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Synthesis and Characterization of Pine Needles Reinforced RF Matrix Based Biocomposites

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Abstract: Synthesis and characterization of pine needles reinforced thermosetting resin (Resorcinol-Formaldehyde) which is most suitable as composite matrix has been reported. The polycondensation reaction between resorcinol and formaldehyde (RF) in different molar ratios has been applied to the synthesis of RF polymer matrix. A thermosetting resin based composite, containing approximately 10, 20, 30 and 40% of natural fiber by weight, has been obtained by adding pine needles to the Resorcinol-Formaldehyde (RF) resin. The mechanical properties of randomly oriented intimately mixed particle reinforced (Pine needles) composites were determined. Effect of fiber loading in terms of weight % on mechanical properties such as tensile, compressive, and flexural and wear properties have also been evaluated. The reinforcing of the resin with Pine needles was accomplished in particle size of 200 micron by employing optimized resin. Present work reveals that mechanical properties of the RF resin increases to extensive extent when reinforced with Pine needles. Thermal (TGA/DTA) and morphological studies (SEM) of the resin, fiber and polymer composites thus synthesized have also been carried out.

Keywords: Natural fibers, Biocomposites, Reinforcement, Mechanical properties.

Introduction

At present there is a mounting need to develop natural fiber based products¹⁻². In the last few years, the production of polymeric material from renewable resources such as natural fibers has been a topic of major research efforts due to the increasing environmental awareness throughout the world³⁻⁶. Natural fibers abundantly found in nature are now considered as most suitable

material for use in various fields due to their enormous eco-friendly advantages. These natural fibers obtained from various resources are able to impart the polymer composite materials with various benefits such as: no health hazards; low price, relatively high specific strength, low density; light weight, less machine wear than that produced by mineral reinforcements; and a high degree of flexibility as compared to their synthetic counterparts⁷⁻¹⁰. It has been observed that mechanical properties of the polymer matrices are improved to a significant extent when natural fibers are incorporated in this matrices¹¹⁻¹². It has been observed that the behavior of natural fibers generally depends on different factors such as source of fiber, harvest period, weather variability, the quality of the soil, the climate at the specific geographic location, and preconditioning. Depending on the origin in thereof, natural fibers can be classified as seed, bast, leaf or fruit fibers. Polymer composite are materials made by embedding fibers in a polymeric matrix material to improve its mechanical, thermomechanical, electrical, and sound-damping properties, among others. Common uses range from aerospace, automotive and military applications to applications in sports equipment and civil infrastructure.

Among various types of natural biomasses, pinus trees are abundantly found in Himachal Pradesh. Pine needles of these trees are a major cause of fire during summer season when plants shed these needles. The burning of this biomass causes not only environmental pollution but also destroy the other flora and fauna. The literature review has revealed that a very little work has been done on utilizing these pine needles as reinforcing material in the polymer composites. Though the Himachal Pradesh is full of natural biomass yet this precious wealth of nature is not exploited for better end products. In the present communication we have reported the fabrication of pine needles reinforced, Resorcinol-formaldehyde (R-F) based polymer biocomposites.

Experimental

Material and fabrication

Resorcinol-formaldehyde resin (RF) was synthesized by the standard method developed in our Applied Chemistry Research laboratory¹³. Pine needles of dimension (200 micron) 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 compression molding technique described somewhere else². 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 ranges from 3-4 MPa depending on the loading of reinforcing material. All the specimens were then post cured at 50°C for 12h.

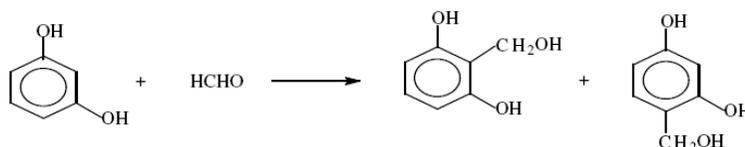
Test methods

Tensile, compressive and flexural strength tests were performed on Computerized Universal Testing Machine (HOUNSFIELD H25KS). Tensile test was conducted in accordance with ASTM D 3039 method. The specimens of dimension 100 mm × 10 mm × 5 mm were used for analysis. Compression strength test was conducted in accordance with ASTM D 3410 method. The three-point bend flexural test was conducted in accordance with ASTM D 790 method. The wear test of the sample was conducted as per ASTM D 3702 method on Wear & Friction Monitor (DUCOM- TR-20L). Weights of the samples were taken on Shimadzu make electronic balance (LIBROR AEG- 220), curing of samples was done on compression molding machine (SANTECH INDIA Ltd) thermal studies were carried out on thermal analyzer (Perkin Elmer) and SEM micrographs were taken on (LEO 435VP).

Results and Discussion

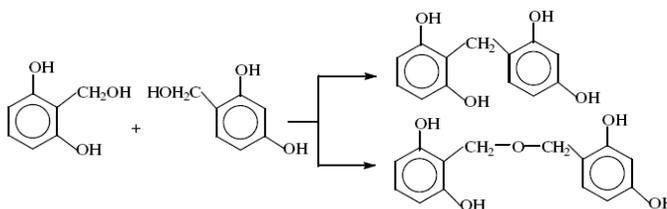
Mechanism of synthesis of resorcinol – formaldehyde resin

Resorcinol is a reactive compound and readily combines with formaldehyde to form methylene derivative¹⁴. In this reaction methylol group occupy either the position *ortho* to both hydroxyl groups or *ortho* to one and *para* to other as shown in scheme 1.

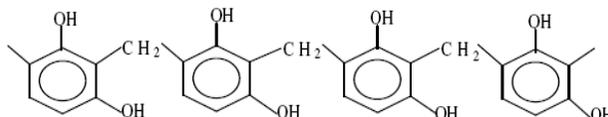


Scheme 1. Formation of methylol derivative

The reaction is carried out in neutral medium as resorcinol is very reactive towards formaldehyde. Hence, proper care must be taken while carrying out the reaction. Methylolated resorcinol condense with formaldehyde molecules and other resorcinol molecules to form polymeric structure as shown in scheme 2. In this reaction resorcinol nuclei are joined together through methylene bridges to give complex molecule. Complete methylene bridging is shown in scheme 3



Scheme 2. Condensation reaction between methylated resorcinol to form polymeric structure



Scheme 3. Methylene bridging in polymerized resorcinol molecules.

Optimization of resorcinol – formaldehyde resin

Optimization of Resorcinol-formaldehyde resin was done by taking the mechanical properties such as tensile strength, compressive strength, flexural strength and wear resistance into consideration. It has been observed that in case of tensile strength test RF samples of ratio 1.0: 1.5 bear more load at a particular applied load as compared to samples of other ratios. This ratio (1.0:1.5) could bear a load of 250.8 N with an extension of 2 mm (Figure 1a). On the other hand, samples of other ratios bear low loads. In compressive test from the (Figure 1b) it is evident that the samples of ratio 1.0: 1.5 could bear a load of 1370 N at a compression of 2.17 mm.

From (Figure 1c) it is evident that the samples of ratio 1.0: 1.5 could bear a maximum load of 117.8 N at a deflection of 1.0 mm. Further from Figure 1d it has been observed that wear rate of samples of ratio 1.0:1.5 was less as compared to any other samples. In case of

wear test loss of material was due to abrasion and friction of samples with disc. This result also supports the tensile, compressive and flexural results. This ratio (1.0:1.5) of resorcinol and formaldehyde showing optimum mechanical properties was taken for further preparation of biomass reinforced resorcinol- formaldehyde biocomposites.

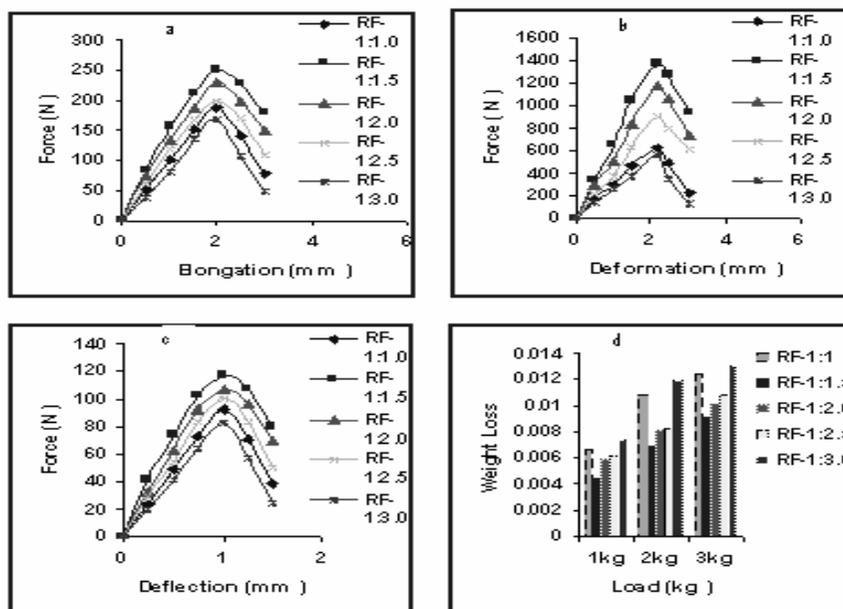


Figure 1. Load elongation/deformation/deflection & wear resistance curve of RF resin (a, b, c, d).

Effect of pine needles reinforcement on the mechanical properties of R-F polymer matrix based composites

It has been observed that mechanical properties of composites increase on reinforcement with pine needles. In tensile strength test composites with 30% wt. loading bear maximum load followed by 40%, 20%, and 10% (Figure 2a). Polymer composite with 30, 40, 20 and 10 % loading bear loads of 825.47N, 735.0 N, 620.0 N and 531.47 N respectively.

In compressive test (Figure 2b), initially force increases with the increase in fibre content but after 30% loading a significant decrease in compressive strength is observed. It is clear from the Figure that composite with 30, 40, 20 and 10 percent loading bear a load of 4527.8 N, 4170.8 N, 3523.5N & 2776.3 N respectively.

The flexural properties of samples as a function of force (in terms of load) and deflection are shown in Figure 2c. Similar trends as obtained in tensile strength and compressive strength tests have been observed for flexural strength results. It is clear from the Figure that composite with 30; 40, 20 and 10 percent loading bear a load of 363.47N, 301.0 N, 1250.0 N and 191.47 N respectively.

As evident from (Figure 2d) that wear rate of RF matrix decreases appreciably when reinforcement with pine needles. It was observed that particle reinforcement decreases the wear rate to a much more extent as compared to the polymer matrix. Maximum wear resistance behaviour is shown by composite with 30% loading followed by 40, 20 & 10% loading.

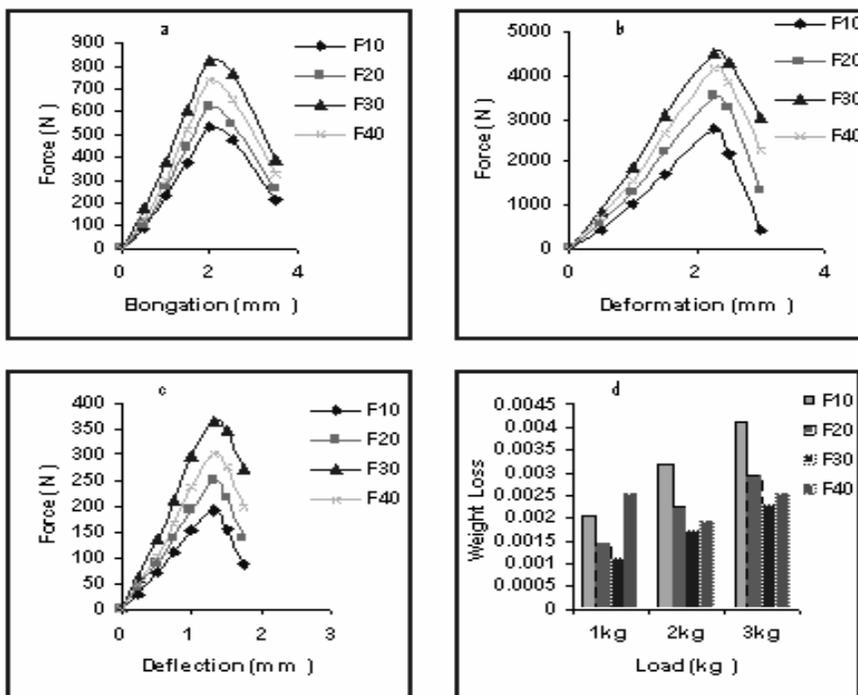


Figure 2. Load elongation/deformation/deflection & wear resistance curve of fiber reinforced composites (a, b, c, d)

The stress-strain curves of these composites have the same shape as the respective load-elongation/compression/deflection curve (Figure 3-a, b, c).

From the tensile/compressive/flexural stress-strain curve various parameters such as ultimate tensile Stress N/mm², yield strength N/mm², fracture stress N/mm² and modulus N/mm² of are obtained which are shown in Table 1-3.

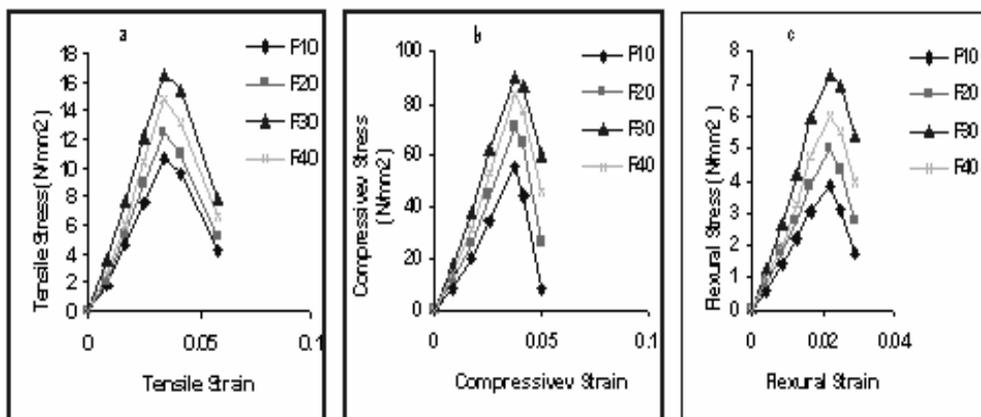


Figure 3. Stress strain curves of composites under tensile, compressive and flexural tests (a, b, c).

Table 1. 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	10.61	8.29	9.75	1.37	296.92
20	12.40	9.97	11.41	1.75	347.79
30	16.50	13.37	14.87	1.46	467.57
40	14.70	12.51	13.34	1.91	427.31

Table 2. Parameters obtained from compressive stress-strain curve 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
10%	55.53	44.56	49.7	1.89	1443.4
20%	70.47	58.40	64.9	1.94	1831
30%	90.44	76.40	83.1	2.26	2370
40%	83.40	70.57	77.93	1.99	2176

Table 3. Parameters from flexural stress-strain curve for different percentage 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
10	3.82	1.87	2.79	1.24	153.57
20	5.00	3.42	4.17	1.77	201.50
30	7.26	5.41	6.71	1.52	307.84
40	6.02	4.25	5.52	1.76	241.48

From these results it is clear that interfacial strength between the cellulosic raw fibre and polymer matrix is the most essential factor for achieving good fibre reinforcement. The interface acts as a 'binder' and transfers 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 fibre surface. Still higher bond strength obtained for RF resin matrix is due to the possible reaction between the methylol groups of the resin with the hydroxyl group of cellulose. Mechanical properties of composites increase up to 30% fibre loading and then decreases. The mechanical strength of composites levels off at high fibre loading. This behaviour can be explained by the fact that at higher fibre loading the fibre-fiber contact predominate the resin matrix-fiber contact which decrease the mechanical properties beyond 30% loading.

Morphological and thermal behaviour of polymer composites

Morphological results (Figure 4) clearly show that when resin matrix is reinforced with the different loadings of fiber, morphological changes take place depending upon the interfacial interaction between fibre and matrix.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of raw fiber, polymeric resin and composites are shown in Table 4 & 5. The values for composite are between the degradation temperatures observed for matrix and the fiber. This indicates that the presence of cellulose fibers affects the degradation process of the composites. This was consistent with results reported earlier¹⁵.

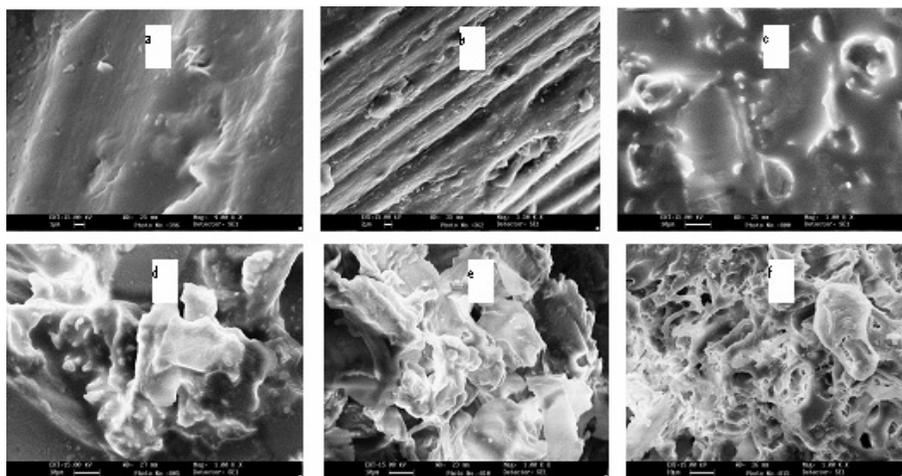


Figure 4. SEM images of (a) RF resin (b) Pine Needles (c, d, e & f) composite with 10, 20, 30 & 40% loadings.

Table 4. Thermogravimetric analysis of RF, PN and P-Rnf-RF composites

S. No.	Sample Code	IDT, °C	% wt. loss	FDT, °C	% wt.loss	Final Residue, %
1.	PN	223	23.45	507	64.44	35.66
2.	RF Resin	299	22.64	990	51.78	48.22
3.	P-rnf-RF	252	13.57	948	58.00	42.00

Table 5. Differential thermal analysis of PN, RF and P-Rnf-RF composites

S. No.	Sample Code	Exothermic/Endothermic peaks °C, μ V
1.	PN	333.2 [10.3]; 478.1 [29.9]
2.	RF Resin	65 [-1.0]; 244 [8.0]; 280 [6.0]
3.	P-Rnf-RF	84 [-11.7]

Conclusions

The mechanical properties of pine needle reinforced polymer composites have been investigated as a function of the chemical nature of matrix polymer and the content of the reinforcing material. Pine needles have a potential ability to work as the reinforcement for polymer matrix. The mechanical properties of pine needles reinforced polymer matrix are higher than that of matrix polymer. High weight content of pine needles enables the pinus composites to increase their strength in the most effective way, when the pine needles are modified into the 'particle size'. The pine needles have the potential to be an ideal substitute fiber of synthetic fibers for synthesis of green composites. These composites can be future materials for the fabrication of eco-friendly materials.

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