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Synthesis and properties of sandwiched films of epoxy resin and graphene/cellulose nanowhiskers paper

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ABSTRACT

Graphene (GN)-based composite paper containing 10 wt.% cellulose nanowhiskers (CNWs) exhibiting a tensile strength of 31.3 MPa and electrical conductivity of 16800 S/m was prepared by ultrasonicating commercial GN powders in aqueous CNWs suspension. GN/CNWs freestanding paper was applied to prepare the sandwiched films by dip coating method. The sandwiched films showed enhanced tensile strength by over two times higher than the neat resins. The moduli of the sandwiched films were around 300 times of the pure resins due to the high content of GN/CNWs paper. The glass transition temperature of the sandwiched films increased from 51.2 °C to 57.1 °C for pure epoxy (E888) and SF (E888), and 49.8 °C to 64.8 °C for pure epoxy (650) and SF (650), respectively. The bare conductive GN/CNWs paper was well protected by the epoxy resin coating, which is promising in the application as anti-static materials, electromagnetic interference (EMI) shielding materials.

1. Introduction

Epoxy resin is one of the most important and widely used thermosetting polymer matrix used for developing advanced composites. Because of its unique mechanical properties, chemical resistance, low cost, ease of processing and good adhesion to many substrates, it can be used in number of applications from electronics to aerospace, such as coatings, adhesives, semiconductor encapsulation, electronics and aerospace [1–5]. However, the non-conductivity restricts its usage as engineering thermal conducting materials, anti-static materials, electromagnetic interference (EMI) shielding materials, and conductors [6]. One commonly used method is adding a variety of conducting fillers such as, metal fibers/flakes/nanoparticles, carbon materials (graphite, carbon black, carbon nanofibers, carbon nanotube, graphene), intrinsically conducting polymers, or their combinations to the polymer matrix to contribute electrical conductivity to the polymer composites [7–10]. Carbon nanostructured materials are still the most effective reinforcements for developing conductive polymer composites because they are able to enhance the mechanical and thermal properties along with electrical conductivity at a very low loading. The insulator-to-conductor transition of the epoxy resin took place for nanotube concentration between 0.5% and 1 wt.% was acquired [7]. Yan et al. obtained a low electrical percolation threshold of 0.1 wt.% single walled carbon nanotubes (SWCNTs) of epoxy-based composites by modifying SWCNTs with amino-containing pyrene derivatives (AmPys) [8]. Rubiolo et al. found that the percolation threshold of the epoxy resin-based composite was 0.06 wt.% for aligned carbon nanotubes, one order of magnitude of smaller (0.5 wt.%) than for a similar composite with randomly oriented nanotubes [9]. Ghaleb et al. reported that commercial graphene nanoplatelets showed lower electrical percolation threshold volume fraction in epoxy resin-based thin films than carbon nanotube at same ultrasonic time [10]. In terms of research and industrial application, carbon nanostructures show the promising reinforcing fillers in polymer matrix.

Another common used method is producing composites using foams, mats, or films to create continuous conductive pathway solving the dispersion problem. Thus a high conductivity value with improved mechanical property is easy to achieve [11]. Han et al. produced the carbon nanotube buckypaper/thermoplastic polyurethane composites having excellent comprehensive properties. These composites containing 42.6 vol.% exhibited much higher modulus of 6 GPa, strength of 123 MPa, corresponding to 3.4-fold improvement in elastic modulus, 9.6-fold improvement in failure strength, and 50-fold improvement in toughness, compared to those of the as-prepared bulky paper [12]. Li et al. reported epoxy nanocomposites with carbon nanotube skeleton showed very high electricity up to 1000 S/cm and Young's modulus up to 30 GPa [13].

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Wang et al. have developed epoxy-based shape memory polymer sandwiched films cored by chemically reduced graphene oxide paper. The composites film showed the recoverability of approximately 100% taking only 5 s under 6 V [14]. The composite structured with the conductive paper as the core and the polymer as the skin are promising in the application as smart materials.

Graphene paper shows some advantages including higher density and mechanical strength over its fibrous carbon nanotube counterpart [15,16]. Graphene paper is usually obtained by thermal/chemical reduction graphene oxide paper, or by filtrated from the dispersion of exfoliated graphite in organic solvent. The properties of graphene paper are generally affected by the morphology and size of precursors, reduction methods. Graphene paper showed higher strength and conductivity when larger graphene oxide sheets were used [17]. Ranjbartoreh et al. produced thermally reduced graphene paper with high tensile strength of 78 MPa by flow-directed assembly of graphene nanosheets [18]. An electrically conductive alkylated graphene paper via chemically reduction of amine-functionalized graphene oxide paper was obtained. The electrical conductivity and tensile strength of the paper increased by more than 25 times and 50% after annealed at 300 °C for 3 h [19]. A high conductivity value of 35100 S/m for the combination of chemical and thermal reduction was reported for the graphene paper [20]. The hybridization of carbon nanostructures is applied to acquire improved properties. Graphene oxide/reduced graphene oxide is found to be very effective to enhance the strength and conductivity value of carbon nanofiber-based paper [21]. The minor addition of carbon nanotube improved the mechanical behavior of graphene oxide paper [22]. The hybrid films of carbon nanotube and nanographite platelets showed superior properties over neat films of carbon nanotubes or nanographites [23].

Recently, we produced graphene paper by adding a small amount of cellulose nanowhiskers (CNWs) into aqueous commercial graphene powders directly followed by the sonicating treatment and casting methods for the first time. Graphene powders are not dispersible and stable in water, which makes it difficult to prepare graphene film without any modification at aqueous state. It was found that the minor addition of CNWs facilitate to disperse graphene powders in water and form the graphene paper. The content of graphene of the resultant GN/CNWs is up to 99 wt.%, while the paper showed high electrical conductivity and good dimensional integrity. This process is simple, efficient and free of toxic organic solvents, which is promising for industrial scale application. CNWs are renewable and can be easily extracted from wood pulp, plant fibers, sea creatures, microbial, or even agricultural products [24]. The graphene-based composite paper exhibited good mechanical flexibility and strength, and electrical conductivity, which is promising in energy storage materials [25,26]. In order to prepare the sandwich films GN/CNWs paper was prepared as the preformed core structure and the epoxy resin solution as the skin structure. The sandwiched films were prepared by dip coating of the paper into epoxy resin solution and subsequent curing at ambient temperature. The structural, morphological, thermal, electrical, and mechanical properties of the sandwiched films were investigated. The epoxy resin coated graphene paper sandwiched films are promising in the applications in the electronics, aeronautics and astronautics industries.

2. Experimental methods

2.1. Materials

Graphene nanoplatelets (GNs), was purchased in powder form from Sichuan Jinlu Group Co., Ltd., Deyang, China. The GNs are consist of 5–8 layers single graphene sheets, the lateral size is around 10–20 μm, the ratio of C and O is 80–100. The raw material for extracting cellulose nanowhiskers, husk of *Xanthoceras sorbifolia* Bunge, was kindly supplied by Shenyang Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang. Bisphenol-A diglycidyl ether E44 (6101), with the epoxy degree of 0.41–0.47, the curing agent – E888 (amine value: 460–480 mgKOH/g) and low molecular weight polyamide 650 (amine value: 200–240 mgKOH/g) with a molecular weight of 600–1100, are domestically commercial products that were brought from Shenyang Zhentraid anti-corrosion materials Co. Ltd., Shenyang. Epoxy resin was dissolved in acetone with an epoxy:acetone weight ratio of 2:5. The curing agents 650 and E888 were added into epoxy/acetone solution. The ratios of epoxy to curing agent were 2:1 and 4:1 for 650 and E888, respectively. 650 and E888 were selected due to their low cost, industrial availability. 650 and E888 are generally used in floor coating and glass fiber reinforced plastics fields. Pure epoxy resin and sandwiched films were cured at ambient temperature. Acetone, sulfuric acid, sodium hydroxide, sulfuric acid, glacial acetic acid, toluene, ethanol, hydrogen peroxide were purchased from Shenyang Xindongbao Scientific Instrument Co., Ltd., Shenyang, China.

2.2. Preparation of the GN/CNWs paper and sandwiched films

Cellulose nanowhisker was extracted from husk of *X. sorbifolia* Bunge by sulfuric acid method as previously reported [27]. The homogeneous aqueous dispersion of GN/CNWs was obtained by ultrasonicating (KH-1600TDE, Kunshan, China) graphene and cellulose powders in water at a frequency of 80 kHz and power of 1600 W until the uniform dispersion was achieved. GN/CNWs paper was obtained by casting the mixture onto plastic petri dish followed by the water evaporation at ambient temperature. The sandwiched films acquired by dip coating the rectangular GN/CNWs paper in the resin solution for 60 s, were named sandwiched film 650 (SF-650) and sandwiched film E888 (SF-E888). The sandwiched films were completely cured at ambient temperature for 24 h. The process for preparing the sandwiched film is shown in Fig. 1.

2.3. Characterization

The cross sectional morphology of the composites was investigated using scanning electron microscope (SEM, JSM-6301F, JEOL, Japan). X-ray diffraction (XRD, D/Max2500PC, Rigaku, Japan) measurements were performed using Cu Kα radiation at a scan speed 0.02° s^{-1} from 5° to 50°. Thermal behavior of the composites was studied on differential scanning calorimetry (DSC, Q20, TA instruments, USA) at a heating rate of 10 °C/min. Thermal stability analysis was carried out with thermogravimetric analysis (TGA, TA Instruments Q500, USA). Samples were heated in open platinum pan from room temperature to 700 °C, under a nitrogen atmosphere in order to avoid thermoxidative degradation due to oxygen, at a heating rate of 20 °C/min. Fourier transform infrared (FTIR, Agilent Technologies Cary 630, Australia) spectroscopy was used to analyze the chemical structures of the specimens. All spectra were collected after 32 continuous scans at a wavelength range of 4000–600 cm^{-1}. The static tensile strength was tested with dynamic mechanical analysis machine (DMA, TA instruments Q800, USA) with a loading rate of 0.25 N/min at room temperature. Storage modulus, loss modulus and glass transition temperature were determined by testing the samples on dynamic thermal mechanical analysis (DMTA, Q800, USA) at a heating rate of 3 °C/min, and pre-strain of 0.01% at a constant frequency of 1 Hz as a function of temperature from −60 to 120 °C. The samples for mechanical testing were cut in rectangular shape with the