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Preparation and Radiation-resistance Characterization of LDPE/phPOSS Nanocomposites

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Abstract - In this study, we demonstrated that low-density polyethylene (LDPE)/octaphenyl polyhedral oligomeric silsequioxanes (phPOSS) nanocomposites exhibited the improved radiation resistance in comparision to that of pure LDPE. The LDPE/phPOSS nanocomposites were prepared by melt blending at the different compositions and then exposed to γ-irradiation at the various doses ranging from 50 to 500 kGy. The radiation resistance of the irradiated nanocomposites were investigated in terms of tensile property, oxygen induction temperature, decomposition temperature, and oxidation extent. The various analytical results revealed that the incorporation of phPOSS into the LDPE matrix could enhance the radiation resistance of pure LDPE because of the protective effect of the phenyl groups existing in the phPOSS. This simple and effective strategy can be used in the development of new radiation-resistant materials for the equipments and components of nuclear power plants.

Key words : Low density polyethylene, Polyhedral oligomeric silsequioxanes, Nanocomposites, Radiation resistance

INTRODUCTION

Radiation resistance of polymers used in the cable insulators and jackets has been considered as one of crucial components for the safety and long service life of nuclear power plant (Placek *et al*. 2003; Seguchi *et al*. 2011; Boguski *et al*. 2014; Alshaketheep *et al*. 2016). That is because polymers more easily deteriorate than metal or inorganic materials when exposed to the chronic and high-energy radiation environment (Singh 1999; Davenas *et al*. 2002; Chang *et al*. 2016). Thus, to improve the radiation resistance of polymers, research works have been performed mainly through a synthetic approach for the introduction of radiation-resistant structure or blending approach using radiation-protective fillers (Hedrick *et al*. 1986; Ferry *et al*. 2012; Liao *et al*. 2018; Sharma *et al*. 2018). Recently, the polymer naocomposites research via blending with nanofillers has been carried out to obtain the improved radiation resistance with maintaining the desirable properties of polymers (Nambiar and Yeow 2012; Borjanovic *et al*. 2016; Christian *et al*. 2016; Pallon *et al*. 2016). However, there still is a high demand for the development of new polymer nanocomposite with better radiation-resistance due to the high concerns of safety and maintenance expenses.

Among the various nanofillers, polyhedral oligomeric silsequioxanes (POSS) have been considered as a promising nanofiller for the development of the radiation-resistant polymer nanocomposites (Li *et al*. 2002). The POSS nanofiller possesses several intriguing characteristics including outstanding mechanical and thermal robustness (stemming from the silicon-oxygen bounded siloxane cage) and easy tuning of surface functionality to meet the miscibility with other polymer (Laine and Roll 2011; Blanco *et al*. 2012). Thus, it has been extensively utilized as a nanofiller to enhance the mechanical and thermal properties of polymers (Ayandele *et*

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al. 2012). Among types of POSSs, octaphenyl polyhedral oligomeric silsequioxanes (phPOSS) is interesting because of its phenyl moiety enabling the improvement of radiation resistance (Deldes 1980; Diao *et al*. 2011). However, the study on the development of radiation-resistant polymer nanocomposites using phPOSS has rarely been performed yet.

The present research was intended to prepare a phPOSS-reinforced low density polyethylene (LDPE/phPOSS) nanocomposites and investigate their radiation resistance. The LDPE was chosen as a matrix because it is the most generally used insulating polymer for the electrical cable insulation (Dadbin *et al*. 2002; Jung *et al*. 2013). The LDPE/phPOSS nanocomposites with different composition were prepared by melt blending and underwent the exposure to γ-irradiation at different doses. To investigate the radiation-protective effect of POSS, the irradiated nanocomposites were characterized in terms of mechanical, thermal and chemical properties.

MATERIALS AND METHODS

1. Materials

Low density polyethylene (LDPE, LUTENE FB0800, LG chemical Co (South Korea)) was used as a matrix polymer in this research. Octaphenyl polyhedral oligomeric silsequioxanes (phPOSS) was purchased from Hybrid Plastic (USA). All the chemicals were used as received.

2. Preparation of LDPE/phPOSS nanocomposites

To produce the LDPE/phPOSS, a melt blending of LDPE and phPOSS at different formulations (Table 1) was performed in twin screw extruder (Nam-Yang Tech. Co. (South Korea)) at the temperature of 150°C with a rotation speed of 60 rpm for 20 min. After the melt blending, the resulting mixtures were compression-molded into 2.0 mm-thick sheets under a pressure of 25 MPa at the temperature of 160°C for 10 min. For comparison, 2.0 mm-thick control LDPE sheet was prepared as well.

Table 1. Composition of LDPE/phPOSS nanocomposites

Samples	LDPE (wt%)	phPOSS (wt%)
Control LDPE	100	0
LDPE/phPOSS-4	96	4
LDPE/phPOSS-8	92	8

3. Gamma-ray irradiation on LDPE/phPOSS nanocomposites

The prepared control LDPE and LDPE/phPOSS nanocomposites were put into a plastic bag, and then were irradiated by γ-rays from a ^{60}Co source (Korea Atomic Energy Research Institute in South Korea) under ambient atmosphere. Doses ranged from 50 to 500 kGy and the dose rate was fixed at 10 kGy·hr^{-1}. After the irradiation, the samples were kept in a desiccator at room temperature to reduce the effect of environmental degradation (Hakkarainen and Albertsson 2004).

4. Characterization

Tensile properties such as tensile strength and elongation-at-break were measured on a universal testing machine (UTM, Instron Model-4210, Instron Engineering Co. (USA)) following to ASTM D638. Oxidation-induction temperature (OIT) was determined using differential scanning calorimeter (DSC, TA instrument, Q1000) in the temperature between 30 and 250°C at a heating rate of 10°C·min^{-1} under the ambient atmosphere. The OIT value was taken as the onset point of the decomposition curve. Thermogravimetric analysis (TGA) was carried on a TGA 2950 model (TA instrument (USA) in a temperature span of 50 to 600°C at a heating rate of 10°C·min^{-1} under an inert atmosphere. The decomposition temperature (T_d) was taken as a temperature for the maximum peak of derivative thermogravimetry (DTG) curve. Chemiluminescence (CL) analysis was conducted on a chemiluminescence analyzer (CLA, CLA-FSI, Tohoku Electronic Industrial Co. Ltd. (Japan)) at a temperature of 25°C for 20 min under an ambient atmosphere.

RESULTS AND DISCUSSION

To investigate the phPOSS effect on the tensile properties of LDPE, the tensile strength and elongation-at-break of the control LDPE and LDPE/phPOSS nanocomposites after the exposure to γ-ray at different does was analyzed by UTM and the results are shown in Fig. 1. As presented in Fig. 1(a) and (b), the tensile strength of the control LDPE showed a tendency to slightly increase with an increasing dose up to 200 kGy and then significantly decrease above the that, indicating the evident change in the tensile properties of the LDPE caused by γ-ray irradiation-induced crosslinking or chain session (Jung *et al*. 2013). Likewise, the LDPE/

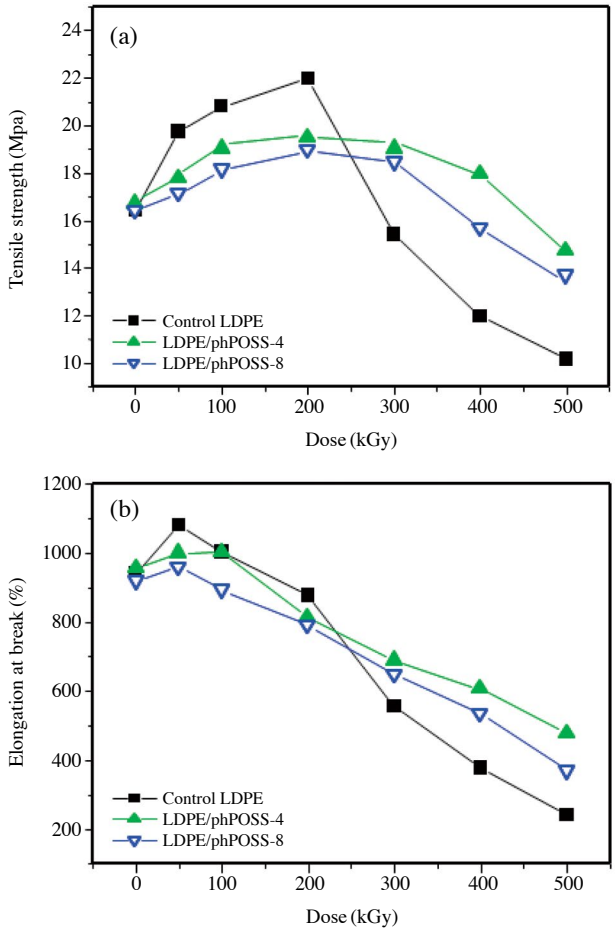

Fig. 1. Tensile strength (a) and elongation-at-break (b) of control LDPE and LDPE/phPOSS nanocomosites at different doses.

phPOSS nanocomposites exhibited a similar tendency as that of control LDPE. But, at all the given doses, the extent of the overall change in the tensile strength was much smaller than that of control LDPE. The LDPE/phPOSS-4 and -8 showed the similar tendency, indicating that the incorporation of 4 wt% phPOSS seemed to be enough to improve the radiation-resistance of LDPE. Furthermore, as shown in Fig. 1(b), the elongation-at-break of the control LDPE was significantly dropped from 930% to 250% with an increasing dose. On the other hand, the LDPE/phPOSS nanocomposites showed the less drop in the elongation-at-break at the given doses. The overall change in the elongation-at-break of the LDPE/phPOSS-4 at the given doses is almost similar to that of LDPE/phPOSS-8 as mentioned in the tensile strength. Therefore, These results indicate that the presence of 4 wt% phPOSS is enough to improve the radiation resistance of LDPE matrix. This effect of POSS in the tensile strengths and elongation breaks of LDPE is probably attributed to the

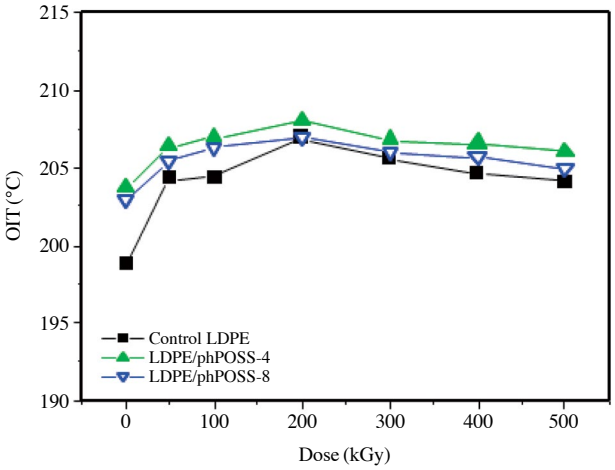

Fig. 2. Oxidation induction temperature (OIT) of the control LDPE and LDPE/phPOSS nanocomposites at the different doses.

fact that the phenyl moiety of the phPOSS dissipates the energy in the aromatic resonance structure before the C-H or C-C bond breakage and thereby the occurrence of the cross-linking or chain scission (responsible for the change in tensile properties) is much reduced in the LDPE matrix, resulting in the improved radiation-resistance (Lee *et al*. 1999; Diao *et al*. 2011).

To examine the phPOSS effect on the oxidation stability of the LDPE, the oxidation induction temperatures (OIT) of control LDPE and LDPE/phPOSS nanocomposites were measured by DSC under oxygen atmosphere (Schmid *et al*. 2006). As shown in Fig. 2, the OIT of control LDPE (198°C) was evidently increased to 205°C with an increasing dose up to 200 kGy and then leveled off over the dose. On the other hands, although the non-irradiated LDPE/phPOSS nanocomposites is higher than that of control LDPE due to flame-retarding effect of phPOSS (Ayandele *et al*. 2012), the irradiated nanocomposites exhibited lower fluctuation in the OIT at the given doses. Furthermore, the LDPE/phPOSS-4 and -8 showed the similar fluctuation in the OIT at the given doses. Therefore, this result reveals that the LDPE/phPOSS nanocomposites even at the amount of 4 wt% phPOSS have better resistance against radiation-induced oxidative degradation in comparison to that of control LDPE owing to the energy-absorption and eventually dissipation ability of phPOSS.

To further investigate the phPOSS effect on the thermal decomposition stabilities of LDPE, the decomposition temperatures (T_d) of control LDPE and LDPE/phPOSS nanocomposites were analyzed by TGA under nitrogen atmosphere. As

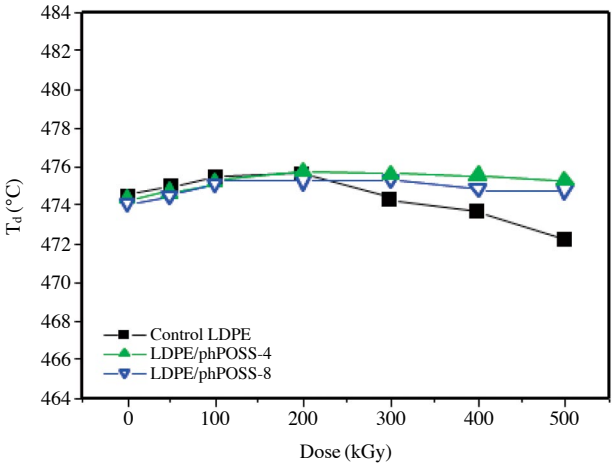

Fig. 3. Decomposition temperature (T_d) of control LDPE and LDPE/phPOSS nanocomposites at different doses.

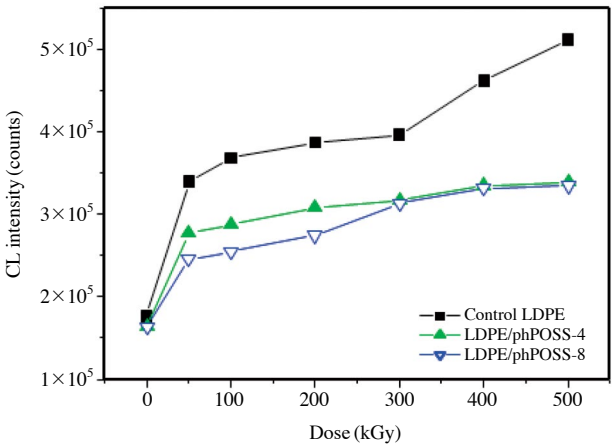

Fig. 4. Chemiluminescene (CL) intensity of control LDPE and LDPE/phPOSS nanocomposites at different doses.

shown in Fig. 3, the T_d of the control LDPE was sightly increased with an increasing dose up to 200 kGy, above which it was more evidently decreased, indicating that the pure LDPE underwent radiation-induced chemical deterioration and thereby resulting in the change in the thermal decomposition temperatures. On the other hand, the LDPE/phPOSS nanocomposites showed no significant changes with the dose and phPOSS content. Thus, this result implies that the LDPE/phPOSS containing above 4 wt% have increased thermal stability at the given doses due to the radiation-protective effect of the phPOSS (Deldes 1980; Diao *et al*. 2011).

To figure out the phPOSS effect on the radiation-induced oxidative deterioration, control LDPE and LDPE/phPOSS was analyzed by CLA, which is capable of measuring the relative extent of oxidized species resulting from the radiation-induced oxidative degradation. As presented at Fig. 4, the CL intensity of the control LDPE increased considerably with an increasing dose in comparison to that of non-irradiated one. This clearly indicates the occurrence of radiation-induced oxidative deterioration which results in more formation of oxidized species in the LDPE (Setnescu *et al*. 2004). In contrast, the LDPE/phPOSS nanocomposites showed much lower CL intensities at the given dose than those of pure LDPE and a similar tendency with the amounts of POSS. Thus, this result could be ascribed to the fact that the lower formation of the radicals by γ-ray irradiation-breakage of C-H or C-C bond is attenuated by the energy absorption and dissipation effect of phPOSS.

CONCLUSION

The LDPE/phPOSS nanocomposites was fabricated by melt-blending method and their higher radiation resistance over control LDPE was demonstrated in this study. It was confirmed from these overall analytic results from the UTM, DSC, TGA, and CL that the LDPE/POSS nanocomposites even at the amount of 4 wt% POSS is more resistant against γ-irradiation-induced deterioration when compared to control LDPE. This improvement could be attributed to the radiation-protective effect of phPOSS originating from the aromatic resonance structure of its phenyl groups. The thermal acceleration test for the LDPE/phPOSS nanocomposites is further underway to predict their lifetime comparing to that of control LDPE. This LDPE/phPOSS naocomposites can be used in the development of high radiation-resistant electrical cable materials for the nuclear power plant.

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