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Microstructure-rheological percolation-mechanical properties correlation of melt-processed polypropylene-multiwall carbon nanotube nanocomposites: Influence of matrix tacticity combination

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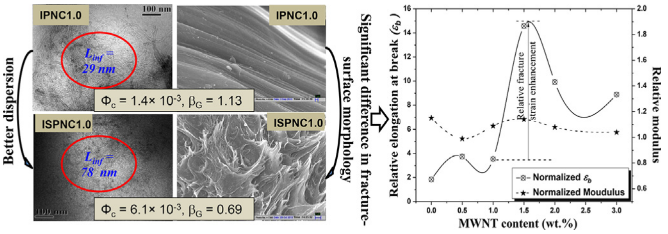
HIGHLIGHTS

- Four-fold enhancement in relative fracture strain due to tacticity modification of PP matrix.
- Rheological percolation shifts to higher loading of MWNT in stereoregularity modified PP.
- van-Gurp Palmen plot reiterates composition dependence of rheological percolation transition.
- Constitutive modeling confirms the role of strain-component in non-Newtonian flow dynamics.

GRAPHICAL ABSTRACT



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ABSTRACT

Isotactic and blend of iso-tactic: syndio-tactic (70:30) polypropylene (PP) matrices based melt-mixed PP/MWNT nanocomposites are comparatively evaluated with regard to morphological, rheological and mechanical properties. Relatively increased mean free space lengths (l_f) between nanotubes in syndio-tactic blended PP/MWNT nanocomposites with its manifestations on the rheological percolation up to a higher extent of MWNT loading ($ø_c \sim 1.4 \times 10^{-3}$ in isotactic to $ø_c \sim 6.1 \times 10^{-3}$ in iso–syndio blend) vis-à-vis enhanced normalized (~four-times) tensile failure strain has been observed. The rheological percolation confirming the formation of a mechanically responsive network structure was ascertained following the power-law relationship between storage modulus and critical volume fraction. Construction of van-Gurp Palmen plot indicated a transition in the rheological response attributed to the network morphology getting shifted to higher concentration of MWNT in the syndio-modified than the iso-unmodified nanocomposites. Constitutive modeling of complex viscosity response of the nanocomposites functionally demonstrated the percolation and relaxation dynamics of polymer chains. The T_g remained affected more by the polymer–nanotube entanglements in iso–syndio than in iso-only system. The increase in strain at break has been attributed to an overall reduction in crystallinity in the syndio-modified PP/MWNT nanocomposites.

1. Introduction

Achieving mechano-functional performance enhancement of carbon nanotube reinforced polypropylene has remained a challenge despite wide spread reports and attempts pertaining to dispersion morphology, mechanical properties, electrical and

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thermal conductivity, flame resistance and fracture and fatigue properties. However, the bulk micromechanics of such nanoscale filler incorporated composites fundamentally rests upon the nanomechanical response of the polymer–nanofiller interactions and molecular level entanglements, which may have a conceptual relevance in further understanding their intrinsic potential for various low-cost engineering and day-to-day applications. In this context compilation of the state of the art vis-à-vis efforts directed towards further increasing their strength/toughness potential are practically crucial.

From application perspectives, isotactic polypropylene (i-PP) with higher modulus and heat distortion temperature is technically more exploited than the other two stereo-specific forms, i.e., less-crystalline syndiotactic polypropylene (s-PP) and highly-amorphous waxy atactic polypropylene (a-PP) [1]. Amongst them s-PP exhibits a relatively higher toughness, lower melting point while being soft and with better clarity than i-PP. Structurally s-PP forms needle like morphologies in contrast to spherulitic morphologies in i-PP. Nevertheless when they are blended the two stereo-regular forms tend to indicate low inter-diffusion at the crystalline boundaries of the two phases as they crystallize separately. s-PP with complex polymorphic behavior when oriented exhibits unusual elasticity combined with superior electrical properties [2]. From chain dynamics point of view i-PP has a 3:1 double helix structure whereas s-PP has a 2:1 double helix conformation. These topological attributes of PP originating from their differences in stereo-regularity essentially renders them immiscible melts and thereby enabling them crystallize separately [3]. Slow crystallization rate of s-PP is normally overcome by addition of effective micro fillers like glass beads and/or talc [4] which leads to an increase in the crystallization temperature from ~69 °C to ~78 °C. Even though the glass beads filled s-PP composites have a lower Young's modulus and tensile strength as compared to i-PP, s-PP has a higher impact strength and relatively stronger interfacial adhesion between low stereo-regular s-PP and inorganic fillers [4]. Guadagno et al. [5] also reported that incorporation of *i*-PP-g-MA increases the crystallization rate of the s-PP and a further strong increase in crystallization rate with incorporation of organically modified layered silicate and the improvement of the crystallization rate of s-PP is much higher as compared to the micro-filler. Carbon nanotube filled s-PP nanocomposites reportedly show the same crystalline form I (arising from helical form I) of s-PP with different degrees of perfection viz. percentage of chain helical conformation, crystal dimension and the crystallinity, apart from exhibiting a decreasing trend of the crystallization temperature on increasing the carbon nanotube content. A similar trend is also observed in case of i-PP/MWNT nanocomposites.

Carbon nanotubes have a tendency to form agglomerate because of van der Waals force of attraction between the nanotubes and in polymer–CNT nanocomposites. These agglomerated CNTs reduce the surface area and hinder the formation of network structure, which otherwise is essential to improve the mechanical properties. Therefore the primary aim of the processing is to disperse these agglomerates to maximum possible extent. In the reported literature the most common fabricating methods of CNT/polymer composites are solution mixing via sonication of nanotubes [6], melt blending [7] and in situ polymerization [8]. Due to inherent limitations of solution mixing and in-situ polymerization techniques in terms of their complexity in sonications and solvent mediation they remain commercially nonviable and environmentally contentious. On the other hand melt processing of nanocomposites being a solvent-free process enables fast production, cost effectiveness apart from offering environmental benefits. Hence, this technique is a promising method to produce CNT filled polymer composites. Among several melt mixing methods/processes, extrusion has captured a considerable interest due to its industrial importance and effective ability to disperse the nanotubes in polymer matrix. For better dispersion of CNTs in the polymer matrices researchers have applied various techniques including surface treatment of CNTs, which is generally carried out by adopting approaches of surface treatment. The first is the surface functionalization or covalent approach or by the physically coating CNTs by some surfactant or non-covalent approach [9–12]. The second method involves sonication of CNTs in deca-hydronaphthalene solutions followed by dissolution of polypropylene granules by mechanical stirring. However, the main drawback of dissolution-sonication process is during sonication length of the CNTs decreases [13]. Lately, second phase (compatibilizer) incorporation has also become an acceptable process to disperse the CNTs in the polymer matrix. Some researchers have used PP-g-MA as a second phase [14,15]. Recently, grafting of PP onto the MWNTs has also been adopted as another process for efficient dispersion of CNTs in PP matrix [16]. It was evident from the exclusive literature reports, based on CNTs filled PP composites concerning their mechanical properties, that the incorporation of various forms of carbon nanotubes such as MWNT, SWNT, DWNT, CNF, on one hand, increases tensile modulus (Young's modulus) and tensile strength of PP based nanocomposites while on the other hand the elongation (strain) at break (ε_b) decreases significantly and even at times abruptly [17]. Theoretically ε_b is considered as a strong material performance indicator since it essentially portrays the inherent ability of the material to undergo yielding/flow that eventually manifests in the toughness of the composites. The enhancement of ε_b as a measure of fracture strain conceptually rests upon the morphology evolution, polymer–nanotube entanglements and the rheological consequences of the relative movement of polymer chains in heterogeneous nano-filled polymer systems. Therefore, the rheological percolation and its effect on the dynamics of quasi static mechanical response holds key to not only enhancing the fracture strain but also the response integrity of the polymer–nanotube network.

The influence of different types of MWNTs on rheological response of PP/MWNT nanocomposites was reported vis-a-vis their electrical properties where modeling of complex viscosity following Carreau-Yasuda model was also discussed by Chafidz et al. [18]. The assessment of rheological and mechanical properties of PP/MWNT systems prepared by master-batch dilution route was reported by Prasantha et al. [19] where a better correlation between rheological network efficiency and Charpy impact strength was established. Similarly, Lee et al. [20], while investigating PP/MWNT nanocomposites prepared by mater-batch dilution route with PP-g-MA as a compatibilizer have reported that compatibilization could effectively enhance the dispersion which in turn facilitated the attainment of a mechanically responsive polymer–nanotube network. In a unique attempt Menzer et al. [21] have investigated on the rheological percolation behavior of PP/MWNT systems with nanotubes of altered lengths during processing. It was conceptually suggested therein that to achieve a percolated network structure an effective agglomerate interaction radius depending on the dimensional characteristics of the nanotubes is crucial. In another interesting study by Teng et al. [22], the effect of MWNT content on rheological and dynamic–mechanical properties of such composites in the shear rate range of $\sim 10^2$–10^4 corresponding to extrusion and injection molding processes respectively, have concluded that the crystalline phase of PP may get significantly affected leading to an increase in T_g with increasing MWNT content. Thus the literature amply discussed on the influence of MWNT related attributes on dynamic interrelations between rheological, dynamic–mechanical and quasi-static mechanical response of the composites without any reference of the role of matrix modification (such as changes in