



Combined effect of expanded graphite and multiwall carbon nanotubes on the thermo mechanical, morphological as well as electrical conductivity of *in situ* bulk polymerized polystyrene composites



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ABSTRACT

Synergetic effect of multiwalled carbon nanotube (MWCNT) and expanded graphite (EG) on the properties of polystyrene matrix has been studied extensively. PS/EG, PS/MWCNT, PS/EG/MWCNT nanocomposites were prepared by bulk polymerization method. Thermo mechanical and electrical conductivity were increased with individual or combined addition of MWCNT and EG to the polystyrene. Raman and FTIR study confirmed acid modification of MWCNT. DMTA and DSC analysis revealed PEM (composite of polystyrene with 1 wt% expanded graphite and modified MWCNT) composite has the highest storage modulus and glass transition temperature. TGA analysis showed that the incorporation of dual filler enhanced the thermal stability of nanocomposites to a large extent. Dispersion of both the nanofillers was found to be better in presence of each other.

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1. Introduction

Polymer nanocomposites with conducting fillers have been the focus for many research groups in past few decades. Mainly the polymer composites with conducting carbon based nanofillers (i.e. Multiwalled carbon nanotube (MWCNT), Multilayer graphene (MGP), carbon nanofiber) have versatile applications. These applications mainly include electromagnetic shielding, anti-static, corrosion resistant coatings, batteries, fuel cells, etc. [1]. Addition of MWCNT or natural graphite flake can amend the mechanical properties, electrical and thermal conductivity. Among the various conducting fillers, natural graphite, which possesses good electrical conductivity of about 10^4 S/cm at ambient temperature, has been widely used [2,3]. The plausible reason for this is the sheet-like structure of natural graphite where the atoms are strongly bonded on a hexagonal plane but weakly bonded normal to that plane. If these sheets/layers could be separated down to a nanometer thickness, they would form high aspect ratio (200–1500) and high modulus (~ 1 TPa) graphite nanosheets [4]. Still two main factors confine the application of the polymer nanocomposites with carbon nanofillers: (i) the poor dispersion in polymer matrices, which restricts the potential enhancement of polymer composites and (ii) high cost [5]. Furthermore expanded graphite (EG) is composed of multi graphene layers and these layers are

situated at a large distance than the natural flake graphite [6]. The graphite nanosheets could have an enormous surface area (up to 2630 m²/g) considering both sides of the sheets are accessible [7]. The EG shows anticipation for application as nanofillers materials in polymer composites due to their high aspect ratio, graphitized plane structure, high conductivity and low manufacturing cost [8–10]. In general a high contact area between EG plates and the polymer chain enhances the reinforcing effect of EG. The EG platelets restricted the motion of polymer chain segments and enhances storage modulus of the nanocomposites by maximizing the load or stress transfer from polymer matrix to nanofiller and makes the polymer composites thermo-mechanically stable [11]. As EG sheet has high surface area and high aspect ratio, so graphite intercalated compound has high thermal conductivity and it could be a good candidate for thermal management systems and could be used where high thermal dissipation is required [12,13]. It has been shown that multi-pores of the EG morphology and functional acids containing –OH groups will facilitate physical and chemical adsorption of polymer solution in between the EG [14–16]. Zhao et al. has shown that ultrasonically dispersed expanded graphite/PPS (PPS/S-EG) nanocomposites has shown higher conductivity, mechanical strength and thermal stability than the PP/EG nanocomposite due to the small particle size of S-EG [17]. Fawn et al. [18] studied the mechanical properties of PA-6/graphite nanocomposites, using pristine graphite, expandable graphite and expanded graphite. When they compared to PA-6/montmorillonite clay nanocomposites of similar filler

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dispersion, the PA-6/graphite nanocomposites showed higher improvements in flame retardant properties, especially by using the expandable graphite due to its heat resistance behavior, but not as good thermo-mechanical properties as the PA-6/clay nanocomposite equivalents. Fukushima et al. has shown that addition of expanded graphite to the polymer nanocomposites accelerates the crystallization process of the nanocomposites [19].

Multiwalled carbon nanotubes (MWCNTs) exhibit excellent mechanical strength (Young's modulus ~ 2 TPa). The tensile strength, tensile modulus and poison ratio of nanotubes have been reported to be in the range of 37–100 GPa, 0.9 TPa [20] and 0.14–0.28 [21], respectively. MWCNTs have high flexibility [22] and excellent electrical property [23]. These properties make MWCNTs an ideal filler material in composites [24].

Bulk polystyrene is an important colorless polymer and resistant to chemical and light corrosion. Polystyrene resins are the most popular materials for building and construction applications, like Insulation foam, roofing, siding, panels, bath and shower units, lighting, plumbing fixtures. However, bulk PS often lacks suitable thermal stability and mechanical properties. Thus, to improve these different properties nanomaterial has been used as fillers in bulk polystyrene. Suckeveriene et al. [25,26] has shown the polymerization technique of styrene in the presence of nanosilica nanoparticles and the grafting of PS chains on the surfaces of nanoparticles via a peroxide bulk polymerization method.

Recently polymer based nanocomposites reinforced with expanded graphite have shown substantial improvements in mechanical, electrical conductivity and barrier properties in several polymers, such as poly (methyl methacrylate) (PMMA), polyamide-6 (PA-6), polyethylene (PE) [1,6,27]. The reason for this is that graphene sheets/layers characterized by high modulus (1 TPa), could be separated down to a nanometer thickness, with high aspect ratio (200–1500). Furthermore, the graphite nanosheets could have an enormous surface area (up 2630 m²/g) considering that both sides of the sheets are accessible [28]. Therefore, the dispersion of such nanosheets in a matrix can play a key role in the improvement of both physical and mechanical properties of the resultant nanocomposites [29,30]. Since the expanded graphite are composed of small thin graphene layer and they are bound by strong π - π interaction force so it is very difficult to disperse the expanded graphite uniformly in the polymer matrix. Thus, the performance of graphene-based polymer composites is limited by the aggregation and stacking of MGP sheets. Although acid modification of expanded graphite may increase the dispersion of expanded graphite in polymer composites but the severe reaction conditions of acid oxidations may cause serious damage on the graphitic structure, and loss of the intrinsic properties of nanocomposites.

The key purpose of this study is to investigate the improved thermo-mechanical, electrical and thermal conductivity of the PS/EG/MWCNT nanocomposites. For this we have chosen long, tortuous and one dimensional MWCNT which can penetrate into the inter gallery of the layer of expanded graphite [5]. This also helps for the potential penetration of the polymer chain into the inter gallery expanded graphite layer. This result is in an increased contact surface area between EG/MWCNT structures and the polymer. So a notable combined effect of expanded graphite, MWCNTs on the enhanced mechanical properties and conductivity of these polystyrene composites was demonstrated.

2. Experimental

2.1. Materials details

Styrene used was of synthesis grade and procured from Merck, Germany. (ii) Benzoyl peroxide (BP), was obtained from

Sigma-Aldrich. MWCNTs (MWCNTs-1000) were procured from Ijin Nano Technology, Korea. The diameter; length and aspect ratios were 10–20 nm, 20 μ m and ~ 1000 , respectively. The density of MWCNT is 2.16 gm/cm³. Expanded graphite was supplied by Timcal Belgium S.A. as TIMREX BNB90. The THF was procured from Sigma-Aldrich and H₂SO₄, HNO₃ both were supplied by Ekta International (Export Division of Navin Chemicals), Mumbai.

2.2. Preparation of functionalized MWCNTs (MWCNT-COOH)

Pure MWCNTs (2 gm) were first ultrasonicated in Tetrahydrofuran (THF) for 1 h at room temperature and then refluxed at 120 °C for 4 h using a round bottom conical flask with a magnetic stirrer (mild stirring). After cooling, the mixture was washed with distilled water. Then unmodified MWCNTs were dispersed in an acid solution consisting of 3:1 concentrated H₂SO₄/HNO₃ mixture (200 ml) and were refluxed for 24 h at 80 °C. After refluxing, the solution was filtered with distilled water and acetone until the pH reached 6–7. The purpose of acid modification is to exfoliate graphite layers [31,32]. It etches away the ends and a sidewall defect sites, where ring strain is large enough to allow chemical attack, and incorporate carboxylic acid groups. A schematic diagram of the whole process has been depicted in Fig. 1.

2.3. Preparation of nanocomposites

For the preparation of nanocomposite styrene (250 ml) was taken in a 500 ml separating funnel and 20 ml of 5% NaOH solution was added to it. The mixture was shaken for 15 min and the purified styrene was decanted into a 250 ml beaker. This process was continued for five times. Finally, after washing with de-ionized water, the purified styrene was collected. 40 ml purified styrene monomer was taken in a 250 ml round shape three-neck glass reactor. Then the reactor, connected with the refluxing condenser and nitrogen inlet to one of the three necks, was immediately placed on a hot plate magnetic stirrer. Required amount (1 wt.%) of the benzoyl peroxide, as polymerization initiator, was added to the styrene under constant stirring (magnetic stirrer) and the reactor temperature was gradually increased to 85 °C. The reaction was continued for 5 h under nitrogen atmosphere with constant temperature and stirring. Finally it was dried in an air oven at 60 °C for 24 h. The final bulk polymerized polystyrene was weighed and it was found to be 32 gm. In order to make 1% MWCNT/PS composite, desired amount of MWCNT (0.32 g) was dispersed in 40 ml styrene monomer in a 250 ml round shape three-neck glass reactor. The MWCNT/styrene dispersion was ultrasonicated for 2 h at room temperature. Then the styrene dispersed with MWCNT was subjected to bulk polymerization through the above mentioned method. Similarly, by this method four composites (PE, PC, PEC and PEM) were prepared. The compositions of the composites are given in Table 1.

2.4. Characterizations

2.4.1. IR measurement

Fourier Transformation Infrared Spectroscopy (FTIR) was recorded on a NEXUS 870 FTIR (Thermo Nicolet) instrument to detect the functional group incorporated on the surface of MWCNT after acid modification. The tests were conducted in a moisture free atmosphere at room temperature from 400 to 4000 cm⁻¹.

2.4.2. Raman study

Raman spectra were recorded in between 1100 and 1900 cm⁻¹ in a Raman imaging system WITEC alpha300 R with 532 nm wavelength.

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