EFFECT OF ELECTRON BEAM IRRADIATION ON PROPERTIES OF POLY(LACTIC ACID) AND KENAF/POLY(LACTIC ACID) BIOCOMPOSITES IN THE PRESENCE OF TRIALLYL ISOCYANURATE AS MULTI-FUNCTIONAL MONOMER

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Abstract

Poly(lactic acid)(PLA) films were prepared using PLA pellets containing triallyl isocyanurate (TAIC) of 3.3 wt% as multi-functional monomer produced by twin screw extrusion technique. Kenaf/PLA biocomposites with 30 wt% kenaf fibers un-irradiated and pre-irradiated (0-30 kGy) prior to composite processing were fabricated by compression molding. The effects of electron beam irradiation on the physical and thermal properties of PLA films (0-400 kGy) and on the dynamic mechanical and flexural properties of kenaf/PLA biocomposites (0-100 kGy) were investigated. The electron beam irradiation done to the PLA films and the biocomposites contributed to enhancing their properties, being in agreement with each other. The best properties were obtained when kenaf fibers were pre-irradiated at 5 kGy and then the biocomposites were irradiated at 10-50 kGy, depending on the targeting properties.

1 Introduction

Recently, environmental problems due to petroleum-derived plastics wastes have been increasingly key-issued all over the world, due to increasing environmental regulations and social consciousness. In order to solve such problems, natural-based materials or biodegradable polymers can be used for replacement of the petroleum-derived plastics. A large number of research efforts have been devoted to do so in academia and industries. Poly(lactic acid)(PLA) is one of the attractive biodegradable polymers based on renewable resources. PLA, which can be used as alternative of polypropylene in many applications, exhibits good mechanical properties, thermal stability, translucence, and biodegradability, whereas it has brittleness and low heat deflection temperature [1]. In order to overcome the shortcomings of PLA properties, many studies on biodegradable polymer blends and natural fiber-based biocomposites have been done for the last decade [2-4].

The fiber-matrix interfacial adhesion is critically important in biocomposites as well as in conventional fiber-reinforced polymer composites to enhance the properties and performances of composites. Therefore, there have been a large number of papers dealing with the modification of natural fibers like kenaf, jute, hemp, flax, sisal, henequen, and banana to increase the properties of biocomposites consisting of natural fibers [5-7]

Electron beam processing is a dry, clean and cold method with advantages such as energy-saving, high throughput rate, uniform irradiation and environmental safety. Electron beam technique has often been utilized for surface modification and property improvement of polymer materials like fibers, films, plastics and composites for the last decades. It may remove surface impurities and alter surface characteristics at appropriate irradiation conditions, leading to the property improvement of materials of interest.

For recent years, Cho *et al*. have reported a number of papers [8-11] demonstrating the electron beam irradiation effect of natural fibers on the interfacial properties as well as on the thermal and mechanical properties of biocomposites. They reported that the electron beam exposed to natural fibers was effective to increase not only the interfacial adhesion between the natural fibers and the polymer matrix but also the thermal and mechanical properties of biocomposites at an appropriate electron beam absorption dose. However, the electron beam effect on biocomposites with PLA and kenaf has been scarcely reported. Kenaf is one of the most attractive cellulose-based natural fibers in biocomposite fields, particularly in automotive applications, due to acceptable mechanical properties, processibility, and its relatively high absorption capability of carbon dioxide in nature during cultivation.

Some research efforts to explore the characteristic changes occurring in biodegradable polymers by introducing electron beam irradiation technique have also been reported recently [12-14]. The work has been based on that electron beam irradiation may contribute to enhancing the properties of biodegradable polymers through crosslinking reaction in the presence of multi-functional monomers.

Consequently, the objectives of this study are primarily to investigate the effect of electron beam irradiation on the physical, mechanical and thermal properties of PLA films, which were fabricated with PLA pellets containing triallyl isocyanurate (TAIC) as multi-functional monomer, and ultimately to explore the effect of electron beam irradiated to biocomposites on the mechanical and thermal properties of kenaf/PLA biocomposites. In order to understand the effect of electron beam irradiation on the properties of kenaf/PLA biocomposites, three different types of biocomposites were fabricated at a fixed kenaf content of 30 wt%, as follows: 1) biocomposites fabricated with chopped kenaf fibers and PLA without any electron beam irradiation. 2) biocomposites irradiated at various electron beam absorption doses (0-100 kGy) after fabricated with chopped kenaf fibers and PLA without electron beam irradiation 3) biocomposites irradiated at various absorption doses (0-100 kGy) after fabricated with kenaf fibers pre-irradiated with different absorption doses (0-30 kGy) and PLA.

2 Materials and testing methods

2.1Materials

PLA(Model: 2003D) used in this work was supplied from NatureWorks (USA). The melting temperature of the PLA is 156℃ and the glass transition temperature 55℃, and the crystallization temperature 100-120℃. TAIC, purchased from TCI(purity 96%) (Japan), was used for curing by electron beam irradiation. The freezing point of liquid-type TAIC is 24℃ and the boiling point is 140℃. The chemical structure of TAIC is shown in Figure 1.

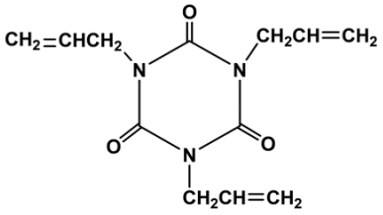

Figure 1. Chemical structure of triallyl isocyanurate (TAIC).

Kenaf bundles supplied from the Bangladesh Jute Institute, Bangladesh were used. They were chopped to 5±2 mm in average by using a fiber chopper (Model: KM105HK1, Man Pyung Ind., Korea). The chopped fibers were used as reinforcement of kenaf/PLA biocomposites.

2.2 Processing of PLA pellets

In order to compound and process PLA pellets without and with TAIC, a modular intermeshing co-rotating type twin screw extruder with the screw diameter of 30 mm and the L/D ratio of 42(LG, Model: BT-30-S2-421) was utilized. PLA was dried in a convection oven for 24 hours prior to use. 4 wt% TAIC against neat PLA was initially fed to the extruder after uniformly mixing the PLA and TAIC. After compounding and extruding, it was found that 3.3wt% TAIC was remained in the PLA pellets due to removal of TAIC in the extruder during the process. The screw speed was 100 rpm.

2.3 Fabrication of PLA films and kenaf/PLA biocomposites

PLA pellets without and with TAIC were used to fabricate neat PLA and PLA films at 180℃ using a hot-press, respectively. Hereinafter, PLA films designate the films made with PLA/TAIC pellets, Neat PLA films do not contain TAIC at all. The dimensions of each film were 170 mm by 150 mm and the thickness of each film was about 250 ㎛ in average. About 30 films of each sample were prepared for electron beam processing.

PLA/kenaf bicomposites were fabricated by using a compression molding method. The PLA pellets containing TAIC and the chopped kenaf fibers were uniformly mixed and the composite fabrication was performed in a stainless steel mold using a hot-press. The biocomposites containing kenaf fibers un-irradiated and pre-irradiated with electron beam prior to composite processing were fabricated, respectively. The kenaf fiber contents were fixed to 30 wt%. The dimensions of each biocomposite plaque were 100 mm by 150 mm. The thickness was varied, depending on the specimen requirement of each test. Kenaf/neat PLA biocomposites were also made for comparison under the same fabrication conditions.

2.4 Electron beam processing

The following materials were irradiated at various electron beam absorption doses using industrial-level electron beam facility: 1) neat PLA and PLA films, 2) kenaf bundles, and 3) kenaf/PLA biocomposites (with kenaf fibers un-irradiated and pre-irradiated before biocomposite fabrication). All the films, kenaf fibers and biocomposites were fully dried prior to electron beam processing. The electron beam processing was performed at ambient temperature at EB Tech., Daejeon, Korea. An electron accelerator (ELV-8) was used. With the films and biocomposites, the electron beam energy used was 2.5 MeV and the current was 9.8 mA. With the kenaf fibers, the electron beam energy of 1.5 MeV was applied and the current of 3.65 mA was used. The electron beam absorption doses applied were in the range of 0-30 kGy for kenaf fibers, 0-400 kGy for films, and 0-100 kGy for biocomposites. The irradiation was done in the electron beam channel, at which the samples to be irradiated were placed in a conveying cart. The electron beam doses were controlled by the number of sample irradiations exposed in the channel.

2.5 Characterization

The PLA films immersed in chloroform were rested at ambient temperature for 24 hours. After 24 hours, uncured PLA resin in the solution was removed using a filter paper with the pore size of 100 ㎛ and with the paper diameter of 150 mm. The percent gel fraction of PLA films was obtained by measuring the weight change occurred in the sample before and after immersing each sample in chloroform.

Differential scanning calorimetry (DSC 200, NETZSCH) was performed to measure the glass transition temperature and heat flux changes of PLA films. The heating rate was 10℃/min to 200℃ and the second heating rate after cooling down to 0℃ was 5℃/min to 200℃. The thermal stability of neat PLA and PLA films was examined to 600℃ by using a

thermogravimetric analyzer (TGA Q500, TA Instruments). The heating rate was 20℃/min. The initial weight of each sample was about 20 mg.
The dynamic mechanical properties of PLA films and kenaf/PLA biocomposites were measured from 30℃ to 110℃ by using a dynamic mechanical analyzer (DMA Q800, TA Instruments). The tension mode and the dual cantilever mode were used for the films and the biocomposites, respectively. The width of the film specimens was 5 mm and the length was 18 mm. the dimensions of the biocomposite specimens were 60 mm x 12 mm x 2.5 mm. The heating rate was 2℃/min. The amplitude was 0.1 mm and the frequency was 1 Hz.
Three-point flexural tests were performed by using a universal testing machine (UTM, Instron 4467) according to ASTM D 790M. A load cell of 30 kN was used. The span-to-depth ratio of rectangular bar specimens was 16:1. The crosshead speed was 0.85 mm/min. The average flexural strength and modulus were obtained from 6 specimens of each.
The impact strength of kenaf/PLA biocomposites was explored by performing the Izod impact test (Tinius Olsen, 892) according to ASTM D256. The V-type notch (2.5 mm in depth) of each specimen was made using a notch cutter prior to the test. The test speed was 3.46 m/s. The impact energy given to the specimen was 12.66 J. The impact distance was 610 mm. The dimensions of each specimen were 63.5 mm x 12 mm x 2.5 mm. The average impact strength was obtained from 6 specimens of each.

3 Results and Discussion

Figure 2 shows the variations of the gel fraction (%) occurred in PLA films as a function of electron beam absorption dose. It was found that neat PLA and PLA films exhibited the low gel fraction of about 2% and 7%, respectively, in the absence of electron beam irradiation. With increasing the absorption dose, the gel fraction of PLA films containing 3.3 wt% TAIC was abruptly increased up to about 70% only at 10 kGy, to about 80% at 30 kGy, and to about 90% at 100 kGy. Above 100 kGy, the gel fraction was not significantly increased with increasing the dose because a large fraction of PLA molecules was readily crosslinked by the electron beam irradiation. At 400 kGy, the gel fraction was about 97%. It was clearly elucidated that PLA films can be effectively crosslinked by electron beam in the presence of TAIC, particularly at a low energy of electron beam.

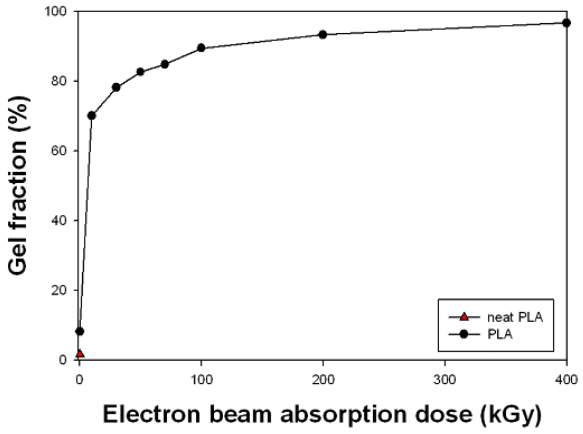

Figure 2. Effect of electron beam absorption dose on the percent gel fraction of neat PLA and PLA films.

Figure 3 exhibits the variations of glass transition temperature (T_g) of PLA films as a function of electron beam absorption dose, being determined by an onset method and a half-height method in the glass transition region of DSC curves, respectively. As expected, the half-height method resulted in about 3-4℃ higher T_g than the onset method in the whole

absorption dose range. The T_g of PLA films with TAIC was abruptly increased by electron beam irradiation up to 70 kGy and the increase was not considerably high at above 100 kGy, exhibiting a similar tendency of the variation as a function of electron beam absorption dose, as indicated in Figure 2. Without electron beam irradiation the T_g of PLA film was 1-2℃ (onset) and 3-4℃ (half-height) higher than that of neat PLA due to the presence of TAIC. Also, even at 10 kGy, the T_g of PLA film was slightly lower than that of neat PLA film. This can be explained by that the PLA film may have TAIC, which was not participated in the crosslinking reaction at such a low dose of 10 kGy and the unreacted TAIC may act as low molecular component, which can decrease the glass transition temperature.

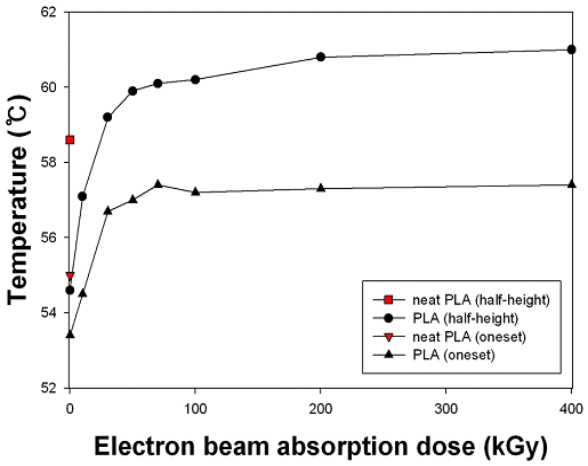

Figure 3. Variations of the glass transition temperature of neat PLA and PLA films as a function of electron beam absorption dose, determined by half-height and onset methods, respectively.

Figure 4 displays the variations of the dynamic storage modulus measured at 40℃ as a function of electron beam absorption dose. As similarly found from the T_g result, the storage modulus of PLA film was lower than that of neat PLA film when the dose was lower than 30 kGy. The storage modulus of PLA film at 50 kGy was greater than that of neat PLA. The greatest modulus was obtained at 100 kGy. Above 100 kGy, the storage modulus was significantly decreased with increasing the dose due to chain scission of PLA molecules or deterioration of the PLA property by high electron beam intensity. The DMA result indicates that the electron beam irradiation at the low absorption below 30 kGy does not significantly contribute to increasing the dynamic mechanical property of neat PLA.

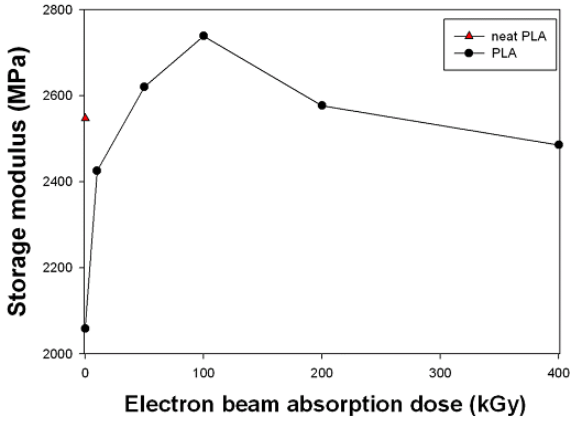

Figure 4. Variations of the storage modulus at 40℃ of neat PLA and PLA films as a function of electron beam absorption dose.

Each figure in Figure 5 exhibits the variations of the storage modulus of kenaf/PLA biocomposites not only as a function of temperature but also as a function of electron beam absorption dose exposed to the biocomposite. In addition, the result also informs on the effect of pre-irradiation of electron beam done to kenaf fibers prior to biocomposite processing on the dynamic mechanical property. As seen, the storage modulus was increased with increasing the absorption dose, showing the highest value when kenaf fibers were pre-irradiated at 5 kGy and subsequently the biocomposites were irradiated at 50 kGy. The tan δ peak temperature also depends on the pre-irradiation of kenaf fibers as well as on the electron beam irradiation of kenaf/PLA biocomposites.

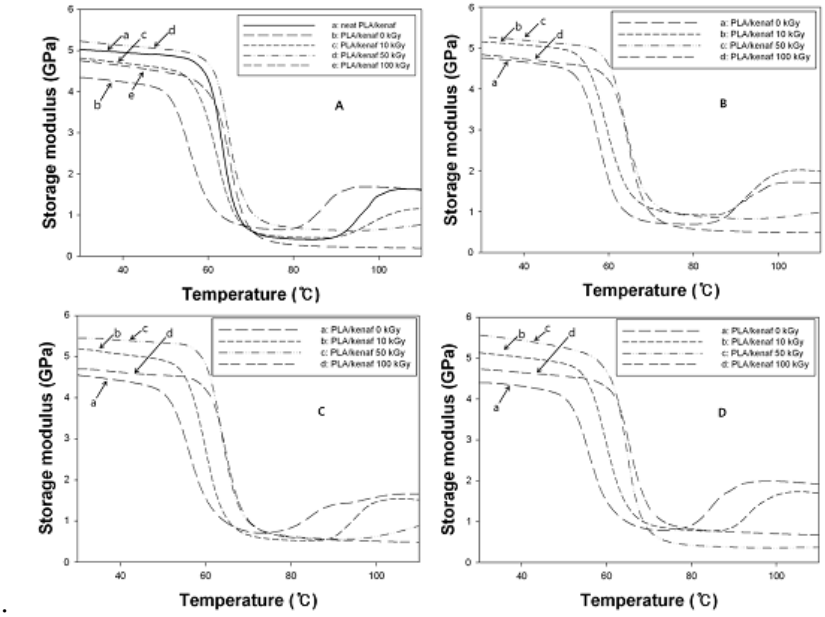

Figure 5. Variations of the storage modulus for PLA/kenaf biocomposites irradiated at various electron beam absorption doses. The kenaf fibers in the biocomposites were un-irradiated and pre-irradiated with different electron beam absorption doses prior to biocomposite fabrication. A: un-irradiated, B: pre-irradiated at 5 kGy, C: pre-irradiated at 10 kGy, D: pre-irradiated at 30 kGy.

Figure 6 shows the effect of electron beam irradiation on the flexural strength of kenaf/PLA biocomposites. The flexural strength and modulus of neat PLA/kenaf biocomposite, which was not exposed to the beam at all, were 90.7 MPa and 6.1GPa, respectively. In the case of biocomposites with kenaf fibers pre-irradiated at 5 kGy, the great flexural strength was obtained when the biocomposite was irradiated at 30 kGy. On the other hand, In the case of biocomposites with kenaf fibers pre-irradiated at 10 kGy, the great flexural strength was obtained when the biocomposite was irradiated at 10 kGy. The pre-irradiation of kenaf at 30 kGy, and the irradiation of biocompoiste at 50 kGy and higher resulted in a decrease of the flexural strength. This may be ascribed to the increase of microstructural defects in the kenaf fiber surface formed at 30 kGy and also the deterioration of intrinsic PLA property by high electron beam at above 50 kGy.

4 Conclusions

In the present study, incorporation of 3.3 wt% triallyl isocyanurate (TAIC) as multi-functional monomer into PLA resin by compounding and extruding processes was effective to contribute to crosslinking not only of PLA films but also of kenaf/PLA biocomposites by electron beam process at appropriate absorption doses.

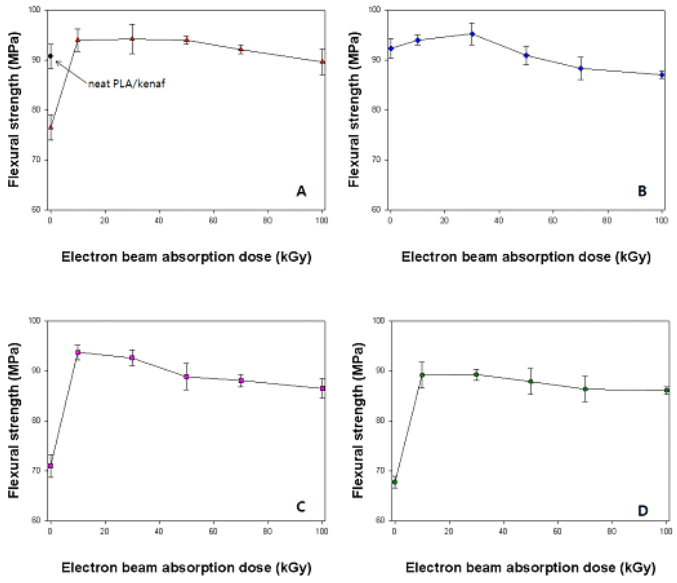

Figure 6. Variations of the flexural strength for PLA/kenaf biocomposites irradiated at various electron beam absorption doses. The kenaf fibers in the biocomposites were un-irradiated and pre-irradiated with different electron beam absorption doses prior to biocomposite fabrication. A: un-irradiated, B: pre-irradiated at 5 kGy, C: pre-irradiated at 10 kGy, D: pre-irradiated at 30 kGy.

The gel fraction of PLA films was increased with increasing the electron beam absorption dose, particularly at the initial stage of the irradiation. The storage modulus of PLA films significantly depended on the absorption dose, exhibiting the highest at 100 kGy. The glass transition temperature of PLA films was increased with the absorption dose, showing a similar tendency with the variation of the gel fraction.

The effects of electron beam irradiation on the properties of kenaf/PLA biocomposites and of pre-irradiation of kenaf fibers done prior to composite fabrication on the biocomposite properties were studied as follows. It was found that the storage modulus of kenaf/PLA biocomposites was highest at 50 kGy and the modulus was further increased by reinforcing with kenaf fibers pre-irradiated at 5 kGy. The flexural strength and modulus depended on the electron beam absorption dose of kenaf fiber pre-irradiation as well as the biocomposite.

The result demonstrated that the mechanical and thermal properties of neat PLA can be marginally increased by an electron beam irradiation according to the absorption dose used. In addition, the properties can also be further increased by incorporating cellulose-base natural fiber kenaf and they were also considerably enhanced by the electron beam irradiation of the biocomposite as well as the kenaf fibers therein.

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