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Rheological properties of epoxy/MWCNT suspensions associated with the surface modification of MWCNT by physisorption of aromatic ionic salts

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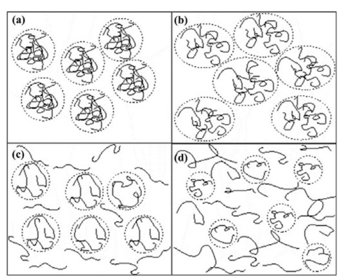
HIGHLIGHTS

- Dilation effect that viscosity of epoxy/MWCNT suspension increases with shear rate was discovered.
- Dilation effect was attributed to the excess epoxy resin trapping in the aggregated domain of MWCNT.
- The transition point that the dilation effect changes to shear thinning effect was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

The multi-walled carbon nanotubes (MWCNTs) physisorbed by aromatic ionic salts such as 10-methyl-acridinium iodide (MAcI) were found to well disperse in diglycidyl ether of bisphenol-A epoxy resin. As they were subjected to the rheological study at 30 °C, the gelation of epoxy/MWCNT-MAcI suspension occurred at 0.75 wt% MWCNT-MAcI, which was less than that using pristine MWCNT. As to the viscosity measurements, the dilation effect that the viscosity of epoxy/MWCNT suspension increases with shear rate was found and more pronounced by incorporating MWCNT-MAcI. According to the Thomas-modified Einstein viscosity equation, the dilation effect was attributed to the excess amount of epoxy resin trapping in the aggregated domain of MWCNT. By increasing the shear rate to a certain point, the shear thinning effect that the viscosity decreases with shear rate was also observed. Interestingly, the transition point that the dilation effect changes to shear thinning effect shifted to lower shear rate as the content of MWCNT increased and/or MWCNT-MAcI was incorporated. Notably, better dispersion and less aggregated domains for the suspensions with MWCNT-MAcI compared to pristine MWCNT were further supported by small angle x-ray scattering and transmission electron microscopy.

1. Introduction

Multi-walled carbon nanotube (MWCNT), which possesses excellent mechanical, electrical and thermal properties, was often combined with polymeric materials to fabricate the nano-composites [1–9]. To assess the effectiveness of their fabrication,

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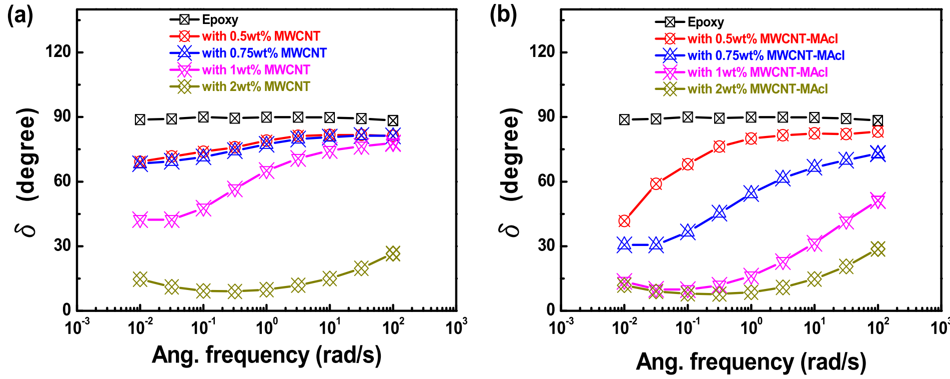


Fig. 1. The degree of phase shift versus angular frequency for the epoxy/MWCNT suspensions with the indicated contents of (a) pristine MWCNT and (b) MWCNT-MAcI measured at 30 °C.

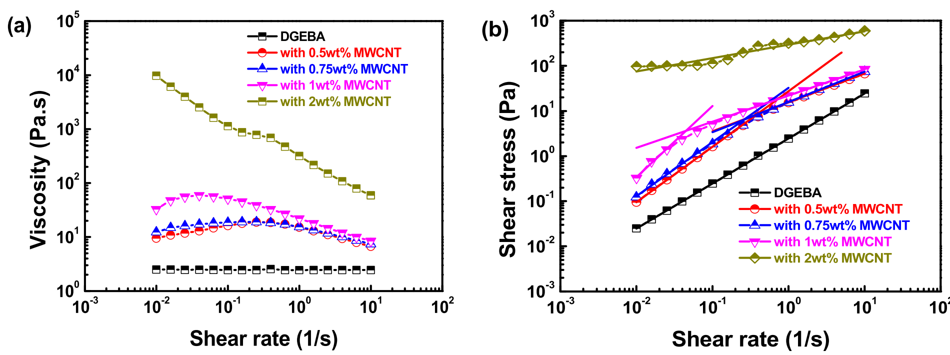
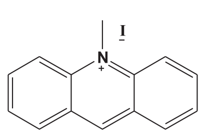


Fig. 2. (a) Viscosity and (b) shear stress as a function of shear rate for DGEBA incorporating the indicated weight percentage of MWCNT measured at 30 °C.

rheological measurements to evaluate the dispersion of MWCNTs in polymer matrix is important. Notably, the rheological properties of epoxy/MWCNT suspensions have been reported to be greatly influenced by the MWCNT content, dispersion, orientation, and formation of network in the epoxy matrix [10–13]. Fan et al. [14] showed that the epoxy suspensions with well-dispersed MWCNTs had higher storage modulus (G') and loss modulus (G") than those with poor dispersion. However, on the contrary, Song et al. [15] reported that the epoxy suspensions with well dispersed MWCNTs had lower storage modulus and viscosity. These contradictory results were frequently reported and are deserved to be further investigated.

Diglycidyl ether of bisphenol-A (DGEBA) is an epoxy resin commonly used for industrial applications owing to its outstanding processing, mechanical, and electrical properties [16–18]. Because it is a Newtonian fluid, it was considered to be a suitable material for the rheological study of epoxy/MWCNT suspensions. To enhance the dispersion of MWCNTs in the epoxy resin, in our previous work we have synthesized 10-methyl-acridinium iodide (MAcI) which is an aromatic ionic salt with the chemical structure shown below [19] and used it to physisorb onto MWCNT through



MAcI

π-π and cation-π interactions [20–23]. The MAcI-physisorbed MWCNT (denoted as MWCNT-MAcI) displayed better dispersion in the epoxy resin and the cured nanocomposite also showed excellent physical, mechanical and thermal properties [19].

In this study, we explored further on the rheological behavior of epoxy/MWCNT suspensions incorporating MWCNTs with and without physisorption of MAcI. The resulting rheological data will be discussed in association with the aggregated domains related to their incorporated MWCNTs. Besides, we also utilized the small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) to investigate the aggregated domains of MWCNT in the epoxy resin and directly observe the dispersion of MWCNTs.

2. Experimental

2.1. Materials

MWCNT of O.D. 10–30 nm, length 0.1–10 μm, >90% carbon basis, was purchased from Aldrich. DGEBA was obtained from Dow Chemical Co. with the trade name of DER 332. Epoxide equivalent weight of DGEBA is 171–175. The synthesis procedure of MAcI has been given in our previous work [19].

2.2. Surface treatments of MWCNT

To physically treat the surface of MWCNT with MAcI, 1 g of MWCNT and 3 g of MAcI in 50 mL dimethylformamide were sonicated in the ultrasonic bath (Delta Model D150H) at the frequency of 43 KHz for 30 min and then stirred for 1 day both at room temperature. The mixture was then poured into large volume of acetone and filtrated through 0.22 μm polyvinylidene fluoride