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Improving the filler dispersion of polychloroprene/carboxylated multi-walled carbon nanotubes composites by non-covalent functionalization of carboxylated ionic liquid

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ABSTRACT

The effect of the non-covalent modification of carboxylated multi-walled carbon nanotubes (MWCNT) by a carboxylated ionic liquid (IL), 1-carboxyethyl-3-methylimidazolium bis(trifluoromethyl sulfony)imide (CMI), on the polymer–filler interactions, filler dispersion, thermal stability, mechanical and dielectric properties of polychloroprene (CR)/MWCNT composites were studied. The better dispersion of MWCNT in CR was attributed to the "cation-π" interaction and π–π stacking between MWCNT and CMI, and other possible intermolecular interactions related to carboxyl groups on MWCNT and CMI. After the introduction of CMI into CR/MWCNT composites, the Payne effect became more pronounced as evidenced by nonlinear viscoelasticity test. After the addition of 16 phr CMI into CR/MWCNT (100/8) composite, the storage modulus greatly increased from 277 MPa to the maximum value of 389 MPa. Meanwhile, the tensile strength increased from 12.5 to 18.2 MPa, and the elongation at break increased from 411% to 464%. This improvement in mechanical properties was accounted from stronger polymer–filler interactions and the plasticizing effect arising from CMI. The presence of CMI ions as permanent dipole and the less possibility for MWCNT to aggregate together gave rise to a big increment in permittivity of CR/MWCNT composites.

1. Introduction

Enjoying the combination of good processability of polymers and excellent functional properties of carbon nanotubes (CNTs) [1,2], polymer/CNTs composites have drawn a worldwide attention in the past decades. However, the dispersion of CNTs is one of several crucial parameters determining the improvement extent of both basic properties and functionality. Different covalent (chemical) and non-covalent (physical) functionalization methods were used to improve the dispersion of CNTs in polymers, including solution [3], ultrasonic dispersion [4], coagulation [5], melting blending [6], microemulsion [7], oxidation and functionalization of side wall [8] and the assistance of surfactants [9]. The covalent functionalization usually involves in a hybridization change from sp^2 to sp^3 and an unavoidable damage of π-conjugation system, which could endow polymer/CNTs composites with enhanced polymer–filler interactions but consequently decrease the electrical and thermal conductivity of CNTs at the same time. Meanwhile the covalent functionalization usually can not be conducted without using environmentally unfriendly strong acids or oxidants. Compared with covalent functionalization, non-covalent functionalization has more advantages, such as low cost, simple operation and small environmental pollution. Polymer wrapping, surfactant adsorption and endohedral method are three main ways to implement the non-covalent functionalization of CNTs [10]. According to the work of Ma [3], these ways are respectively achieved through van der Walls interactions and π–π stacking between polymers and CNTs, physical adsorption of surfactants, and storage of guest atoms or molecules through capillary effect.

In recent years, ionic liquid (IL) has been reported to improve the dispersion of CNTs in polymer/CNTs composites as a new surfactant. In 2003, Fukushima [11] fabricated a thermally stable gel (bucky gel) from IL and single-walled carbon nanotubes, and confirmed that the local ordering of IL rather than the entanglement of carbon nanotubes gave rise to a physical crosslinking in the bucky gel. CNTs dispersed in IL were further used in sensors, actuators and electrochemistry [12]. The improved dispersion of CNTs arising from the non-covalent modification by IL has been proved

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by many researchers, however, there is still a big division in explanations for the better dispersion of CNTs. Most of researchers attributed it to the "cation-π" interaction and π–π stacking between IL and CNTs [13]. But other researchers thought IL interacted with CNTs through weak van de Waals interaction rather than "cation-π" interaction [14]. No matter what the interactions are, their existence induces IL to form a separation layer on the surface of CNTs so that CNTs will not entangle with each other to form agglomerates. Because carboxylated multiwalled carbon nanotubes had a stronger interaction with CR than common multiwalled carbon nanotubes [15], the former should be a better filler for CR. In this work, we proposed a new carboxylated IL, 1-carboxyethyl-3-methylimidazolium bis(trifluoromethyl sulfony)imide (CMI), to conduct a non-covalent functionalization of carboxylated multiwalled carbon nanotubes (MWCNT) and fabricated different CMI modified CR/MWCNT composites. Fig. 1 shows the way used to fabricate CMI modified CR/MWCNT composites and the different interactions between CMI and MWCNT. As shown in Fig. 1, CMI can adhere on the surface of MWCNT *via* "cation-π" interaction, π–π stacking and other possible intermolecular interactions between CMI and MWCNT. These other intermolecular interactions may be the dipole interactions between polar groups and the hydrogen bonds between carboxyl groups of MWCNT and CMI [14,16]. The interactions between CMI and MWCNT were expected to be stronger than that between 1-butyl 3-methyl imidazolium bis(trifluoromethylsulphonyl)imide (BMI) and non-functional MWCNT, and an improved dispersion of MWCNT in CR could be achieved. Then CR/MWCNT composites with good mechanical properties, dielectric properties and thermal properties could be fabricated.

As CMI is not a liquid at room temperature, its bucky gel cannot be fabricated *via* simply grinding it with CNTs together. Das [17] found the predispersion of CNTs with ethanol before mixing CNTs with styrene-butadiene rubber or butadiene rubber could significantly enhance CNTs dispersion in polymers. Inspired by this, we prepared bucky gel from CMI and MWCNT *via* an ultrasonic dispersion of them in ethanol (Fig. 1). After mixing this bucky gel with CR, residual ethanol was removed. Similar to the fabrication of bucky gel by grinding non-functional MWCNT with BMI together [13,18], this approach also has advantages of operation simplicity and little environmental pollution. Meanwhile, the high CMI concentration is proved unnecessary for the dispersion of MWCNT *via* the fabrication of bucky gel. This work is also expected to provide a universal method for the fabrication of bucky gel from non-room temperature IL: mixing IL and CNTs together *via* a favorable solution. And the usage of carboxylated IL is hoped to make IL a promising additive in the production of more novel polymer/CNTs composite materials suitable for the field of electrochemistry [18].

2. Experiments

2.1. Materials

CR (M-40, ML [1 + 4] at 100 °C is 48) was produced by Denka, Japan. Carboxylated multiwall carbon nanotube (MWCNT) with a diameter of 10–30 nm and a carboxyl group content of 1.55% was purchased from Chengdu Organic Chemicals, China. 1-Carboxyethyl-3-methylimidazolium bis(trifluoromethyl sulfony) imide (CMI) was purchased from Lanzhou Greenchem ILS, China. Magnesium oxide (MgO), zinc oxide (ZnO), steric acid (SA) and ethylene thiourea (ETU) were purchased from Kyowa Chemical Industry (Japan), Mitsui Ming & Smelting (Japan), Sinopharm Chemical Reagent (China) and Kawaguchi Chemical Industry (Japan), respectively, and used as received.

2.2. Preparation

2.2.1. Non-covalent modification of MWCNT

Preparation process of CMI modified CR/MWCNT composites contains two steps: the non-covalent modification of MWCNT by CMI, the fabrication of CR/MWCNT composites. Firstly, CMI was

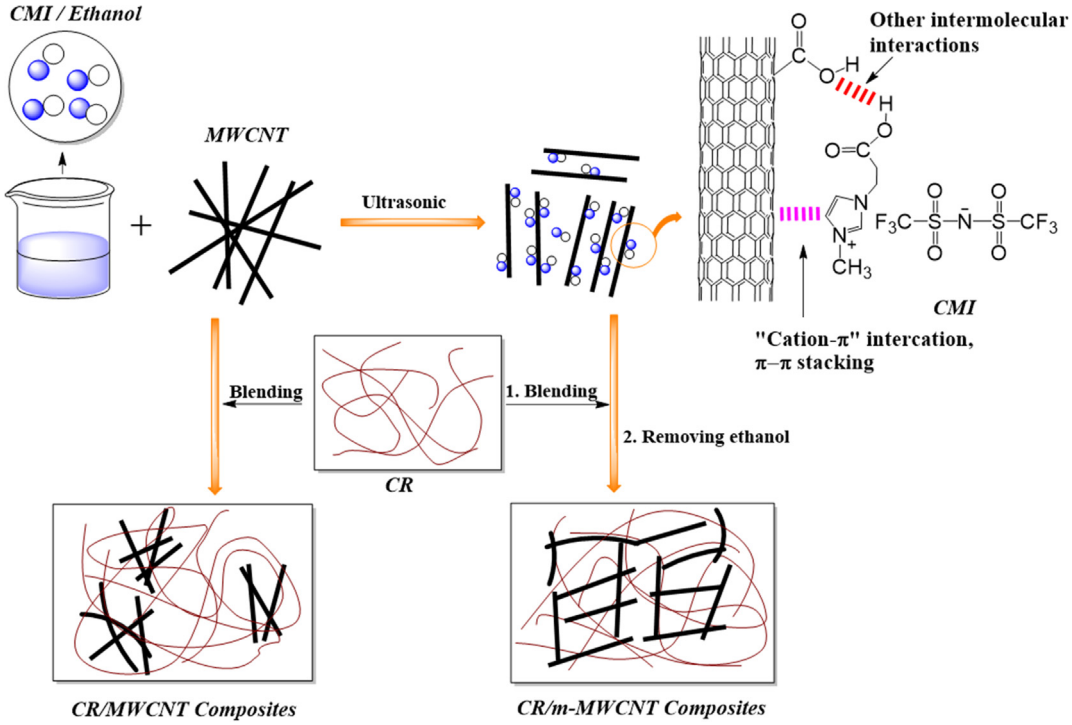

Fig. 1. Fabrication process of CR/MWCNT (CR/m-MWCNT) composites and the schematic diagram of different interactions between CMI and MWCNT.