Radiation-Induced Crosslinking and Mechanical Properties of Blends of Poly(lactic acid) and Poly(butylene terephthalate-*co*-adipate)

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ABSTRACT: Blends of poly(L-lactic acid) (PLLA) and poly(butylene terephthalate-*co*-adipate) (PBTA) were prepared at ratios of 50 : 50, 60 : 40, and 80 : 20 by melt blending in a Laboplastomill. Improved mechanical properties were observed in PLLA when it was blended with PBTA, a biodegradable flexible polymer. Irradiation of these blends with an electron beam (EB) in the presence of triallyl isocyanurate (TAIC), a polyfunctional monomer, did not cause any significant improvement in the mechanical properties, although the gel fraction increased with the TAIC level and dose level. Irradiation of the blends without TAIC led to a reduction in the elongation at break (E_b) but did not show a significant effect on the tensile strength. E_b of PBTA was unaffected by EB radiation in the absence of TAIC. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3321–3328, 2008

Key words: biodegradable; crosslinking; electron beam irradiation; mechanical properties; polyesters

INTRODUCTION

Poly(lactic acid) is a biodegradable polymer made from renewable resources. It is one of the first synthetic absorbable polymers found to be suitable for biomedical applications,[1] and it is available in two enantiomeric forms, namely, poly(L-lactic acid) (PLLA) and poly(D-lactic acid). PLLA is a semicrystalline plastic material with a glass-transition temperature around 58°C and a melting point around 178°C. It is one of the polymers that has attracted much attention during the last decade as a biodegradable polymer in the wake of severe environmental impact caused by the disposal of nonbiodegradable polymers. Previously, PLLA has mainly been found in the medical industry as a biocompatible polymer for such applications as drug-delivery systems, implant material for bone fixation, and surgical suture.[2] Apart from medical applications, PLLA has been found, because of its higher costs, in restricted applications, mainly in the packaging industry as high-value films, rigid thermofoams, food and beverage containers, and coated papers.[3] The recent development of low-cost production methods[4] of lactic acid through the carbohydrate fermentation of corn dextrose and subsequent polymerization of lactide formed by the condensation of two molecules of lactic acid monomer has paved the way for applications of PLLA in a vast array of general plastics products.

PLLA possesses very favorable properties, including high transparency, strength, biodegradability, biocompatibility, and barrier properties.[3] Nonetheless, brittleness, low deformation at break, and lack of flexibility limit its applications.

Several modifications, such as copolymerization, plasticization, and polymer blending, have been proposed to improve the mechanical properties of PLLA.[2,5] Blends of PLLA with various nonbiodegradable polymers and biodegradable aliphatic polyesters, such as poly(ε-caprolactone),[6–8] poly(butylene succinate),[9,10] and poly(hydroxyl butyrate),[11,12] have been investigated. An investigation was recently reported[13] on the modification of PLLA by its blending with another biodegradable aromatic flexible polymer, poly(butylene terephthalate-*co*-adipate) (PBTA). This attempt was made to modify PLLA by its blending with PBTA, commercially available under the trade name Ecoflex,[14] and irradiation with an electron beam (EB) in the presence of a polyfunctional monomer (PFM), namely, triallyl isocyanurate (TAIC). TAIC was found to be the most effective crosslinking agent for PLLA in a previous study.[15] The main aim of the study was to improve thermal properties of the blends by irradiation. Both the mechanical properties and thermal properties of the blends were studied in this investigation. This article presents the mechanical properties of both the

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unirradiated and irradiated blends. The thermal properties will be discussed in a separate article.

EXPERIMENTAL

Materials

The PLLA used in the experiments was LACEA H100J grade supplied by Mitsui Chemicals Corp. (Tokyo, Japan), and PBTA (Ecoflex) was supplied by BASF (Tokyo, Japan). The PFM TAIC used was supplied by Nippon Kasei Chemical Co, Ltd. (Tokyo, Japan).

Both PLLA and PBTA were dried *in vacuo* at 40°C for 6 h before use in the experiments. This was done to ensure the prevention of the hydrolytic degradation of PLLA.

Preparation of the blends

PBTA and PLLA were mixed at different blend ratios at 180°C for 10 min in a Laboplastomill model 50C150 (Tokyo Seiki Seisaku-Sho, Ltd., Tokyo) at a rotor speed of 60 rpm. TAIC was incorporated into the mixture before it was mixed in the plastomill.

Preparation of the films

The films were prepared from the blends at 180°C with a hot press at a pressure of 150 psi. The samples were preheated for 3 min on the press at the same temperature before the pressure was applied for another 3 min. The films were then quenched at the same pressure with running water at room temperature for 5 min with a cold press. The film thicknesses were 0.5 mm.

Irradiation of the films

The films were enclosed in radiation-resistant polythene bags and vacuum-sealed before irradiation at different doses from 0 up to 200 kGy with an EB accelerator (Nisshia High Voltage (NHV) Co., Inc., Tokyo, Japan). The acceleration energy, beam current, and dose rate were 2 MeV, 2 mA, and 10 kGy/pass, respectively.

Characterization of the irradiated blends

The gel content of the irradiated blends was estimated by the method described as follows.

About 0.05 g of the samples were placed in 325-mesh sachets and boiled under reflux for 12 h in chloroform. The sachets with gel were first washed thoroughly with fresh chloroform and dried in a vacuum oven at 50°C for 4 h. The weights of the wet gel and dry gel were determined:

$$\text{Gel fraction} = (W_2/W_1) \times 100$$

$$\text{Swelling ratio} = (W_2/\text{Weight of the wet gel}) \times 100$$

where W_1 is the weight of the irradiated sample and W_2 is the weight of the dry gel.

Tensile properties

The tensile properties were tested at room temperature (27°C) with a Toyoseiki Strograph VE50 (Tokyo Seiki Seisaku-Sho, Ltd.) at a crosshead speed of 10 mm/min according to ASTM D 1822.

RESULTS AND DISCUSSION

Crosslinking by irradiation

The gel fraction gave us an idea of the extent of crosslink formation. The gel fractions of the blends containing different percentages of PLLA irradiated at different levels of TAIC at various dose levels are delineated in Table I. The 80/20 PBTA/PLLA blend was irradiated at 50 kGy only, and therefore, the gel fraction of this blend is shown in Table I at 50 kGy only. Also, the 40/60 and 20/80 PBTA/PLLA blends were not irradiated at 200 kGy. The gel fraction in all of the blends irradiated without TAIC was zero, regardless of the dose level, except in two samples that were irradiated at 200 kGy, the highest dose level investigated. One of the samples was PBTA, which showed a very small gel fraction of 30%, whereas the 50/50 PBTA/PLLA blend showed a very insignificant gel fraction, as low as 4%. These results, therefore, confirm that crosslinks were formed in all of the blends when they were irradiated at comparatively lower doses in the presence of TAIC, as evident by their corresponding gel fractions. The higher dose levels required for crosslink formation can be reduced drastically by the incorporation of a PFM in individual polymers or polymer blends before irradiation. However, it has been reported that EB and γ irradiation of PLLA without crosslinking agents leads to degradation.[1,16,17] In the presence of TAIC in the blend, increasing the dose level increased the gel fraction, regardless of the PBTA content. At a dose level of 50 kGy, which was considered to be the optimum dose level as far as the gel fraction was concerned, the gel fraction dramatically increased when the PLLA content in the blend was increased above 50%, provided that the TAIC level in the system was above 3% (Fig. 1). Another important observation was that the gel fraction was reduced at this dose level in blends containing more than 50% PLLA with a TAIC level of less than 2%. On the other hand, a higher gel fraction was seen for the blends irradiated with TAIC levels of less than 2%, when the PBTA content was higher in the blend. According to these observations,

TABLE I
Gel Fraction of the PLLA/PBTA Blends Irradiated with Different TAIC Levels at Various Dose Levels

		Dose level (kGy)							
PLLA (%)	TAIC level	0 ↓	5 ↓	10 ↓	20 ↓	30 ↓	50 ↓	100 ↓	200 ↓
0	0	0	0	0	0	0	0	0	33.21
	1	0	0	9.23	34.91	48.03	55.17	64.65	73.73
	3	0	0	3.53	24.32	43.00	60.42	75.64	82.30
	5	0	0	1.31	19.06	40.56	59.79	80.41	86.94
20	0	—	—	—	—	—	—	—	—
	1	—	—	—	—	—	52.72	—	—
	3	—	—	—	—	—	54.15	—	—
	5	—	—	—	—	—	55.16	—	—
50	0	0	0	0	0	0	0	0	4.40
	1	0	0	2.77	5.01	10.71	14.44	43.72	19.39
	3	0	0	8.10	46.64	54.29	62.04	82.96	85.96
	5	0	0	4.74	29.55	54.98	78.99	90.07	90.29
60	0	0	0	0	0	0	0	0	—
	1	0	0	1.08	1.32	0.74	17.83	4.96	—
	3	0	0	5.31	29.78	50.49	68.92	65.72	—
	5	0	2.22	14.90	55.10	81.05	87.73	96.02	—
80	0	0	0	0	0	0	0	0	—
	1	0	0	0	0	3.15	20.65	7.60	—
	3	0	0	3.84	46.80	56.10	66.83	76.30	—
	5	0	5.32	31.27	64.64	78.32	89.06	95.35	—
100	0	0	0	0	0	0	0	0	0
	1	0	0	0	0	2.93	25.08	33.25	19.66
	3	0	1.11	32.68	64.63	70.85	78.52	92.34	90.91
	5	0	5.06	36.39	59.38	75.01	93.36	99.32	99.55

it is clear that crosslink formation in the blends was influenced by both the level of TAIC and the polymer content. The degree of gel formation seemed to be dependent on the concentration of PFM, the dose level, and also, to a lesser extent, the PLLA content in the blend. PLLA gave the highest gel fraction with a TAIC level above 3% at doses above 10 kGy. However, PBTA gave a considerable gel fraction at comparatively low levels of TAIC. A reasonably high gel fraction was observed at 50 kGy for almost all of the blends having a TAIC level above 3% (Fig. 1). The gel fraction in PBTA and in the blends containing less than 20% PLLA showed hardly any variation with TAIC level at 50 kGy. The results of the gel fractions of the irradiated blends indicate that an optimum gel fraction was obtained when the blends were irradiated at 50 kGy. Considering the previous observations, we regarded a dose level of 50 kGy and a TAIC level of 3% as the optimum conditions for irradiation of the blends in the presence of TAIC. It has been reported in a previous study that almost the same level of gel fraction was achieved in PLLA with TAIC levels of 3 and 5% at a radiation dose of 50 kGy.[18]

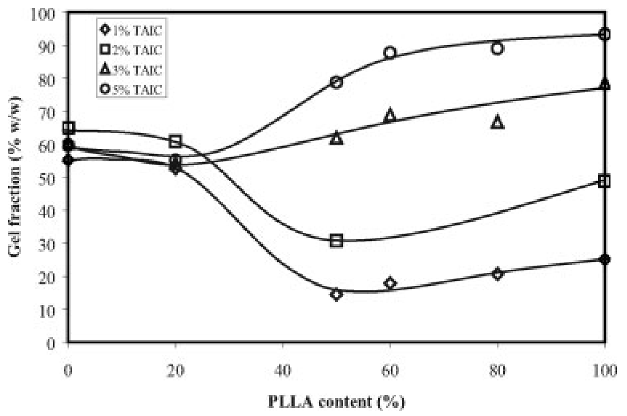


Figure 1 Variation of the gel fraction of different blends irradiated at 50 kGy with different TAIC levels.

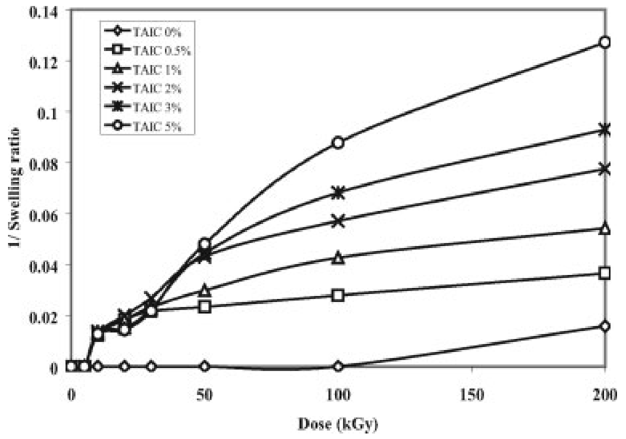


Figure 2 Effect of the dose and TAIC level on the degree of crosslink formation in PBTA.

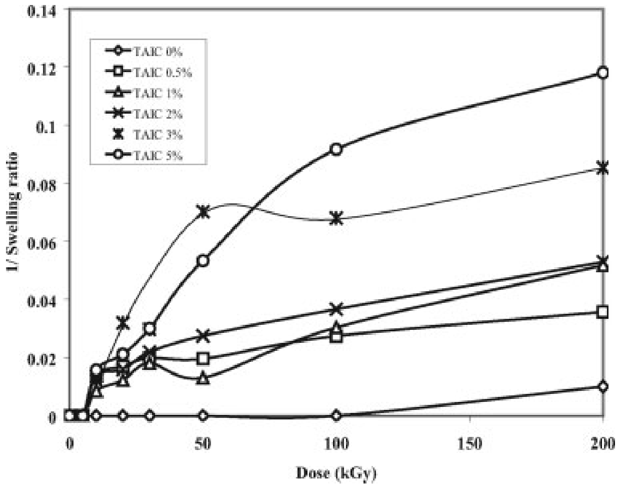


Figure 3 Effect of the dose and TAIC level on the degree of crosslink formation in 50/50 PBTA/PLLA.

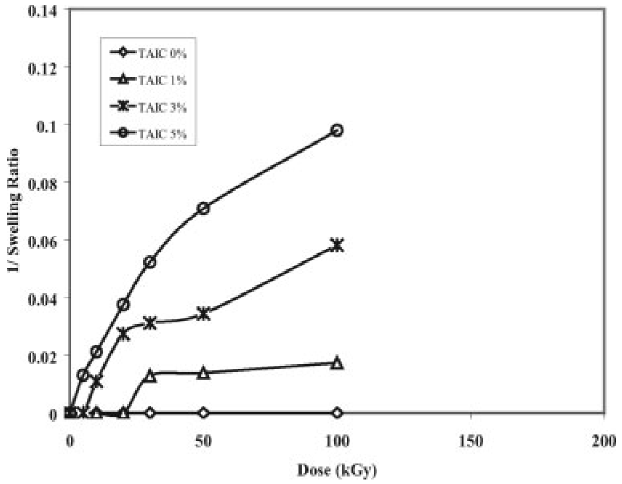
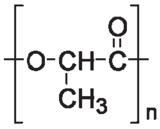


Figure 5 Effect of the dose and TAIC level on the degree of crosslink formation in 20/80 PBTA/PLLA.

Crosslink formation was also studied by the analysis of the swelling ratio. Figures 2–6 confirm that the degree of crosslinking rapidly increased when the dose level was increased up to 100 kGy, beyond which no further significant increase was observed. Samples were not irradiated at 200 kGy for the 40/60 and 20/80 PBTA/PLLA blends, and therefore, points at 200 kGy are not shown in Figures 4 and 5. There was a very clear difference in the degree of crosslinking between PBTA and PLLA, where the degree of crosslinking of PLLA was influenced by the TAIC level beyond doses of 20 kGy and that of PBTA was influenced by the TAIC level beyond doses of 30 kGy. It was also clear that when the PLLA component was increased in the blend, the degree of crosslinking improved significantly at comparatively lower doses. It was evident from these data that crosslink formation in PLLA was easier than in PBTA. This was attributed to the fact that free radicals generated during radiation had easy access to PLLA molecules, whereas crosslink formation was rather difficult in PBTA because of the obstruction caused by bulky aromatic rings along the PBTA molecule. The molecular structures of PLLA and PBTA[14,19] are as follows:



$$\left[-\mathrm{O}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]_n$$

Poly(lactic acid)

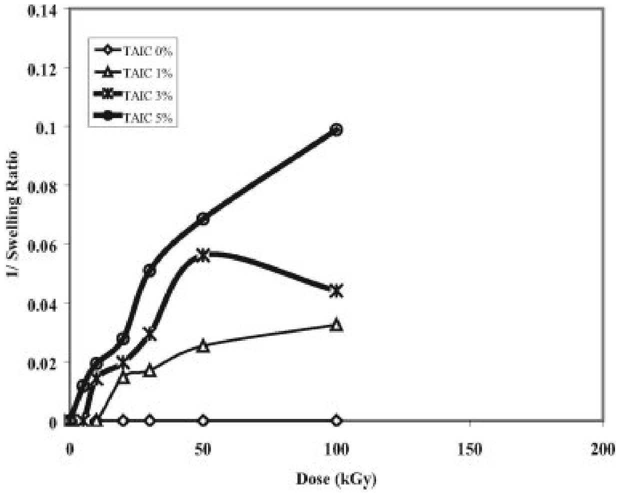


Figure 4 Effect of the dose and TAIC level on the degree of crosslink formation in 40/60 PBTA/PLLA.

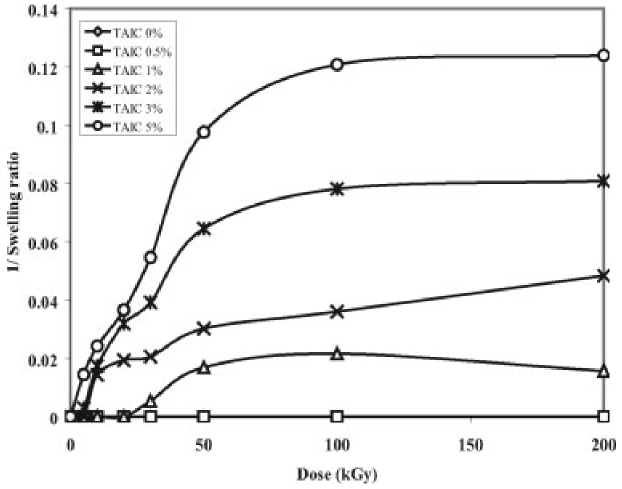


Figure 6 Effect of the dose and TAIC level on the degree of crosslink formation in PLLA.

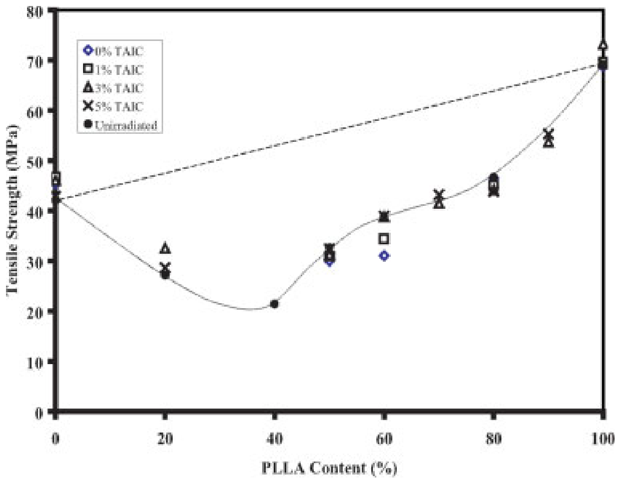
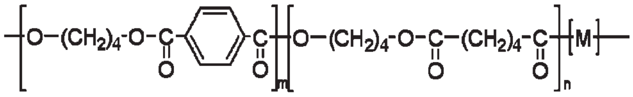


Figure 7 Effect of the PLLA content and TAIC level on T_s of the PBTA/PLLA blends irradiated at 50 kGy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Ecoflex (PBTA)

Mechanical properties

PLLA has superior strength properties at room temperature but lacks flexibility. On the other hand, PBTA is a flexible polymer that shows moderate strength at room temperature (see Fig. 7). The tensile strength (T_s) and elongation at break (E_b) were tested at room temperature (27°C) for both PLLA and PBTA and also for their blends (80/20, 60/40, 40/60, and 20/80 PBTA/PLLA). As shown in Figure 7, T_s dropped gradually with the incorporation of PLLA in the blend, and a minimum value of about 20 MPa was shown when the blend contained 40% PLLA; further increasing the proportion of PLLA in the blend increased T_s again. This blend system showed an antagonistic effect as far as T_s was concerned, which was attributed to the incompatibility of the constituent polymers in the blend system. The compatibility of two polymers can be predicted by their solubility parameters (δ_s's), and a δ_s difference of more than 3 $(\mathrm{cal/cm^3})^{1/2}$ between two polymers indicates incompatibility of the polymers in the system.[2] The δ_s of PLLA was reported as 10.1 $(\mathrm{cal/cm^3})^{1/2}$,[2] and that of PBTA, calculated according to the group contribution method,[20] was 22.95 $(\mathrm{cal/cm^3})^{1/2}$. The difference in δ_s between PBTA and PLLA indicated the incompatibility of the system. The images of the smoothed and cryofractured surfaces of the unirradiated blends shown in Figure 8(a,b) also confirm the incompatibility of the two polymers. The surfaces were examined with a Hitachi SEMEDX type N scanning electron microscope (Hitachi High Technologies Co., Inc., Tokyo, Japan).

Also shown in Figure 7 are the T_s values of blends containing PLLA at 50, 60, and 80% irradiated at 50 kGy with various TAIC levels of 0, 1, 3, and 5%. T_s values of the blends containing PLLA at 20, 70, and 90% irradiated at 50 kGy with various TAIC levels of 3 and 5% are also shown in Figure 7. It was clear that a significant variation in T_s of the samples irradiated at different levels of TAIC was not observed. The blends irradiated at various dose levels with different levels of TAIC too did not show a significant variation in T_s. Figure 9 shows the variation in T_s of blends irradiated at different dose levels with 3% TAIC. T_s of the samples containing more than 50% of PLLA irradiated above 100 kGy could not be tested because it was not possible to cut the test pieces because of the extreme brittle nature of these

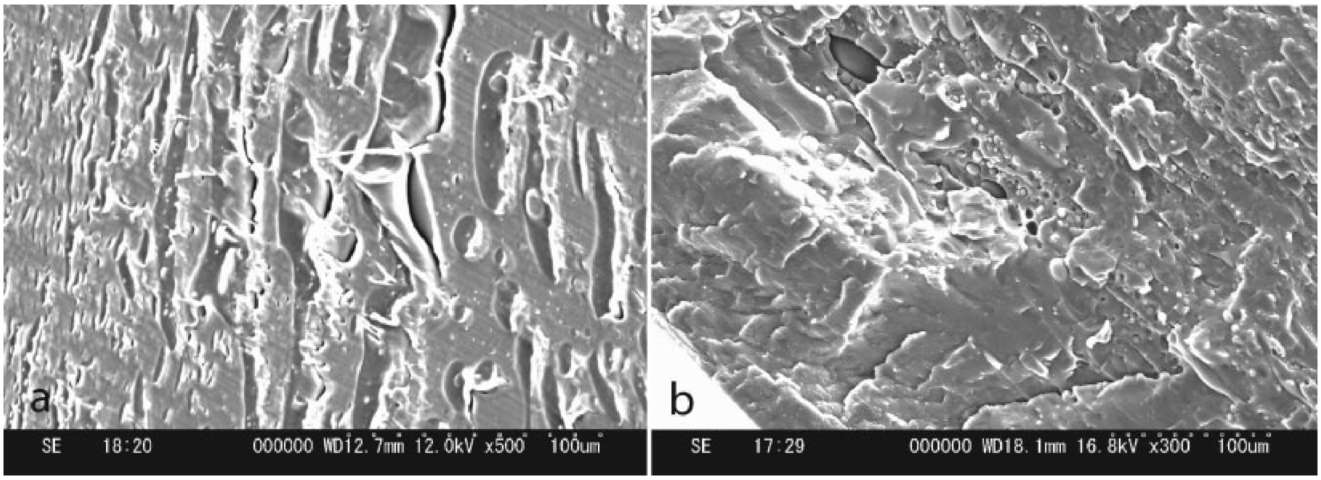


Figure 8 Scanning electron micrographs of the unirradiated 50/50 PBTA/PLLA blends with 0% TAIC: (a) surface smoothed (500× magnification) and (b) cryofractured surface (300× magnification).

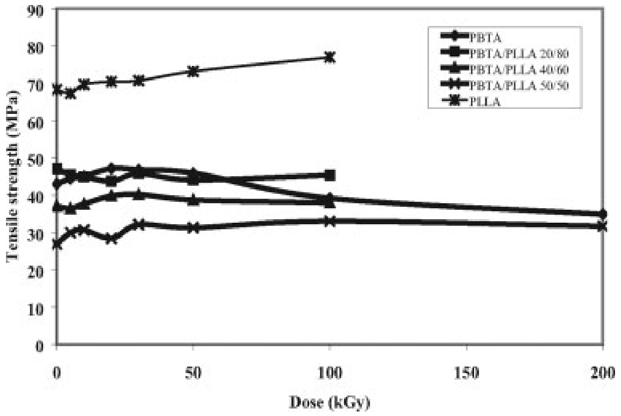


Figure 9 Effect of the dose level on T_s of the PBTA/PLLA blends irradiated with 3% TAIC.

samples. According to Figure 9, the increase in crosslink density (Figs. 2–6) with increasing dose seemed to have no significant effect on T_s, which was attributed to chain scission during irradiation, which might have offset the effect of crosslinking. However, it is rather difficult to explain why the T_s did not drop when the blends were irradiated without TAIC because we expected that chain scission would occur in the PLLA component. A plausible explanation for this observation is that the crystallinity of PLLA may have been affected by irradiation. It was shown by DSC analysis in an earlier study that main-chain scission occurs both in the amorphous and crystalline phases during irradiation,[1] and the shorter chain molecules formed had the ability to align themselves easily, which in turn, would favor crystallization. The individual lamellae thus formed became thinner and were in a state of stretched-form shortened chain crystals,[21] which accounted for the interconnectivity of the network, which led to high T_s values.[22] Also, the increased crystalline domains could have acted as stress concentrators, which would have increased the yield stress and resulted in a brittle material[23] and, hence, a higher T_s. The argument for the formation of shortened chain crystals during irradiation was further supported by the observation of the extreme brittle nature of the samples containing more than 50% PLLA irradiated above 100 kGy.

In contrast to T_s, E_b was dramatically improved by the incorporation of PBTA in the blend, as shown in Figure 10, where PBTA showed the highest E_b. An interesting adverse effect on E_b of the blends was observed when the blends containing PLLA were irradiated in the absence of TAIC. We postulated that during irradiation, severe molecular degradation of PLLA occurred because of chain scission, whereas PBTA possibly resisted the degradation, and therefore, E_b of PBTA was unaffected (Fig. 10). Irradiation in the presence of TAIC dramatically improved E_b of the blends by the formation of crosslinks. The formation of a polymer network structure, either chemical or physical, is essential for improved elongation.[24] However, analysis of results of E_b of the samples irradiated at 50 kGy and tested at room temperature (27°C) showed that although there was an improvement of E_b by irradiation when TAIC was incorporated in the previous blends, it was still slightly inferior to that in the unirradiated blends with no incorporated TAIC (see Fig. 10). This observation confirmed that the molecular degradation of PLLA took place during irradiation and that the physical polymer network structure broke as a result. Nonetheless, crosslinks formed between the molecular chains in the presence of TAIC due to irradiation formed a chemical network structure, which may have restricted the molecular segmental mobility on stretching and, therefore, may have reduced E_b compared to that with a physical network structure. This was further made obvious from the fact that increasing the TAIC level too increased the crosslink density in the irradiated blends and, hence, reduced E_b further because of the formation of more chemical crosslinks. The irradiation of PBTA without TAIC did not change its E_b, which confirmed that it was more resistant to degradation on irradiation. With the formation of crosslinks in PBTA by irradiation in the presence of 3–5% TAIC, the molecular segmental mobility was restricted to a small extent, and hence, E_b was reduced by about 100%. It is clear that the molecular segmental mobility was reduced more by an increased number of crosslinks with a higher level of TAIC (3 and 5%) than by a lesser number of crosslinks formed with lower levels of TAIC, that is,

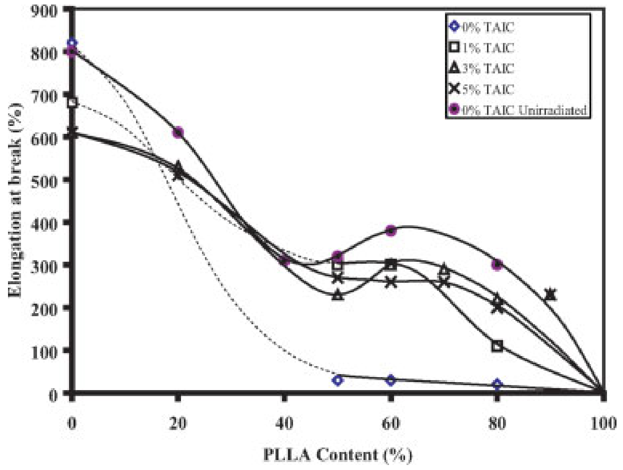


Figure 10 Effect of the TAIC level and blend ratio on E_b in the PBTA/PLLA blends irradiated at 50 kGy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

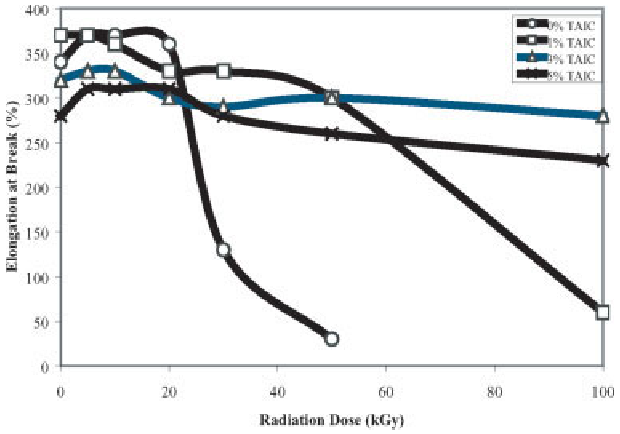


Figure 11 Effect of the concentration of TAIC and radiation dose on E_b of 40/60 PBTA/PLLA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1% (see also Fig. 2). PLLA showed its brittle nature, as evident from it having no elongation at all.

As shown in Figure 10, differences were also observed in E_b for different polymer blends irradiated at 50 kGy with TAIC. It was highest for PBTA levels between 600 and 800%. It was lowered to around 300% in the blend with equal proportions of the two polymers, whereas it was negligible in PLLA. The 40/60 PBTA/PLLA blend showed an E_b between 250 and 400%, whereas E_b was between 200 and 300% in 20/80 PBTA/PLLA at all doses, except in the blends with TAIC at 1%, where a drop was observed beyond doses of 30 kGy, as shown in Figures 11 and 12. From these observations, it is obvious that the incorporation of 20–40% PBTA into PLLA improved E_b of the resulting blend to 300–350%, which was a substantial improvement when compared to an E_b of 200% achieved by the incorporation of a plasticizer in a previous study.[16]

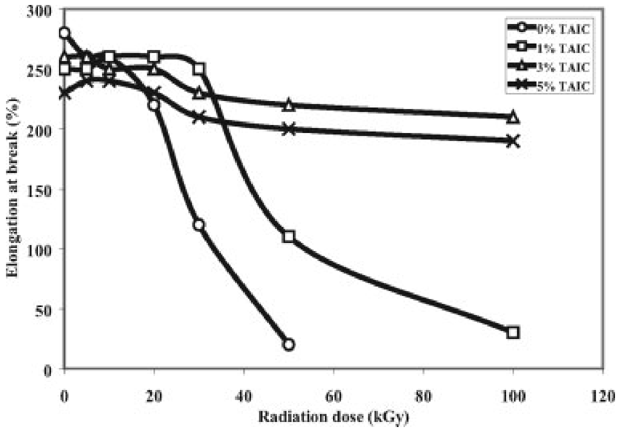


Figure 12 Effect of the concentration of TAIC and radiation dose on E_b of 20/80 PBTA/PLLA.

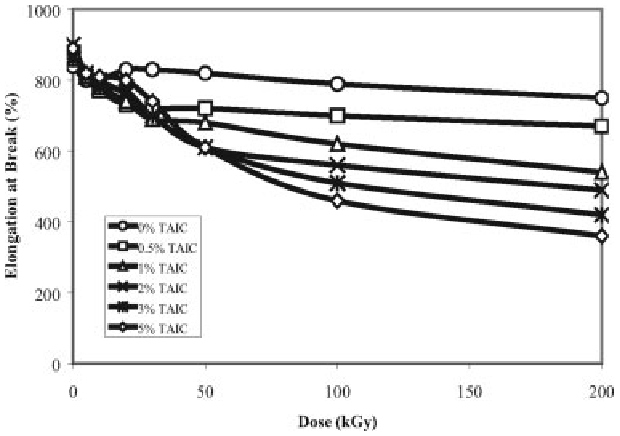


Figure 13 Effect of the concentration of TAIC and radiation dose on E_b of PBTA.

Analysis of results from individual blends indicated that irradiation in the absence of TAIC had the smallest effect on E_b of PBTA (Fig. 13), whereas the blends containing PLLA showed a rapid decline in E_b with increasing radiation dose in the absence of TAIC (Figs. 11 and 12). This was attributed to the rapid chain scission of PLLA molecules during irradiation, as shown in a previous molecular weight study,[1] compared with very minimal chain scission in the PBTA molecules. Because of the possible rapid chain scission in PLLA by irradiation, the polymer network, which is essential for elasticity,[24] would also have been disturbed. On the other hand, because of the very slow chain scission, the disturbance of the physical polymer network in PBTA was very minimal, which thereby prevented the fall of E_b.

As far as T_s and E_b are concerned, the best compromise of the properties was seen when the ratio of PBTA/PLLA in the blend was between 40/60 and 20/80.

CONCLUSIONS

The results of this study indicate that E_b of PLLA was improved when it was blended with PBTA, although at the expense of its strength to a small extent. Hence, the brittle PLLA could be used to produce a tough material by the incorporation of PBTA while still retaining its strength to a considerable extent. The results also indicate that the best compromise of mechanical properties was obtained when 20 to 50% of PBTA was blended with PLLA. A level of 3 parts of TAIC in the blend was sufficient to achieve an optimum level of gel fraction after crosslinking by EB radiation. Nevertheless, crosslinking by irradiation in the presence of PFMs showed no significant improvement in the mechanical properties at room temperature, although it reduced the solubility of the polymer/polymer blend in chloroform and, hence, improved the resistance to solvents.

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