Chemical Engineering Journal 247 (2014) 33–41

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Strain sensing behavior and dynamic mechanical properties of carbon nanotubes/nanoclay reinforced wood polymer nanocomposite

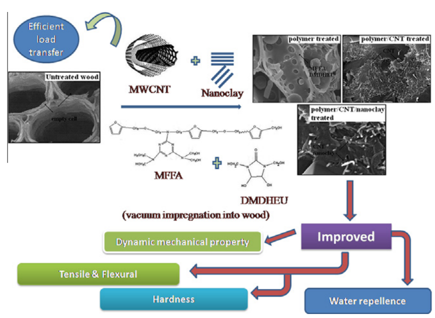
Ankita Hazarika, Tarun K. Maji *

Department of Chemical Sciences, Tezpur University, Assam 784028, India

HIGHLIGHTS

- Wood polymer nanocomposites (WPNC) were prepared by impregnation method.
- Modification of MWCNT was studied by Raman spectroscopy.
- Efficient load transfer was found from MWCNT to wood/polymer.
- WPNC exhibited an improvement in dynamic mechanical properties.
- Activation energy for the relaxation process increased for the composites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form 21 January 2014
Accepted 21 February 2014
Available online 12 March 2014

Keywords:
Wood
Nanocomposites
Multiwalled carbon nanotubes
Raman spectroscopy
Mechanical properties

ABSTRACT

Wood polymer nanocomposites (WPNC) was prepared consisting of multiwalled carbon nanotubes (MWCNT) and nanoclay by vacuum impregnation of melamine formaldehyde furfuryl alcohol copolymer and 1,3-dimethylol 4,5-dihydroxy ethylene urea, a crosslinking agent. X-ray diffraction study indicated a decrease in crystallinity of wood cellulose in the composites. Strain dependent Raman spectroscopy showed efficient load transfer from the wood/polymer to the nanotubes indicating better interfacial interaction. The surface morphology of the composites was studied by scanning electron microscope. Dynamic mechanical analysis showed an enhancement in elastic modulus, loss modulus and damping index for the WPNC. At a fixed nanoclay loading, with the increase in the content of MWCNT in the composites, the apparent activation energy for the relaxation process in the glass transition region increased. Tensile, flexural, hardness and water repellence properties improved significantly after incorporation of MWCNT into the composites.

1. Introduction

Wood polymer composites (WPC) have gained significant popularity in the recent years as it can be a replacement for solid wood due to its advantageous properties for different construction purposes and outdoor applications. The service life of wood can be enhanced through chemical modification by the use of suitable chemicals [1]. Fig wood (*Ficus hispida*), a type of softwood, is not appropriate for structural applications due to its poor dimensional, mechanical and other physical properties. This wood can be made value added by forming composites with polymers. WPC prepared by vacuum impregnation of polymers are suitable for various applications like outdoor deck floors, railings, fences, cladding and siding, park benches, window and door frames and indoor furnitures [2,3]. The application of vacuum during the process of impregnation evacuates air from the pores of the wood samples and helps in penetration of monomers and nanofillers into its empty spaces. However, the simultaneous use of the combination of vacuum and pressure leads to better penetration of polymer/

* Corresponding author. Tel.: +91 03712 267007x5053; fax: +91 03712 267005.
E-mail address: tkm@tezu.ernet.in (T.K. Maji).

http://dx.doi.org/10.1016/j.cej.2014.02.069
1385-8947/

nanofillers into the wood so as to attain further improvement in properties. The properties of WPC can be improved further by the use of nano materials.

The application of nano materials such as nanoclay and carbon nanotubes (CNT) to reinforce polymer composites has drawn the attention with the advancement of nanotechnology. Nanoclay treated WPC as in situ reinforcement has been reported to improve its properties significantly [4]. CNTs are considered to be new emergent multifunctional materials that have outstanding mechanical and thermal properties which make it a potential contender for a wide variety of applications [5]. Poor interfacial interaction between polymer and CNT as well as sturdy intermolecular Van der Waals interactions among the nanotubes render formation of its aggregates [6]. Therefore it is essential to modify the surface of CNT with some functional groups [7]. Apart from improvement in mechanical properties, incorporation of CNT in combination with nanoclay in poly(methylmethacrylate) has been reported to enhance thermal stability and flame retardancy of the composites [8]. Few reports are available pertaining to the combined use of CNT and nanoclay in WPC. Hence there is lot of scope to do further work in this area.

The use of water as a solvent has drawn special attention for a sustainable environment instead of using petroleum based diluents. Furfurylated wood results in significant improvement in dimensional stability and durability but the treated wood does not show improvement in the bending strength and the modulus of elasticity (MOE) [9]. Melamine formaldehyde resin is capable of forming hydrogen bonds leading to an improvement in dimensional, mechanical and thermal properties of the composite [10]. Therefore a copolymer of melamine formaldehyde and furfuryl alcohol (MFFA) can lead to an overall improvement in properties of the composites.

Dynamic mechanical analysis (DMA) is an effective tool to study the viscoelastic behavior of the materials under various conditions of stress, temperature for diverse applications. The dynamic parameters such as storage modulus E', loss modulus E'' and mechanical damping $\tan\delta$ of nanocomposite provide an important insight to study the interaction between wood, polymer and the nanoparticles [4].

The vibrational modes and the structure of CNTs have been widely studied by the Raman spectroscopic technique [11]. The characteristic features of Raman spectroscopy of multiwalled carbon nanotubes (MWCNT) are appearance of peak at about 1345 and 1572 cm^{-1} which can be assigned to the D-band and the G-band of MWCNT respectively [12]. D-band is associated with the scattering of an electron by phonon emission by the disordered sp^3 hybridized carbon network and the local defects that initiate from structural imperfections. G-band is related to the ordered sp^2 hybridized carbon network that is associated with the tangential C–C stretching vibration [13]. A local strain will induce in CNT as mechanical load is transmitted from polymer matrix to CNT. The C–C bond vibration that occurs due to the local strain can be analyzed by Raman spectroscopy [14].

Keeping the above in view, the present work has been aimed to prepare MFFA prepolymer and 1,3-dimethylol 4,5-dihydroxyethylene urea (DMDHEU) for impregnation into wood in presence of MWCNT and nanoclay. The main objective is to study the synergistic effect of MWCNT and nanoclay on Raman peak shift due to the strain sensing behavior of the composites under loading, DMA, tensile, flexural and water repellent properties of the prepared composites.

2. Methods

2.1. Materials

Fig wood (*F. hispida*) was collected locally. Melamine, furfuryl alcohol, glyoxal, maleic anhydride and formaldehyde were purchased from Merck (Mumbai, India). Nanomer (clay modified by 15–35 wt% octadecylamine and 0.5–5 wt% aminopropyltriethoxy silane, Aldrich, USA), and MWCNT CM-250 (5–10 nm inner diameter, 60–100 nm outer diameter, 250 μm length, Sigma Aldrich, Korea) were used as received. All other chemicals used were of analytical grade.

2.2. Modification of MWCNT

A mixture of potassium hydroxide and ethanol was prepared and 5 g of MWCNT was added to it. The reaction mixture was placed in an ultrasonic bath for 24 h at 80 °C. The resulting mixture was filtered and repeatedly washed with deionized water until the pH value reached 7. Finally it was dried overnight in vacuum oven at 45 °C. The product obtained was the MWCNT-OH.

2.3. Preparation of the MFFA copolymer

Melamine (31.53 g) and formaldehyde (60.81 ml) were taken in molar ratio of 1:3 and polymerized by bulk polymerization at 80–85 °C by maintaining pH at 8.5–9.0 with Na_2CO_3. 1 mole of furfuryl alcohol (43.40 ml) was added to the aqueous solution of methylol melamine followed by addition of maleic anhydride as catalyst and finally polymerized for another 45 min. The viscosity (at 30 °C) of different batches of MFFA copolymer thus prepared was almost similar as judged by Ubbelohde viscometer.

2.4. Preparation of DMDHEU crosslinker

The molar ratio of n(glyoxal), n(urea), n(formaldehyde) were taken as 1:1.10:1.95 for synthesis of DMDHEU. Urea (6.6 g) was added slowly to an aqueous solution of glyoxal (4.5 ml) under nitrogen purge .The pH of the reaction mixture was adjusted to a approximately 5.5. The reaction mixture was then heated to 50 °C and allowed to stir for 24 h. The reaction 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 (15.8 ml) solution and pH was adjusted to 8.2–8.5. The reaction mixture was heated to approximately 50 °C and allowed to stir for 24 h. The reaction mixture was then allowed to cool to room temperature, neutralised and kept for subsequent use [15].

2.5. Dispersion of MWCNT and nanoclay in MFFA copolymer

MWCNT and nanoclay were swelled in FA-water mixture for 24 h with mechanical stirring. FA-water mixture can swell the mixture of MWCNT as well as nanoclay and is a good solvent for the MFFA copolymer. The dispersed MWCNT and nanoclay was then sonicated for 30 min. Now MFFA was slowly added to the dispersed MWCNT and nanoclay under stirring condition. This mixture was further sonicated for 15 min and kept ready for use.

2.6. Preparation of wood polymer composites (WPC)

All the samples were cut into dimensions following ASTM (American Society for Testing and Materials) measurements and oven dried at 105 °C to constant weight and was then taken in an impregnation chamber. The samples were cut into 2.5 cm × 1 cm × 2.5 cm for water uptake test and hardness test. The wood samples for tensile and flexural test were cut into 10 cm × 0.5 cm × 2 cm and 1 cm × 1 cm × 16 cm respectively. The samples were cut into 5 cm × 1.25 cm × 0.35 cm for the dynamic mechanical analysis (DMA) test. 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