Polymer Testing 55 (2016) 1–9

Contents lists available at ScienceDirect

Polymer Testing

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

Material Behaviour

Multi walled carbon nanotubes induced viscoelastic response of polypropylene copolymer nanocomposites: Effect of filler loading on rheological percolation

Pawan Verma [a], Meenakshi Verma [a], Anju Gupta [a], Sampat Singh Chauhan [a], Rajender Singh Malik [a, b], Veena Choudhary [a, *]

[a] *Centre for Polymer Science & Engineering, Indian Institute of Technology Delhi, New Delhi 110016, India*
[b] *Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Murthal, Sonepat 131039, India*

A R T I C L E I N F O

Article history:
Received 25 June 2016
Accepted 1 August 2016
Available online 3 August 2016

Keywords:
Rheology
Percolation
Polypropylene random copolymer
Carbon nanotubes

A B S T R A C T

Polypropylene random copolymer nanocomposites having 0.2–7.0 vol% multi-walled carbon nanotubes (MWCNTs) were prepared via melt processing. Transmission electron microscopy (TEM) was employed to determine the nano scale dispersion of carbon nanotubes. Linear viscoelastic behavior of these nanocomposites was investigated using parallel plate rheometry. Incorporation of carbon nanotubes in the polymer matrix resulted in higher complex viscosity (η^*), storage (G') and loss modulus (G'') as compared to neat polymer, especially in the low-frequency region, suggesting a change from liquid to solid-like behavior in the nanocomposites. By plotting storage modulus vs. carbon nanotube loading and fitting with a power law function, the rheological percolation threshold in these nanocomposites was observed at a loading of ~0.27 vol% of MWCNTs. However, electrical percolation threshold was reported at ~0.19 vol% of MWCNTs loading. The difference in the percolation thresholds is understood in terms of nanotube connectivity with nanotubes and polymer chain required for electrical conductivity and rheological percolation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polypropylene random copolymer (PPCP) is a semi-crystalline polymer with high flexibility, better clarity and high impact strength than polypropylene homopolymer (PP) [1–5]. Random addition of ethylene units along the PP backbone promotes the formation of shorter stereoregular blocks which leads to hindrance in crystalline arrangement of polymer molecules, and thus low melting temperature and crystallinity [6–8]. At the same time, they exhibit essentially the same chemical resistance, water vapor barrier properties and organoleptic properties (low taste and odour contribution) as PP. PPCP is mainly being used for blow molding, injection molding and sheet extrusion applications where high clarity is a requirement. These materials are used for food packaging, medical packaging and consumer products. Many studies have already been reported for PPCP. Sahin et al. [6] reported the effect of test parameters on the mechanical properties of polypropylene random copolymer, and they observed that the properties such as the yield stress, elastic modulus and yield strain of the material increase with strain rate, while Charpy impact crack initiation and propagation resistances of the material are rather sensitive to the test temperature. Similarly, the Shore D hardness of the natural PPCP material reduces as temperature increases. Fan et al. [9] studied β-nucleated controlled rheological behavior of polypropylene random copolymer. They observed that degraded samples demonstrate better flowability than undegraded samples, while the addition of β-nucleating agent contributed less effect on the flow properties. L. d'orazio et al. [10] studied rheological and mechanical aspect of injection molded samples of isotactic polypropylene/ethylene-co-propylene (iPP/EPR) blends. They observed that better impact properties are shown by the blends containing the EPR phase with a microstructure typical of a random copolymer. The iPP/EPR blends in this article were classified as 'negative deviation blends'. Hingmann et al. [11] reported rheological properties of a partially molten polypropylene random copolymer during annealing and revealed that, as crystalline

* Corresponding author.
E-mail addresses: veenach@hotmail.com, veenac@polymers.iitd.ac.in (V. Choudhary).

http://dx.doi.org/10.1016/j.polymertesting.2016.08.001
0142-9418/© 2016 Elsevier Ltd. All rights reserved.

material content increases, the shear viscosity also increases at small shear rates, while strain hardening showed uniaxial elongation.

In recent years, to improve polymer properties and expand the application boundary of polymers, various types of fillers and additives have been incorporated in polymer matrices. Among these, carbon nanotubes (CNTs) were identified as a unique material with extraordinary thermal, mechanical, optical and electrical properties [8,12–14]. The combination of high aspect ratio, small size, very low density and, more importantly, excellent physical properties make CNTs an ideal filler for fabricating high strength, light weight polymer nanocomposites with high performance and multifunctionality [3,15–18]. Incorporation of CNTs in the polymer matrix affected the rheological, thermal, electrical and mechanical properties of the resulting composites [19–23]. Pang et al. [19] reported preparation of super-tough conducting carbon nanotube/ultrahigh-molecular-weight polyethylene (UHMWPE) composites using 2.7 vol% of HDPE for loading CNTs. The ultimate strain, tear strength, and impact strength of the composites reached 478%, 35.3 N and 58.1 kJ m^{-2}, respectively. Verma et al. [20,24] reported crystallization behavior and electrical properties of PPCP in the presence of MWCNTs. They observed that MWCNTs acted as nucleating agent and significantly affected the crystallization parameters. Electromagnetic shielding effectiveness and mechanical properties of the composites also showed a significant improvement on incorporation of MWCNTs. Addition of 4.6 vol% MWCNTs gave −47 dB attenuation and ~42% improvement in tensile strength. Seo et al. [21] reported a decrease in electrical resistivity of PP on incorporation of CNTs. The electrical percolation was achieved at a loading between 1 and 2 wt% CNTs. Gupta et al. [22] reported the rheological properties and observed an increase in storage and loss moduli on addition of MWCNTs in poly(trimethylene terephthalate) matrix. They also observed rheological percolation at lower loading ($\rho c = 0.25–1$ wt%). Du et al. [23] reported similar behavior i.e rheological percolation value at 0.12 wt% and electrical percolation at 0.39 wt% in the case of SWCNT/PMMA composites prepared via a coagulation method. The variation in percolation could be due to the dispersion and interfacial bonding of CNTs in a given polymer. A uniform dispersion of CNTs without destroying their integrity and good interfacial bonding is required to achieve significant load transfer across the CNT–matrix interface [25].

To explore the extraordinary properties of CNTs and expand the application boundary of PPCP, we aimed to investigate the effect of MWCNTs on the rheological and electrical properties of PPCP. Rheological properties of CNT/polymer composites in the molten and solid state are important for designing and/or optimizing their preparation and shaping processes i.e., processing behavior such as extrusion and injection molding. It is also important to find out the percolation threshold value as the rheological behavior of nanocomposites changes enormously before and after the percolation threshold. Percolation threshold directly relates to the material's microstructure, the state of nanotube dispersion, aspect ratio, orientation of nanotubes, and the interactions between nanotubes and polymer chains. In this work, an attempt has been made to investigate the effect of MWCNTs on the viscoelastic parameters such as complex viscosity (η^*), elastic modulus and loss modulus. Nanocomposites were prepared using a twin screw extruder (micro compounder) in which there is the provision of recirculation of polymer melt to facilitate better mixing of MWCNTs in polymer matrix. Melt recirculation has also been used by many researchers for the preparation of nanocomposites [25–30].

In our previous work, we reported the successful realization of uniform dispersion of MWCNTs upto 7.0 vol% in PPCP matrix via a continuous melt processing technique using twin screw extruder with melt recirculation [31]. In the present study, the rheological aspects of PPCP in the presence of varying amounts of MWCNTs have been investigated and an attempt has been made to develop a correlation between electrical/rheological percolation and morphology. The use of polypropylene random copolymer (in place of homopolymer) offer processing as well as economic advantages such as low cost, better mechanical properties and lower (20–30 °C less) processing temperature (energetically economical) compared to PP, along with better compatibility with fillers. Presence of more free volume facilitated higher filler loading compared to PP.

2. Experimental

2.1. Materials

PPCP [Repol R120MK] having ethylene content of 3–3.5 wt% and melt flow index 12 g/10 min (230°C/2.16 kg) was procured from Reliance Industries Limited. Multiwalled carbon nanotubes (MWCNT) were synthesized by chemical vapor deposition (CVD) using ferrocene as catalyst and toluene as a carbon source. The purity of MWCNTs was determined by recording a thermogravimetric trace in oxygen atmosphere, which gave ~96%. char yield with about 4% as impurity of iron catalyst present in the samples. The morphological characterization using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed that CNTs are multiwalled with inner and outer diameter varying from ~10 to 12 nm and ~30 to 40 nm, respectively, and a length of ~20–40 μm. The detailed procedure for the preparation and characterization of MWCNTs has been reported in our previous paper [24].

2.2. Melt compounding

PPCP/MWCNT nanocomposites were prepared by melt blending using a co-rotating HAAKE MiniLab II microcompounder under the processing conditions listed in Table 1. Before blending, MWCNT and PPCP were dried at 80 °C for 6 h to remove moisture. The test samples were prepared by compression molding with the processing parameter given in Table 1. The nanocomposites were prepared by mixing PPCP with 0, 0.2, 0.4, 0.9, 1.8, 4.6 and 7.0 vol% of MWCNTs and samples have been designated as PPCP-0, PPCP-0.2, PPCP-0.4, PPCP-0.9, PPCP-1.8, PPCP-4.6 and PPCP-7.0 respectively.

2.3. Characterization

The dynamic frequency (ω) sweep test was carried out in the frequency range of 0.01–100 rad/s and at a strain value of 1% to ensure the tests were performed under linear viscoelastic regime. Morphology of PPCP/MWCNT nanocomposites was investigated using TEM (JEOL 2100F) operating at accelerating voltage of 200 kV. For this analysis, ultra-thin sections (30–80 nm thick) of nanocomposites were prepared using a Leica Ultamicrotome. For dynamic mechanical analysis, a DMA Q800 from TA Instruments was used to study the effect of MWCNTs on the dynamic mechanical properties of PPCP. The DMA scans were recorded in the temperature range of −20–130 °C at a heating rate of 2 °C/min in a single cantilever mode at a frequency of 1 Hz. Rectangular specimens of dimensions 17.5 × 13 × 2 mm^3 were used for recording DMA scans.

3. Results and discussion

3.1. Rheological properties

Viscoelastic properties of PPCP/MWCNT composites as a function of MWCNT loading are presented in Fig. 1 which clearly reveals

Download English Version:

https://daneshyari.com/en/article/5205782

Download Persian Version:

https://daneshyari.com/article/5205782

Daneshyari.com