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Quantifying microstructure, electrical and mechanical properties of carbon fiber and expanded graphite filled cyclic olefin copolymer composites

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ABSTRACT

In this study, micro-structural features and physical properties of cyclic olefin copolymer composites filled with different amounts of carbon fiber (CF) and expanded graphite (EG) were studied. The electrical percolation for the CF and EG were found to be 30 phr (volume fraction of 0.142) and 20 phr (volume fraction of 0.083), respectively. It was also found that the electrical conductivity of double-filler composites was higher than those of single-filler counterparts at a particular filler amount which implied that more conduction pathways were formed via the connection points of CF rods and EG sheets into the structure.

1. Introduction

Carbon filled polymer composites (CPCs) have attracted great industrial and scientific research interests in last decades due to their superior electrical, thermal and mechanical properties and promising applications such as electromagnetic shielding, conductive film applications, bipolar plate material in fuel cell systems, batteries, and sensors [1]. Many of the reported studies on the structural and physical properties of CPCs have generally focused on the preparation of electrically conductive polymer composites filled with various forms of carbon such as carbon black [2–4], single or multi-walled carbon nanotubes [5–9], carbon fibers [10–12], fullerenes [13–15], graphite and graphene derivatives [16–20]. Especially carbon nanotubes (CNTs) have generated great scientific attention since they provide superior physical performance and electrical conductivity at very low loading amounts compared to other types of carbon fillers. But, lack of mass production and cost of carbon nanotubes are still serious drawbacks for their industrial usage in the production of low-cost conductive CPCs as well as fullerenes. On the other hand, carbon black (CB) and graphite (G) have been considered the more versatile and low-cost fillers for preparing of CPCs compared to CNTs. Graphite, the low-cost filler alternative for the CPCs, is a two-dimensional (2D) carbon filler formed by the stacks of one-atom-thick planar graphene sheets which is densely packed carbon atoms in a honeycomb crystal lattice. Expanded graphite (EG) is the physically modified form of graphite. Commercially available grades of EG are generally prepared via the routes of oxidation of stack surfaces with strong acids and oxidants that yields graphite oxide (GO) then the thermal expansion of GO by rapid heating. EG exhibits much lower bulk density, higher surface area and higher porosity than the graphite. Thus, the EG is more effective filler to improve the electrical conductivity and mechanical properties of CPCs compared to graphite at a particular loading amount of filler. Carbon fiber (CF) is a macrofiller which consists of graphene sheets in molecular scale. It has been projected that the CF will become the most widely used reinforcing agent for the engineering applications of polymer based composites due to its high stiffness, tensile strength, chemical resistance and temperature tolerance and low weight and thermal expansion. Chopped fibers, prepregs or fabrics are the most widely used forms of CFs to improve the mechanical performances of resin or thermoplastic based polymer composites especially in aircraft and aerospace industry [21–23].

Using of immiscible polymer blends and combination of various types of conductive fillers into the composite structure have been studied to increase the electrical conductivity of CPCs [24–27]. It has been reported that the using of conductive filler combinations could yield a significant increase in the electrical conductivity of CPCs which called as the "synergic effect" [28,29]. Such improvement cannot be normally achieved by single filler individually at the same amount of filler. Effects of using of dual or triple filler

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combinations on the electrical conductivity of CPCs have been investigated for the "carbon fiber/carbon black" [30], "carbon fiber/graphite" [31] and "carbon fiber/carbon black/graphite" [28] systems.

On the other hand, investigation of effects of various forms of carbon based fillers on the rheological properties of CPCs is another important issue for the melt processing operations because a sufficient electrical conductivity generally requires quite much amount of filler which could lead to significantly increase the melt viscosity of polymers. Many studies have been published about the investigation of rheological and mechanical properties of CPCs [26,32,33]. In these studies, variation in viscoelastic parameters such as shear modulus (G', G'' or E', E''), dynamic viscosity (η^*), compliance (J^*) and phase angle ($\tan\delta$) have been measured via rheological and dynamic mechanical measurements and concluded depending on the compositional variations. Motlagh et al. investigated the electrical and rheological properties of CPCs prepared with carbon fiber (CF) and carbon black (CB) by melt compounding [34]. They reported that the electrical percolation thresholds of the CB and CF were about 2.7% (v/v) and the using of higher amount of carbon fiber (CF) than the carbon black (CB) into the matrix lead to better processability.

Cyclic olefin copolymers (COC) are new type olefinic copolymers, obtained from the copolymerization of linear and cyclic olefins, exhibit superior mechanical properties, excellent transparency, low moisture absorption and good resistance to solvents. Various cyclic olefins, derivatives of norbornene and dicyclopentadiene, can be used to synthesize COCs. Norbornene is the most widely used bicyclic olefin monomer in the COC structure. Chemical structure of poly(ethylene-norbornene) copolymer is given in Fig. 1. Depending on the mole or weight ratio of the norbornene units in the structure, COCs exhibit relatively high glass transition temperatures compared to other polyolefin copolymers and thus provide long service life without a significant loss in physical properties. Preparation and investigation of physical properties of COC nanocomposites including various types of inorganic fillers such as silica [35,36], titania (TiO_2) [37], organoclay [38] and polyhedral oligomeric silsesquioxanes (POSS) [39] have been studied. To the best of knowledge, only few works have been reported on the preparation and characterization of COC composites filled with conductive fillers [32,34].

In this study, morphological, electrical and mechanical properties of cyclic olefin copolymer composites reinforced with carbon fiber as a macrofiller and expanded graphite as nano-sized filler were investigated in detail for the first time. Micro-structural features and physical properties of a series of composites including different amounts of CF and EG were studied. Synergistic effects of fillers on the electrical conductivity of composites were also analyzed.

2. Experimental

2.1. Materials

The cyclic olefin copolymer (COC) used in this study was a commercial grade copolymer, Topas® 5013, kindly donated by Ticona. Commercial grades of carbon fiber (AKSACA®) and expanded graphite (TIMREX® BNB90) were also kindly provided by AKSA (Turkey) and TIMCAL (Switzerland). Carbon fiber is a chopped strand of surface modified grade with a phenoxy-based resin. Some physical properties of the polymer and fillers employed in the study are listed in Table 1.

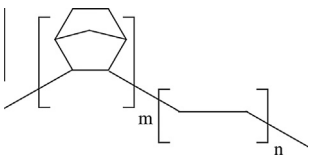

Fig. 1. Chemical structure of cycloolefin copolymer.

2.2. Sample preparation

Composite samples were prepared by the melt processing method in a lab-scale, co-rotating twin screw extruder (Rondol Micro Lab., UK, D: 10 mm, L/D: 20) with a screw speed of 70 rpm. Intermeshing screws of the extruder were configured as including 3D of 4 × 60° followed by 2D of 4 × 90° kneading segments. A temperature profile of 190–220–230 °C was applied throughout the barrel from the feeding zone to die. A rod die with the diameter of 2 mm was used and the extrudates were granulated. Before the melt processing, all materials were dried in a vacuum oven overnight at 70 °C. For conductivity and dynamic mechanical tests, test specimens (5 × 1 × 0.1 cm in length, width and thickness) were prepared by compression molding under the pressure of 5 tones at 220 °C. Sample compositions are designated as CF*x*, EG*y* and CF*x*EG*y* where *x* and/or *y* indicated the filler amount into the composition as phr (part of filler per hundred of polymer). Sample compositions systematically varied in the single and double filler containing composites. Amount of filler varied in the range of 5–80 phr for the series of composites prepared with the CF and in the range of 5–40 phr for the series of samples prepared with the EG.

2.3. Scanning electron microscopy (SEM) study

Morphologies of the fillers and composites were investigated by a field emission scanning electron microscope (FE-SEM, FEI Quanta FEG 450) operated at 30 kV. Fractured surfaces of the test specimens into liquid nitrogen were directly imaged in the electron microscope after a proper sample preparation.

2.4. Electrical conductivity measurements

Electrical conductivity measurements were carried out both an impedance spectroscopy analyzer (Solartron SI 1260 Impedance/gain-phase analyzer and Solartron dielectric interface 1296 devices) which works with alternative current (AC) at 100 mV between the frequency ranges of 10^6–10^0 Hz and a multimeter (Keithley 2100/120 $6_{1/2}$-Digit USB Digital Multimeter) that works with direct current (DC) by four probe method. The surfaces of specimens directly contacted with electrodes were coated with the conductive silver paste to provide better surface contact. Conductivity measurements were firstly performed with five samples

Table 1
Some physical properties of the materials used in the study.

	COC	Carbon fiber	Expanded graphite
Commercial Name	Topas® 5013	(AKSACA®)	TIMREX® BNB90
Density (g/cm^3)	1.02	1.7–2.0	2.24
T_g[a] (°C)	134		
MVR[b] (ml/10 min.)	48		
Surface area (m^2/g)			28
Particle size (d_{90})		*D*: 8 μm *L*: 3 mm	85.2 μm
OAN[c] (ml/100 mg)			150
Aspect ratio		375	–

[a] Glass transition temperature measured with DSC method.
[b] Melt volume flow index under the test conditions of 260 °C and 2.16 kg (ISO 1133).
[c] Oil adsorption number (ASTM).