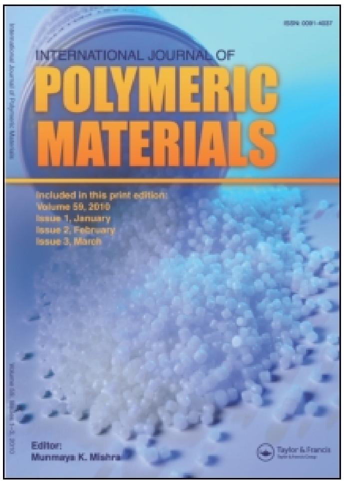

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Mechanical, Morphological and Thermal Properties of Pine Needle-Reinforced Polymer Composites

A. S. Singha[a]; Vijay Kumar Thakur[a]
[a] Material Science Laboratory, National Institute of Technology Hamirpur, Himachal Pradesh, India

To cite this Article Singha, A. S. and Thakur, Vijay Kumar(2009) 'Mechanical, Morphological and Thermal Properties of Pine Needle-Reinforced Polymer Composites', International Journal of Polymeric Materials, 58: 1, 21 — 31
To link to this Article: DOI: 10.1080/00914030802461857
URL: http://dx.doi.org/10.1080/00914030802461857

International Journal of Polymeric Materials, 58:21–31, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030802461857

Mechanical, Morphological and Thermal Properties of Pine Needle-Reinforced Polymer Composites

A. S. Singha and Vijay Kumar Thakur
Material Science Laboratory, National Institute of Technology
Hamirpur, Himachal Pradesh, India

In the present communication, the synthesis and characterization of pine needle (PN)-reinforced urea formaldehyde (UF) polymer matrix-based composites are being reported. These composites were prepared by compression molding technique. The composites were subjected to evaluation of mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance. These composites have been found to possess better mechanical properties than the UF polymer matrix. These properties were found to depend on the different loadings of the pine needle, and to increase until 30% loading of pine needle. Beyond this loading the mechanical properties decrease. Morphological and thermal analysis of the UF matrix, fiber, and fiber-reinforced polymer composites have also been carried out.

Keywords: mechanical properties, natural fibers, pine needle, polymer matrix

INTRODUCTION

Polymeric materials, because of their properties like low density, high specific strength, low abrasion, and high corrosion resistance, are being preferred over traditional materials like metals and ceramics [1–4]. Polymer composites were developed during the 1940s for military and aerospace applications. Since then considerable

Received 9 July 2008; in final form 3 August 2008.

We express our sincere thanks to Director, National Institute of Technology Hamirpur (H.P.) INDIA for providing the basic laboratory facilities. Financial assistance from University Grant Commission (New Delhi) provided through grant no. F.NO.-30-80/2004 (SR) is acknowledged.

Address correspondence to A. S. Singha, Material Science Laboratory, National Institute of Technology Hamirpur – 177005, Himachal Pradesh, India. E-mail: assingha@gmail.com

advances have been made in the use of these materials. Production of polymeric materials from renewable resources is a new area which is being explored extensively because of their eco-friendly nature [5–7]. The lignocellulose materials are now being considered as an alternative to synthetic fibers for use in various fields [8–10]. These natural fibers are being used as reinforcing materials for the synthesis of a variety of polymer matrix-based composites [11–14]. These natural fibers, obtained from a variety of resources, are able to provide the polymer composite materials a variety of benefits such as: low price, light weight, no health hazards, low density, high specific strength, less machine wear than that produced by mineral reinforcements, and a high degree of flexibility as compared to their synthetic counterparts [11–14]. It has been observed that natural fiber-reinforced polymer composites possess good mechanical properties with low specific mass [15–16]. Further more, lignocellulose fiber-reinforced composites have properties similar to those of traditional synthetic fiber-reinforced composites. Lignocellulose fibers are biodegradable and consist of carbohydrates, lignin and extraneous components. The carbohydrate portion of fiber is comprised of cellulose and hemicelluloses. Cellulose is principally responsible for the strength of natural fibers because of its high degree of polymerization and linear orientation. The process of compression molding is one of the methods to prepare natural fiber-reinforced composites. These composites are finding extensive applications in the automotive, construction and packaging industries. Among the various types of natural bio-materials, pine needle have high potential as a reinforcing material in polymer composites. Literature review has revealed that very little work has been done on the use of pine needle as reinforcing material in polymer composites. In the present article we report some of our studies on the synthesis of urea formaldehyde (UF) resin matrix-based biocomposites and evaluation of their mechanical and thermal properties.

EXPERIMENTAL

Materials and Methods

Urea, formaldehyde solution and sodium hydroxide (Qualigens Chemicals Ltd.) were used as received.

Matrix Polymer

Urea formaldehyde (UF) resin was used as matrix material.

Reinforcing Material

Pine needle collected from local sources were used as reinforcing materials. Pine needle were initially washed thoroughly with detergent solution. After this, these needles were soaked in hot distilled water for 3 h and dried for 48 h in air at room temperature. Then these fibers were further dried at 100°C for 24 h to adjust the moisture content (1–2%) and subsequently stored in a vacuum dessicator. Prior to use the pine needle were chopped into fibers of 3 mm length.

Synthesis of Urea Formaldehyde Resin

Urea formaldehyde resin was synthesized by the standard method developed in our material science laboratory [3]. The resin synthesized was then transferred to specially designed molds. Resin sheets of size 150 mm × 150 mm × 5.0 mm were prepared under pressure (4.0 MPa) by a closed-mold method as described elsewhere [4–6].

Synthesis of Polymer Composites

Dried pine needle of dimension 3 mm were mixed thoroughly with urea formaldehyde resin using mechanical stirrer with different loadings (10, 20, 30 and 40%) in terms of weight. Then, each mixture was poured into specially designed molds whose interior surfaces were coated with oleic acid to avoid adhesion of the mixture and to allow easy removal of the composites. The mixture was then spread uniformly on the surface of the mold. Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by compression molding technique [4–6]. The material was first placed in a hot open mold and left for about 5 min. Then the mold was closed. Composite sheets were prepared by hot pressing the mold at 130°C for 30 min under an applied pressure ranging from 3–4 MPa depending on the loading of reinforcing material. All the specimens were then post-cured at 130°C for 12 h.

Mechanical Properties

Tensile, compressive, flexural and wear tests were performed on specimens cut from the above fabricated polymer matrix and composite materials. For tensile, compressive and flexural strengths the measurements were carried out on a Computerized Universal Testing Machine (HOUNSFIELD H25KS). The wear testing was done on Wear & Friction Monitor (DUCOM-TR-20L). Specimens of dimension 100 mm × 10 mm × 5 mm were used for analysis. The tensile and compression tests were conducted in accordance with ASTM D 3039 and ASTM D 3410 methods, respectively. The three-point bending flexural and wear resistance tests of the composites were conducted in accordance with ASTM D 790 and ASTM D 3702 methods, respectively. Seven specimens of each sample were used for the measurement of the mechanical properties and average results are reported.

RESULTS AND DISCUSSION

Mechanism of Synthesis of Polymer Resin

The reaction between urea and formaldehyde is supposed to follow two-step reaction paths [3]. The first step involves the reaction between urea and formaldehyde to form methylol urea. Since urea is tetrafunctional the initial reaction may lead to the formation of tetramethylol derivative of urea (as shown in Figure 1a) in the

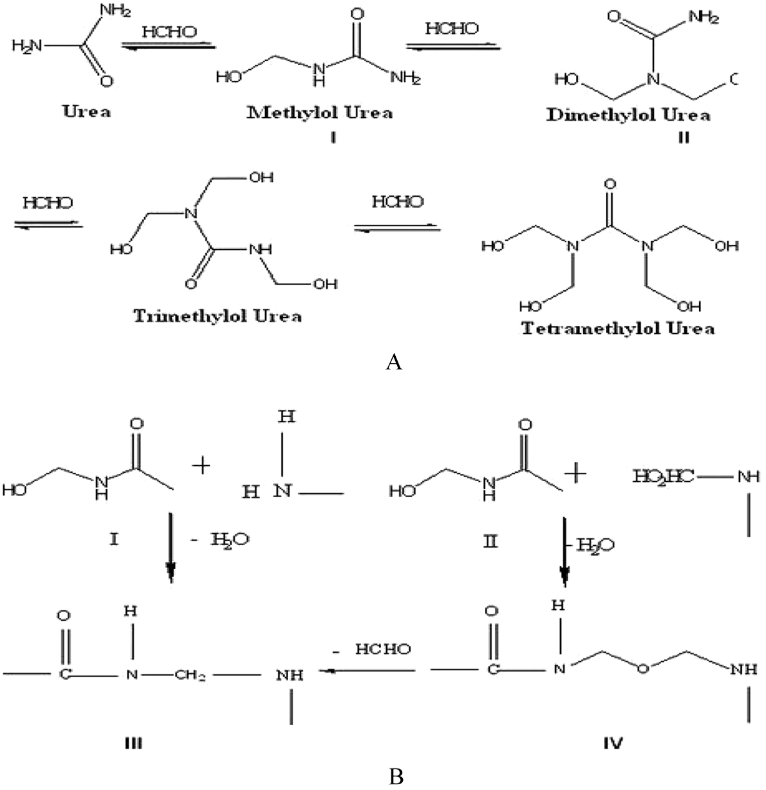

FIGURE 1 (a) Formation of methylol derivatives of urea; (b) Condensation of methylol urea by elimination.

presence of an excess of formaldehyde. The rate at which the reaction between methylol urea (I) and dimethylol urea (II) takes place depends upon temperature, pH and the ratio of formaldehyde to urea (F/U). The formation of dimethylol urea takes place in slightly alkaline conditions at a pH range of 7–8. The next step during the polymerization reaction involves condensation between the nucleophilic nitrogen of monomeric methylolurea and the electrophilic carbonyl carbon of formaldehyde to form polymer molecules. The further reaction was carried out at 80–90°C in an acidic medium to control the rate of reaction (pH 5.5–6). Under acidic conditions methylol urea condenses by the elimination of water between any of four steps (as shown in Figure 1b). The degree of crosslinking was checked at regular intervals to avoid the formation of gel at the cost of resin. Finally, the reaction was arrested by neutralization (pH 7.5–8).

Effect of Reinforcement on the Mechanical Properties of Polymer Matrix

Prior to the preparation of polymer composites, optimization of urea formaldehyde (UF) resin was done by evaluating the mechanical properties such as tensile strength, compressive strength, flexural strength and wear resistance [4–6]. It has been observed that urea formaldehyde (UF) resin in the ratio of 1.0:2.5 exhibits optimum mechanical properties. Urea and formaldehyde resins of this ratio were subsequently used for further preparation of fiber-reinforced green composites.

Tensile Strength

In the tensile strength test, UF samples of ratio 1.0:2.5 bear more load as compared to samples of other ratios. This ratio (1.0:2.5) could bear a maximum load of 128.125 N with an elongation of 1.84 mm. Further more, it has been observed that the tensile strength of the composites increases on reinforcement with pine needle. Composites with 30% wt loading bear maximum load followed by 40%, 20%, and 10% loadings. The numerical results are shown in Table 1.

Compressive Strength

In the compressive strength test, the samples of ratio 1.0:2.5 could bear a load of 991 N with a deformation of 3.51 mm. The compressive strength of the UF matrix has been found to increase when reinforced with pine needle. The compressive properties of the composites as a function of load are presented in Table 1. From the table it is evident that at first the compressive force increases with the increase in fiber

TABLE 1 Tensile, Compressive, Flexural and Wear Resistance Results of Optimized UF Resin and its Fiber-Reinforced Composites

Sample	Force (N) under tensile test	Force (N) under compression test	Force (N) under flexural test	Load (Kg) under wear test	Weight loss (Kg)
UF Resin 1:2.5	128.12	991.00	59.00	3	0.0107
Composite with 10% Loading	200.50	1775.00	80.00	3	0.00670
Composite with 20% Loading	241.47	2193.50	102.00	3	0.003242
Composite with 30% Loading	347.00	2703.00	125.00	3	0.002547
Composite with 40% Loading	305.00	2450.00	117.00	3	0.002891

content, but beyond 30% fiber content a significant decrease in compressive strength is observed.

Flexural Strength

In the flexural strength test the samples of ratio 1.0:2.5 could bear a maximum load of 59 N at a deflection of 0.776 mm. Similar trends as obtained in tensile strength and compressive strength tests have been observed for flexural strength results. The flexural properties of samples as a function of force (in terms of load) are shown in Table 1.

Wear Test

It has been observed that the wear rate of samples of ratio 1.0:2.5 was less as compared to any other ratio. Loss of material was due to abrasion and friction of the samples by the disc. The wear rate of UF matrix decreased appreciably when reinforcement was done with pine needle. Maximum wear resistance behavior was shown by composite with 30% loading (Table 1).

Stress-Strain Analysis

Stress-strain analysis gives a relationship between the applied load and the elongation/deformation/deflection of the tested material. Stress-strain behavior is determined from tensile, compressive and flexural tests. Stress is calculated as usual by dividing the applied load with the initial annular cross-sectional area, while strain is defined as the ratio of the displacement and the initial length.

Tensile Stress-Strain Curves

Tensile stress-strain curves have been constructed from the load elongation measurements. The stress-strain curves have the same

TABLE 2 Parameters Obtained from Tensile Stress-Strain Analysis at Different Loadings

Fiber loading (wt.%)	Ultimate tensile stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Tensile modulus N/mm^2
UF Resin	2.56	1.95	2.27	0.97	87.47
10%	4.01	3.25	3.84	1.34	117.92
20%	4.82	3.95	4.57	1.04	141.48
30%	6.94	5.98	6.49	1.17	207.95
40%	6.10	5.4	5.75	1.94	177.25

shape as the load-elongation curves. When the load exceeds a value corresponding to the yield strength, the specimen undergoes gross plastic deformation. It is permanently deformed if the load is released to zero. Various parameters derived from the tensile stress-strain curves are shown in Table 2.

Compressive Stress-Strain Curves

The compressive stress-strain curve has been constructed from load deformation measurements. The compressive stress-strain curve has the same shape as the load-deformation curves. Various parameters derived from the tensile stress-strain curve are shown in Table 3.

Flexural Stress-Strain Curves

Flexural stress-strain curves also have the same shape as the load-deflection curves. Various parameters derived from the tensile stress-strain curves are shown in Table 4.

The performance of natural fiber-reinforced polymer composites is controlled by the properties of the fiber-matrix bonding. Good

TABLE 3 Parameters Obtained from Compressive Stress-Strain Analysis at Different Loading

Fiber loading (wt.%)	Ultimate compressive stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Compressive modulus N/mm^2
UF Resin	19.82	18.07	19.27	1.07	340.00
10%	35.5	29.20	33.76	1.59	597.48
20%	43.87	37.48	40.95	1.46	740.83
30%	54.06	46.95	51.07	1.64	901.00
40%	49.00	42.37	47.23	1.45	830.28

TABLE 4 Parameters from Flexural Stress-Strain Analysis at Different Loading

Fiber loading (wt.%)	Ultimate flexural stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Flexural modulus N/mm^2
UF Resin	17.7	11.35	15.17	1.15	1900.77
10%	24.00	17.067	21.13	1.249	2000.00
20%	30.60	22.73	27.97	1.53	2550.00
30%	37.50	25.98	34.36	1.34	3125.00
40%	35.10	23.09	32.27	1.26	2925.00

interfacial bonding (or adhesion) is a primary requirement to ensure load transfer from matrix to reinforcement. A fundamental understanding of interfacial bonding properties and a quantitative characterization of interfacial bonding/adhesion strength helps in evaluating the mechanical behavior and capabilities of composite materials. The higher the magnitude of bonding and load transfer, the better the mechanical properties. In the case of pine needle-reinforced UF matrix-based composites, extensive bonding takes place probably between the hydroxyl/methylol groups of matrix and hydroxyl groups of lignocellulosic fiber resulting in strong structure which ultimately accounts for better mechanical properties when compared with the mechanical properties of the polymer matrix. The bonding strength also depends on the surface topology of the fiber. The adhesion/bonding between the polymer matrix and the reinforcement is a result of good wetting of the fibers by the UF matrix as well as the formation of a chemical bond between the fiber surface and the UF matrix. It has been observed that beyond 30% fiber loading there is a decrease in the mechanical properties of UF matrix-based composites. This behavior could be explained as due to more fiber–fiber contact in comparison to fiber—matrix contact at higher fiber loading, which results in decreased bonding between the fiber and matrix. In the case of tensile/compressive and flexural tests, when fiber-reinforced UF composites were subjected to a load, stress was transferred from the matrix along the fibers, which results in good mechanical properties. The uniform distribution of stress solely depends on the population and orientation of the fibers. At low levels of fiber loading, due to poor orientation of fibers, the fibers were not capable of transferring load to one another, and stress accumulated at certain points of the composite, which led to lower mechanical properties. At 30% levels of loading the population of the fibers is just right for maximum orientation, and the fibers actively participate in stress transfer and hence the best results are obtained. At higher fiber loading, agglomeration of fibers takes place which results in the partial blockage of stress transfer, and hence accounts for the lowering of mechanical properties above 30% loading.

Morphological Behavior of Biocomposites

Scanning electron microscopy (SEM) studies were carried out in order to evaluate the changes in surface morphology of the fibers and polymer matrix upon reinforcement. The excitation energy used was 5 keV. All samples were first carbon sputtered, followed by sputtering a gold palladium mixture to achieve good electric conductivity before examination. On comparison, these micrographs clearly showed the difference in the morphology of the composites when compared with the morphology of the fiber and the polymer matrix separately (Figures 2a–f). Further, the morphological results clearly show the effect of different loadings on the texture of the composites.

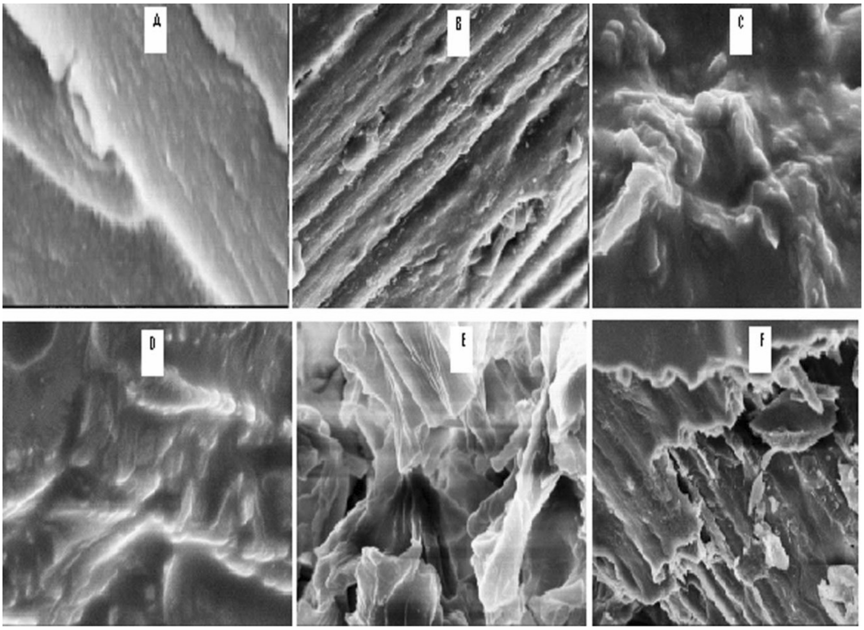

FIGURE 2 SEM images of (a) UF resin; (b) Pine needle (c, d, e, and f) composite with 10, 20, 30, and 40% loadings.

TABLE 5 Thermogravimetric Analyses of UF, PN and SF-Rnf-UF Composites

Sr. No.	Sample code	IDT (°C)	% wt loss	FDT (°C)	% wt loss	Final residue (%)
1	PN	223	23.45	507	64.44	35.66
2	UF Resin	238	22.48	995	87.51	12.49
3	SF-Rnf-UF	226	35.09	805	75.38	24.62

Thermal Analysis of Urea Formaldehyde Resin, Pine Needle and Polymer Composites

Thermogravimetric analysis (TGA) of materials such as raw pine needles, polymeric UF resin and their composites, was carried out as a function of % weight loss with the increase in temperature. In the case of raw fiber, in the beginning of the decomposition, dehydration and glucosan formation took place in the temperature range of 26.0°C to 210.0°C, followed by the cleavage of C–H, C–C and C–O bonds. The initial decomposition temperature (IDT) was found to be 223°C and the final decomposition temperature (FDT) was 507°C. On the other hand, in the case of UF resin, it is a single-stage decomposition and the observed initial decomposition temperature is 238.0°C, which the final decomposition of the resin took place at 995.0°C. It has been observed that for the composites, initial and final decomposition temperatures were 226.0°C and 800.5°C. These results indicate that the presence of cellulose fibers affects the degradation process of the biocomposites. The initial decomposition (IDT) temperature and final decomposition temperature (FDT) data are presented in Table 5. These studies were further supported by differential thermal analysis (DTA) (Table 6). The IDT and FDT values for the composite are between those of the matrix and the fiber, which indicates that the composite is thermally less stable than the resin matrix. These results are consistent with the results reported earlier [4–6].

TABLE 6 Differential Thermal Analyses of PN, UF and SF-Rnf-UF Composites

Sr. No.	Sample code	Exothermic/endothermic peaks°C (μV)
1	PN	333.2 [10.3], 478.1 [29.9]
2	UF Resin	179 [6.8], 253 [5.7], 271 [27.9], 545 [9.4], 725 [−23.0]
3	SF-Rnf-UF	79 [2.4], 266 [20]

CONCLUSIONS

Pine needle can be a potential candidate for the synthesis of natural fiber-reinforced composites. These composite materials have been found to possess appreciable mechanical strength as compared to the parent resin matrix. Percent fiber loading has been found to affect the magnitude of mechanical properties of the pine needle-reinforced UF matrix-based composites. High mechanical properties, low density and the eco-friendly nature of natural fiber have made them a good reinforcing material for the synthesis of smart composite materials.

REFERENCES

[1] Singha, A. S., Anjali, S., and Thakur, V. K., *Bulletin of Material Science* **31**, 7 (2008).
[2] Singha, A. S., Anjali, S., and Misra, B. N., *J. Polym. Mater.* **25**, 91 (2008).
[3] Singha, A. S., and Thakur, V. K. *International J. Plast. Tech.* **11**, 835 (2007).
[4] Singha, A. S., and Thakur, V. K., *Iranian Polymer Journal* **17**, 541 (2008).
[5] Kaith, B. S., Singha, A. S., Kumar, S., and Kalia, S., *Inter. J. Polym. Mater.* **57**, 54 (2008).
[6] Singha, A. S., and Thakur, V. K., *Inter. J. Poly. Mater.* **57**, 1059 (2008).
[7] Misra, B. N., Sharma, R. K., and Singha, A. S., *J. Appl. Polym. Sci.* **27**, 1321 (1982).
[8] Bhatnagar, A., and Sain, M. *J. Reinf. Plast. Compos.* **24**, 1259 (2005).
[9] Chauhan, G. S., Kaur, I., Misra, B. N., Singha, A. S., and Kaith, B. S., *Polymer Degradation and Stability* **69**, 261 (2000).
[10] Singha, A. S., and Anjali, S., *International J. Chem. Sci.* **5**, 1404 (2007).
[11] Sood, D. S., Singha A. S., and Misra, B. N., *J. Macromol. Sci. Chemistry A* **20**, 236 (1983).
[12] Bledzki, A. K., and Gassan, J., *Prog. Polym. Sci.* **24**, 221 (1999).
[13] Sapuan, S. M., and Maleque, M. A., *Materials and Design* **26**, 65 (2005).
[14] Tamer, S., *Materials and Design* **27**, 270 (2006).
[15] Kaith, B. S., Singha, A. S., and Kalia, S., AUTEX *Research Journal* **7**, 119 (2007).
[16] Jacob, M., Francis, B., Thomas, S., and Varughese, K. T., *Polymer Composites* **27**, 671 (2006).