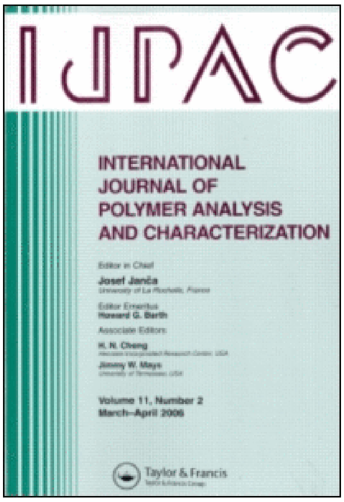

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RENEWABLE RESOURCE-BASED GREEN POLYMER COMPOSITES: ANALYSIS AND CHARACTERIZATION

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Novel "green" polymer composites were successfully synthesized from pine needles and a phenolic matrix by compression molding technique. Various weight contents (10%, 20%, 30%, and 40%) of the pine needles were incorporated in the polymer matrix. Reinforcing of the polymer matrix with pine needles was done in the form of short fibers 3 mm in length. The effect of the fiber weight contents on the mechanical properties of the polymer was investigated. Thermal analysis (TGA/DTA/DTG) and scanning electron microscopy (SEM) were used to study the thermal stability and morphology of the composite systems respectively.

Keywords: Mechanical properties; Morphological and thermal analysis; Polymer composites; Natural fibers

INTRODUCTION

During the past few years countless efforts have been aimed at the utilization of natural fibers in various polymeric materials.[1–4] Natural fiber–reinforced polymers are envisioned as an emerging new class of benevolent composite materials.[5–8] In the present era natural fiber–reinforced composites are making inroads in numerous application areas such as packaging, aerospace, automotive, and housing. Natural fiber–reinforced composites having conventional polymers as matrices have been extensively researched.[9–11] The nonbiodegradability of conventional polymers and the exhausting of petroleum resources have triggered extensive research and development in the field of biobased polymers and their applications. Currently various researchers and material scientists all over the world are focusing their attention on effective utilization of these natural fibers in polymer composites.[12–14] These fibers offer a number of advantages over synthetic fibers. The advantages of natural

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fibers over traditional reinforcing agents such as synthetic fibers are low cost, low density, easy availability, biodegradability, user friendliness, noncorrosiveness, and associated enhanced specific properties.[15–18] Greater attention is being given to the synthesis of polymer biocomposites that can help in resolving future environmental problems.[19,20] The effective utilization of natural fibers obtained from a number of renewable resources as reinforcing material in polymer matrix composites provides constructive environmental benefits and offers abundant advantages over conventional materials including lightness, resistance to corrosion, and ease of processing.[21,22]

Currently, the commercial importance of polymers has driven intense applications in the form of composites in various fields such as automotive, aerospace, marine, and infrastructure.[23–25] A polymer composite consists of two or more materials pooled in such a way that the individual materials generally are not distinguishable. The material properties of the final component are higher than that of the individual components.[26–29] Generally, all natural fibers have proven to be good reinforcements in polymer matrices. Among various types of natural biomass, *Pinus* trees are abundantly found in the Himachal Pradesh state of India. Traditionally, pine needles of these trees belonging to the Himalayan region have been used by the local people for making low-cost articles like ropes, bags, boots, socks, and mats. Also, pine needles of these trees are a major cause of fire during the summer when plants shed these needles. The burning of this biomass not only causes environmental pollution but also destroys other flora and fauna. A literature review has revealed scanty information on utilizing these pine needles as reinforcing material in polymer composites.[1–5] In the present communication we have reported the fabrication of pine needle–reinforced, resorcinol-formaldehyde (RF)–based polymer biocomposites.

The present communication presents the fabrication of green composites from biobased cellulose pine needles and resorcinol-formaldehyde (RF)–based polymer biocomposites by the compression molding technique further developed in our laboratory. Effect of fiber weight contents on the mechanical, morphological, and thermal properties of polymer matrix was studied.

EXPERIMENTAL SECTION

Materials

Resorcinol and formaldehyde solution were kindly supplied by Qualigens Chemicals Ltd and were used as received. Resorcinol-formaldehyde (RF) was used as the polymer matrix. Pine needles were collected from the National Institute of Technology-Hamirpur Campus. Pine needles 3 mm in length were used as the reinforcing material in the polymer composite.

Synthesis of Polymer Resin and Biocomposite

Resorcinol-formaldehyde resin (RF) was synthesized by the standard method developed in our Material Science Research laboratory.[16] Pine needles 3 mm in length after proper purification and drying were thoroughly mixed with resorcinol-formaldehyde resin by different fiber loadings (10, 20, 30, and 40%) in terms of weight. Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by the compression molding technique described previously.[2,3] Compression molding was performed in a hot press using a mold preheated to 50°C. Composite sheets were prepared by hot pressing the mold at 50°C for 30 min. The pressure applied ranged from 3 to 4 MPa depending on the loading of the reinforcing material. All the specimens were then post-cured at 50°C for 12 h.

Testing and Characterization

Analysis of Mechanical Properties of Polymer and Composite Samples.

Tensile Strength Test. The tensile strength test was conducted on a Hounsfield H25KS computerized universal testing machine. Specimens of dimension 100 mm × 10 mm × 5 mm were used for analysis. The tensile test was conducted in accordance with ASTM D 3039 method and at the constant strain rate of 10 mm/min.

Compressive Strength Test. The compression test was conducted in accordance with ASTM D 3410 method. The composite sample was held between the two platforms and the strain rate was fixed at 10 mm/min and the total compression range was 7.5 mm.

Flexural Strength Test. The flexural strength of samples was also tested on the computerized universal testing machine. The three-point bend flexural test was conducted in accordance with ASTM D 790 method.

Wear Test. The wear test of the sample was conducted on a Ducom-TR-20L wear and friction monitor. Wear resistance of composites was carried out per ASTM D 3702 method.

Morphological Studies. Changes in the surface morphology of the composite synthesized with different loadings were analyzed by scanning electron microscopy (SEM). The excitation energy used was 5 keV. To achieve good electric conductivity, all samples were first carbon sputtered followed by sputtering a gold palladium mixture before examination. SEM micrographs of the samples show the morphology of the green composites prepared.

Thermal Properties. Thermal analysis of polymers and other materials gives us good account of their thermal stability in order to carry out their applications in real life. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies of samples were carried out in nitrogen atmosphere on a thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Resorcinol is a very reactive compound and voluntarily combines with formaldehyde to form methylene derivative.[16] In the polymerization reaction between resorcinol polymer and formalin, the methylol group occupies the position either ortho to both hydroxyl groups or ortho to one and para to the other. The abovementioned polymerization reaction is carried out in a neutral medium as resorcinol is very reactive towards formaldehyde and forms a number of products depending upon the reaction conditions. Hence proper care must be taken while carrying out this polymerization reaction. It has been observed that methylolated resorcinol condenses with formaldehyde molecules and other resorcinol molecules to form polymeric structure. Generally in these polymerization reactions, resorcinol nuclei are joined together through methylene bridges to give a complex molecule.

In order to fabricate the pine needle–based polymer composites, first of all resorcinol-formaldehyde resin was synthesized by the standard method developed in our materials science laboratory. After synthesis of the polymer, it was optimized by taking into account mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance. It has been observed that RF samples in the ratio 1.0:1.5 exhibit optimum mechanical properties at ambient laboratory conditions. Hence this ratio (1.0:1.5) of resorcinol and formaldehyde showing optimum mechanical properties was taken for further preparation of pine needle–reinforced resorcinol-formaldehyde polymer biocomposites.

Effect of Pine Needle Reinforcement on the Mechanical Properties of RF Polymer Matrix–Based Composites

It has been observed that mechanical properties of composites increase on reinforcement with pine needles. In the tensile strength test, composites with

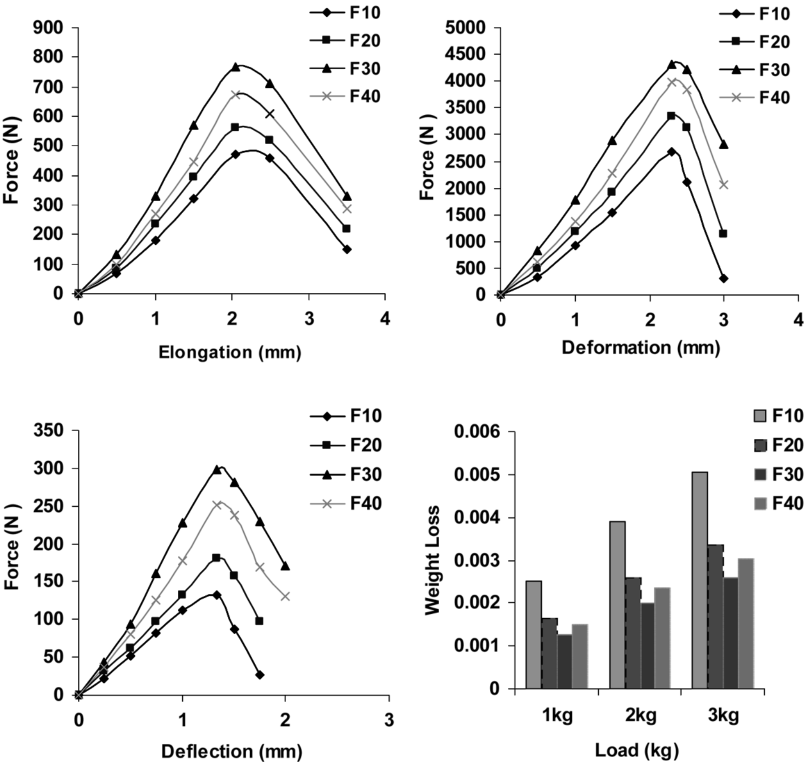

Figure 1. Load elongation/deformation/deflection and wear resistance curve of fiber–reinforced composites.

30 wt.% loading bear maximum load followed by 40, 20, and 10 wt.% (Figure 1(a)). Polymer composites with 30, 40, 20, and 10% loading bear loads of 755.87 N, 665.0 N, 550.0 N, and 461.47 N respectively.

In the compressive test (Figure 1(b)), first, force increases with the increase in fiber content, but after 30% loading a significant decrease in compressive strength is observed. It is clear from the figure that composites with 30, 40, 20, and 10% loading bear loads of 4317.0 N, 3970.8 N, 3333.7, and 2706.3 N respectively.

The flexural properties of samples as a function of force (in terms of load) and deflection are shown in Figure 1(c). Trends similar to those obtained in the tensile strength and compressive strength tests have been observed for flexural strength results. It is clear from the figure that composites with 30, 40, 20, and 10% loading bear loads of 297.32 N, 251.0 N, 131.47 N, and 181.00 N respectively.

As evident from Figure 1(d) the wear rate of the RF matrix decreases appreciably with reinforcement with pine needles. It was observed that reinforcement decreases the wear rate to a much greater extent than that of the polymer matrix alone. Maximum wear resistance behavior is shown by the composite with 30% loading followed by 40, 20, and 10% loading.

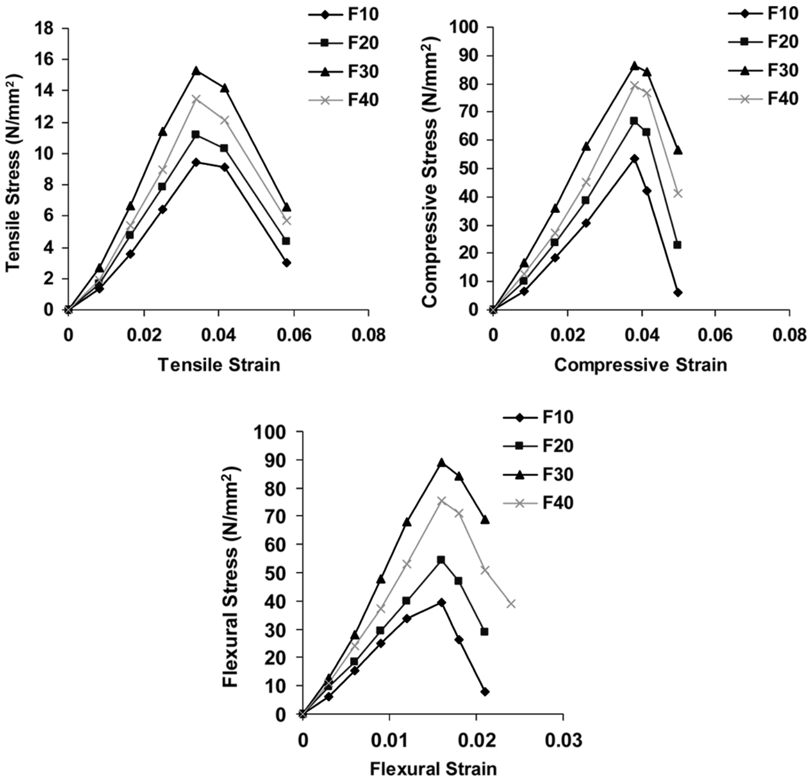

Figure 2. Tensile/compressive/flexural stress-strain curve of fiber-reinforced polymer composites.

Stress-Strain Analysis

The stress-strain curves of these composites have the same shape as the respective load-elongation/compression/deflection curve (Figure 2(a)–(c)).

From the tensile/compressive/flexural stress-strain curves, various parameters such as ultimate tensile stress (N/mm^2), yield strength (N/mm^2), fracture stress (N/mm^2), and modulus are obtained, shown in Tables I–III.

From these results it is clear that interfacial strength between the cellulosic pine needles and polymer matrix is the most indispensable factor for achieving good fiber reinforcement. The interface acts as a "binder" and transfers the load between the matrix and the reinforcing fibers. Different degrees of reinforcement effects are achieved by the addition of pine needles to polymer matrix. This may be due to the different adhesion strength between matrices and fibers. The adhesion is due to formation of hydrogen bonds with hydroxyl groups available on the fiber surface. Still higher bond strength obtained for the RF resin matrix is due to the possible reaction between the methylol groups of the resin and the hydroxyl group of

Table I. Parameters obtained from tensile stress-strain curve 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
10	9.22	8.00	8.95	1.00	271.17
20	11.00	9.43	11.07	1.15	318.52
30	15.11	13.04	14.27	1.29	435.41
40	13.3	12.14	13.00	1.17	487.17

Table II. Parameters obtained from compressive stress-strain curve at different loadings

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
10	49.12	40.24	46.00	1.25	1407.21
20	66.67	57.13	62.70	1.57	1707.48
30	86.34	74.17	81.00	2.26	2233.95
40	79.40	68.57	75.47	1.33	2057.71

Table III. Parameters from flexural stress-strain curve for different loadings

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
10	039.44	030.26	035.97	1.62	2471.24
20	054.30	046.61	051.28	1.74	3402.25
30	089.24	077.49	083.57	1.58	5591.54
40	075.30	063.88	070.92	1.63	4718.04

cellulose. It has been observed that mechanical properties increase up to 30% fiber loading and then decrease. Mechanical strength of RF composites levels off at high fiber loading. This behavior can be explained on the basis that at higher fiber loading the fiber-fiber contact dominates over the resin matrix-fiber contact, which decreases the mechanical properties beyond 30% loading.

Morphological and Thermal Study of Polymer Composites

Morphological results (Figure 3(a)–(d)) clearly show that when the resin matrix is reinforced with the different loadings of fiber, morphological changes take place depending upon the interfacial interaction between the varying loadings of fiber and the resin matrix. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of raw fiber, polymeric resin, and composites are shown in Figure 4 and Table IV. The values for the composite are between the degradation temperatures observed for the matrix and for the fiber. This indicates that the presence of cellulose fibers affects the degradation process of the composites. The thermal degradation behavior of short fiber–reinforced composite is presented in Figure 4. This was consistent with the results reported earlier.[16]

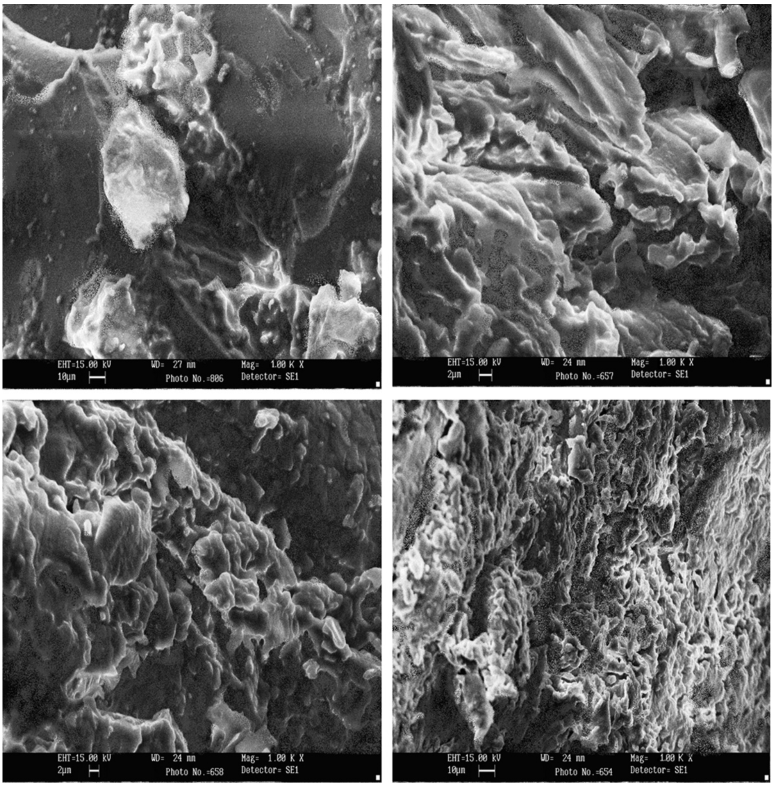

Figure 3. SEM images of pine needle-reinforced composites with 10, 20, 30, and 40% loadings.

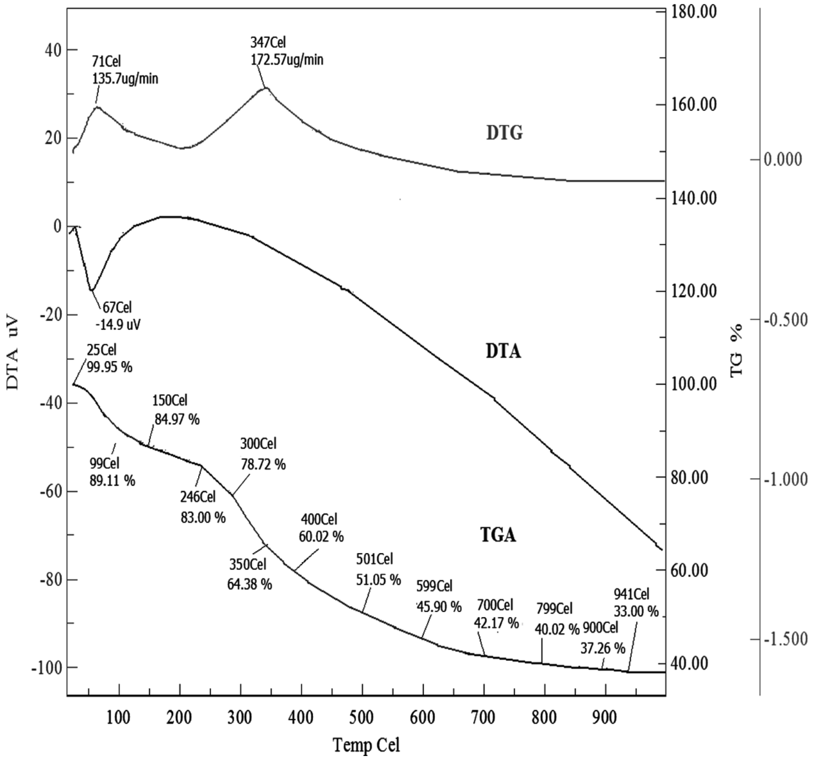

Figure 4. TGA/DTA/DTG analysis of SF-Rnf-RF composites.

Table IV. TGA/DTA analysis of RF, PN, and SF-Rnf-RF composites

No.	Sample code	IDT (°C)	% wt. loss	FDT (°C)	% wt. loss	Final residue (%)	Exothermic/endothermic peaks °C (μV)
1.	PN	223	23.45	507	64.44	35.66	333.2 [10.3]; 478.1 [29.9]
2.	RF resin	299	22.64	990	51.78	48.22	65 [−1.0]; 244 [8.0]; 280 [6.0]
3.	SF-Rnf-RF	246	17.00	941	67.00	33.00	67 [−14.9]

CONCLUSIONS

This study was focused on the fabrication of low-cost, value-added, eco-friendly biodegradable composite materials from a waste biomass such as pine needles and a polymer matrix. Our results show that these pine needles have high potential ability to work as the reinforcing material in polymer matrix. High weight content of pine needles enables the polymer composites to increase their strength in the most effective way when the pine needles are incorporated into the polymer matrix. These pine needles have the potential to be an ideal substitute of synthetic fibers for synthesis of polymer biocomposites. These composites can be future materials for the fabrication of eco-friendly materials.

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