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Effect of amine-functionalized dispersant on cure and electrical properties of carbon nanotube/epoxy nanocomposites

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ABSTRACT

The efficient dispersion of carbon nanotubes, CNTs in epoxy resin is a challenging task to reach the final properties of the competent nanocomposite. In this study, the CNT/epoxy nanocomposite was fabricated by solution mixing process using an amine-functionalized dispersant. The dispersion of CNTs in organic solvent was further improved using an ultrasonic horn. According to the data obtained from UV–vis spectroscopy, a minimum ultrasonication time of 10 min is necessary to obtain proper dispersion of CNTs in organic solvent. The cure behavior of epoxy resin containing different CNT loadings was investigated by dynamic DSC thermograms. The higher CNT loading lowers the initial curing temperature and the peak temperature mainly due to high thermal conductivity of CNT. The SEM micrographs of the fractured surfaces showed the effect of dispersant on proper dispersion of CNTs in epoxy. The electrical percolation threshold was measured at about 0.5 wt% of CNT. However, the conductivity results revealed the adverse effect of dispersant on the nanocomposite electrical properties, mainly due to dispersant adsorption and hence screening the CNTs surface charges.

1. Introduction

Different carbon nanotubes, CNTs have attracted considerable attentions in modern polymeric nanocomposites mainly due to their unique electronic, thermal and mechanical properties [1–3]. The extraordinary mechanical and electronic properties of CNTs make them ideal fillers in light weight composites. However, the development in CNT/polymer composites has been greatly limited by the problems associated with the proper dispersion of CNTs and the load transfer across the CNT/polymer interface [2,3]. There are critical challenges in reaching the uniform dispersion and disaggregation of CNT bundles in a polymer matrix. The tendency of carbon nanotubes to self associate into micro scale aggregates results in products with inferior mechanical and electrical performance [4–6]. Different van der Waals forces on CNT surface and the CNT high surface area are responsible for CNT entanglement or aggregation and hence limitation in the final performance [3,4]. Therefore, the effective dispersion of CNTs has been the focus of many industrial and academic researches in recent years [5].

Different techniques were developed for CNTs dispersion which can be generally categorized into covalent functionalization and non-covalent functionalization. The covalent functionalization involves formation of carboxyl functional groups on CNT surface followed by grafting of the organic moieties on the modified surface. Whereas, the non-covalent functionalization utilize different dispersants, surfactants and organic solvents to promote CNT dispersion [6].

The CNT surface adsorbs the surfactants with hydrophilic or hydrophobic heads in which may be regarded as a simple effective way to enhance the dispersion of CNT without interfering with their performance. The state of CNT dispersion varies from aggregates, bundles, or ropes into separated individual tubes and depends strongly on the characteristics of the hydrophilic groups of surfactant [7]. The surfactants can also stabilize the dispersion of CNT with ionic hydrophilic groups based on the electrostatic repulsion between micellar domains [8]. Whereas, the nonionic surfactants facilitate the CNT dispersion through assembling a large solvation shell from the hydrophilic moieties of the surfactants [9]. The surfactants can effectively disperse CNTs via formation of specific directional π–π stacking interactions with the graphite surfaces of the nanotubes. Since small molecules or polymers can be adsorbed onto CNT surfaces by π–π interactions, conjugated polymers have also been considered as modifiers for CNT surfaces. The strong interactions between CNT and conjugated polymers may result in wrapping a polymer chain around a CNT [10,11].

The adsorbed surfactants on carbon based surfaces may form a hemi-micelle structure and sheath the nanotube surface. The interfacial interactions between CNT in agglomerates can be replaced by mutual interactions between the polar groups of dispersant and the hydroxyl

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groups of CNT [12]. Several factors are decisive issues in choosing the proper surfactant in polymeric media such as the surfactant structure, the CNT/surfactant ratio and the surfactant critical micelle concentration [12,13]. There are some reports about the excellent dispersion of multi-walled carbon nanotubes, MWCNTs in sodium dodecylbenzene sulfonate, SDBS solutions. The mechanism and the associated factors have been studied systematically to improve the efficiency of the sonication driven dispersion by using UV–vis spectroscopy [14,15]. In addition to numerous usefulness of the dispersant, the use of dispersant may results in shorter sonication times. The long ultrasonication times may increase the possibility of nanotubes breakage [14]. The shortening of CNT results in structural damage and hence, lowering the nanotubes superior properties such as mechanical, thermal and electrical properties [18]. Good thermal conductivity of CNTs may facilitate the transfer of the heat in polymer matrix and cause faster cure initiation [13]. Note that the higher CNT loading may also cause reduction in heat of cure due to steric hindrance effects. The electrical conductive network is formed by the well distributed CNTs in the matrix through inducing electrical pathways [19,20].

In this paper, the influence of an amine-functionalized dispersant was evaluated on the ultrasonic-assisted CNT dispersion in epoxy resin. The dispersant was also examined for two of the main properties of CNT/epoxy systems, i.e., the cure behavior and the electrical conductivity.

2. Experimental

2.1. Materials

The epoxy resin (Epon 828) was purchased from Shell Co. USA. The amino polyamide hardener (Crayamid 115) was obtained from Cray Valley HSC USA and was used at a weight ratio of (1:1) to epoxy resin. The hydroxyl functionalized multi-walled carbon nanotubes were supplied by Shenzhen Nanotech Port Co., China with diameter 5–10 nm, length 30 μm and purity > 95. The amine-functionalized dispersant (Disperbyk BYK163) was used from BYK- Chemie GmbH, Germany. Xylene as solvent was purchased from Merck, Germany.

2.2. Preparation of the MWCNT/epoxy nanocomposites

The MWCNT/epoxy nanocomposites were prepared in two steps. In the first step, CNT dispersions were prepared via adding 0.1 g CNT into a beaker of 50 mL xylene. Then the dispersant was added at an equal weight ratio of CNT. All the dispersions were then subjected to ultrasonication process using a horn sonicator. The flask of CNT dispersion was placed in a bath of ice water during sonication in order to prevent unfavorable temperature rise. The horn sonicator operates at 70% power amplitude and a 0.5-s pulse on and 0.5-s pulse off. In order to find the optimum ultrasonication time, the CNT dispersion was subjected to various sonication times up to 20 min. Visual inspections of the dispersion stability were conducted at different storage times up to 48 h after the ultrasonication process. Based on the results of UV–vis spectroscopy, the optimum condition to get the proper CNT dispersion was chosen and was used in the next step.

In the second step, the prepared CNT dispersion was added into epoxy resin through shear mixing at 800 rpm for an hour at room temperature. Then, the organic solvent and the bubbles were removed under vacuum (< 200 mbar) for 60 min. Different nanocomposites were prepared through the inclusion of 0.5, 1, 2, 3 and 4 wt% of CNT based on the total epoxy resin. The curing of all samples were carried out via mixing curing agent into CNT/epoxy nanocomposite in a teflon pan followed by heating at 80 °C for about 45 min. For the sample series without dispersant, the prepared CNT dispersion was immediately mixed with the epoxy resin followed by placing into a ultrasonic bath for a further 10 min.

2.3. Instrumental

The ultrasonication of CNT dispersion was carried out using a Bandelin probe (KE76, Germany). The process time was fixed between 2 and 20 min.

The dispersion of CNTs in xylene was characterized in the visible wavelength range (300–700 nm) using a Shimadzu UV–vis spectrophotometer (UV-1650 PC, Japan). Samples of CNT dispersions were taken regularly during the ultrasonication process and carefully diluted 15 times with xylene to get suitable spectra. The baseline correction in spectrophotometery was carried out using a dispersant solution.

The SEM micrographs were captured in a TESCAN (VEGA, Czech republic) at 20 kV. The dispersion of CNTs in epoxy resin was studied on the cross section area of the cryo-fractured surface followed by sputtering with a thin layer of gold.

The cure behavior of the CNT/epoxy nanocomposites was determined using a differential scanning calorimeter, DSC (Netzsch DSC 200 F3, Germany). The DSC thermograms were obtained from 25 °C to 200 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The samples containing 0.1, 1 and 10 wt% CNT were placed individually into DSC pan immediately after mixing with hardener.

The nanocomposite sample sheets were prepared after curing the nanocomposites at 80 °C for 60 min. The electrical resistivities of the 2 mm thick sheets were measured by the standard two-point test method in Keithley electrometer (model 610C, USA) at room temperature.

3. Results and discussions

3.1. Stability of CNT dispersion

Fig. 1 shows the visual stability of 0.1 wt% CNT dispersions at different times after ultrasonication for 5 min. Each pair of samples (a, b and c) consists of a neat CNT marked as sample 1 and dispersant-treated CNT marked as sample 2.

As shown in Fig. 1, each pair of samples shows two different behaviors. In sample series containing neat CNT, the CNTs precipitate rapidly (< 5 min) and settle at the bottom of test tubes. It is clearly visible that the degree of CNTs sedimentation increased at longer times. In sample series containing the dispersant-treated CNT, the dispersion stability was observed for a relatively long time. The observations indicate the outstanding stability of the dispersant-treated CNT up to 48 h after the ultrasonication process. The dispersion stability of the dispersant-treated CNT may be attributed to lower interfacial surface tension and weakening van der Waals interactions on the CNTs surfaces. The formed mutual interactions and hydrogen bonding between the polar amine groups of dispersant and the hydroxyl groups of CNT may overcome the interfacial interactions in CNT bundles [16]. The adsorbed surfactant molecules on the CNT surface may also decrease the surface tension and separate the CNT large agglomerates by steric hindrance effects.

In order to find the necessary time to obtain proper dispersion of CNTs, different sonication times were examined using 1 wt% dispersant-treated CNT. Fig. 2 shows the UV–vis spectra of CNT dispersions as a function of sonication time.

The UV–vis spectra show maximum absorption at 300 nm followed by a steady reduction at higher wave lengths. The data were highly scattered at lower wave lengths than 300 nm and therefore they were not shown in Figure. The maximum absorption may be used as indication for the dissociation of the CNT bundles [3,13]. The results of UV–vis spectra suggest more effective dissociation of the CNT bundles at longer sonication times which is in agreement with other reports [15,17,18]. However, it is thought that long ultrasonic times could result in possible damage of the nanotubes [14]. The CNT breakage leads to shorter length of the nanotubes, structural damage and hence reduction of the nanotubes superior properties, [18]. It seems that time