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Preparation of polymer/POSS nanocomposites by radiation processing

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Abstract

Multifunctional polyhedral oligomeric silsesquioxane (POSS)-reinforced polypropylene (PP) nanocomposites were prepared by a simple and economical radiation processing, which has a great potential for the preparation of high performance materials.

The tensile strength of PP/POSS nanocomposites increased with an increasing POSS content up to 5 wt% and with an increasing absorption dose up to 50 kGy. The tensile strength of irradiated PP/POSS nanocomposites decreased at high absorption dose due to the main chain scission of PP by radiation.

The PP/POSS nanocomposites showed improved thermal stability due to the formation of crosslinked network between PP and POSS by radiation.

Keywords: nanocomposites; radiation processing; polyhedral oligomeric silsesquioxanes (POSS); mechanical property

1. Introduction

Polymer nanocomposites have attracted a considerable scientific and technological interest because of their extraordinary properties such as unique electronic, optical, and mechanical properties when compared to the conventional composites [Lee et al., 2005; Liu and Brinson, 2008; Schadler et al., 2007]. Thus, the polymer nanocomposties have been investigated by combining various nanofillers such as canbon nanotubes, nanoparticles, nanoclay with common polymers [Bao and Tjong, 2008; Bellucci et al. 2008; Rong et al. 2001].

Recently, polymer nanocomposites with polyhedral oligomeric silsesquioxanes have evoked much interest due to its unlimited surface modification and the relatively excellent compatibility with organic materials differentiating from typical nanofillers [Huang et al., 2005; Joshi and Butola, 2004; Pielichowski et al., 2006]. The polymer nanocomposites containing POSS have been fabricated by various techniques including copolymerization [Xu et al., 2002; Zheng et al., 2001], grafting [Fu et al., 2004], and melt blending [Baldi et al. 2007; Chen et al., 2007].

Recently, the preparation of polymer/POSS nanocomposites by the in-situ radiation-induced graft polymerization of monofunctional POSS was reported by our group [Choi et al., 2008]. In the previous work, the mechanical properties of the

PP/POSS nanocompsoites were much enhanced but the thermal properties were not much improved. Therefore, further investigation on the improvement of mechanical properties and thermal properties of the nanocomposites was required and thus leading to the goal of the present study.

In this work, we prepared PP/POSS (PP/POSS) nanocomposites by using a simple and economical radiation processing applicable for the mass production. The process consisted of melt-blending PP with multi-functional POSS as nanoscale filler followed by γ-ray irradiation on the PP/POSS mixtures. The prepared PP/POSS nanocomposites were characterized by means of FT-IR, UTM, and TGA analyses.

2. Experimental Part

2.1. Materials

PP (B310, MW 523,000) was donated by Honam Petrochemical Co. (Korea) and used as a main matrix for the preparation of nanocomposites. Multifunctional acrylo POSS® (POSS, MA0736, Hybrid Plastics, USA) was used as a nanofiller without further purification.

2.2. Preparation of PP/POSS nanocomposites

PP and oily POSS were melt-blended in a lab-scale Brabender at 180 °C and 64 rpm rotor speed for 10 min according to the composition in Table 1. The PP/POSS mixtures were then hot-pressed into a standard specimen for mechanical tests. The prepared samples were irradiated by γ-ray using ^{60}Co source under various absorption doses up to 100 kGy at a dose rate of 10 kGy/h at room temperature.

2.3. Characterization of PP/POSS nanocomposites

The radiation effect on neat PP and PP/POSS nanocomposites was analyzed by FT-IR spectroscopy (Tensor 37, Bruker, USA). Mechanical properties such as the tensile strength and elongation-at-break were measured by using an Instron (Model 4210, Instron Engineering Co., USA) according to the ASTM Standard D 638. Thermogravimetric analysis of the PP/POSS nanocomposites was carried out on a SDT Q-600 series analysis system (TA Instrument, USA). The measurements were performed under a flowing nitrogen atmosphere from 50 to 700 °C at a scan rate of 10 °C/min. Decomposition temperature in this measurement was defined as 5% mass loss temperature.

3. Results and Discussion

The radiation effect on the chemical changes of PP/POSS nanocomposites was investigated by FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra of neat PP, POSS and POSS10 irradiated at various absorption doses. As shown in the non-irradiated POSS10 spectra, the typical peaks for POSS were observed at 1720 (νC=O), 1640 (νC=C) and 1106 (νSi-O) cm^{-1}. The intensity of the C=C peak at 1642 cm^{-1} in the irradiated POSS10 spectra was reduced upon increasing the dose up to 20 kGy, above which it was almost disappeared. On the other hand, the two peaks corresponding to carbonyl and siloxane were clearly observed even at 100 kGy as seen in Fig. 1. These results indicate that irradiation even at 50 kGy was enough to activate all the double bonds of POSS in order to form the network structure in the PP/POSS nanocomposites.

<Table 1>

<Fig. 1>

Fig. 2 shows the tensile strength and elongation-at-break of PP and PP/POSS nanocomposites as a function of absorption dose. As shown in Fig. 2(a), the tensile strength of the neat PP slightly increased with an increasing dose up to 10 kGy, beyond

which it gradually decreased. This phenomenon can be attributed to the scission of PP backbone during irradiation [Goulas et al., 2004]. In comparison to that of neat PP, the tensile strength of non-irradiated PP/POSS nanocomposites was improved with an increasing content of POSS up to 5 wt% and began to be deteriorated beyond that content. Moreover, in case of the irradiated nanocomposites, tensile strength showed a tendency to increase with an increasing dose up to 50 kGy and gradually decreased above that. Among the irradiated nanocomposites, POSS5-50 showed the highest tensile strength, 30.5 MPa, because the network structure was effectively formed in the nanocomposites as observed in FT-IR analysis. On the other hand, the reduction in the tensile strength of POSS5 irradiated at higher doses above 50 kGy can be explained by the fact that the radiation-induced chain scission of PP backbone in the nanocomposites prevails at higher dose even though the network structure was formed [Choi et al., 2008].

Fig. 2(b) shows the changes in the elongation of neat PP and PP/POSS nanocomposites as a function of dose. Unlike tensile strength, the elongation properties of neat PP and irradiated PP/POSS nanocomposites were heavily affected by γ-irradiation. The elongation of neat PP was rapidly reduced with an increasing dose due to the increase of brittleness by radiation [Goulas et al., 2004]. In comparison with neat

PP, the elongation of the non-irradiated nanocomposites was more diminished with an increasing content of POSS. Furthermore, the reduction in the elongation for all the irradiated nanocomposites became more pronounced than that in the neat PP. These behaviors can be reasoned from the fact that the hard POSS diminished the mobility of PP matrix and the reduced mobility of PP matrix was accelerated by the radiation-induced crosslinking as well as chain scission, resulting in the abrupt reduction of elongation in all the nanocomposites.

<Fig. 2>

The decomposition temperatures of neat PP and PP/POSS nanocomposites as a function of absorption dose are shown in Fig. 3. The decomposition temperature of neat PP and POSS were found to be 431 and 398 °C, respectively. The changes in the decomposition temperatures of neat PP as a function of dose showed the tendency toward the reduction due to the chain scission of PP by irradiation [Krupa and Luyt, 2001]. Likewise, the decomposition temperatures of the nanocomposites decreased with an increasing dose. However, when compared to PP, the decomposition temperatures of all the nanocomposites were overall higher at any given dose of irradiation. Furthermore,

the effect of POSS content on the decomposition temperatures of the nanocomposites was not significant up to 20 kGy, above which the POSS content showed a noticeable effect. These phenomena can be attributed to the fact that neat PP could be mainly degraded during irradiation due to the backbone scission, while the radiation-induced degradation of PP matrix in the composites was minimized by the simultaneous radiation-induced crosslinking due to the presence of multi-functional POSS. Thus, grafting of inorganic particles onto the polymer backbone enables us to improve the mechanical properties of the nanocomposites without adversely affecting the thermal properties.

<Fig. 3>

4. Conclusion

POSS-reinforced PP nanocomposites with different compositions were successfully fabricated by high energy radiation. The Tensile strength increased with increasing the content of POSS and also with the irradiation dose up to 50 kGy above which it started to decrease. In contrast, the elongation was seriously affected by the increasing content of POSS and the absorbed dose due to the increased brittleness by

the addition of multifuncational POSS and chain scission of PP by radiation. The thermal stability of PP/POSS nanocomposites was considerably improved with increasing the content of POSS. The thermal stabilities of all the PP/POSS nanocomposites were better than the neat PP irradiated at the same conditions due to the minimization of PP backbone scission by radiation induced crosslinking with multifunctional POSS.

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Figure Captions

Fig. 1. FT-IR spectra of neat PP, POSS and POSS10 irradiated at various absorption doses.

Fig. 2. (a) Tensile strength and (b) elongation at break of PP/POSS nanocomposites as a function of the absorption dose.

Fig. 3. Decomposition temperatures of PP/POSS nanocomposites as a function of the absorption dose.

Table Caption

Table 1. Formulations for the preparation of PP/POSS nanocomposites.

Table 1

Table 1. Formulations for the preparation of PP/POSS nanocomposites.

Samples	PP (weight%)	POSS (weight%)	Dose Rate kGy/h	Total Absorption Dose kGy
PP-0	100	0	10	0
PP-10	100	0	10	10
PP-20	100	0	10	20
PP-50	100	0	10	50
PP-100	100	0	10	100
POSS2-0	98	2	10	0
POSS2-10	98	2	10	10
POSS2-20	98	2	10	20
POSS2-50	98	2	10	50
POSS2-100	98	2	10	100
POSS5-0	95	5	10	0
POSS5-10	95	5	10	10
POSS5-20	95	5	10	20
POSS5-50	95	5	10	50
POSS5-100	95	5	10	100
POSS10-0	90	10	10	0
POSS10-10	90	10	10	10
POSS10-20	90	10	10	20
POSS10-50	90	10	10	50
POSS10-100	90	10	10	100

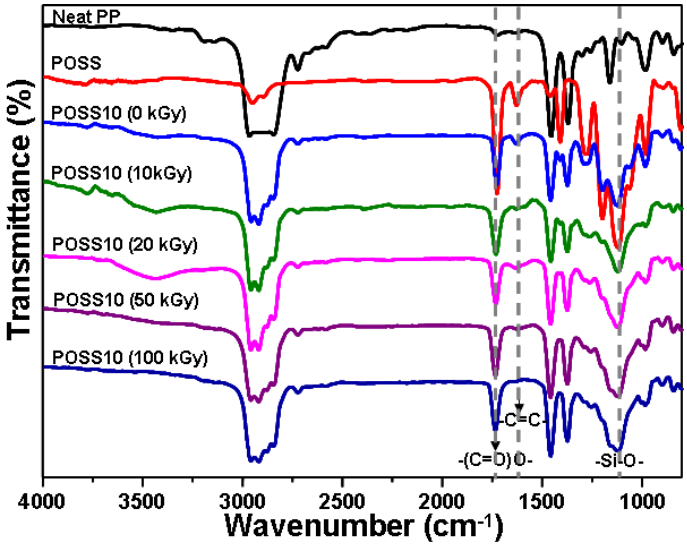
Neat PP
POSS
POSS10 (0 kGy)
POSS10 (10kGy)
POSS10 (20 kGy)
POSS10 (50 kGy)
POSS10 (100 kGy)
Transmittance (%)
-C=C-
-(C=O)O-
-Si-O-
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

Fig. 1.

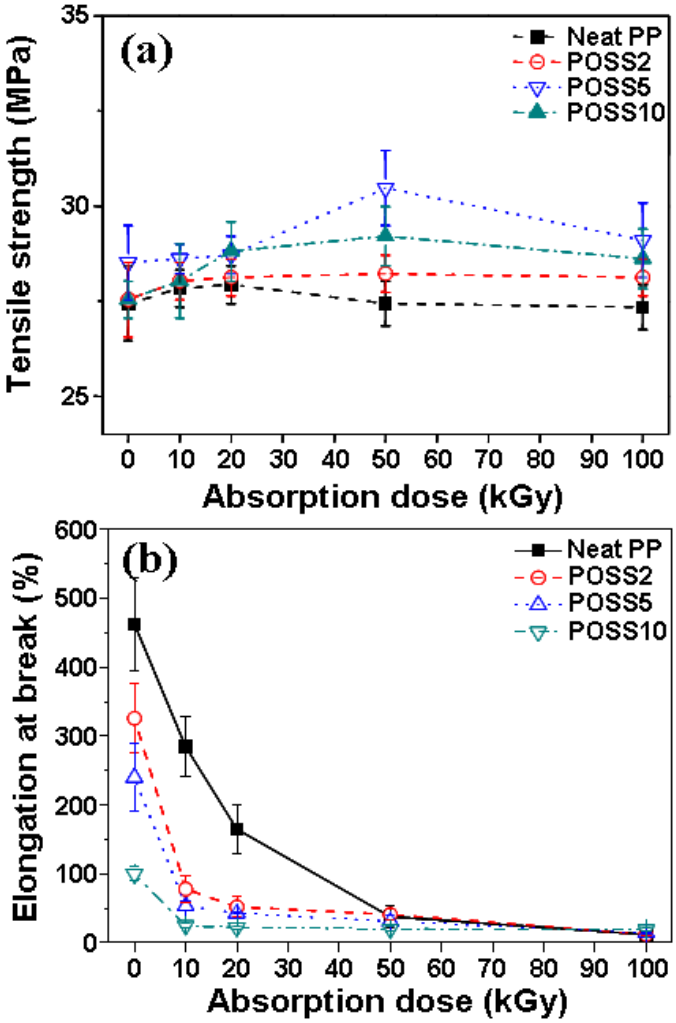
(a)
Neat PP
POSS2
POSS5
POSS10
Tensile strength (MPa)
35
30
25
0 10 20 30 40 50 60 70 80 90 100
Absorption dose (kGy)
(b)
Neat PP
POSS2
POSS5
POSS10
Elongation at break (%)
600
500
400
300
200
100
0
0 10 20 30 40 50 60 70 80 90 100
Absorption dose (kGy)

Fig. 2.

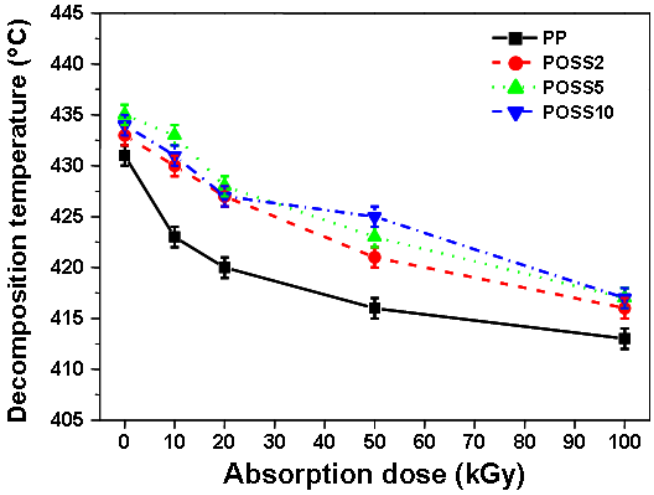
Decomposition temperature (°C)
445
440
435
430
425
420
415
410
405
0
10
20
30
40
50
60
70
80
90
100
Absorption dose (kGy)
PP
POSS2
POSS5
POSS10

Fig. 3.