STUDIES ON MULTIFUNCTIONAL POLYMERIC NANOCOMPOSITES BASED ON POLYURETHANE-HYBRID NANOGRAPHITE

by

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ymeric nanocomposites; Nanographene;
nanomaterial

CERTIFICATE

This is to certify that the thesis entitled "**Studies on Multifunctional Polymeric Nanocomposites Based on Polyurethane-Hybrid Nanographite**" being submitted by **Mr. Amitava Bhattacharyya,** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in the department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Bhattacharyya has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

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ABSTRACT

In this study, hybrid nanographite based nanoparticles (iron coated nanographite and iron-nickel co-deposited nanographite) have been synthesized through fluidized bed electrolysis process and these hybrid nanoparticles have been dispersed in thermoplastic polyurethane (TPU) polymer to develop multifunctional (such as microwave absorbent, conducting, improved gas barrier, weather resistant, etc.) nanocomposites in the form of nanocomposite films, coatings and fibers. Nanocomposite films and coatings are produced through solution route while nanocomposite fibers are formed through melt spinning in twin screw extruder.

Nanographite was first functionalized and exfoliated before metals were deposited on it. Conc. nitric and sulfuric acid (1:3 ratio) was used to functionalize as well as intercalate nanographite in 1:40 material to liquor ratio with 1 h ultrasonic treatment followed by stirring at 600 rpm. It has been found from Fourier Transform Infrared Spectroscopy (FTIR) analysis that 24 h acid treatment (with stirring) is required for the functionalization process which results in generation of carboxyl group (–COOH) at nanographite surfaces. The rapid heating of intercalated nanographite using 2.45 GHz microwave leads to exfoliation of graphene sheets with increased surface area and pore volume. Microwave treatment of 60 s was found to be optimum with reasonable thinning of platelets and the length and width reduction were also not too high as observed in Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) studies.

The deposition of iron group metal has been carried out on functionalized and exfoliated nanographite particles through fluidized bed electrolysis where the cathode

is designed as cylindrical wire net type and anode is placed at the centre of the cell. The fluidized bed is realized using centrifugal force on bed particle i.e. acid functionalized and exfoliated nanographite. The current density, particle concentration, stirring rpm, electrolyte bath composition and deposition time have been optimized considering the quantity and quality of metal deposited on nanographite. The 200 ml bath has a capacity of 0.5 to 1 g nanographite as bed material. For uniform charge transfer from anode to cathode high rpm (more than 1000) is required. The rate of deposition is low at low current density and increases with increase in current density. However, too high current density (>0.4 Am^{-2}) leads to rapid nucleation of metals on nanographite surface which results in poor quality deposition. The deposition is initially high but after 30 min it is very slow. As the deposited iron reacts with atmospheric oxygen to form oxides, nickel deposition and iron-nickel co-deposition is also studied and the respective process parameters are optimized.

For deposition of iron 0.1 M ferrous chloride ($FeCl_2$) solution is used in the electrolyte bath, however, minimum 0.5 M nickel chloride ($NiCl_2$) solution is required for the sufficient ion concentration in nickel deposition bath. During co-deposition, an electrolyte bath of 0.5 M $FeCl_2$ and 0.5 M $NiCl_2$ was used. Nickel, being more novel material, is not deposited as high as iron. In optimized conditions, the iron coated nanographite (FeNG) particles contains approx. 40 wt% iron on total weight of the FeNG particles, while the nickel coated nanographite (NiNG) contains approx. 17 wt% nickel and the iron-nickel co-deposited nanographite (FeNiNG) contains approx. 40 wt% iron and 7 wt% nickel. These particles have been used to prepare nanocomposite films, coatings and fibers for performance evaluation.

It was observed from the optical microscope and phase image of atomic force microscope (AFM) that the combined process of 2 h ultrasonic treatment of 37 kHz and 1 h mechanical stirring at a speed of 1000 rpm was sufficient to disperse these nanoparticles in the thermoplastic polyurethane solution (30 % w/v) used to prepare nanocomposite film as well as nanocomposite coating on nylon fabric. For FeNG and FeNiNG based films the melting peaks in DSC start slightly higher than the other nanocomposite films. A 5 wt% CNF dispersed nanocomposite film shows frequency independent impedance while other nanocomposite films does not have such property though the impedance is less in compare to pure TPU film. It has been observed that the microwave reflection loss is strongly dependant on thickness of films and the filler concentration in the film. The 2 mm thick films are taken for further absorbency tests. A concentration of 10 wt% filler has been found to reduce the microwave reflection a great extent and also retained good flexibility of the films. However, at low frequency range (0.3 – 1.5 GHz), the reflection loss for all films hardly touches 10 dB i.e. the nanocomposite films are not so effective against low frequency radars. In X (8 – 12 GHz) and Ku (12 – 18 GHz) band radar frequencies, the appreciable reflection loss is observed for 10 wt% FeNG and FeNiNG based 2 mm thick film (from 8 to 14 GHz) and its performance is even comparable with one commercial hybrid nanoparticle (NiZnFerrite).

The nanocomposite coated fabrics have been characterized and their performance properties such as microwave absorbency, gas barrier, conductivity, weather resistance, etc. have been evaluated. Microwave absorbency and impedance of the nanocomposite coatings is almost similar in nature as in films. The 2 wt% CNF

dispersed nanocomposite coating is found have frequency independent impedance as the conducting network formation occurs even in 2 wt% dispersion. It has been observed that only 1 wt% of nanofillers such as NG, FeNG and FeNiNG can reduce to tackiness problem of the TPU coating. Because of the huge surface area of NiZnFerrite and layered structure of G and NG, the relative gas barrier property of these nanocomposite coated fabrics is very high in compare to pure TPU. Although, the gas barrier property is improved in case of FeNiNG and FeNG based coatings, it is not so high as compared to NiZnFerrite, G or NG based coated fabrics. The weathering resistance of the nanocomposite coatings has been examined. The strength loss for NG and FeNiNG based coatings is very low even after 30 h of UV exposure. The tendency to form oxides under humid conditions results in degradation of coating surface of FeNG based nanocomposite coatings. The flexural rigidity increase for nanocomposite coated fabrics is not so high in comparison with pure TPU coating.

In the present study, the TPU chips have been explored for their suitability for melt processing in micro twin screw extruder. The thermo-oxidative degradation of the TPU has to be minimized and nanoparticle mixing should be maximized in twin screw compounder during nanocomposite fiber extrusion. The online study of screw force during mixing of nanofillers in polymer melt and the tensile strength studies on TPU and NG based nanocomposite fibers indicate that 4 min mixing at 100 rpm screw speed and 180°C results moderate dispersion and does not initiate much degradation.

The nanoparticles were melt-mixed in the machine and subsequently drawn to develop conducting and semi-conducting nanocomposite fibers. These nanocomposite fibers were tested for their electrical conductivity as well as other

morphological features. FeNG based nanocomposite fibers show some higher onset of softening and melting peak in DSC compared to other nanocomposite fibers. The expansion of fibers under thermo mechanical analysis shows that the NG and FeNG based fibers have very good thermal stability. The d.c. conductivity of TPU fiber is in the range of 10^{-8} S/m. It increased more than 10^{3} times with very low amount of conducting nanofillers. The incorporation of nanofillers significantly decreases the impedance of nanocomposite fibers. However, even 3.5 wt% CNF can not impart conducting network in the nanocomposite fiber while 2 wt% CNF dispersed in polyurethane matrix shows excellent conductivity in form of solution cast film. It has been found that the tremendous shear experienced by the CNF fibers during mixing in TSE breaks its length substantially and although the fillers are dispersed properly, the reduction in length inhibits them to form a conducting network.

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