

Enhancement of Physical Properties of Boehmite/HDPE nanocomposite film by Electron Irradiation

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1. Introduction

High density polyethylene (HDPE) has excellent mechanical properties due to its linear nature and high crystallinity. The intrinsic properties of HDPE can be enhanced by adding inorganic fillers, such as SiO₂ [1], TiO₂ [2], and Al₂O₃ [3] as nanoparticles to form a polymer nanocomposite. The HDPE nanocomposite can then be processed into a film and be used in various industrial fields such as those involving food packaging, power cable insulation, radiation shielding, and the fabrication of lithium-ion battery separators. The main issues of fabricating polymer nanocomposites exist in requiring the nanofillers to adhere well and be thoroughly dispersed within the polymer matrix. To address these issues regarding dispersion and interfacial adhesion, the surfaces of the nanoparticles are usually silanized. Among the possible nanocomposite filler materials, aluminum oxide, or more specifically, boehmite (AlO(OH)), has the highest hydroxyl group content, allowing the material to react readily with silane coupling agents. However, to create a thermoplastic-based nanocomposite with optimal properties, covalent bonds must form between silane and the thermoplastic matrix. Such covalent bonds can be generated by applying a process such as incorporation of a radical initiator, however, the addition of a radical initiator such as dicumyl peroxide produces noxious methane gas [4]. An alternative method using electron beam irradiation can accomplish the same goal without the use and the production of harmful chemicals, making the method very attractive [5]. Unlike other conventional procedures involving harmful chemicals and convoluted steps, in this study, a silanized boehmite/HDPE nanocomposite film was irradiated with electrons to enhance the interfacial adhesion between the nanofiller and the HDPE matrix. By enhancing the interfacial adhesion, a significant improvement in the mechanical properties of the nanocomposite film was able to be achieved.

2. Materials and Methods

2.1 Preparation of Samples

The boehmite nanoparticles were surface treated with vinyltrimethoxysilane prior to film fabrication. Neat HDPE, boehmite(BA)/HDPE, and surface treated BA(vBA)/HDPE films were fabricated by melt blending using a BA-11 twin screw extruder equipped with a film

dispensing unit (Bautek Co., Korea) (Fig. 1). The loading levels of the nanocomposite films were set to 8wt%. During cast film fabrication, the screws on the extruder were rotated at 400 rpm and the temperature profile from the hopper to the die was set to 180-185-190-190-200-210-220 °C. The average range of 50 keV electrons in HDPE was calculated to be 42.1 μm, thus, the films were fabricated with a thickness of 30 μm to ensure irradiation at all depths.



Fig. 1. Film manufacturing equipment and fabricated films

2.2 Electron Irradiation

The samples were homogeneously irradiated with a thermionic electron gun equipped with a tantalum cathode in a vacuum chamber under a pressure of 10⁻⁶ torr. The energy and the current density of the electron beam was set to 50 keV and 0.5 μA cm⁻², respectively. The electron beam was circular with a diameter of 6 cm. The electron fluences delivered to the samples ranged from 10¹⁴ cm⁻² to 10¹⁵ cm⁻².

2.3 Characterization

To examine the morphology of the sample cross sections, samples were fractured in liquid nitrogen and the fractured surfaces were analyzed with a scanning electron microscope (SEM, SU5000, Hitachi).

To assess the effects of silanization and electron irradiation on nanocomposite films, a Fourier-transform infrared spectrometer (FTIR, Nicolet iS50, Thermo Fisher Scientific Instrument) was used in attenuated total reflection (ATR) mode to obtain the FTIR spectra of relevant samples.

The elastic modulus, tensile strength, and elongation at break of 100 mm × 20 mm samples were determined using a universal testing machine (Instron5848, Instron) with a load of 5 kN at room temperature. The gauge length and crosshead speed were set to 30 mm and 50 mm/min, respectively.

3. Results

3.1 Morphology

To evaluate the dispersion and interfacial adhesion of BA in HDPE, cryo-fractured cross sectional SEM images of the nanocomposite films were acquired and shown in Fig 2. In the case of untreated BA in the HDPE matrix, the nanoparticles have agglomerated due to their high surface energy to form particles that are micrometers in size (Fig. 3(a) – (c)). With surface treated BA, particle agglomeration is rare (Fig. 3(d) – (f)), showing that the surface treatment process enhances the dispersion property of the nanoparticles. The interfacial adhesion can be evaluated by analyzing the cavities formed from the interaction between the nanofiller and the polymer matrix. Vacant cavities indicate that the nanoparticles that originally occupied the cavities were displaced due to not being strongly adhered to the matrix. It is apparent from the SEM images that the electron irradiation process enhances interfacial adhesion but more so for surface treated BA.

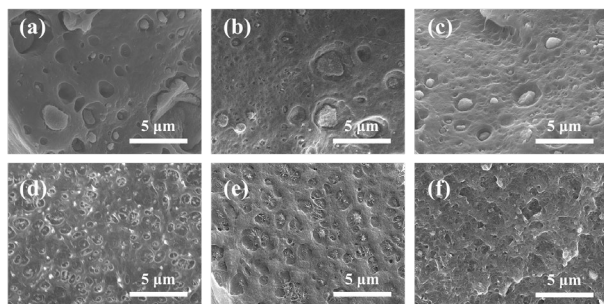


Fig. 2. SEM images of cryo-fractured surfaces of pristine BA/HDPE (a) and pristine vBA/HDPE (d). SEM images of BA/HDPE (b, c) and vBA/HDPE (e, f) irradiated with EB fluences of $5 \times 10^{14} \text{ cm}^{-2}$ (b, e) and $1 \times 10^{15} \text{ cm}^{-2}$ (c, f)

3.2 ATR-FTIR Analysis

Fig. 3 shows the ATR-FTIR spectra of irradiated samples. The spectra all exhibit C=O peaks at 1745, 1720, and 1645. The EB irradiation of BA can produce oxygen radicals that can react with polyethylene to form C=O bonds. In the case of BA/HDPE, the hydroxyl groups on the BA surface form hydrogen bonds with the ketone groups on HDPE. For vBA/HDPE, the vinyl functional groups found in VTMS form ester bonds with HDPE by utilizing the oxygen radicals generated during irradiation. The formation of ester bonds corresponds to the peak at 1745 cm^{-1} in the ATR-FTIR spectrum of vBA/HDPE. It can be inferred from the formation of these ester bonds that C-C bonds also form from radical grafting.

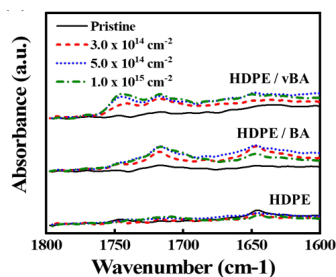


Fig. 3. ATR-FTIR absorption spectra of irradiated HDPE, HDPE/BA, HDPE/vBA at the wavenumber range of $1800 \sim 1600 \text{ cm}^{-1}$

2.5 Mechanical Properties

The effects of EB irradiation on the mechanical properties of the unmodified BA and modified BA are presented in Fig. 4. The nanofillers restrict the chain mobility of the polymer, enhancing the strength of the polymer to resist when subjected to extension. Therefore, significant increase in elastic modulus and tensile strength can be observed when nanofiller is added to a neat HDPE film. Electron irradiation can also serve to restrict chain mobility by crosslinking.

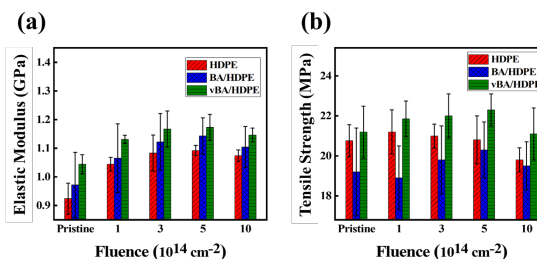


Fig. 4. Mechanical properties of HDPE, BA/HDPE, and vBA/HDPE

3. Conclusions

The effects of electron irradiation and nanofiller on the physical properties of polymer nanocomposite films have been analyzed and presented in this work. EB irradiation not only causes the crosslinking of the HDPE matrix, but also enhances the interfacial adhesion between the matrix and the nanofiller by generating hydrogen bonds. In the case of vBA, the vinyl functional groups found on the nanofiller covalently bonded to the HDPE chains by irradiation-induced radical grafting, causing the HDPE/vBA film to exhibit excellent mechanical properties.

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