Composites Part B 80 (2015) 101–107

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Mechanical, flow and electrical properties of thermoplastic polyurethane/fullerene composites: Effect of surface modification of fullerene

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ARTICLE INFO

Article history:
Received 12 December 2014
Received in revised form
5 May 2015
Accepted 6 May 2015
Available online 14 May 2015

Keywords:
A. Polymer-matrix composites (PMCs)
A. Particle-reinforcement
D. Mechanical testing
E. Extrusion

ABSTRACT

Thermoplastic polyurethane (TPU) composites with fullerene loadings varying from 0.5 to 2 weight% were prepared by melt-mixing method. Nitric acid oxidation and silanization were applied to fullerene surface to improve interfacial interactions with TPU matrix. The influence of surface modifications of fullerene on mechanical, melt flow and electrical properties of TPU based composites were investigated. Incorporation of fullerene leads to nearly twofold increase in tensile strength and Young's modulus of the composites in addition to enhancing the flexibility. The best results are obtained in nitric acid and silane modified fullerene containing composites at the lowest concentration (0.5%). Higher MFI values were observed for composites loaded with surface treated fullerenes compared to pristine fullerene because of their better dispersion in TPU. Electrical properties of TPU also improved by the addition of surface modified fullerene particles. Surface oxidation and silanization gave rise to dispersion homogeneity which may be the reason of both tensile strength and strain improvements at the same time.

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1. Introduction

Fullerene is a member of carbon nanostructures family which has zero-dimensional structure. Research efforts based on fullerene chemistry with combination of macromolecular chemistry led to develop easily processable fullerene-containing polymeric materials [1]. However, organic modifications are required since pristine fullerene tends to form aggregates very easily and is difficult to handle. Formation of self-aggregation causes poor miscibility of fullerene and limits its applications [2,3].

Polymer composites containing fullerenes have great potential for versatile applications which include optical interrupters, polymer photoconductors, electrodes in lithium batteries, electro-optical structures in nano-electronics, nonlinear optics and photovoltaic devices [4–9]. Reinforcing ability of carbonaceous fillers is mainly related to mechanical performance and electrical conductivity improvement for polymer composite applications [10–12]. Incorporating nano-fillers in polymeric matrices has been applied in three different ways such as solution, in-situ and melt mixing. Many of the lab-scale studies have been made by using mainly first two methods but melt compounding is the one that is most practical and suitable for large scale composite production in industrial applications. The efforts towards fullerene reinforced composites for practical applications that have been performed by using melt compounding are very limited in academic field. Fullerene has been used as additive in several thermoplastic polymers including polyethylene [13,14], polypropylene [15,16], polyamide [17] and poly(ethylene-co-acrylic acid) [18] with melt mixing method.

Thermoplastic polyurethane (TPU) has desirable properties such as excellent mechanical properties, chemical resistance and easy processibility. Beside these general characteristics, TPU is a fully recyclable polymer that makes it cost-effective. Majority of TPU application is across a range of markets including automotive, sporting goods, medical devices, tubes, hoses, wires and cables. In addition to these general applications, polyurethane can gain shape memory actuation when they are loaded with conductive

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http://dx.doi.org/10.1016/j.compositesb.2015.05.013
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carbonaceous fillers [19–21], they can be used in electronic packaging thanks to their high flexibility [22], because of their electro-striction effect, they can be used as an actuator [23,24] and they can gain gas barrier property [25] with the addition of fullerene particles.

To our best knowledge, this research is the first study that investigates the properties of fullerene filled TPU with melt blending method. In the current study, fullerene is functionalized by using nitric acid and amino functional silane coupling agent. Pristine and surface modified fullerenes were incorporated in TPU matrix by using melt mixing method. In order to characterize fullerene surfaces, fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray spectroscopy (EDX) techniques were used. Mechanical properties, melt flow characteristics, thermal properties and electrical conductivities of composites were evaluated by tensile test, melt flow index (MFI) test, differential scanning calorimetry (DSC) analysis and dielectric measurements, respectively. Dispersion of fullerene particles into TPU matrix was examined by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Fullerene carbon soot was purchased from Acros Organics (USA) (180–200 mesh) used in this study. The commercial polyester-based thermoplastic polyurethane (Texalan® 485A) was obtained from Pasific (Covina, USA). It has a density and hardness of 1.20 g/cm^3 and 85 (Shore A), respectively. 3-Aminopropyltriethoxysilane (APTES), ethanol and nitric acid (HNO_3, 65%) were supplied from Merck.

2.2. Surface modifications of fullerene

Fullerene soot was annealed at 450 °C for 4 h, initially. The pristine fullerene is coded as C_{60}. Chemical oxidation of fullerene was carried out by using similar methods employed by Toppare et al. [26] and others [27,28]. 1.6 g of C_{60} was refluxed at 120 °C with 70 ml concentrated HNO_3 solution for 48 h. The mixture was diluted with distilled water and filtrated, then the product was washed with distilled water and dried under vacuum for 2 h. The nitric acid treated fullerene was coded as Ni–C_{60}. During silane treatment, Ni–C_{60} was mixed in 2 wt% APTES/ethanol solution for 80 min by using ultrasonication at room temperature. After silane treatment, product was washed with ethanol several times. The silane modified fullerene was coded as Si–C_{60}.

2.3. Preparation of TPU/fullerene composites

TPU was dried at 100 °C for 2 h prior to compounding. TPU based composites were prepared via melt mixing in counter rotating twin screw microextruder (15 ml microcompounder, DSM Xplore, Netherlands) at a screw speed of 100 rpm at 210 °C for 8 min. Fullerenes were incorporated at four different compositions of 0.5, 1, 1.5 and 2 weight% in TPU matrix. Test samples were prepared by injection molding instrument (Microinjector, Daca Instruments) at a barrel and mold temperature of 215 °C and 40 °C, respectively.

2.4. Characterization methods

FTIR measurements in attenuated total reflectance (ATR) mode were performed by using IR-spectrometer (Bruker VERTEX 70) at a resolution of 2 cm^{-1} with 32 scans between 600 and 3800 cm^{-1} wavenumbers. Modified and untreated surfaces of C_{60} and cyro-fractured surfaces of composites were examined by FEI Quanta 400F Field Emission Scanning Electron Microscope. The SEM photographs were taken at different magnifications varied from ×50,000 to ×200,000. The measurements of the tensile properties were carried out by using Lloyd LR 30 K universal tensile testing machine with load cell of 5 kN at crosshead speed of 5 cm/min according to the standard of ASTM D-638. Tension tests were conducted on dog-bone shaped samples (7.4 × 2.1 × 80 mm^3). Tensile strength, percentage elongation at break and tensile modulus values were recorded. All the results represent an average value of five samples with standard deviations. Thermal properties of composites were determined by differential scanning calorimetry (DSC 4000, Perkin Elmer) from −50 °C to 250 °C under nitrogen atmosphere at heating rate of 10 °C/min. MFI measurements were studied by using Coesfield Material Test, Meltfixer LT. The test was carried out at 215 °C under specified load of 5 kg. The MFI values of TPU and its composites were reported as the average of ten measurements. For dielectric measurements, the surfaces of the samples were covered with silver paste to form electrodes. The dielectric measurements were performed between 500 Hz and 1 MHz frequency range at different temperatures (80 K–400 K) by using Agilent 4284A LCR Meter. The real part of dielectric constant was calculated by using following equation:

$$\varepsilon' = C_P d/\varepsilon_0 A$$

Where, C_p is the capacitance of the sample, ε_0 (dielectric permittivity in vacuum), A is the effective surface area, and d is the thickness of the samples. AC-conductivities (σ_{ac}) of the samples were calculated with the following equation:

$$\sigma_{ac} = \omega C_P d \tan \delta / A$$

Where; tanδ is dielectric loss factor, ω is the angular frequency ($2\pi f$).

3. Results and discussion

3.1. SEM/EDX analysis

SEM images with 50,000 magnifications and EDX data of pristine and surface treated C_{60} samples are shown in Fig. 1 and Table 1, respectively. According to SEM images, Ni–C_{60} and Si–C_{60} are seen in more bulky form relative to pristine C_{60} which may be arise from the increasing of the intermolecular forces such as hydrogen bonding after nitric acid and silane treatments. It is clearly observed from the elemental analysis on Table 1 that oxygen content rises by a factor of two times after nitric acid modification due to hydroxyl groups on fullerene surface and remarkable silicon percentage is observed after silanization which indicates the formation of siloxane units at the surface of fullerene after the reaction of silane coupling agent with surface hydroxyl groups. Oxygen content also increases somewhat possibly due to siloxane adsorption on the fullerene surface.

3.2. FTIR analysis

FTIR spectra of C_{60} and surface treated C_{60} samples are shown in Fig. 2. The four intense peaks at 530, 580, 1180 and 1430 cm^{-1} are the characteristic C_{60} peaks that appear in all spectra [29]. Absorption bands from 1000 to 1500 cm^{-1} range indicate the oxygen functionalities such as C–O stretching at broad peak from 1100 to 1200 cm^{-1} in which absorption increment of the peak for Ni–C_{60} can be clearly seen. Si–O–Si vibration band at 1050 cm^{-1} and Si–O–C vibration band at 1100 cm^{-1} present for Si–C_{60} only due to the formation of siloxane units after silane treatment [30,31]. The absorption band at 875 cm^{-1} indicates the Si–OH bond which corresponds to hydrolyzed silane portion during silanization [32].

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