



Fracture toughness and deformation mechanism of un-vulcanized and dynamically vulcanized polypropylene/ethylene propylene diene monomer/graphene nanocomposites



M. Haghnegahdar, G. Naderi*, M.H.R. Ghoreishy

Department of Polymer Processing, Iran Polymer and Petrochemical Institute, Tehran, Iran

ARTICLE INFO

Article history:

Received 16 November 2016

Received in revised form

14 January 2017

Accepted 18 January 2017

Available online 20 January 2017

Keywords:

Fracture toughness

Impact behavior

Nano composites

Notch

Fractography

ABSTRACT

Polypropylene (PP)/Ethylene propylene diene monomer (EPDM)/graphene nanocomposites were prepared by melt mixing process via an internal mixer (Brabender plasti-corder). The effect of multi-layer graphene (MLG), few-layer graphene (FLG) and dynamic vulcanization on microstructure and fracture toughness of the multicomponent system were investigated. The morphology of the samples were characterized by wide X-ray diffraction (WAX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which revealed that graphene mostly was dispersed into the PP phase and the size of the dispersed phase (EPDM) was decreased with incorporation of graphene, more specifically FLG, in both un-vulcanized and vulcanized systems. The concept of essential work of fracture (EWF) was used to analyze the fracture toughening behavior and deformation mechanism of PP/EPDM/graphene nanocomposites. In the case of un-vulcanized polymer, the total work of fracture improvements (+23.5%) was noted for PP/EPDM/FLG in which FLG platelets with higher aspect ratio were used, showed the better dispersion and higher ductility fracture behavior compared with MLG. The fracture mechanism of un-vulcanized samples occurs due to debonding and/or cavitation of the dispersed phase (EPDM), while for vulcanized samples the fracture mechanism proceeds through creation of nanovoids and cavitation in the dispersed phase which lead to the shear yielding of PP matrix. The graphene platelets acted as crack initiation sites as well as obstacles against crack propagation. The results of microstructure properties along with the fracture analysis data showed that the aggregated MLG platelets act as stress concentration and facilitate the initiate cracks while the FLG platelets hindered the crack path. Improvement in toughness behavior and matrix resistance were attributed to higher voiding stresses and finer dispersion of graphene.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

In the past decades, the toughening of polypropylene (PP) has been the subject of considerable research because of the brittle fracture of PP matrix at high impact rate or low temperature [1–3]. One of the most simple but impressive methods to improve PP impact toughness is the melt blending of PP and elastomers such as ethylene–propylene rubber (EPR), styrene–butadiene–styrene (SBS) copolymer, 4 butyl rubber, and ethylene–propylene–diene rubber (EPDM) [4,5]. Among these rubbers, EPDM is considered as one of the most effective impact modifiers for PP matrix.

A thermoplastic elastomer (TPE) is category of a polymeric material with functional performance, mechanical and elastic properties of similar to those of a conventional vulcanized rubber [6,7]. TPE is a special class of copolymers with unique features such as melt processability, low compression set and recyclability [6]. One of the well-known TPE categories is a dynamically cured blend termed thermoplastic vulcanized (TPV). Dynamic vulcanization is the procedure where curing agents are used to selectively cross-link the elastomeric phase during melt mixing [8,9]. The process always needs to be carried out under high shear, above the melting temperature of the thermoplastic component and at the processing conditions to activate and pursue the process of vulcanization of the rubber component. In fact, the mechanism of rubber toughening usually sacrifices the stiffness and modulus of PP. Hence, the incorporation of a reinforcing filler to toughed PP is substantially

* Corresponding author.

E-mail address: G.Naderi@lppi.ac.ir (G. Naderi).

crucial in order to hold the balance between stiffness and toughness. The introduction of nanofillers into PP/EPDM blends can restore the required strength and stiffness [6,10].

Among the nanofillers, graphene has effective reinforcing effects because of its large aspect ratio and high Young's modulus (~1 TPa), high tensile strength (130 ± 10 GPa) and extensive specific surface area (SSA) [11–13]. Graphene is basically a single atom thick layer of graphite with crystal lattice comprised of hexagonally arranged sp^2 bonded carbon atoms of interconnected benzene rings [14–16]. Expanding the high performance of polymer/graphene nanocomposites, requires strong interfacial interactions between graphene and polymeric matrix which certifies the effective load transfer from polymeric matrix to graphene layers [17,18]. Graphene layers are usually aggregated in polymeric matrix because of the strong affinity of graphene layers to each other via π -stacking and Vander Waals force [19,20]. The aggregated state of graphene may be highly compliant which can decrease the efficient aspect ratio of the graphene layers, and diminish the reinforcing effect through the creation of microscopic defects form [21,22]. Additionally, strong interfacial adhesion between graphene layers and polymer matrix is also crucial for effective reinforcement [23–25]. In order to improve the compatibility of graphene layers with polymer chains and also restrict the aggregation and stacking structure of graphene layers in polymer matrix, addition of compatibilizer such as Maleic anhydride grafted polypropylene (PP-g-MA) are generally employed in order to reach a fine dispersion of graphene layers in the PP/EPDM and enhance stiffness [26–28]. It is expected that achieving nanoscale dimensions of dispersed graphene layers in the polymer matrix leads to a substantial improvement of stiffness without considerable loss of impact strength [29,30].

Furthermore, no studies regarding the effect of graphene on the fracture toughness behavior and deformation mechanism based on PP/EPDM in un-vulcanized and vulcanized systems have been reported to this date. The main objective of this work is to study the parameters affecting fracture toughness and deformation mechanism. For this purpose, initially, PP/EPDM nanocomposites were prepared via melt blending process, subsequently, the influence of graphene type such as multi-layer graphene (MLG) and few-layer graphene (FLG) in addition to PP/EPDM composition and also dynamic vulcanization on fracture toughness behavior were investigated using the essential work of fracture (EWF) method. The morphology of fractured surface and subsurface of EWF test were investigated in which morphology development of the fracture surface of notched Izod impact test and fractured subsurface of the tensile EWF measurements was evaluated. The aim was to obtain more insight into the effect of different kinds of graphene (MLG and FLG) on fracture characteristics of toughened PP/EPDM blends. The effect of different dispersion state and aspect ratio of graphene were investigated on the nano and micro-deformation mechanisms that were included in the toughening of such PP/EPDM and its nanocomposites.

2. Experimental

2.1. Materials

The basic specifications of PP (MOPLN-MR230C), EPDM (KEP270) and graphene N002-PDR (designated as FLG) from Angstrom Materials, Inc. (Dayton, OH), employed in this study are reported in Table 1. The maleic anhydride-modified polypropylene (PP-g-MA) Epolene G3015 (acid number = 15 mg of KOH/g PPMA, MW = 47,000 g mol, MA = 1.3%) was obtained from Eastman Chemical company. The curing system Zinc Oxide (ZnO), Stearic Acid (St.Ac), Sulfur (S), Tetramethylthiuram Disulfide (TMTD) and

2-Mercaptobenzothiazyl Disulfide (MBTS) were supplied from Malaysia, Korea Kumho polychem and Bayer Company, respectively.

2.2. Preparation of PP/EPDM nanocomposites

For the preparation of un-vulcanized and vulcanized PP/EPDM and theirs nanocomposites, melt-mixing was performed using an internal mixer (Brabender plasti-corder) with the rotor speed ratio of 2: 3, roller blades, chamber volume 55 cc and fill factor 0.75. For un-vulcanized specimens in the first step of the process, the graphene powder, PP pellets and PP-g-MA were dry-mixed in a bag to ensure that the materials were well distributed at the macro scale level. In all instances, graphene and PP-g-MA were dried in a vacuum oven at 120 °C for more than 12 h before the melt mixing process. The mixture was then melt-mixed at 180 °C to obtain a master batch (PP/PP-g-MA/graphene nanocomposites) using the mixer at a rotor speed of 100 rpm for 10 min to give the desired composition (Table 2). In the second step, PP/graphene nanocomposite and EPDM were mixed prior to being fed to the mixer and then the same processing conditions were applied. The preparation of vulcanized specimens have an additional step after loading EPDM as follows: ZnO and St. Ac. were added to the mixer, after MBTS, TMTD and sulfur was added to the mixer and mixed for 1 min, sulfur was added followed by continuous mixing for 5 min. The composition of curing system of vulcanized samples are given in Table 3. Finally sheets with 1 mm thickness were cut into rectangles for EWF test after being prepared by hydraulic hot press according to ISO 293.

2.3. Characterization

Raman spectroscopy was performed with Labram Raman spectroscopy (Horiba, Jobin-Yvon spectrometer) in the range of 1000–3000 cm^{-1} at room temperature using a 632.8 nm laser. The C1s and O1s binding energies of the graphene (FLG and MLG) was measured by using an X-ray photoelectron spectrometer (XPS, X-TOL, ULVAC-PHI.) equipped with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV).an X-ray photoelectron spectrometer. Wide X-ray diffraction (WAX) measurements were performed on a diffractometer Bruker D8 to measure d-spacing of nanoparticles in the PP/EPDM using Bragg's equation: $2d\sin\theta = n\lambda$, where n is an integer determined by the given order and λ is the X-ray wavelength and crystallinity of PP phase at room temperature was obtained within the wide angle range ($2\theta = 5\text{--}30^\circ$), Cu K radiation, $\lambda = 1.54 \text{ \AA}$, generator voltage of 40 kv, current 40 mA and scanning rate of 0.1°/min. Transmission electron microscopy (TEM) (TFR430) at an acceleration voltage of 150 kV. The samples for TEM observation were prepared as ultrathin sections microtome using an ultra-microtome (Model MT-6000, Du Pont Company, USA) in liquid nitrogen. The ultrathin sections with a thickness of 80 nm were transferred from liquid nitrogen to copper grids before observation. Phase morphology studies were carried out using a scanning electron microscopy (SEM) (TESCAN Co, Germany). The morphology of the prepared nanocomposites was studied by preferential and partial etching of EPDM phase in n-heptan for 24 h (un-vulcanized samples) and PP phase in boiling xylene for 5min (vulcanized samples). The samples were then dried in a vacuum oven at 70 °C for 5 h to remove the traces of solvents present. Prior to morphological analysis, the surface of samples were covered with a thin layer of gold to prevent electrostatic charging build-up during observation. The morphology of fractured surface and subsurface of the EWF test was also investigated. The area of fractured subsurface and surface of EWF test were shown in Fig. 1b. The EWF test was measured using $100 \times 20 \times 1$ mm double edge notched

Download English Version:

<https://daneshyari.com/en/article/5022262>

Download Persian Version:

<https://daneshyari.com/article/5022262>

[Daneshyari.com](https://daneshyari.com)