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Development of carboxyl-functionalized multi-walled nanotube/polydimethylsiloxane novel polymeric nanodielectric material

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ABSTRACT

In this paper, we develop a new type of polydimethylsiloxane (PDMS)-based nanocomposite by incorporating carboxyl-functionalized multi-walled nanotube (MWCNT) to the polymer matrix as fillers. The dispersion of MWCNT during the material processing plays a significant role in deciding the final properties of the nanocomposites. A rapid evaporation and stirring method was used to minimize re-aggregation of the fillers during MWCNT/PDMS composites fabrication processing by solution blending. Furthermore, dispersions of MWCNT in solvents were investigated to correlate the degree of dispersion state with Hansen solubility parameters. The result indicated that carboxyl group can impart negative charges and create the long-term electrostatic stability of MWCNT in the solvents. The resultant MWCNT/PDMS composites exhibited high permittivity, low dielectric loss, and low percolation threshold.

1. Introduction

As one of novel functional materials, high-permittivity (high-*k*) polymer composites have a great potential application in gate dielectrics [1], embedded components [2], energy storage devices [3,4], piezoelectric generators [5] and electromechanical transducers [6], due to their high permittivity, light weight and good processability. The dielectric permittivity is an important index to represent one property of the polymer matrix flexible high-k dielectric composites [7].

One common approach to increase the dielectric permittivity of these materials is to incorporate conductive fillers in the polymer matrix. Based on percolation theory, the effective permittivity is substantially improved near the percolation threshold of the conductive filler. Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [8], CNTs have become one of the most actively studied materials because of their excellent properties, including low mass density, high flexibility, and remarkable mechanical, electrical, and thermal properties [9]. To date, multi-walled CNTs (MWCNTs) have been widely used as conductive fillers due to their reasonable cost, wide range of types, better availability, easy dispersion and low electrical percolation thresholds (f_c) [10,11].

In this work, polydimethylsiloxane (PDMS) was selected as polymer matrix. PDMS can be easily made into composite film by mixing nanoparticles or other nanostructures [12,13], which has been used extensively for nano-generators [14,15], nano-devices [16] or nano-sensors [17]. Simultaneously, carboxyl-functionalized multi-walled nanotube (MWCNT) was used as conductive filler and we dispersed MWCNT into PDMS by solution blending method which is simple and effective. Herein, introduction of carboxyl functional groups not only can improve MWCNT solubility in various solvents, but also are useful for the further chemical link with other compounds. However, the re-aggregation of fillers during the fabrication processing of solution blending is common, especially for carbon-based 1D or 2D nanomaterials [18,19]. To overcome these problems, a rapid evaporation and stirring method was used to minimize re-aggregation of the fillers during fabrication processing. Our goals are to develop high-permittivity MWCNT/PDMS composites with minimum possible percolation threshold.

2. Experimental

2.1. Materials

The PDMS (Sylgard 184) prepolymer and curing agent was supplied by Dow Corning Corporation. The carboxyl-functionalized multi-walled nanotube with1.55 wt% —COOH (denoted as

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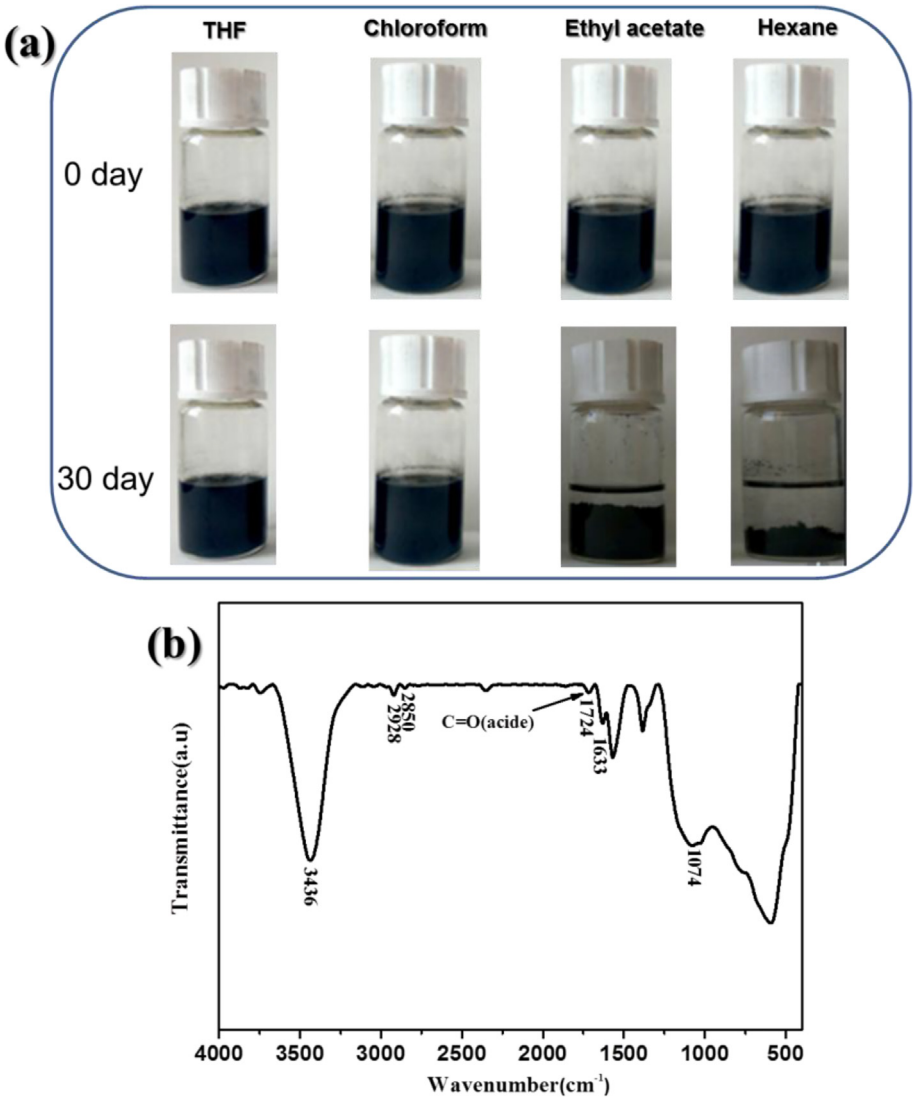

Fig. 1. (a) Dispersion conditions of MWCNTs in four solvent and (b) FT-IR spectra of carboxyl-functionalized multi-walled nanotube.

Table 1
Surface tensions and Hansen solubility parameters of solvents [25].

Organic solvents	ST (mJ m^{-2})	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)
Chloroform	26.67	17.8	3.1	5.7
Tetrahydrofuran	26.59	16.8	5.7	8
Ethyl acetate	23.75	15.8	5.3	7.2
n-hexane	17.89	15.3	0	0

MWCNT) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences and were used without further purification. The MWCNT bundles were 10–30 nm in diameter and 10–30 μm in length. Chloroform, tetrahydrofuran, ethyl acetate, hexane and other chemicals were of analytical grade and used as received.

2.2. Preparation of MWCNT/PDMS composites

The MWCNT/PDMS composites were prepared through the solution blending method to obtain a good dispersion of MWCNTs in the PDMS matrix. First, the MWCNTs with the content ranging from 0.0 to 3.0 wt% were dispersed in aqueous solvent by ultrasonic treatment and careful stirring in order to form a stable MWCNT suspension. Then, the MWCNT suspension was mixed with the PDMS pre-polymer followed by careful stirring. The MWCNT/PDMS compounded solution was first concentrated by heat-stirring technique in order to get rid of the solvent quickly and thus can effectively prevent the re-aggregation of MWCNT. After most of the solvent was removed, curing agent was added to the MWCNT/PDMS mixture to a concentration of 10 wt% with respect to the total weight of the PDMS. The concentrated solution was poured onto a mould and completely cured at 60 °C for 24 h to obtain the MWCNT/PDMS films. Finally, the MWCNT were immobilized in the PDMS matrix. The thickness of the film was controlled by changing the amount of the solution poured onto the mould.

2.3. Characterization

The morphology of MWCNT/PDMS composite was observed using a JEOL -JSM-7500F scanning electron microscope. For the observation of cross-section morphology, MWCNT/PDMS composite samples were cryogenically fractured in liquid nitrogen (−170 °C) and then coated with platinum before observations under the scanning electron microscope. The dielectric properties of MWCNT/PDMS composite films (diameter 25 mm and thickness