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Original Research

Enhancement of the thermo-mechanical properties and efficacy of mixing technique in the preparation of graphene/PVC nanocomposites compared to carbon nanotubes/PVC

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Abstract

Thin films of poly vinyl chloride (PVC)/multiwalled carbon nanotubes (MWCNT) and PVC/graphene (GN) nanocomposites were prepared by mixing in the presence of different quantities of nanoparticles. Film casting was performed using tetrahydrofuran as a solvent. The as-prepared PVC/MWCNT and PVC/GN nanocomposites were characterized by scanning electron microscopy, Raman spectroscopy, X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and diffused reflectance spectroscopy. Only the PVC/GN nanocomposite films were evaluated further for detailed mechanical analysis because of the poor dispersion of MWCNTs in PVC. The PVC/GN nanocomposite films were thermo-mechanically more stable than the PVC films. These nanocomposites have potential as a replacement material for PVC and PVC/MWCNT owing to their better dispersion and high stability.

Keywords: Nanocomposite; Mechanical strength; Thermal stability; Band gap

1. Introduction

The advances in the synthesis of nanomaterials have encouraged research towards their possible use in the fabrication of nanocomposites [1,2]. Nanocomposites have attracted considerable attention because the physical properties of the host materials can be enhanced easily by the incorporation of suitable nanoscale materials. On the other hand, the selection of both an appropriate nano-filler and host material is essential for fabricating a nanocomposite towards a particular application.

Graphene (GN), a single layer of sp^2-hybridized carbon atoms in two dimensions, has attracted enormous attention in recent years on account of its outstanding thermal, mechanical and electrical properties [3–5]. Carbon nanotubes (CNTs), on the other hand, also have many unique properties, such as low-weight, high aspect ratio, and high electrical and thermal conductivity. Owing to their remarkable properties, both GN and CNTs have found applications in various fields, such as nanoelectronic devices, photovoltaic devices, transparent electrodes, sensors, super capacitors, and conducting composites, as well as in the automotive, aeronautic and aerospace industries [6–14].

Poly vinyl chloride (PVC) is the most widely used polymer after polyethylene and polypropylene. Moreover, it is inexpensive, chemically stable, biocompatible, and sterilizable [15]. The low thermal stability of PVC, however, has limited its application in fields requiring working at high temperatures [16]. Polymer nanocomposites show substantial property enhancement at much lower loadings than polymer composites with conventional micron-scale fillers (such as glass or carbon fibers) [17]. Sajini et al. [18] reported that GN-filled PVC nanocomposites have flexible conductivity, high mechanical strength and thermal stability. CNTs have also been used as a filler to improve the electrical and thermal conductivity of PVC [19]. Fillers, such as clay [20], wood fibers [21] and calcium carbonate [22] have also been used to improve the thermal and mechanical performance of PVC.

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Nanocomposites based on GN may have different physico-chemical properties than those based on MWCNTs because of the differences in the dispersion and aggregation behavior of these nanomaterials in the PVC matrix. To the best of the authors' knowledge, there are few reports on the interactions of MWCNTs or GN with the PVC matrix, which would affect their dispersion or agglomeration in PVC. Therefore, more research is needed on the preparative conditions as well as the physico-chemical difference of MWCNTs or GN composites with PVC to produce uniform dispersions of these nanomaterials for a range of applications. This paper reports the preparation of PVC/MWCNT and PVC/GN nanocomposite thin films from THF solutions produced using a mixing technique. The surface morphology, thermal properties and mechanical properties in terms of aggregation were also investigated.

2. Experimental

2.1. Materials

PVC (average molecular weight ~1020) was purchased from Yakuri pure chemicals, Japan and GN was obtained from Iljin Nano Tech, Seoul, Korea (thickness ~8 nm and mean length ~500 nm). MWCNTs (diameter ~10–20 nm and average length ~20 μm with 95% purity) were purchased from Hanwha Nanotech, Korea. Tetrahydrofuran (THF) was supplied by Duksan pure chemicals, Korea, and used as received.

2.2. Preparation of PVC/MWCNT and PVC/GN nanocomposites

Nanocomposites of PVC/MWCNT and PVC/GN were prepared by mixing MWCNT or GN in a PVC matrix using THF as the solvent. In a typical process, PVC was first dissolved in 50 mL of THF with continuous stirring until 24 h for complete dissolution. The MWCNT or GN was mixed separately with the above solution under continuous stirring and occasional shaking in an ultrasonic bath for the appropriate dispersion of these nanomaterials inside the THF solution of PVC. Subsequently, the films of the PVC/MWCNT and PVC/GN nanocomposites were prepared on the glass plates using a solvent casting technique. The films were then peeled off from the glass plates after evaporation of the solvent at room temperature. The prepared films were labeled PVC, PVC/MWCNT-1% and PVC/GN-1%, and PVC/GN-2% and PVC/GN-3%, as listed in Table S1.

2.3. Characterization

Structural analysis of the samples were carried out by X-ray diffraction (XRD, PAN analytical, X'pert PRO-MPD) over the range, 10–90° 2θ, using Cu Kα radiation ($\lambda = 0.15405$ nm). Raman spectroscopy (InVia Reflex UV Raman microscope, Renishaw, UK) was performed to examine the type of interactions between PVC and GN and between PVC and MWCNT in the nanocomposite films. The surface morphology was examined by scanning electron microscopy (SEM, Hitachi-4200). The optical properties were determined by ultraviolet-visible-near infrared (UV–vis–NIR, VARIAN, Cary 5000, USA) spectrophotometry. Thermogravimetric analysis (TGA, SDT Q600, USA) was carried out from 25 °C to 800 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere. Mechanical analysis was performed using a DMA Q800.

3. Result and discussion

3.1. Preparation of PVC, PVC/MWCNT and PVC/GN films

The PVC/MWCNT and PVC/GN nanocomposites were prepared using mixing technique. The PVC/MWCNT films were not smooth due to the aggregation of MWCNTs in different regions of the films, as shown in Fig. 1.

In contrast, the PVC/GN films showed a uniform distribution and good dispersion of GN in the PVC matrix. The basic difference between CNTs and GN is their shape. CNTs are cylindrical, whereas GN is sheet-like, which is responsible for their different interactions in solvents. The main hindrance to the widespread use of CNTs is their poor wettability [23–25] and the tendency to rope up in the solvents [26]. CNTs are found in the form of ropes or bundles, 10–25 nm in diameter and a few micrometers in length, owing to their high van der wall forces. The CNT ropes were entangled together in the solid state to form highly dense and complex structures, making them resistant to wetting [27–29]. The various areas of such films are expected to respond differently when studied for mechanical characterization due to the aggregation of MWCNTs in different regions of the films. Only PVC and PVC/GN nanocomposite films were tested by mechanical strength analysis due to the poor dispersion of MWCNT in PVC.

3.2. Aggregation/dispersion behavior of MWCNT inside PVC/MWCNT film

The PVC/MWCNT nanocomposites were prepared by mixing MWCNTs in a PVC solution (made in THF), and thin films of the PVC/MWCNT nanocomposites were prepared

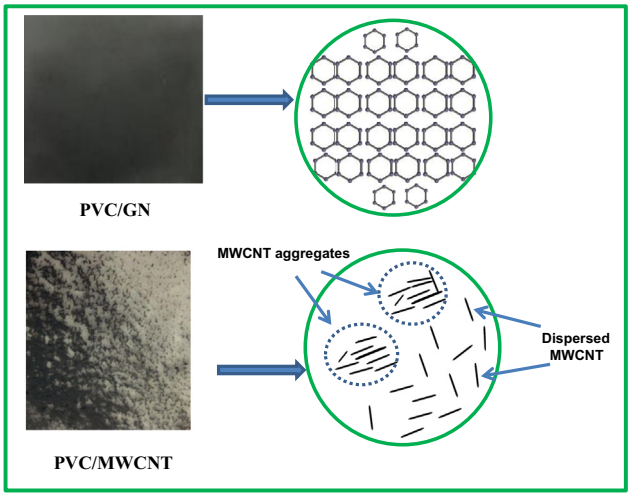

Fig. 1. Digital photograph of PVC/GN-1% and PVC/MWCNT-1%.