

**COMPARATIVE STUDIES ON DEFORMATION AND FRACTURE
BEHAVIOUR OF MULTIWALL CARBON NANOTUBE FILLED
ISOTACTIC AND ISOTACTIC-SYNDIOTACTIC MIXED
POLYPROPYLENE NANOCOMPOSITES**

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By

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Centre for Polymer Science and Engineering

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



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*Dedicated
To My
Parents*

CERTIFICATE

This is to certify that the thesis entitled “**Comparative studies on deformation and fracture behaviour of multiwall carbon nanotube filled isotactic and isotactic-syndiotactic mixed polypropylene nanocomposites**” being submitted by **Mr. Dibyendu Das**, to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in the Centre for Polymer Science and Engineering, is a record of bonafide research work carried out by him. Mr. Das 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

Two different series of multi wall carbon nanotubes (MWNT) filled polypropylene (PP) based nanocomposites viz. IPNC (i-PP/PP-g-MA/ MWNT) and ISPNC (i-PP:s-PP (70:30)/PP-g-MA/ MWNT) and two different series of functionalized-MWNT (MWNT-NH₂) filled PP based nanocomposites viz. IPNC-NH₂ (i-PP/PP-g-MA/ MWNT-NH₂) and ISPNC-NH₂ (i-PP:s-PP (70:30)/PP-g-MA/ MWNT-NH₂) were fabricated via melt mixing in a twin screw extruder in the composition range of 0–3 wt. %. The structural, morphological, thermal, rheological, mechanical, dynamic mechanical and fracture properties of the nanocomposites have been comparatively investigated. The structural aspects of the nanocomposites have been obtained by conducting Wide Angle X-ray Diffraction (WAXD) and Fourier transform infra red spectroscopy (FTIR). The details of the nanotube dispersion/distribution aspects are characterized by Transmission electron microscopy (TEM) and their possible macroscopic consequences on dynamic mechanical properties, tensile (quasi-static) mechanical response and glass transition temperatures of the nanocomposites have been discussed. Rheological percolation phenomena and transition in rheological response were discussed to understand the mechanical functioning of network morphology. Constructaion of van-Gurp Palmen plot indicated a transition in the rheological response attributed to the network morphology getting shifted to higher concentration of nanotubes in the *iso/syndio*-based nanocomposites than the only *iso*-based nanocomposites. Constitutive modeling of complex viscosity (viz. Cross model, Carreau-Yasuda model, Berzin et al. model and Dorigato et al. model) response of the nanocomposites functionally demonstrated the percolation and relaxation dynamics of polymer chains. The micromechanical properties of the nanocomposites were critically analyzed using various composite theories such as Einstein, Guth and Smallwood, Kerner, Thostenson and Qian et al. models to understand the interfacial effects and its role on the stress transfer mechanisms.

Substantial improvement of elongation at break (ϵ_b) in *iso/syndio*-based nanocomposites than the only *isotactic*-based nanocomposites are critically explained on the basis of overall reduction in crystallinity, immobilized volume fraction of the polymer chains and radius of gyration of the matrix.

Furthermore, the fracture mechanical responses of these nanocomposites have been rigorously evaluated following essential work of fracture (EWF) approach based on post-yield fracture mechanics (PYFM) principles. The fracture kinetic parameters such as crack extension (Δa), crack tip opening displacement (CTOD; δ) and crack extension rate have also been investigated. The J-integral assessments were also carried out and the methodic correspondence between PYFM and EPFM (elastic plastic fracture mechanics) has also been entailed in the thesis. The fracture kinetic parameters are quantified from the time synchronized deformation data prior to failure were acquired as images at various time scales and were overlapped to the deformation stages in the load-displacement diagrams for double edge notch tension (DENT) specimens corresponding to different compositions used in the evaluation of post-yield fracture behavior. The improvement of resistance to crack initiation and crack propagation in *iso/syndio*-based nanocomposites than the only *iso*-based nanocomposites are extensively explained on the basis of fracture kinetic parameters.

The strain field characteristics have been analyzed using the strain data recorded as a function of time during the uni-axial tension of DENT specimens by high-speed optical video-camera interfaced with a digital image correlation assisted ARAMIS-GOM software computation set-up for the real-time understanding of the dynamics of crack growth. The kinetics of crack propagation (KCP) and strain field analysis (SFA) have been discussed to understand the matrix-composition and nanotube-content dependence of fracture toughness. The thematic outcomes of

the thesis highlights on the feasibility of a new pathway to design toughened PP/MWNT based nanocomposites (by controlling crack blunting mechanism) by altering the stereo-regularity of PP from isotactic to an asymmetric blend of isotactic/syndiotactic forms or by the use of functionalized nanotubes that enables the modification of the interfacial interaction. Furthermore, the strain field analysis has been found to be uniquely successful in demonstrating the differential strain localization attributes in the various fracture process zones.

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