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Dynamic mechanical analysis, biodegradability and thermal stability of wood polymer nanocomposites

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ABSTRACT

Melamine formaldehyde-furfuryl alcohol copolymer (MFFA) and 1,3-dimethylol 4,5-dihydroxy ethylene urea (DMDHEU) were synthesized and vacuum impregnated into wood with nanoclay to prepare wood polymer nanocomposite (WPNC). MFFA, DMDHEU and WPNC were characterized by Fourier Transform Infrared Spectroscopy (FTIR). Transmittance Electron Microscopy (TEM) study confirmed impregnation of nanoclay into the composites. Treated samples showed an improvement in elastic modulus, loss modulus and damping index as indicated by dynamic mechanical analysis (DMA). The incorporation of nanoclay improved the thermal stability of the composites. The apparent activation energy for the relaxation process in the glass transition region increased with the increase in the amount of nanoclay. Untreated wood exhibited maximum biodegradability whereas polymer treated wood showed minimum biodegradability. Addition of nanoclay improved the biodegradability of the polymer treated wood samples as evidenced by decay evaluation, soil burial and scanning electron microscopy (SEM) study.

1. Introduction

Wood modification has been expedited in the last decade due to increased environmental awareness, availability of tropical hardwood species and rise in demand for a high quality timber for various engineering and structural applications so as to enhance its service life. It is, naturally available composite, composed of cellulose fiber embedded in an amorphous matrix of lignin. The carbohydrate polymeric constituents of wood contain abounding hydroxyl groups which render wood with some unfavorable properties like poor dimensional stability, mechanical strength, susceptible to rot caused by wet weather and humid condition etc.

The drawbacks associated with the properties of wood can be overcome through the formation of wood polymer composites (WPC) [1–3]. Chemical modification of wood involves bond formation between the reagents and the polymeric constituents of wood cell wall. Modification with both thermosetting resin as well as thermoplastic brings out some changes in the chemical and physical properties of the wood to a great extent. Therefore, the substrate is difficult to be recognized by the enzymes responsible for metabolizing the cell wall polymers. The moisture content of the cell wall is not enough for fungal attack due to reduction in the accessible hydroxyl groups [4,5].

Nanobased treatment of WPC offers it with potentially effective products to meet its end-use applications [6]. WPC treated with layered silicate nanoclays as in situ reinforcement has been reported to enhance its properties significantly [7]. Cai et al. has reported that WPC modified with aluminosilicate nanofillers can significantly improve the wood properties, including surface hardness, modulus of elasticity, dimensional stability and water repellence [8].

The replacement of petroleum-derived raw materials with renewable ones is very worthy and challenging. The utilization of water as a solvent instead of petroleum based diluents is of special interest from environmental point of view. Furfuryl alcohol, obtained from sugarcane bagasse, has been reported to enhance significantly the dimensional stability and durability of the treated wood [9,10]. But, the bending strength and the modulus of elasticity (MOE) of the furfuryl alcohol based composites are same as that of untreated wood [11]. The important feature of melamine formaldehyde (MF) is their ability to form hydrogen bonds which leads to dimensional, mechanical and thermal properties [12]. It is also one of the hardest polymeric resins. Therefore furfuryl alcohol can be copolymerized with MF resin to get overall improvement in the properties of the composites.

As the wood polymer nanocomposites (WPNC) can be subjected to various types of dynamic stressing during service, studies regarding the structures and viscoelastic behavior of these materials for determining their relevant stiffness and damping character-

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istics for diverse applications are of great importance [13]. The dynamic parameters such as storage modulus (E') denote the elastic part of the sample and thus describes the ability of the sample to bear a load. The loss modulus (E'') is equivalent to the dissipated energy and thus signifies the viscous response of the sample. The damping capability of the sample is denoted by the loss factor tan δ. Ornaghi et al. has performed dynamic mechanical analysis (DMA) of glass/sisal hybrid composites and reported an increase in the storage, loss modulus and shift in glass transition temperature for higher glass loading. They have also reported that an increase in activation energy for the relaxation process occurs in the glass transition region as the filler content increases [14].

Keeping the above into account, the present work has been focused to prepare MFFA copolymer and impregnate it into wood in presence of 1,3-dimethylol 4,5-dihydroxyethylene urea (DMDHEU) as crosslinker and nanoclay. The main objective is to study the dynamic mechanical analysis, thermal stability and biodegradability of the prepared composites.

2. Experimental section

2.1. Materials

Fig wood (*Ficus hispida*) was collected from a local forest. Melamine, furfuryl alcohol (FA), glyoxal and formaldehyde were purchased from Merck (Mumbai, India). Maleic anhydride was obtained from G.S. Chemical Testing Lab. & Allied Industries (India). Nanomer (clay modified by 15–35 wt.% octadecylamine and 0.5–5 wt.% aminopropyltriethoxy silane, was received from Aldrich, USA. All other chemicals used were of analytical grade.

2.2. Preparation of the MFFA and DMDHEU

Melamine and formaldehyde were taken in molar ratio of 1:3 and polymerized by bulk polymerization method at 80–85 °C by maintaining pH at 8.5–9.0 with Na_2CO_3. Furfuryl alcohol (1 mol) was added to the aqueous solution of methylol melamine followed by addition of maleic anhydride as catalyst and finally polymerized for another 45 min.

Urea (1.1 mol) was slowly added to an aqueous solution of glyoxal (1 mol) under nitrogen purge adjusting the pH to 5.5. The reaction mixture was heated to 50 °C and allowed to stir for 24 h. It was cooled to room temperature, neutralized and evaporated to near dryness by rotary evaporator to yield crude 4,5-dihydroxyethylene urea (DHEU). DHEU was added to an aqueous formaldehyde solution (1.95 mol) and pH was adjusted to 8.2–8.5. The temperature of reaction mixture was raised to approximately 50 °C, and stirred for 24 h [15].

2.3. Preparation of wood polymer composites (WPNC)

All the samples were oven dried at 105 °C to constant weight and were then taken in an impregnation chamber. Vacuum was applied for a specific time period for removing the air from the pores of the wood samples before addition of the respective prepolymeric mixture. The samples were kept immersed in the impregnation chamber for 6 h after attaining atmospheric pressure. The samples were then wrapped in aluminium foil and cured at 90 °C for 24 h in an oven. The cured samples were then Soxhlet extracted to remove homopolymers, if any, formed during impregnation.

2.4. Bacterial media

The following composition was taken for the preparation of mineral salt medium for bacterial growth. 2.0 g Na_2HPO_4, 100 mg $CuSO_4$ $7H_2O$, 4.75 g KH_2PO_4, 10 mg H_3BO_3 $5H_2O$, 10 mg MoO_3, 70 mg $ZnSO_4$ $7H_2O$, 2.0 g $(NH_4)_2SO_4$, 0.5 mg $CaCl_2$ $2H_2O$, 100 mg $MnSO_4$ $5H_2O$, 1 mg $FeSO_4$ $7H_2O$ and 1.2 g $MgSO_4$ $7H_2O$ were dissolved in 1000 mL of demineralised water. A 50 mL conical test tube was taken and to it 3 mL of this liquid culture medium was poured. It was then sterilized using autoclave at 121 °C and 15 lbf pressure for 15 min. The autoclaved media were then allowed to cool down to room temperature and WPC samples were added into the media under sterile condition inside a laminar air flow hood. Media containing only polymer samples were also cultured as negative control.

2.5. Bacterial strains

Bacillus sp. Cd-3 culture was developed by means of nutrient broth at 37 °C for 18 h. 1 mL of bacterial cultures were centrifuged at 6000 rpm for 20 min at room temperature and the pellets were washed with 0.9% NaCl and re-suspended in 1 mL of mineral salt medium. Now 0.5 mL of the culture medium containing 1×10^8/mL microbes was inoculated to the test tube containing 50 mL media for each test. The test tubes were then incubated under sterile condition at 37 °C and 100 rpm for the degradation study.

3. Measurements

The treated and untreated samples were ground and FTIR spectra were recorded by using KBr pellet in a Nicolet (Madison, USA) FTIR Impact 410 spectrophotometer.

Transmission Electron Microscopy (TEM) was performed to study the dispersion of silicate layers. An ultramicrotome fitted with a diamond knife was used for Ultrathin sectioning (approximately 100 nm thick) of the transverse film surfaces. The samples were embedded with epoxy resin for the preparations of (ultra) thin as well polished sections. The sections were stained with 1% (wt.%) uranyl acetate for sufficient contrast. The sections were then mounted on grids and examined with a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 80 kV.

The morphologies of microbial-degraded, and soil burial-degraded samples were studied by using (JEOL JSM-6390LV) scanning electron microscope at an accelerated voltage of 5–10 kV. The fractured surface of the samples was used for the study. These were sputtered with platinum and deposited on brass holder.

The DMA was performed using TA instruments Q800. Specimens were scanned over a temperature range of 25–200 °C. Frequency of the oscillation was performed at 1 Hz, 3 Hz, 5 Hz, 10 Hz ramped at 2 °C/min to 200 °C. Storage modulus, loss modulus and mechanical loss factor (tan δ) were recorded and plotted against temperature.

Thermal properties of WPCs were measured in a thermogravimetric analyser (TGA) (TGA-50, shimadzu) at a heating rate of 10 °C min^{-1}up to 600 °C under nitrogen atmosphere.

The microbial degradation was studied spectrophotometrically by using a UV visible spectrophotometer (CECIL CE7400) at 600 nm against blank culture media under sterile condition.

The hardness of the degraded samples was measured by using a durometer (model RR12) according to ASTM D2240 method and expressed as shore D hardness.

The flexural strength of the microbial-degraded, and soil burial-degraded samples was measured by UTM-HOUNSEFIELD, England (model H100K-S) with a cross head speed of 2 mm/min and by calculating the modulus of elasticity (MOE) and modulus of rupture (MOR) according to ASTM D-790 method.

MOR was calculated as follows:

$$\mathrm{MOR} = 3\,WL/2bd^2$$