STUDIES ON CARBON NANOFIBER REINFORCED POLYPROPYLENE COMPOSITES

by

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CERTIFICATE

This is to certify that the thesis entitled **"Studies on Carbon Nanofiber Reinforced Polypropylene Composites"** being submitted by **Ms. Sangita Nandi** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy**, in Polymer Science and Technology, is a record of bonafide research work carried out by her. Ms. Sangita Nandi has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and 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

Carbon nanofibers (CNF) have attracted attention due to their one-dimensional structure, excellent electrical and thermal conductivity, together with their excellent mechanical properties. These novel properties of CNF have generated scientific and technical interest in the development of nanofiber-reinforced polymer composites. The performance of a composite depends largely on the dispersion behavior of the filler in polymer matrix, which depends primarily on the properties of the matrix and filler, the surface characteristics of the filler, the interface between the two components as well as the mode of stress transfer at the interface. In case of nanofillers, the dispersion presents great challenges due to their extremely small dimensions, high surface areas, and high surface energies. The dispersion of the nanofillers in polymer matrix depends on filler characteristics, interfacial properties, entanglement state of the as-received nanofibers and the flowability of the matrix resin as well as on processing conditions. Thus, evaluation of processibility of these nanofiber composites becomes important to understand both the processing behavior as well as state of dispersion.

The composites based on three different MFI grades of polypropylene (PP) were prepared in a DSM conical twin-screw microcompounder using 2%, 5% and 8% CNF concentration at 220^{0}C. The processability of carbon nanofiber (CNF) filled PP composites was analyzed through torque rheometry and oscillatory rheological studies. Dispersion of CNFs in polypropylene matrix during processing was studied w.r.t. CNF content, melt flow index (MFI) of PP, processing time and screw rpm. Attempts were made to correlate torque rheometry, morphology development and electrical resistivity to study the dispersion of CNFs during compounding. Increasing CNF loading from 2% to 5% resulted in 8 order of magnitude reductions in surface resistivity, which indicated an electrical percolation threshold at 3.5 wt% of CNF.

The melt rheological analysis of the PP/CNF composites was performed in a parallel plate rheometer at different temperatures and a frequency range of 0.05 to 50 Hz. The influence of frequency, temperature and nanofiber content on complex viscosity, storage and loss modulii and damping behavior was investigated. A shear thinning behavior at high frequencies was observed for all the compositions. Both the viscosity and modulus increased significantly at low frequencies for CNF loading more than 2wt%, suggesting an onset of pseudo-solid-like behavior due to the formation of interconnected network of CNFs (rheological percolation). The crossover frequency approached to lower value with CNF loading, which indicated higher relaxation time for the composites due to restrictions imposed by CNFs on the matrix flow behavior. Lower rheological percolation threshold as compared to electrical percolation threshold is due to the fact that denser CNF network is required for electrical conductivity, while a less dense CNF network can impede the motion of polypropylene chain.

Thermogravimetric analysis of the composites showed the samples to have negligible moisture uptake and an enhancement in resistance to thermal degradation as compared to those of the unfilled PP samples. The melting temperatures of the composites showed a slight increase as compared to unfilled PP. The non-isothermal crystallization kinetics studies indicate that the addition of CNF led to an increase in the rate of PP crystallization with no change in nucleation mechanism, as analyzed by the Avrami method. Both the Jeziorny method and Mo method described the crystallization

kinetics of composite satisfactorily. Moreover, the method proposed by Kissinger was used to evaluate the activation energy of the composites. The results showed that the activation energy of the composites decreased with increasing CNF content as well as with decreasing MFI of PP.

The tensile modulus and yield strength were found to increase with increasing concentration of CNF while elongation % decreased irrespective of MFI of PP. Although flexural modulus showed an increasing trend with CNF loading but flexural strength remain relatively independent of CNF content. Both the storage modulus (G') and loss modulus (G") increased in presence of higher CNF concentration. Although T_g was not affected much and remained almost independent of nanofiber loading, but tanδ peak became significantly broadened in presence of CNF. In general, composites based on lower MFI grade (higher molecular weight) yielded superior composite properties as compared to composites made from higher MFI grade polypropylene.

Achieving appropriate fiber/matrix adhesion is the key to imparting good mechanical properties to a polymeric composite. In order to improve the nanofiller/matrix interactions, functionalization of the nanofiller surface is essential. The functionalization of CNFs could enhance their chemical compatibility with the matrix and hence dispersion and interfacial properties are expected to improve. In this research, the chemical modification was carried out by refluxing the as-received CNF in a mixture of conc. sulphuric acid and conc. nitric acid (1:9, v/v) at 100^0C with constant stirring for different chemical treatment time. The oxidized CNF (O-CNF) was purified and characterized by FTIR spectroscopy, NaOH titration, Methylene blue adsorption and morphological analysis. The results suggest that acid oxidation leads to fiber surface etching and the

CNF lengths decreased drastically with oxidation time. The composites of 2 wt% O-CNF and PP were prepared in presence of 2 wt% of maleic anhydride grafted PP compatibilizer. The thermal, mechanical and electrical properties were evaluated and compared with those of composites made with untreated CNF. Studies on crystallization behavior indicated the nucleating action of both unmodified and chemically modified CNF. Thermogravimetric analysis indicated an increase in thermal stability of the composites. The electrical conductivity was lower than untreated CNF and was decreased with chemical treatment time because oxidation process probably damage graphitic structure of CNF and caused less number of π-electron available for electron transport. In case of O-CNF based composites, the aspect ratio was reduced due to oxidation and consequently, caused a reduction in tensile and dynamic mechanical properties.

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