PC05: ผลของรังสีต่อความเสถียรทางความร้อนของพอลิเมอร์ผสมระหว่างพอลิแลคติคแอซิดและเซลลูโลสอะซิเตต

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บทคัดย่อ

งานวิจัยนี้ได้ทำการผสมเซลลูโลสอะซิเตตกับพอลิแลคติคแอซิด เพื่อวัตถุประสงค์ที่จะปรับปรุงความเสถียรของพอลิแลคติคแอซิดเมื่อโดนความร้อน ในขณะที่ไม่สูญเสียความสามารถในการย่อยสลาย ไตรอัลลิล ไอโซไซยานูเรต (Trially isocyanurate, TAIC) ถูกใช้เป็นสารเหนี่ยวนำให้เกิดการคลอสลิงค์ระหว่างเซลลูโลสอะซิเตตและพอลิแลคติคแอซิด พอลิเมอร์ผสมแบบที่เติมและไม่เติม TAIC ถูกฉายรังสีโดยใช้เครื่องเร่งอนุภาคอิเล็กตรอน ผลการทดลองจากการหาค่าสัดส่วนของเจล และกราฟที่ได้จากเครื่อง Differential Scanning Calorimeter (DSC) แสดงให้เห็นว่ารังสีช่วยเหนี่ยวนำ TAIC ในการคลอสลิงค์พอลิเมอร์ผสม ในขณะที่ผลการทดลองด้วยเครื่อง Thermo Mechanical Analyzer (TMA) แสดงให้เห็นว่าเซลลูโลสอะซิเตตช่วยปรับปรุงความเสถียรทางความร้อนของพอลิแลคติคแอซิด

คำสำคัญ: รังสี พอลิแลคติคแอซิด เซลลูโลส ความเสถียรทางความร้อน

Effects of Radiation-Induced Crosslinking on the Thermal Stability of Poly(Lactic Acid) and Cellulose Acetate Blends

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Abstract

Poly(lactic acid) (PLA) was blended with cellulose acetate to improve the thermal stability of PLA, while simultaneously retaining the inherent compostability of both polymers. The blends were irradiated by an electron beam accelerator, both with and without triallyl isocyanurate (TAIC) as a crosslinking agent. Results from gel fraction and differential scanning calorimeter (DSC) showed that blends with TAIC were able to undergo crosslinking reactions induced by radiation, whereas results from thermo mechanical analyzer (TMA) showed that the presence of cellulose acetate improved the thermal stability of PLA.

Keywords: Radiation Crosslinking, Polylactic Acid, Cellulose Acetate, Thermal Stability

1. Introduction

Poly(lactic acid) or polylactide (PLA) is a compostable thermoplastic aliphatic polyester obtained by ring-opening polymerization of lactide monomers which can be derived from renewable resources such as starch or sugarcanes. In recent years, PLA has been receiving a great deal of attention, essentially due to its degradability[1-2]. With this environmental-friendly property, along with a highly transparent appearance similar to that of polyethylene terephthalate (PET), PLA has undoubtedly become one of the most promising alternatives to non-biodegradable synthetic polymers conventionally derived from petroleum-based chemicals. Nonetheless, two of the most important factors that prevent PLA from being commercially and widely used are its thermal stability and high cost, compared to commercial plastics such as polyethylene (PE) or PET commonly used in packaging materials. This work focuses on two techniques, blending and radiation-induced crosslinking, as proposed solutions to overcome the aforementioned shortcomings associated with PLA.

Blending is one of the most convenient and practical techniques used to modify properties and expand applications of various polymers. Blending PLA with other polymers has been applied in a number of works[3-7]. In this work, blending PLA with polysaccharide derivatives has been proposed to both reduce the cost and improve the thermal stability of PLA. Renewable resources such as starch and cellulose are relatively inexpensive and therefore able to offer a competitive commercial strategy. Moreover, these natural polymers have high heat stability. Originating from renewable resources as well as being biodegradable, cellulose is the most abundant polysaccharide that is inexpensive and has high thermal stability. As one of the cellulose derivatives increasingly gaining attraction, cellulose acetate (CA) has excellent transparency, high thermal stability as well as toughness[8]. The proposed blends between PLA and CA are designed to combine the processability and PET-like properties of PLA with the high thermal stability of CA.

Crosslinking is another technique utilized to improve thermal stability of polymers. Crosslinking can be induced by chemical or radiation treatments. Unlike chemical treatments, radiation can induce crosslinking at ambient temperature, in solid state. With these advantages, radiation has proven to be a highly effective technique to induce the crosslinking between polymer molecules and as a result modify their properties. PLA normally degrades under direct ionizing radiation[9]. Nonetheless, when mixed with appropriate crosslinking agent, PLA is able to undergo radiation-induced crosslinking[10-11]. This work aims to take advantages that both blending and radiation-induced crosslinking have to offer to improve the thermal stability of PLA.

2. Experimental

2.1 Materials

Poly(L-lactic acid) (Ecoplastic S12) was considerately supplied by Toyota Motor Co. Ltd., Japan. Cellulose diacetate (LT-55) was kindly contributed by Daicel Chemical Industry Co. Ltd., Japan. Triallyl isocyanurate (TAIC) was contributed by Nippon Kasei Chemical Co. Ltd., Japan. Chloroform (Wako Pure Chemical Industries, Ltd., Japan) was used as received.

2.2 Sample preparation and irradiation

The blends between PLA and CA with different ratios (100:0, 90:10, 80:20, 70:30, 60:40, 50:50 and 0:100) were prepared by dissolving PLA, CA and TAIC (5phr) in chloroform at room temperature. After the solvent was evaporated at ambient temperature, the blends were dried in a vacuum oven at 50 ºC for 48h. To form 150 x 150 x 0.2 mm films, the blends were preheated at 180 ºC for 5min, hot pressed at 180 ºC for 5min and subsequently cold pressed for another 5min. The blends were then vacuum sealed in a polyethylene / nylon bag prior to EB-irradiation by a 2 MeV at a dose rate of 10 kGy / pass.

2.3 Gel fraction measurements

Fraction of insoluble part in samples was determined by submerging samples in chloroform for 48 h at room temperature. The following equation was used to gravimetrically calculate the gel fraction of the samples;

$$\text{Gel fraction (\%)} = [\, W_d / W_i \,] \times 100 \qquad (1)$$

where W_i is the initial weight of the dried samples after irradiation and W_d is the weight of the dried samples after extraction with chloroform.

2.4 Thermal properties

A DSC from TA Instruments, DSC Q100, was used for DSC measurements. Each sample was weighed and sealed in an aluminum pan. DSC scans were performed in modulated mode with a period of 60 s at a scan rate of 1 ºC/min. All DSC experiments were done under nitrogen purge, with a heating rate of 10 ºC/min from 0 ºC to 225 ºC.

Thermal stability of the samples was studied using a TMA-60 thermomechanical analyzer from Shimadzu. The 5 x 5 x 0.2 mm sample film was fixed in a holder and heated from ambient temperature to 220 ºC in a nitrogen atmosphere under a constant load of 0.5 g with a heating rate of 20 ºC /min.

3. Results and Discussions

3.1 Gel fraction

Figure 1 shows the gel fraction of two PLA samples, with and without TAIC. From the figure, it is obvious that without TAIC, PLA was unable to crosslink. On contrary, PLA sample mixed with TAIC were able to form gel. The gel fraction of PLA mixed with TAIC increased with increasing dose. The results from the gel fraction experiments of the blends prepared by systematically varying the ratio between PLA to CA are shown in Figure 2. Generally, most of the blends showed similar trend. At 20 and 50 kGy, the gel fraction values are relatively comparable for all the blends, whereas, at 100 kGy the gel fraction of the blends increases with increasing content of PLA. This may stem from the fact that CA is more likely to degrade at high dose, while PLA is able to crosslink further.

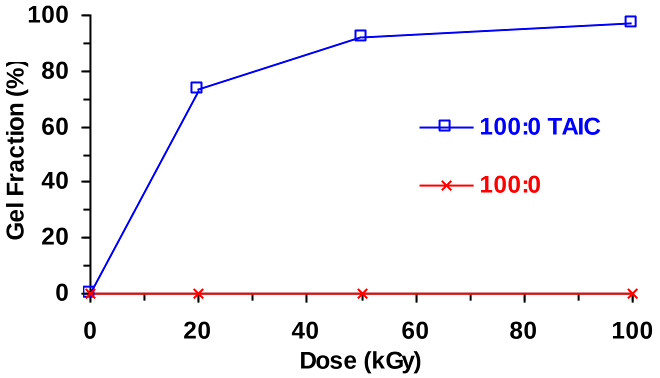

Fig. 1 Gel fraction of PLA with and without TAIC, irradiated at 0, 20, 50 and 100 kGy.

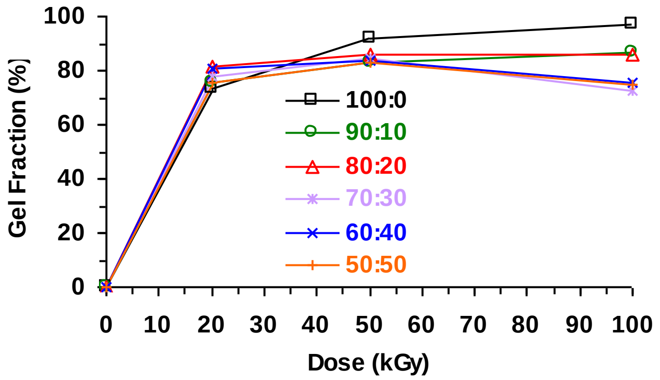

Fig. 2 Gel fraction of the blends at different ratios of PLA to CA,

with TAIC, irradiated at 0, 20, 50 and 100kGy.

3.2 DSC thermograms

DSC experiments were performed to trace changes in thermal properties of samples caused by radiation-induced crosslinking. Figure 3 displays the DSC thermograms of PLA samples without TAIC; irradiated at four different doses. In general, the four thermograms exhibit minor changes. All four samples have similar glass transition temperature (T_g), cold crystallization temperature (T_c) and melting temperature (T_m) centered at approximately 57, 98 and 174 ^{o}C, respectively. The insignificant changes of irradiated samples compared with the unirradiated sample agreed well with those from gel fraction experiments, confirming that, without TAIC, PLA was unable to undergo radiation-induced crosslinking.

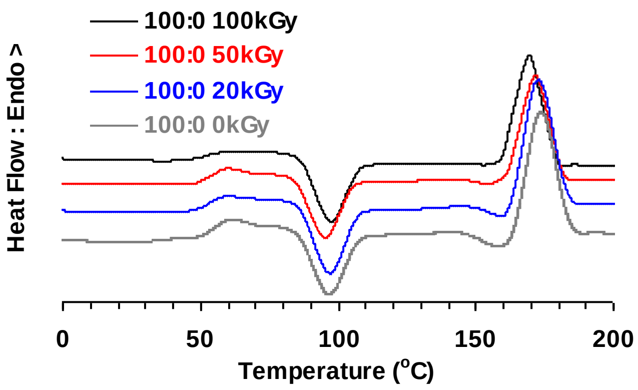

Fig. 3 DSC thermograms of PLA, without TAIC, irradiated at 0, 20, 50 and 100 kGy.

The DSC thermograms of PLA samples mixed with TAIC are shown in Figure 4. Unlike their TAIC-free counterparts, the TAIC-containing samples irradiated at different doses showed drastic differences in their thermograms. The DSC thermogram of the unirradiated sample showed all three peaks, similar to those of samples without TAIC. Upon irradiation, T_g increased with dose, but very slightly. On contrary, the cold crystallization peaks shifted towards higher temperatures, while the melting peaks moved towards lower temperatures. At 100kGy, only T_g is observable, while T_c and T_m are no longer present.

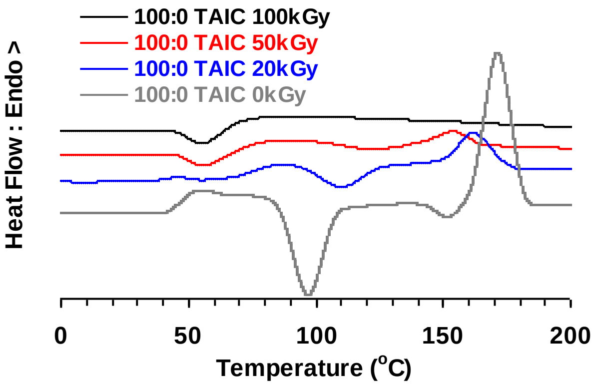

Fig. 4 DSC thermograms of PLA, with TAIC, irradiated at 0, 20, 50 and 100 kGy.

The drastic changes in the DSC thermograms of these samples confirmed that they underwent radiation-induced crosslinking. This can be explained from the fact that crosslinking fixes PLA molecules and therefore prevents crystallization and melting. As for the blends between

PLA and CA, DSC results of all the blends at different ratios also showed similar pattern. The unirradiated sample showed all three peaks (T_g, T_c and T_m) in their DSC thermograms. With increasing dose, T_c and T_m shifted towards higher and lower temperatures, respectively. The size of T_c and T_m peaks decreased with dose and finally disappeared at 100 kGy. For an example, DSC thermograms of the 80:20 blends are displayed in Figure 5.

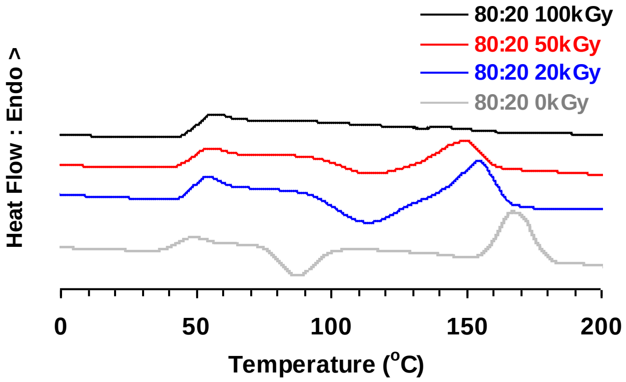

Fig. 5 DSC thermograms of the PLA:CA blend (80:20), with TAIC, irradiated at 0, 20, 50 and 100kGy.

3.3 Thermal stability

Figure 6 shows TMA thermograms of PLA (100:0) and CA (0:100) with TAIC, irradiated at 0 and 100 kGy. The unirradiated PLA started its elongation at about 70 °C. The blend continued to gradually extend until about 150 °C, after which the elongation seemed to level off. However, after 200 °C the blend drastically elongated. Its deformation suddenly increased from 8% at 200 °C to 27% at 225 °C. After TMA experiments, the sample badly deformed and was torn apart.

The PLA irradiated at 100 kGy also showed slow deformation at the beginning. However, unlike its unirradiated counterpart, the PLA irradiated at 100 kGy was able to maintain its gradual elongation without drastic deformation. At 225 °C, its deformation is less than 7%. After the experiment, the sample remained fairly intact. These results suggested that radiation-induced crosslinking further improved the thermal stability of PLA.

As for CA (0:100), both the unirradiated and irradiated samples show similar TMA thermograms. Both samples remained thermally stable until 170 °C. This is not unexpected since CA is known to have high thermal stability. Nonetheless, after 170 °C both samples began to shrink.

The thermal shrinkage of CA samples is caused by the breaking of acetyl group from cellulose molecules. With heat exposure, the acetyl groups break from the long chains of cellulose molecules, acetic acid is then released. The release of acetic acid shortens the polymeric chains and finally leads to shrinkage.

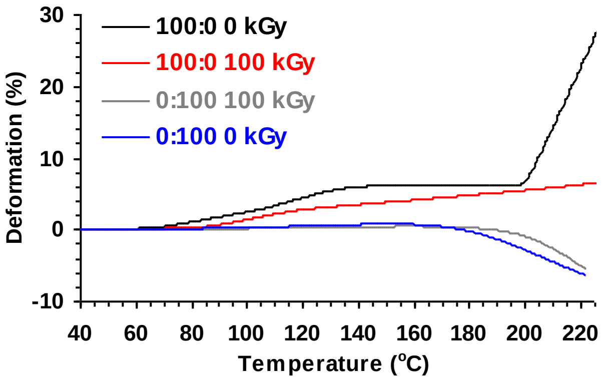

Fig. 6 TMA thermograms of PLA (100:0) and CA (0:100), with TAIC, irradiated at 0 and 100kGy.

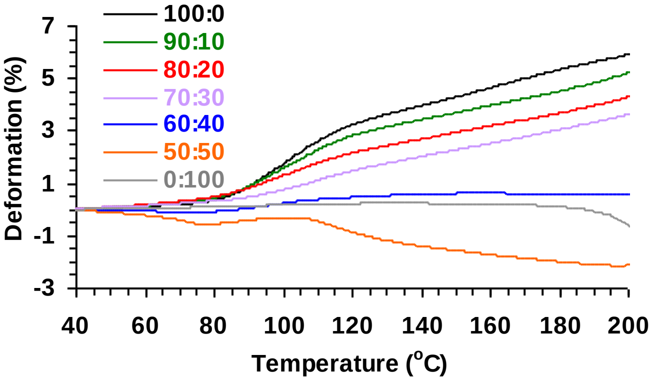

Fig. 7 TMA thermograms of the blends at different ratios of PLA to CA, with TAIC, irradiated at 100kGy.

TMA thermograms of the blends at different ratios of PLA to CA are shown in Figure 7. From the figure, it can be seen that the thermal stability of the blends systematically increased with CA content. At 200 °C, the deformation of 100:0, 90:10, 80:20, 70:30 and 60:40 blends are 5.9, 5.2, 4.3, 3.6 and 0.6%, respectively. Note that the blends with the ratio of PLA to CA higher than 60:40

showed thermal expansion, while the blend at the ratio of 50:50 started showing thermal shrinkage. Meanwhile, the blend with the ratio of 60:40 showed comparatively slight change in thermal deformation, at 200 °C its deformation was less than 1%. These results showed that the presence of CA helped improve the thermal stability of the blends.

5. Conclusions

The blends with different ratios of PLA and CA were systematically prepared and characterized. The results from both gel fraction and DSC experiments implied that without TAIC, the blends cannot form gels, while the presence of TAIC enabled the blends to undergo radiation-induced crosslinking. The results from TMA experiments entailed that the presence of CA improved the thermal stability of the blends.

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