The Properties of Polymer Blends between Poly(lactic) Acid and Epoxidized Natural Rubber Irradiated in the Rubber Phase

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Abstract: The objective of this work was to study the properties of new biodegradable packaging materials by radiation crosslinking in the rubber phase in a poly(lactic)acid (PLA)/epoxidized natural rubber blend. As a result of increasing problems with regards to disposal of domestic waste, particularly plastics, a new class of polymer especially designed to be biodegradable, has been undergoing development. The mechanical properties indicated that the 90/10 composition of the PLA/ENR blend had the highest modulus, elongation at break and tensile strength compared to other blend compositions. This research will therefore employ this ratio to investigate the effect of pre-irradiation of epoxidized natural rubber on the properties of the poly (lactic) acid / epoxidized natural rubber blend. The impact strength of the polymer blend increases with an increased radiation dose irradiated into the rubber phase because the increase in the radiation dose leads to an increase in the crosslink density within the rubber phase. Moreover, the TGA thermograms of polymer blends without irradiation in the ENR phase are compared with pre-irradiation in the ENR phase. It could be concluded that at a particular temperature weight loss from irradiation in the ENR phase at 30 kGy is higher than from other radiation doses and also no radiation dose, indicating that no radiation provides more thermal stability. Thus it could be seen that degradation being the predominant process during irradiation causes the scission of the rubber chains and this chain scission is associated with the weight loss.

Keywords: radiation, rubber, polylactic acid, biodegradable plastic

1. Introduction

Due to increased public attention to environmental problems, the research into biodegradable polymers has gained considerable momentum in recent years.

One of these biodegradable polymers is poly(lactic acid) (PLA) which is derived from renewable resources, thus it is appropriate for packaging applications. However, PLA is brittle, which limits its uses.

Blending PLA with epoxidized natural rubber (ENR) which can also be biodegradable will improve its toughness [1, 2] because there is a reaction between the OH group of the PLA and the expoxide group of the ENR to form a hydrogen bonding.

In this research work, ENR was irradiated prior to being blended with PLA by γ-rays from ^{60}Co source which caused a crosslinking reaction in the irradiated ENR. This lead to better properties in the polymer blends. In addition, the reason why this research selected the radiation method to vulcanize ENR was because radiation vulcanization offers several advantages over the conventional thermo-chemical methods viz. products are free from residual chemicals like nitrosamines, sulphur, zinc oxide, they possess low cytotoxicity, are more transparent, soft and have less rubber proteins that cause allergic responses [3].

Thus, this paper reports the effects of irradiating the rubber prior to melt mixing with poly (lactic acid). Also on the thermal properties and physical properties of polymer blends between poly(lactic) acid and epoxidized natural rubber irradiated in the rubber phase.

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2. Experimental

2.1. Materials

Epoxidized natural rubber, grade “Epoxyprene 50” with 50% epoxidation level (ENR 50) was purchased from Guthrie Polymer Ltd.; poly (lactic acid) was purchased from Thantawan Industry Company Limited with a weight-average molecular weight of 2.4×10^5. Furthermore, PLA was dried in a hot oven at 60 °C for 24 hrs before processing.

2.2. Experimental procedure

Blend preparations: Irradiation of ENR 50 was carried out using γ-rays from ^{60}Co source, available from the Office of Atoms for Peace by varying the radiation dose at a dose rate 4.8 kGy/h and then blending with

poly (lactic) acid by using a twin-screw extruder.

The temperature profile from hopper to die ranged from 150-160 ^{o}C. The samples from the extruder were palletized into granules at 600 rpm. The granules were heated at 55 ^{o}C for 2 days, and then formed into sheet by hot press equipment at 190 ^{o}C, 10.5 MPa.

Swelling studies: For swelling studies a known weight of film was left to swell in toluene till no further increase in weight of the film was observed. This was considered as the equilibrium swelling weight of the film. The swollen film was vacuum dried to a constant weight. The swelling ration was calculated using simple mathematical relations.

Mechanical Properties: Molded samples were cut into dumbbell shaped specimens according to ASTM D638 for tensile tests and further impact strength tests according to ASTM D256.

Table 1. The tensile properties and impact strength of PLA/ENR binary blend.

PLA/ENR (wt/wt)	Modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)	Impact strength (KJ/m^2)
100/0	1874.34 ± 1.62	2.26 ± 1.84	44.67 ± 1.62	3.33 ± 0.98
90/10	885.67 ± 1.08	2.86 ± 0.92	18.34 ± 1.62	5.56 ± 1.56
80/20	815.67 ± 1.15	0.93± 0.98	8.00 ± 0.56	4.40 ± 0.65
70/30	175.00 ± 0.98	0.70± 1.35	0.70 ± 0.26	4.50 ± 1.47
60/40	138.34 ± 1.82	0.75± 1.88	1.17 ± 0.73	10.80 ± 0.87
50/50	29.00 ± 1.41	0.70± 1.64	0.86 ± 0.11	10.30 ± 1.18

TGA studies: Thermogravimetric analysis was done using a Thermal Analyser (TG-DTA, Perkin-Elmer, Pyris diamond) in the temperature range of 30- 800^{o}C at a heating rate of 4^{o}C/min.

Results and discussions

The effect of PLA and ENR blending on the modulus, elongation at break, tensile strength and impact strength is shown in Table 1. As expected, the addition of ENR reduced the modulus and strength significantly, while it improved the impact strength. However, at the composition of ENR of more than 10%, the elongation at break dropped dramatically, and so do the modulus and the tensile strength.

The impact strength increased upon increasing the amount of ENR. This may be attributed to the elastomeric behavior of ENR. The improvement of impact strength when ENR is added to PLA probably

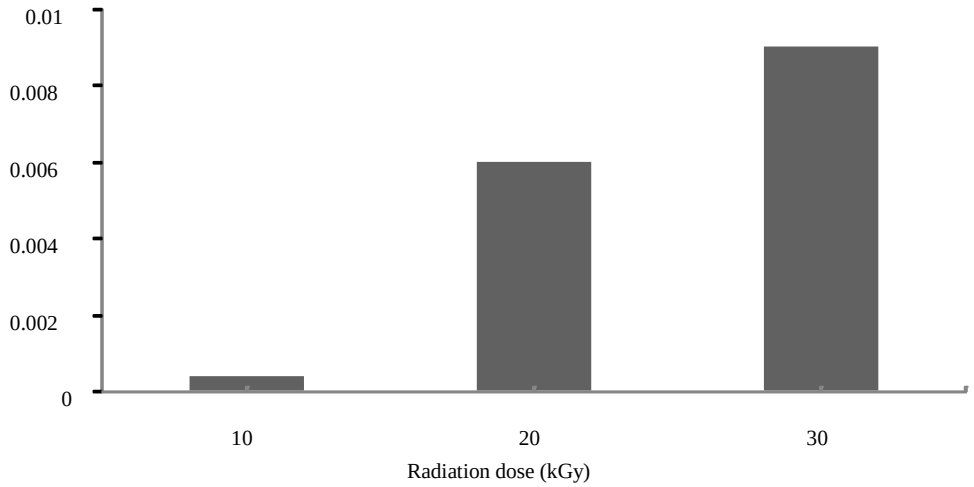

Figure 1. ***The effect of radiation doses on a swelling ratio of 90/10 poly(lactic) acid/epoxidized natural rubber blend (PLA/ENR) pre-irradiated in ENR***

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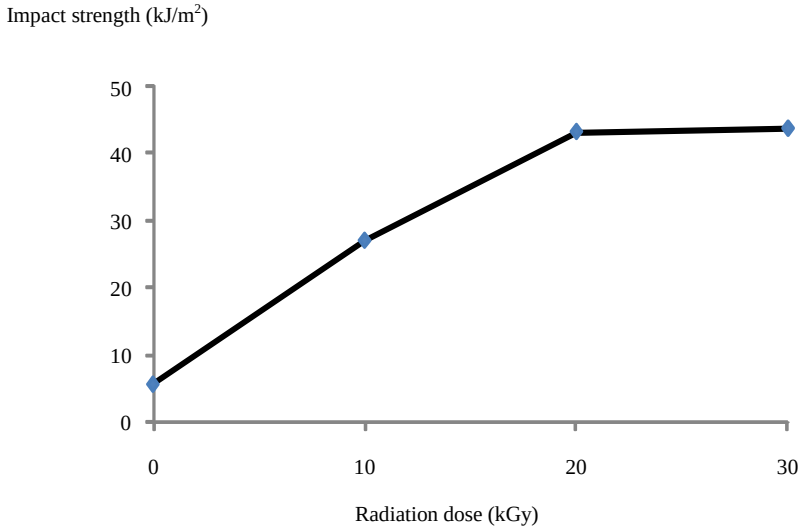

Figure 2. ***The effect of radiation dose on impact strength of 90/10 polylactic acid/epoxidized natural rubber blend (PLA/ENR) pre-irradiated in ENR.***

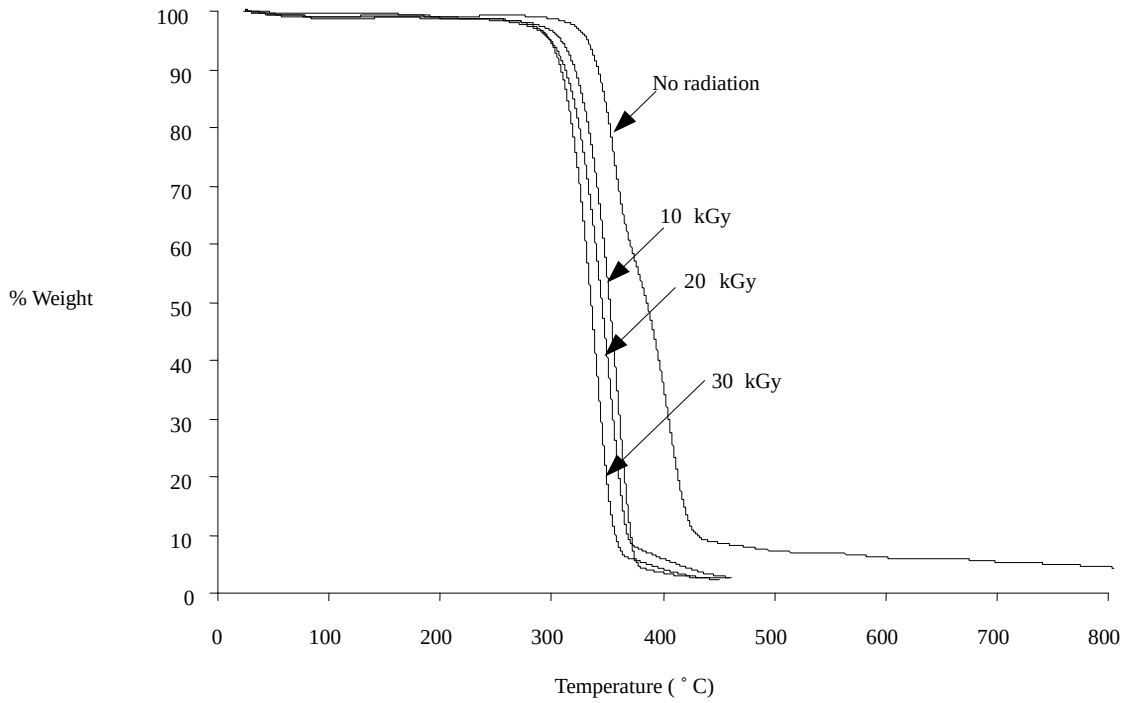

Figure 3. ***TGA thermograms of 90/10 polylactic acid/epoxidized natural rubber blend (PLA/ENR) both without irradiation and pre-irradiation in ENR phase.***

occurs as a result of a chemical reaction between the oxirane group of ENR and the hydroxyl group in PLA.

The results from the mechanical properties indicated that the 90/10 composition of the PLA/ENR blend had the highest modulus, elongation at break and tensile strength compared to other blend compositions.

This research will therefore employ this ratio to investigate the effect of pre-irradiation of epoxidized natural rubber on the properties of the poly(lactic) acid / epoxidized natural rubber blend.

The impact strength of the polymer blend is one of the most important properties for certain applications, therefore changes in the impact strength of this polymer blend was investigated.

Polymers undergo crosslinking as well as degradation simultaneously, however the predominant process determines the final affects of the irradiation.

Figure 2. shows the changes in the impact strength of the polymer blend with various doses of gamma rays.

It is clear from the figures that impact strength of the polymer blends increases with radiation doses of up-to a dose of 20 kGy and after that it remains constant up-to 30 kGy indicating that initially up-to a dose of 20 kGy crosslinking is the predominant process.

Figure 1. shows the results of changes in the swelling ratio with changes in the radiation doses. It is clear from results that the swelling ratio increases with increase in radiation doses because of the increas in crosslinking density in the rubber phase.

Figure 3. shows TGA thermograms of 90/10 poly(lactic) acid/epoxidized natural rubber blend (PLA/ENR) both without irradiation and pre-irradiation in ENR phase, radiation vulcanized to a dose of 30 kGy.

Comparing TGA profiles of polymer blends without irradiation in the ENR phase with pre-irradiation in the ENR phase it can be seen that at a particular temperature weight loss from irradiation in the ENR phase at 30 kGy is higher than from other radiation doses and also no radiation dose, indicating that no radiation provides more thermal stability. Thus it could be concluded that degradation being the predominant process during irradiation causes the scission of the rubber chains and this chain scission is associated with the weight loss.

Conclusions

The properties of polymer blends between poly(lactic) acid and epoxidized natural rubber irradiated in the rubber phase has been investigated. The samples were characterized for their swelling ratio, impact strength and thermal stability as a function of the radiation dose. The swelling ratio and impact strength of these polymer blends were found to increase with increased radiation doses. Whereas thermal stability decreases with increases in radiation doses due to the degradation effect being the predominant process.

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