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Rheological and mechanical properties of polyamide 6 modified by electron-beam initiated mediation process

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HIGHLIGHTS

- PA6 was modified by the electron-beam initiated mediation process.
- Maximum increase in complex viscosity of modified PA6 was 75 times higher than virgin PA6 at 0.1 rad/s.
- Mechanical properties were improved without scarifying of processability.
- The GMA as a mediator played a key role in the electron-beam initiated mediation process.

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ABSTRACT

Polyamide (PA6) has been modified by electron-beam initiated mediator process to improve drawbacks of PA6. Glycidyl methacrylate (GMA) was chosen as a reactive mediator for modification process of PA6. The mixture of the PA6 and GMA was prepared by using a twin-screw extruder, and then the mixture was exposed to electron-beam irradiation at various doses at room temperature. The modified PA6 were characterized by observing rheological and mechanical properties and compared virgin PA6. Thermal properties, water absorption, and gel fraction were also investigated. Tight gel was not found even when PA6 was irradiated at 200 kGy. Complex viscosity and storage modulus of PA6 were remarkably increased by electron-beam irradiation with medium of GMA. Maximum increase in complex viscosity was 75 times higher than virgin PA6 at 0.1 rad/s when it was irradiated at 200 kGy with the GMA. Mechanical properties were also improved without scarifying of processability. The reaction mechanisms for the mediation process with the reactive mediator of GMA were estimated to elucidate the cause of significantly enhanced rheological and mechanical properties without loss of thermoplasticity.

1. Introduction

PA6 is a large volume commodity polymer that possesses unique properties such as tough, strong, and abrasion resistant (Li and Zhang, 1997; Dadbin et al., 2005; Pramanik et al., 2009). Therefore, it finds wider range of uses both in domestic and engineering applications. However, PA6 has still insufficient properties to apply for many specific uses and higher water absorption causing decrease in mechanical properties and dimensional stability due to a plasticizer effect of water. In addition, PA6 is sharp melting with low viscosity which can limit it form versatile applications such as higher melt strength process and much care is needed during processing to avoid overheating, combat with drooling, and maintain low shearing (Dadbin et al., 2005).

Much effort has been devoted for overcoming these drawbacks of polyamide by crosslinking modification method with/without a crosslinking agent (Gering and Zyball, 1995; Clough, 2001; Dadbin et al., 2005; Pramanik et al., 2009; Sengupta et al., 2006; Okabe et al., 2005). High energy radiation crosslinking process has been already adopted for modifying polymers (Gering and Zyball, 1995; Clough, 2001; Dadbin et al., 2005) and crosslinking agents such as triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), and other multi-functional monomers have been eventually added to polymers for effective crosslinking process. However, the crosslinked polymer enables no melt processing above its normal melting temperature and does not dissolve in its usual solvent completely, which seems to become another limit for the application of modified polyamides. Also, cross-liked polymer is difficult to recycle, which is not good for solving plastic waste problem. Therefore, most industrial applications are converged on exposure of molded or extruded products to high-energy radiation.

In this study, we devoted to introduce PA6 modified by grafting, which improved drawbacks of PA6 without disregarding its

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processability unlike crosslinking modified PA6. The graft reaction of molecules was performed by electron-beam irradiation with a reactive mediator (Bhattacharya et al., 2008; Shin et al., 2010). The GMA was chosen as the reactive mediator for grafting process because GMA has two reactive sites, which are an epoxy functional group and a double bond. The epoxy group can react with other functional groups in polymers during melt mixing and the double bond can be easily opened by an electron-beam initiated radical and then it links polymer chain to another chain. Hence, the molecular weight of PA6 might be increased and temporary physical network resulting from increased entanglement might be suggested (Chae et al., 2001; Di et al., 2005). The grafted PA6 might be expected to have similar excellent physico-mechanical properties as a crosslinked PA6, while it still maintains thermoplasticity without disregarding its processability. We also proposed electron-beam initiated reaction mechanisms, which were believed to be occurred with the medium of GMA.

2. Experimental

2.1. Materials

Polyamide 6 (domamid® 24) with a density of 1.14 g/cm^3 was obtained from DOMO Caproleum GmbH. Glycidyl methacrylate (GMA) and formic acid were provided by Sigma-Aldrich (WI, USA).

2.2. Melt mixing of nylon and GMA

The PA6 and GMA were mixed in a plastic bag before being extruded in a twin-screw co-rotating extruder (SM PLATEK Co. Ltd., TEK 30, Korea). The screw diameter was 30 mm with an L/D ratio of 36. The extruder was operated at 150 rpm with a constant feed rate of 15 kg/h. The barrel and die temperatures were set at 200–240 °C and 235 °C, respectively. GMA content was 3 parts per hundred resin (phr) on the basis of PA6 weight. The extrudate was cooled in chilled water (~20 °C) and cut into pellets with diameter less than 1 mm. Then the pellets were dried for 24 h at 80 °C prior to the electron-beam irradiation.

2.3. Electron-beam irradiation

The mixture with maximum chip diameter of 1 mm was irradiated using a commercial electron-beam accelerator (ELV-0.5, BINP, Russia, with a maximum beam current of 40 mA and electron energy of 0.5–0.7 MeV) under a nitrogen atmosphere. The irradiation doses were 5, 10, 20, 50, 100, and 200 kGy, which were controlled by varying both the beam currents of 0.5–10 mA and the conveyor speeds of 1–2 m/min, and the irradiation dose was measured by film dosimeters (B3 WINdose Dosimetry, GEX Co.) and dosimeters (GENESYS 20, Thermo SCIENTIFIC Co.). Acceleration voltage was 0.7 MeV and the effective penetration depth was about 2 mm for the substrate with 1 g/cm^3 of density (Woods and Pikaev, 1994; Han et al., 2006). The irradiated samples were dried in an oven at 80 °C for 12 h to eliminate any residual radicals.

2.4. Characterization

Thermal properties were determined using differential scanning calorimetry (DSC; TA INSTRUMENTS Q200). Samples were heated from room temperature to 270 °C at a rate of 20 °C/min and maintained at 250 °C for 3 min to remove the thermal history. Subsequently, they were quenched to −30 °C then reheated to 270 °C at 10 °C/min under a nitrogen atmosphere. The degree of crystallinity, X_c, was calculated as:

$$X_c\ (\%) = (\Delta H/\Delta H_m^o) \times 100$$

where ΔH is the heat of fusion of specimen and ΔH°_m is the heat of fusion of 100% PA6 equal to 188.1 J/g (Dadbin et al., 2005).

The rheological property was measured using an ARES (Advanced Rheometric Expansion System: Rheometric Scientific Co. Ltd. U.S.) rotational rheometer. The equipment was run in the parallel plate configuration at a temperature 235 °C with a strain of 2% in the angular frequency range of 0.1–100 rad/s.

The mechanical properties of PA6 and modified PA6 were determined using INSTRON 4464 tensile tester (INSTRON). Tests were performed on tensile bars (type II) that were compression molded according to the KS M3600 test method using a hot press (Model 3851-O, Carver Inc.) at a set temperature of 240 °C and a molding pressure of 14 MPa. The experiment was performed at room temperature with a gauge speed of 10 mm/min and a gauge length of 35 mm. The average value determined from 4 tests was employed as the tensile value.

The gel contents of the irradiated samples were determined by extracting the soluble fraction with boiling formic acid in a soxhlet extractor. The gel content was calculated as follows:

$$\text{Gel content}\ (\%) = W_r/W_0 \times 100$$

where W_r is the mass of residue after extraction with boiling formic acid W_0 is the mass of specimen before extraction.

To calculate water absorption all the specimens were vacuum dried for a day at 60 °C and weighted, and then the specimens were located in a constant humidity room maintained at 100% relative humidity at room temperature for 1–31 days. The water absorption was calculated as follows:

$$\text{Water absorption}\ (\%) = (W_i - W_i)/W_i \times 100$$

where W_t is the mass of wet specimen which was stored in the constant temperature and humidity room. W_i is the mass of vacuum dried specimen. The values obtained were the average of three readings.

3. Results and discussion

3.1. Thermal properties and gel content

The melting temperatures, crystallinity, and gel content of virgin PA6 and modified PA6 are tabulated in Table 1. The melting temperature was not affected by the electro-beam irradiation and the crystallinity was slightly decreased by the electro-beam irradiation. There was no significant gel content by electron-beam irradiation. The gel content of was 1.3% even when PA6 with GMA was irradiated at 200 kGy. In former research for the crosslinked nylon 6 by electron-beam induced crosslinking with/without crosslinking agent, Dadbin et al. reported that the melting

Table 1
Melting temperature, crystallinity, and gel content of samples.

Sample code	Irradiation dose (kGy)	T_m (°C)	Crystallinity (%)	Gel content (%)
virgin PA6	0	218	32	0
EB0	0	218	28.7	0
EB2.5	2.5	217	28.5	0
EB5	5	219	28.7	0
EB10	10	217	28.9	0
EB20	20	218	28.7	0
EB50	50	218	28.7	0
EB100	100	218	27.5	1.1
EB200	200	216	27.9	1.3