RHEOLOGICAL AND CONDUCTIVE PROPERTIES OF INJECTION- AND COMPRESSION-MOLDED CARBON NANOTUBE POLYMER COMPOSITES

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ABSTRACT

In the present study we show that carbon nanotube network formation and morphology play significant roles on the rheological, mechanical, and electrical properties of polymer-based nanocomposites. Results show that the formed network is in majority constructed of nanotube bundles, which geometrically entangle at a critical volume fraction ϕ_{cv} (geometrical percolation threshold). The geometrical entanglement of carbon nanotubes significantly affects the rheological performance regardless of the network morphology which improves the mechanical properties. On the other hand, nanotube configuration affects the electrical performance even if the network is not fully established (below ϕ_{cv}). In this case, random configuration moves the transition from isolator to conductor ϕ_{cv}^{e} (electrical percolation threshold) to much lower nanotube content and profoundly improves the conductivity of the nanocomposite.

INTRODUCTION

Carbon nanotubes-CNTs are widely accepted as exceptional nanofillers with superior strength and effective electron transfer, which can be utilized to improve functional performance of host materials. They establish randomly connected network within polymers, where they serve as mechanical reinforcement or conductive pathway, which can be used in numerous cutting-edge technologies[1]. Nevertheless, the functional performance of such materials mainly depends on network formation and its morphology. CNT network in polymer-based nanocomposites is generally established in melt and governs the properties of such materials in solid state. Within this research we focus on the rheological properties and electrical conductivity of CNT polymer-based nanocomposites.

Up to date there are numerus research works reporting on the improvement of mechanical properties with the addition of CNTs. Recent studies in this field observed percolation event in mechanical properties, explaining that particle interactions additionally reinforce the material[2]. However, none of these studies explicitly correlate the improvements with network formation and its morphology. Furthermore, since the effective electron transfer is one of the key features of CNTs, extensive research has already been conducted on electrical conductivity of such nanocomposites[3]. While there are some reports that geometrical entanglement of CNTs is a key factor for the establishment of conductive network, there are others showing that randomness in CNT configuration increases the probability to enable electron transfer. Therefore, the aim of the present research was to investigate network formation, its morphology, and their effects on the rheological and conductive properties of CNT polymer-based nanocomposites.

EXPERIMENTAL PART

Low-density polyethylene-LDPE was used as matrix material, while single-walled carbon nanotubes-SWCNTs were selected as nanofiller. Nanocomposites preparation process was performed in three phases: (i) the preparation of SWCNT/LDPE mixtures with uniformly dispersed nanofiller in the matrix material by using twin-screw extrusion; the preparation of the samples with different network morphologies by (ii) injection molding (aligned network configuration) and (iii) compression molding (random network configuration). The morphology of SWCNT network was investigated by plasma etching technique coupled with SEM. The SWCNT network formation and growth was observed through rheological analysis, i.e., complex viscosity η*, viscoelastic storage G'(ω) and loss G"(ω) modulus as a function of frequency ω. Tests were conducted at constant temperature (150°C) in the linear viscoelastic regime by using a modular rotational rheometer MCR 302 (Anton Paar, Austria) coupled with plate-plate sensor system (PP25, 1 mm gap). Electrical conductivity was investigated by utilizing custom build 4-wire and 2-wire DC measurement rig. In the measured voltage range, all samples showed Ohmic behavior, thus the specific conductivity σ was determined from the linear slope of the *I-U* curves.

RESULTS AND DISCUSSION

From the rheological tests, the frequency dependency of the relative viscosity ($\eta_{\mathrm{rel}} = \eta'/\eta_{\mathrm{m}}$; η' - real part of complex viscosity, η_{m} - viscosity of matrix material) was determined. Two regimes can be observed (Fig. 1a): dilute and semi-dilute regime, separated by the critical volume fraction ϕ_{cv} indicating SWCNT network development. Below ϕ_{cv} (in the dilute regime) no particle interactions are present and SWCNT bundles behave as individual entities, mainly interacting with the host material. The mechanical reinforcement can be understood as a transfer of external load from host material to nanoparticles. However, above ϕ_{cv} (in the semi-dilute regime), the bundles form randomly connected network, where interactions by adjacent rods become significant. Bellow ϕ_{cv}, where bundles are unconstrained, two configurations were obtained, namely the aligned configuration formed in injection molding samples and the random configuration formed in compression molding samples. However, those configurations provide no particular change in the rheological behavior η_{rel}. Above ϕ_{cv}, the movement of the bundles is constrained and randomly connected network is formed regardless of the process method used, resulting in approximately the same mechanical reinforcement.

The electrical conductivity σ of nanocomposites was normalized to relative conductivity as $\sigma_{\mathrm{rel}} = \sigma/\sigma_{\mathrm{m}}$, ($\sigma_{\mathrm{m}}$ is electrical conductivity of matrix material, Fig. 1b). The most interesting and significant finding of this work is that the electrical percolation threshold ϕ_{cv}^{e} distinctly differs and is not associated with the geometrical percolation ϕ_{cv}; moreover, it may occur at considerably lower concentrations. Below ϕ_{cv} the aligned configuration of injection molded samples does not allow the charge transfer, while the random configuration of compression molded samples allows the charge transfer although the network has not been fully established.

This was observed by surge of σ_{rel} for ~10^{10} times. Above ϕ_{cv} the movement of rods is constrained and only one configuration is possible. As such, the injection molding samples also become conductive.

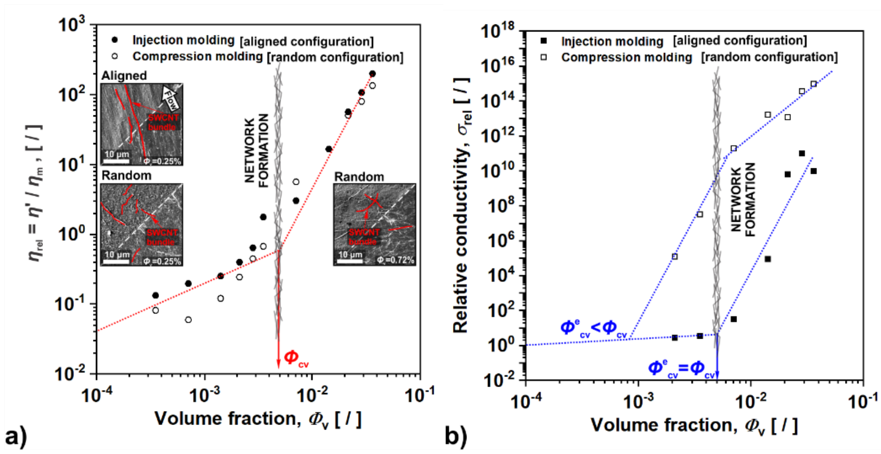

Figure 1: Effect of SWCNT content on a) rheological and b) electrical properties of nanocomposites

CONCLUSIONS

It was shown that CNT network formation and morphology play significant roles on the mechanical and electrical properties of LDPE nanocomposites. Network is in majority constructed from nanotube bundles, which geometrically entangle at a critical volume fraction. The mechanical and rheological properties were found to be independent of nanocomposite morphology, while the electrical performance was strongly dependent on the morphology. Random configuration significantly decreases the transition of nanocomposites from an isolator to a conductor.

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