Compos Part A 2004, 35, 321.
16. Ashori, A.; Nourbakhsh, A. Ind Crops Prod 2008, 28, 225.
17. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609.
18. Ashori, A. Polym-Plast Technol Eng 2006, 45, 1133.
19. Nourbakhsh, A.; Ashori, A.; Kouhpayahzadeh, M. Reinforced Plast Compos, to appear.
20. Vun, R. Y., Wu Q., Monlezun, C. J. Forest Prod J 2004, 54, 233.
21. Widyorini, R.; Xu, J.; Umemura, K.; Kawai, S. J Wood Sci 2005, 51, 648.
22. Lee, S.; Shupe, T. F.; Hse, C. Y. Forest Prod J 2004, 54, 71.
23. Lee, S.; Shupe, T. F.; Hse, C. Y. Holz als Roh - und Werkstoff 2006, 64, 74.
24. Adel, A. M. Appl Polym Sci 2007, 104, 1887.
25. Yachmenev, V.; Negulescu, I.; Yan, C. J Ind Textiles 2006, 36, 73.
26. Talavera, F. J. F.; Guzmán, J. A. S.; Richter, H. G.; Dueñas, R. S.; Quirarte, J. R. Ind Crops Prod 2007, 26, 1.
27. Pasquini, D.; Teixeira, Ed. M.; Curvelo, A. A. D. S.; Belgacem, M. N.; Dufresne, A. Compos Sci Technol 2008, 68, 193.
28. Kazayawoko, M.; Balatinecz, J. J.; Matuana, L. M. J Mater Sci 1999, 34, 6189.
29. Mahalberg, R.; Paajanen, L.; Nurmi, A.; Kivisto, A.; Koskela, K.; Rowell, R. M. Holz als Roh- und Werkstoff 2001, 59, 319.
30. Hon, D. N. S.; Ren, S. Reinforced Plast Compos 2003, 22, 957.
31. Li, H.; Law, S.; Sain, M. Reinforced Plast Compos 2004, 23, 1153.
32. Khalil, R.; Chryss, A. G.; Jollands, M.; Bhattacharya, S. J Mater Sci 2007, 42, 10219.
33. Yang, H. S.; Wolcott, M. P.; Kim, H. S.; Kim, S.; Kim, H. J Compos Structures 2007, 79, 369.
34. Thunwall, M.; Boldizar, A.; Rigdahl, M.; Banke, K.; Lindström, T.; Tufvesson, H.; Högman, S. Appl Polym Sci 2008, 107, 918.
35. Gu, R.; Kokta, B. V. Thermoplastic Compos Mater 2008, 21, 27.

36. Maldas, D.; Kokta, B. V. Polym-Plast Technol Eng 1990, 29, 119.
37. American Society for Testing and Materials. Annual book of ASTM standards; West Conshohocken, PA, 1999, 19428.
38. American Society for Testing and Materials. Annual book of ASTM standards; West Conshohocken, PA, 1997, 19428.
39. Maldas, D.; Kokta, B. V. Wood Fibres/Polymer Composites: Fundamental Concepts, Processes, and Material Options; Forest Product Society: Madison, WI, 1993; p 112.
40. Mueller, D. H.; Krobjilowski, A. J Ind Text 2003, 33, 111.
41. Zhang, M. Q.; Rong, M. Z.; Lu, X. Compos Sci Technol 2005, 65, 2514.
42. Ashori, A.; Nourbakhsh, A. Polym Compos 2008, 29, 574.
43. Meyrs, E. G.; Chahyadi, I. S.; Gonzalez, C.; Coberly, C. A. Wood Fibres/Polymer Composites: Fundamental Concepts, Processes, and Material Options; Forest Product Society: Madison, WI, 1993.
44. Stark, N. M.; Rowlands, R. E. Wood Fiber Sci 2003, 35, 167.
45. Yin, S.; Rials, T. G.; Wolcott, M. P. Crystallization behavior of polypropylene and its effect on wood fiber composite properties. In Fifth international conference on wood fiber-plastic composites; 1999 May 26–27; Forest Products Society: Madison, WI, 1999; p 139.
46. Sanadi, A. R.; Caulfield, D. F.; Jacobson, R. E. Paper and Composites from Agro-based Resources; CRC Lewis Publishers: Boca Raton, FL, 1997.
47. Oksman, K.; Clemons, G. J Appl Polym Sci 1998, 67, 1503.
48. Bledzki, A. K.; Gassan, J. Prog Polym Sci 1999, 24, 221.
49. Rozman, H. D.; Yeo, Y. S.; Tay, G. S.; Abubakar, A. Polymer Testing 2003, 22, 617.
50. Nourbakhsh, A.; Ashori, A. Polym Compos 2008, 29, 569.
51. Nourbakhsh, A.; Ashori, A. Polym Polym Compos 2008, 16, 283.