Thermally and Mechanically Enhanced Boehmite/HDPE Hybrid Nanocomposite Film Prepared by Electron Irradiation

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1. Introduction

High density polyethylene (HDPE) is the most widely used polymer because of its low cost and high production capacity with good mechanical properties. The intrinsic properties of HDPE can be enhanced by adding inorganic fillers, such as SiO_2, TiO_2 [2], and Al_2O_3 [3] as nanoparticles (NPs) 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 power cable insulation, thermally conductive films in electronics, and the fabrication of lithium-ion battery separators. To achieve the desired thermal and mechanical properties of nanocomposite film, the NPs is required to adhere well with matrix as well as thoroughly dispersed. The dispersion of NPs can be achieved by coating silane coupling agents which can generate covalent bonds with hydroxyl groups on NPs. Therefore, the NPs covered with abundant hydroxyl groups are excellent candidates for fillers in nanocomposites in terms of better dispersion. Therefore, 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, although strong covalent bonds between NPs and silane coupling agent has been formed, the bond between the silane coupling agnet and the polymer matrix is still weak. 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. 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. In this study, we are going to fabricate HDPE nanocomposite film containing unmodified boehmite NPs and boehmite NPs modified by various silane coupling agnets. Then, the effects of electron irradiation on mechanical and thermal properties of nanocomposite films are analyzed, and the results obtained by various alkyl chain length and end groups of surface modifiers are compared.

2. Methods and Results

2.1 Preparation of boehmite/HDPE nanocomposite films

The boehmtie nanoparticles were surface treated with various silane coupling agents; Vinyltriemthoxysilane (vinyl), Octyltrimethoxysilane (C8), Octadecyltrimethoxysilane (C18), Trimethoxy(7-octen-1-yl)silane (C6-vinyl), and 10-undecenyltriethoxysilane (C9-vinyl). The HDPE nanocomposite films containing NPs were fabricated by melt blending using a BA-11 twin screw extruder equipped with a film dispensing unit (Bautek Co., Korea). The loading levels of the nanocomposite films were set to 10 wt%. 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 120-200-220-250-250-250-250-250 °C. The films were fabricated with a thickness of 120 µm (Fig. 1).

Fig 1. Fabricated boehmite/HDPE nanocomposite films containing nanoparticles coated with various modifiers.

2.2 Electron Irradiation

The samples were homogeneously irradiated with electron accelerator equipped at EB-tech in Daejeon (Fig. 2). The electron energy was set to 1 MeV, and the samples were put on slowly moving conveyor belt. A dose of 12.5 kGy was irradiated each time it passed the beam extraction window. To assure the homogeneity along the irradiation depth, all samples were firstly irradiated with half the dose and then turned over to irradiate the remaining half dose. The electron dose delivered to the samples ranged from 100 to 600 kGy.

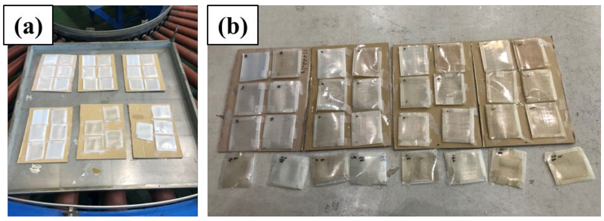

Fig 2. (a) Electoron irradiation and (b) irradiated samples

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 micro-scope (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 In-strument) was used in attenuated total reflection (ATR) mode to obtain the FTIR spectra of relevant samples.

The tensile yield strength 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.

The thermal properties were characterized by thermomechanical analyzer (TMA) and thermal conductivity using laser-flash analysis (LFA

3. Results

The intrinsic hydrophilic characteristic of boehmite were changed to hydrophobic by silane coupling agents. The degree of hydrophobicity were simply evaluated by dropping little amount of modified NPs on DI water. The more hydrophobicity, the more the NPs floated without being mixed with DI water. The NPs coated with longer alkyl chain shows the more hydrophobicity (Fig. 3). Therefore, C18 represents highest hydrophobicity among the samples in this study.

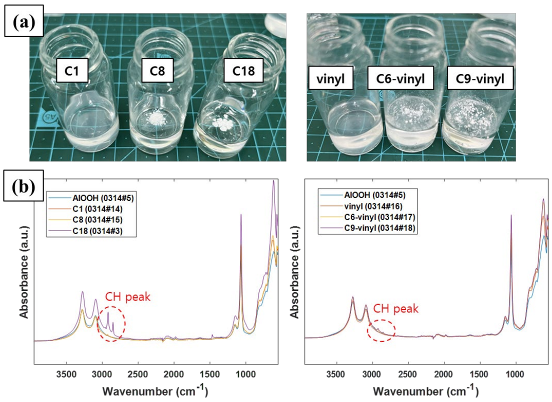

Fig 3. (a) Affinity with water and (b) FTIR results of boehmite NPs unmodified and modified with various modifiers.

The dispersion of NPs were evaluated by cryo-fractured SEM images (Fig. 4). All samples containing modified NPs show better dispersion than unmodified. The NPs modified with C18 and C9-vinyl, however, represent much higher dispersion compared to other samples, indicating that the dispersion is related to the hydrophobicity of NPs.

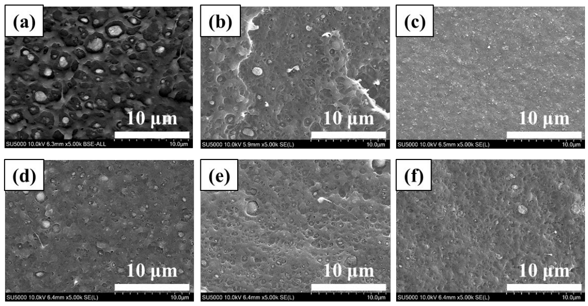

Fig 4. Cross sectional morphology of nanocomposite films containing (a) unmodified boehmite NPs and boehmite NPs modified with (b) C8, (c) C18, (d) vinyl, (e) C6-vinyl, and (f) C9-vinyl.

The effects of EB irradiation on the yield strength nanocomposite films are presented in Fig. 4. Due to the weak interfacial adhesion between the NPs and polymer matrix, stress can be concentrated at that point subjected to extension. The crosslinking by electron irradiation intensified the interfacial adhesion and polymer matrix itself. Especially, the vinyl end group show high improvement of yield strength.

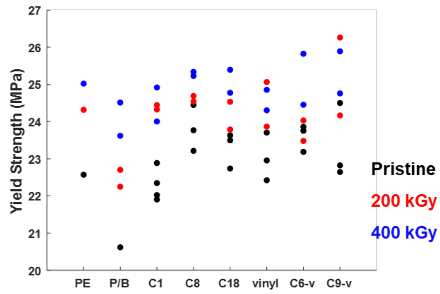

Fig 5. Yield strength of nanocomposite films

The thermal properties were evaluated through the TMA (Fig. 6) and thermal conductivity (Fig. 7). Both of the results show the better properties for the electron irradiated nanocomposite film containing modified NPs. Further crosslinking at the interface between NPs and polymer matrix results in high restriction to thermal stress and enhanced thermal conductivity.

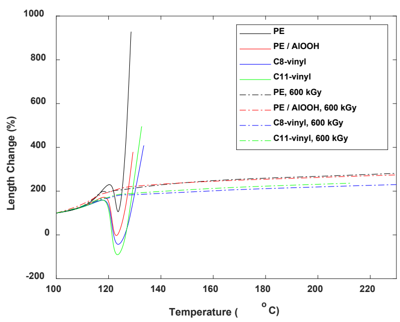

Fig 6. TMA results of nanocomposite films

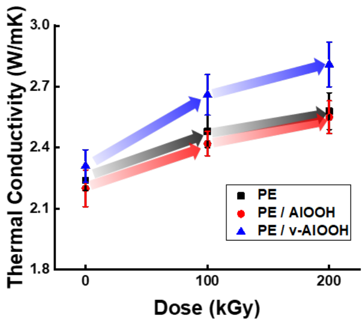

Fig 7. Thermal conductivity of nanocomposite films

3. Conclusions

The enhancement of thermal and mechanical properties of HDPE nanocomposite film filled with boehmite NPs by electron irradiation have been 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 NPs. Especially, the vinyl functional groups at the outermost shell of the modified NPs covaently bonded to the HDPE chains by irradiation-induced radical grafting, causing the nanocomposite film to exhibit excellent properties.

REFERENCES

[1] F. H. Ruddy, A. R. Dulloo, J. G. Seidel, F. W, Hantz, and L. R. Grobmyer, Nuclear Reactor Power Monitoring Using Silicon Carbide Semiconductor Radiation Detectors, Nuclear Technology, Vol.140, p. 198, 2002.
[2] F. H. Ruddy, A. R Dulloo, J. G Seidel, J.W.Palmour, and R. Singh, The Charged Particle Response of Silicon Carbide Semiconductor Radiation Detector, Nuclear Instruments and Methods In Physics Research, Vol.505, p.159, 2003.
[3] J. F. Ziegler, J. P. Biersack, "SRIM-2000, 40: The Stopping and Range of Ions in Matter", IBM-Research, Yorktown, NY 2000.