

Preparation of Melting-Free Poly(lactic acid) by Amorphous and Crystal Crosslinking under UV Irradiation

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ABSTRACT: The poly(lactic acid) (PLA) with 3.6% mol of benzophenone (BP) per repeat unit of PLA can be crosslinked to a gel fraction of 98.5% at UV energy of 160 J/cm². From NMR analysis, the photocrosslinking of PLA was attributed to the recombination of primary and tertiary carbon radicals in the repeating units which were generated by the hydrogen abstraction of BP. With increasing crosslinking, melting peak disappeared and glass transition temperature elevated with loss of crystallinity, indicating that the crosslinking occurred in the crystalline region as well as in the amorphous region. The thermal stability of the crosslinked PLA also improved as shown by higher onset temperature as much as 56°C and higher maximum decomposition temperature compared with the pristine PLA. The higher toughness of the crosslinked PLA film was obtained together with the improvement in tensile strength and modulus with increasing crosslinking density. In addition to photocrosslinking of amorphous region, the crosslinking of crystalline region can have significant influence in the improvement of thermal and mechanical properties. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Several polymers have been intensively studied as environmentally friendly materials since they are biodegradable, biocompatible, and nontoxic. Biodegradable polymers such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(ϵ -caprolactone) (PCL), poly(dioxane) (PDO), poly(trimethylene carbonate) (PTC) have been applied for food packaging and various biomedical materials including absorbable sutures, skin grafts, implants, controlled drug delivery system.^{1,2} Thermoplastic PLA is an enantiomeric aliphatic polyester consisting of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), which can be obtained by the ring-opening polymerization of corresponding lactides which can be produced from renewable resources such as corn or sugar cane.

Although PLLA has a relatively high melting temperature (T_m) as high as ca. 180°C in comparison with other biodegradable polyesters, it is not high enough for some high temperature applications such as hot beverage containers. In addition, PLLA is a semicrystalline polymer that usually crystallizes at a very low rate, which produces amorphous products whose modulus drops rapidly above the glass-transition temperature (T_g) of ca. 50 to 65°C. Therefore, an improvement of the thermal stability of PLLA is indispensable for widening its commercial exploitation.

Several techniques have been developed to improve the thermal stability and mechanical properties of PLA-based materials such as PLA blends with other polymers and nanocomposites.^{3,4} One of the fundamental techniques used to enhance melting temperature of PLA is the introduction of stereocomplex crystals which can be formed in a blend of PLLA and PDLA.⁵

Chemical and irradiation treatments have been used to introduce crosslinking between macromolecular chains including thermal treatment, gamma or electron-beam irradiation, and UV irradiation. A thermal treatment method have used triallyl isocyanurate (TAIC) and dicumyl peroxide as a crosslinker and an initiator, respectively.⁶ In order to improve the flexibility and strength of PLA, a small amount of methacryloyloxyethyl isocyanate was reacted with PLA to obtain a ductile PLA with markedly improved mechanical properties.⁷

The γ -irradiation or electron beam has been often utilized to sterilize biomedical devices for medical and veterinary applications. However, high energy radiation can damage medical devices made from fragile polymers even at a minimum sterilization dose of 25 kGy. Radiation sterilization especially damages biodegradable polymers such as PLLA and PGA which can be decomposed under the radiation. The crosslinked PLLA by γ -irradiation has been reported to produce a gel fraction of 88% or less

when PLLA plate was mixed with 3% of TAIC and irradiated at 50 kGy.^{8–11} In the crosslinking of PLLA under electron beam irradiation, blends of PLLA and poly(butylene terephthalate-*co*-adipate) were also crosslinked by electron beam irradiation in the presence of TAIC.¹² The presence of 3% TAIC was also found to be the most effective in producing a crosslinked PLLA of a gel fraction of 83%.¹³ The absorption of TAIC to stereo blends of PLLA and PDLA can be controlled by supercritical carbon dioxide treatment with 30 kGy radiation dose. Although tensile strength and Young's modulus of PLA blends were reduced by the CO₂ treatment, the crosslinked samples by the radiation crosslinking became harder and tougher.¹³

The ionizing radiations are known to lead either to the structuration of polymers or to their degradation.^{14,15} Photooxidation, one of the two major mechanisms involved in the photodegradation of polymers, mainly involves the oxidation initiation by photolysis of hydroperoxides, propagation by chain reactions, and termination through bimolecular reactions of alkyl peroxy radicals. Nearly all commercial thermoplastic polymers are sensitive to photo-oxidation, eventually resulting in loss in their physical properties.^{16,17} Because PLA has recently gained much attention, more durable PLA is required especially with regard to thermal and light resistance. The atomic linkage of PLA consists of C-C, C-H, C-O, and C=O bonds. Because the excited state of the C=O group exhibits an antibonding and biradical property by $n-\pi^*$ transition, the photoexcitation of C=O tends to cause photochemical reactions, such as α and β cleavages, atom abstraction, radical addition, and electron abstraction or electron transfer.^{18,19} Ikada²⁰ and Tsuji²¹ suggested that the main chain scission of both PLA randomly occurred by UV irradiation not via Norrish Type I reaction but via Norrish Type II. Janorkar et al.²² proposed two mechanisms of PLA degradation under UV irradiation: one involves photolysis of the backbone at C=O leading to dehydrogenation and the other involves the photo-oxidation of PLA leading to formation of hydroperoxide derivatives that subsequently degraded to compounds containing a carboxylic acid and unstable diketones. PLA originally has low wettability and poor compatibility to cells due to its hydrophobicity. Therefore some attempts have been made to solve this problem by ionized beam irradiation²³ and UV/ozone irradiation.²⁴ UV-induced crosslinking of polymers has become increasingly popular due to continuous and environmentally friendly process, energy and space saving as well as cost-effectiveness. UV-induced crosslinking under argon or vacuum of solid PEO containing benzophenone (BP) obtained a gel fraction of 92% and maximum water swelling of 2500%,^{25,26} which was prepared by solution casting or press-molding.²⁷ New photolytic products of BP and detailed photo-reduction mechanism in the photocrosslinking of polyethylene (PE) have been reported.²⁸ And the effect of more miscible BP derivatives containing long alkyl chains with PE resin was investigated in the photocrosslinking.²⁹ The poly(vinyl alcohol) films under UV irradiation was crosslinked in the presence of sodium benzoate.³⁰ Dense films of poly[(4-ethylphenoxy)(phenoxy)phosphazene] containing two kinds of BP derivatives where ethylphenoxy side chains were used for photocrosslinking³¹; 1,4-phenylene-*bis*-acrylic acid was incorporated into polyesters such

as poly(ethylene terephthalate) and poly(butylene terephthalate), which was crosslinked by a cycloaddition pathway rather than by the radical processes.^{32,33}

The purpose of this study is to improve the thermal stability and mechanical properties of a commercial PLA by the photocrosslinking of crystalline region as well as amorphous region. Until now, the preparation of melting-free PLA by crystal crosslinking has not been investigated. The most probable crosslinking mechanism of the crystal crosslinking of PLA is also suggested.

EXPERIMENTAL

Materials

A commercially available PLA (below 1% D type enantiomer, M_v 276,500) was supplied from Nature Works LLC. Benzophenone (BP) was purchased from Aldrich Chemicals.

Preparation of PLA Films and UV Irradiation

PLA powders containing different concentrations of BP were hot-pressed at 190°C for 2 min under a pressure of 10 MPa. The mold was allowed to quench under pressure in ice water. The thickness of the films was measured to ca. 200 μm . A continuous UV irradiation was applied at a conveyor speed of 2 m/min, 2.5 J/cm² per pass, on both sides of films with a UV irradiator containing UV bulb of a power of 80 W/cm. A Fe-doped lamp was chosen to maximize photocrosslinking effect of the longer wavelength region. UV energy was adjusted to find optimal irradiating condition for the samples at room temperature.

¹H NMR and Solid State ¹³C NMR Analyses

The unirradiated and crosslinked PLA samples were dissolved in chloroform at room temperature and the insoluble gel fraction was removed. The filtered polymer solutions were dried under vacuum and subsequently dissolved in CDCl₃. ¹H NMR spectra of a 0.1% solution of the untreated PLA and the soluble fraction of the crosslinked PLA were acquired by a 400 MHz NMR spectrometer (Avance Digital 400, Bruker). The quantitative analysis was fulfilled to find out the photocrosslinking mechanism. The solid-state ¹³C NMR spectra of the pristine and crosslinked PLA films were also obtained to identify the photocrosslinking mechanism using a 600 MHz solid-state NMR spectrometer (Unity NOVA600, Varian).

Gel Fraction and Degree of Swelling

The irradiated PLA was immersed in acetone to extract unreacted photoinitiators. The extracted PLA samples were weighed and then again dissolved in chloroform at room temperature for 24 h. The remaining undissolved gel was dried under vacuum at 40°C for 12 h and weighed to calculate the gel fraction. Gel fraction (%GF) was calculated using the following equation:

$$\%GF = \left(\frac{W_g}{W_0} \right) \times 100 \quad (1)$$

where W_0 and W_g are the vacuum-dried weights of the PLA films and the gels after dissolution in chloroform, respectively.

The obtained gel was immersed in chloroform for 48 h, and the swelling degree (the weight ratio of the absorbed solvent to the dried gel) was calculated with the following equation:

$$\%DS = \frac{W_S - W_g}{W_g} \times 100 \quad (2)$$

where W_g is the weight of the dried gel; W_S is the weight of the solvent-swollen gel of the same crosslinked sample at room temperature.

XRD Analysis

The crystal structures of the photocrosslinked PLA films were investigated by X-ray diffraction method. X-ray diffraction patterns were recorded in the reflection mode with a Rigaku X-ray diffractometer with Ni-filtered Cu-K α radiation (40 kV and 150 mA) at a scanning rate of 2°/min. The X-ray diffraction could be analyzed by the spacing between the planes in the atomic lattice (d) using Bragg's equation:

$$d = \frac{\lambda}{2 \sin \theta} \quad (3)$$

where λ is the X-ray wavelength ($\lambda = 1.54 \text{ \AA}$) and θ is the angle between the incident ray and the scattering planes. The degree of crystallinity of the films was estimated using the area under amorphous and crystalline peaks with the following relationship.

$$X_C = \frac{A_c}{A_c + A_a} \times 100 \quad (4)$$

where A_c and A_a are the areas of the crystalline and amorphous peaks, respectively.

Thermal Properties

Thermal properties of PLA samples were measured at the second heating cycle with a Perkin-Elmer Diamond DSC under nitrogen atmosphere. The melting point (T_m), glass transition temperature (T_g), and enthalpy of melting (ΔH_m) of each sample were searched over -10°C to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$. The DSC crystallinity was determined as the ratio of the experimental melting enthalpy to the melting enthalpy of a 100% crystalline polymer (135 J/g).¹⁶ The thermal stability of the samples was also investigated with a thermalgravimetric analyzer (TA-Q500) under nitrogen until 550°C at a heating rate of $20^\circ\text{C}/\text{min}$.

Mechanical Properties

The tensile properties of the samples were measured at room temperature using a tensile tester (Instron 4467) with a cross-head speed of 0.5 mm/min. Dynamic mechanical properties were investigated using a dynamic mechanical analyzer (DMA-Q800). Samples in the form of strips (7 mm \times 3 mm \times 0.2 mm) were measured in tensile mode at a constant frequency of 1.0 Hz as a function of temperature from 0° to 165°C at a heating rate of 2°C per minute under nitrogen atmosphere. The storage modulus is assumed to be proportional to the crosslinking density of crosslinked polymers. The molecular weight between crosslinks (M_C , g/mol) can be derived from the storage modulus measurement of the irradiated films.²⁴

$$M_C = \frac{3\rho RT}{E} \quad (5)$$

where ρ is the density of PLA ($\rho = 1.248 \text{ g/cm}^3$), R is the gas constant ($8.32 \text{ cm}^3 \text{ MPa/Kmol}$), and T is the temperature fixed

Table I. The Gel Fraction and Degree of Swelling Depending on Crosslinking Condition

Condition			
BP content (% mol/repeat unit)	UV energy (J/cm ²)	% GF	% DS
0	0	0	0
	160	0	0
2.0	0	0	0
	40	38.4 \pm 0.3	2,078 \pm 25
	80	69.4 \pm 0.4	1,660 \pm 20
	100	74.3 \pm 0.3	1,421 \pm 15
	200	91.3 \pm 0.5	991 \pm 12
1.2	160	91.6 \pm 0.4	972 \pm 15
2.0		93.0 \pm 0.5	903 \pm 13
2.8		95.4 \pm 0.7	877 \pm 11
3.6		98.5 \pm 0.8	770 \pm 10

at 434 K to evaluate M_C from the rubbery modulus values of the crosslinked polymers. Crosslinking density of the crosslinked gels and films is calculated by the following equation.²⁵

$$d_x = \frac{1}{vM_C} \quad (6)$$

here, v is the specific volume of PLA polymer.

RESULTS AND DISCUSSION

Photocrosslinking of PLA

The gel fraction of the crosslinked PLA samples containing various BP concentrations depending on the UV energy are shown in Table I. No gel fraction was found for the UV-irradiated PLA films without benzophenone (BP) even at a UV energy of up to 160 J/cm^2 . The gel fraction of the crosslinked PLA increased with increasing UV energy and the highest gel fraction of 98.5% was obtained at 160 J/cm^2 for the sample containing 3.6% mol BP per repeating unit. The structure of the crosslinking network was influenced by the characteristics of the constituents and the crosslinking density, which was related to the distance between crosslinking points. The higher the UV energy applied, the larger the number of radicals that can be produced. However, the sample irradiated with 200 J/cm^2 produced lower gel fraction than that with 160 J/cm^2 , where the higher UV energy was not desirable for the higher crosslinking because of concomitant chain degradation of the UV irradiated samples.²⁴ The degree of swelling (DS) of the crosslinked PLA in chloroform reduced with the increase in gel fraction, which implied that the crosslinking hindered the molecular expansion during swelling. The crosslinked PLA of larger crosslinking density can be obtained with a higher BP concentration. The gel fraction increases proportionally with increasing BP concentration, indicating that the higher gel fraction may be resulted from the larger numbers of polymeric radicals generated by the added BP. The dose of 1.2% mol BP per repeating unit may be enough to introduce a

Table II. M_C and d_x of the Crosslinked PLA Films

% GF	Dynamic mechanical analysis			
	T_g (°C)	\dot{E} (MPa)	M_C (g/mol)	d_x (10^{-4} mol/cm ³)
0	67.9 ± 0.1	–	–	–
69.4	68.3 ± 0.1	2.83 ± 0.01	4.867 ± 17	2.56 ± 0.05
93.0	70.3 ± 0.1	4.09 ± 0.02	3.359 ± 16	3.72 ± 0.03
98.5	70.5 ± 0.1	7.08 ± 0.03	1.942 ± 8	6.43 ± 0.01

gel fraction of 91.6% in the PLA samples. The molecular weight between crosslinks (M_C) and crosslinking density (d_x) of the crosslinked PLA samples depended on the gel fraction as shown in Table II. With increasing the gel fraction, the M_C was decreased and d_x increased accordingly.

The ¹H NMR analysis was carried out to elucidate the photocrosslinking mechanism as shown in Figure 1. The pristine PLA showed well-defined spectrum where methine (a) and methyl (b) protons appeared in quartet and doublet peaks at 5.15 and 1.57 ppm, respectively. The soluble fraction of the UV-irradiated PLA samples with a gel fraction of 38.4% showed a new sharp peak of methylene (c) at 2.15 ppm, while a sample with higher

gel fraction of 93.0% showed dominant methylene protons at the same chemical potential over the methyl and methine protons. The peak area calculation of the ¹H NMR spectra of the soluble fraction of the two crosslinked samples indicated degrees of crosslinking of 12.1% and 53.5%, respectively.

The solid-state ¹³C NMR analysis was carried out to identify crosslinked carbon structure as shown in Figure 2. The pristine PLA showed well-defined spectrum where peaks of methyl (a), methine (b) and carbonyl (c) carbons appeared at 16.6, 69.0, and 169.6 ppm, respectively. The crosslinked PLA (93.0% GF) showed new peaks of methyl (d), methylene (f), methine (g), and quaternary (e) carbons appeared at 20.6, 30.9, 74.2, and 72.1 ppm, respectively, indicating the methylene crosslinking. As shown in Figure 3, UV irradiation may generate tertiary (A) and primary (B) radicals from PLA main chains by the hydrogen abstraction of the excited triplet benzophenone under UV irradiation. When the radicals may recombine to form covalent crosslinks between chains, the (A + A) type reaction can be difficult to occur due to the steric hinderance. Also in the (B + B) type reaction, the decrease in the peak area of the methine proton could not be explained. The (A + A) and (B + B) type crosslinking seemed not to occur and only (A + B) type linkage was attributed to the observed crosslinking of PLA. Therefore the PLA photocrosslinking may take place by the recombination of primary and tertiary carbon radicals by (A + B) type crosslinking. The UV irradiation itself can encourage the photocrosslinking of PLA main chain (α -cleavage) which can generate recombinable polymer radicals. However, no crosslinking of the PLA without BP implied that the UV irradiation alone may produce polymer radicals by photocrosslinking of the ester bonds, which may not be efficient enough to induce crosslinking. The photoinitiator addition may be indispensable for the present photocrosslinking system.

The XRD patterns of different untreated and crosslinked PLA samples irradiated at 160 J/cm² are shown in Figure 4 and Table III. The pristine PLA sample (a) shows the peaks of homocrystallites around 19.6°. The 2θ of the crosslinked samples reduced and shifted to 16.6°, where crystallinity was disappeared above a gel fraction of 95.4%. This tendency has also been reported in the radiation crosslinking of PLLA/PDLA stereocomplex under electron beam.²² In addition the interplanar spacing of the atomic lattice remarkably increased with increasing the gel fraction. It clearly indicates a structural transition from packed structure to disordered state with the increase in crosslinking. To verify the crystal crosslinking, the PLA was annealed in absence or presence of photoinitiators at 90°C for

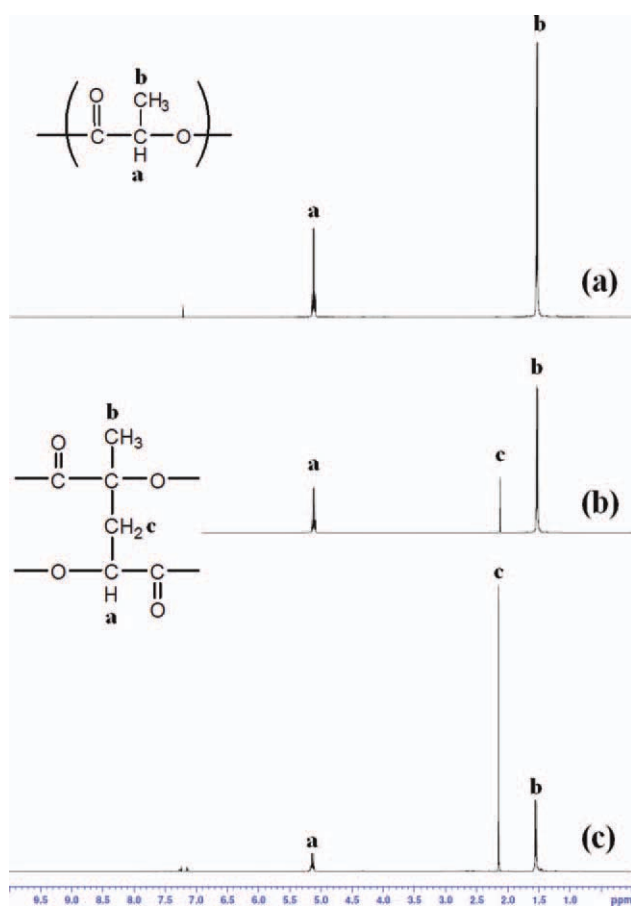


Figure 1. The ¹H NMR spectra of (a) pristine and crosslinked PLAs with a gel fraction of (b) 38.4% and (c) 93.0%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

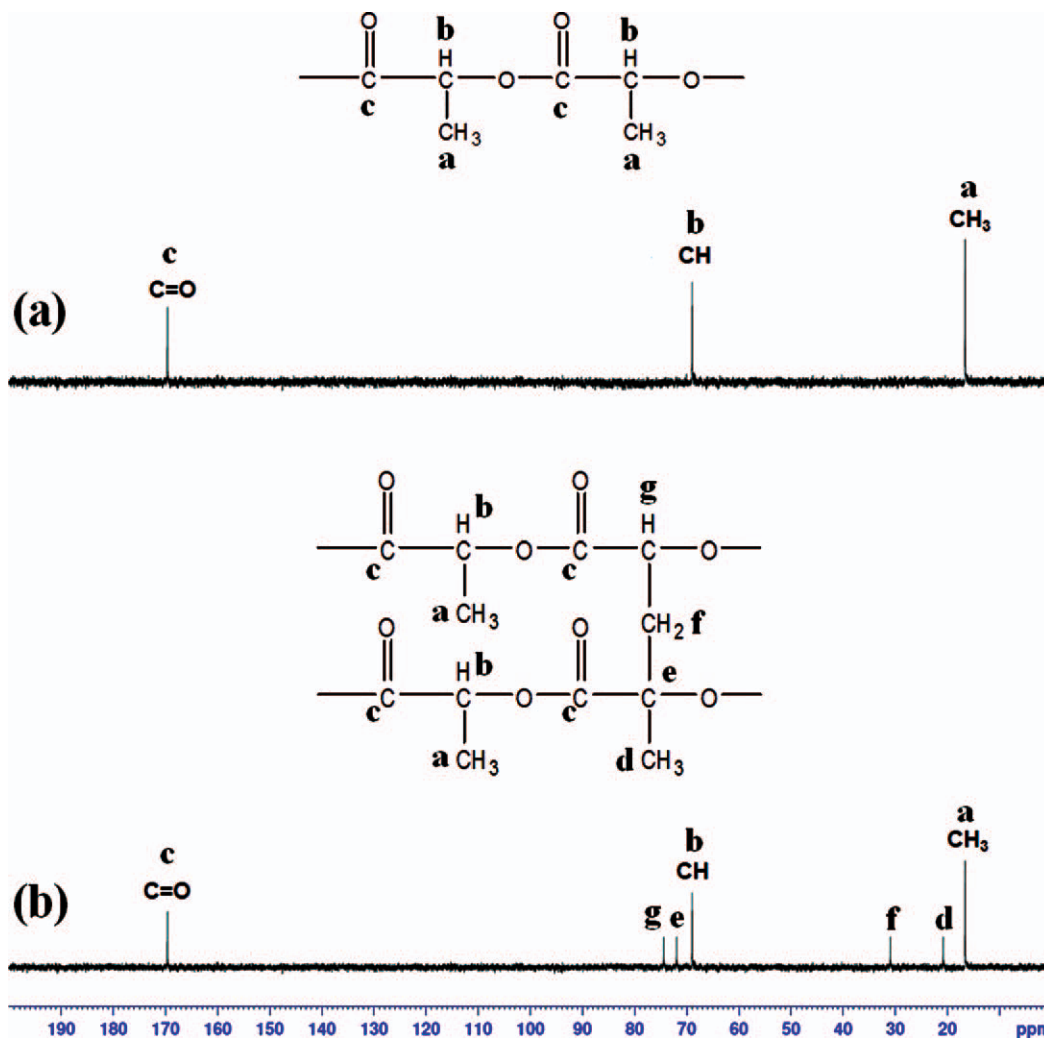


Figure 2. The solid state ^{13}C NMR spectra of (a) pristine and (b) crosslinked PLA film with a gel fraction of 93.0%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

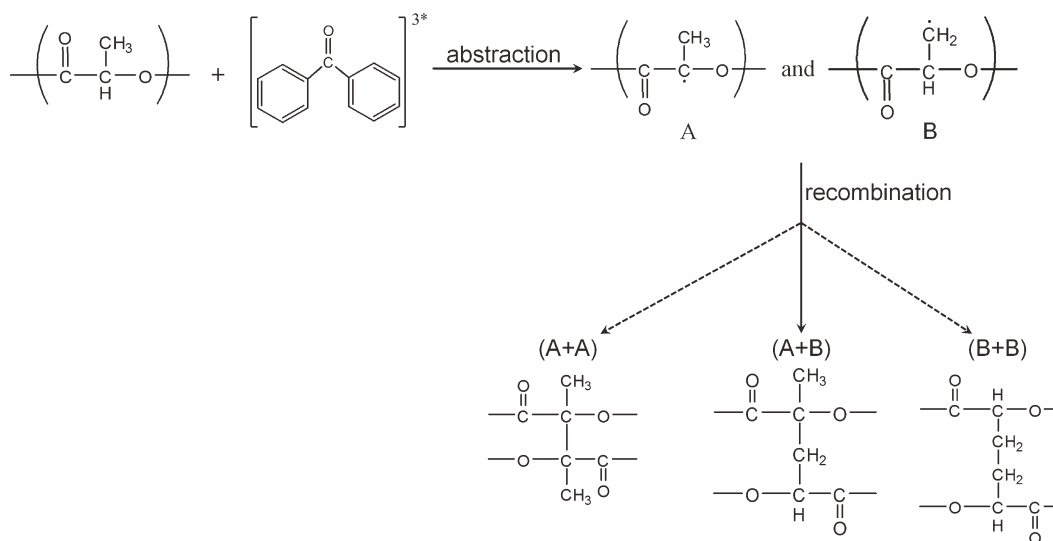


Figure 3. The proposed photocrosslinking mechanism of PLA.

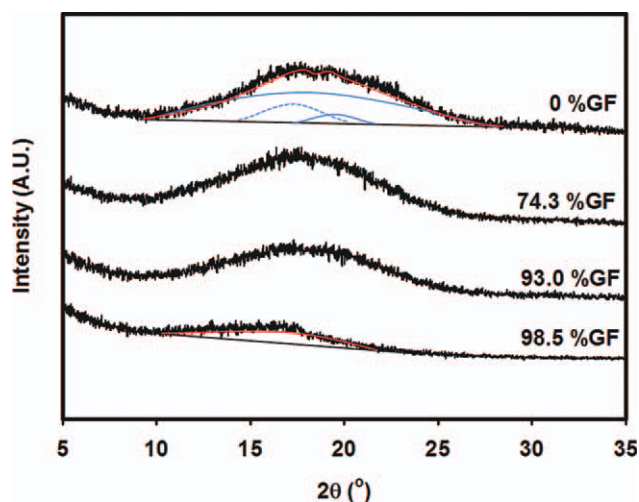


Figure 4. XRD curves of crosslinked PLA depending on the gel fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

60 min before UV irradiation. The crystal crosslinking effect has also been shown for the recrystallized PLA (Table III). Without BP, no crosslinking was observed again. The XRD crystallinity of the annealed PLA was 73.4% initially and the crystallinity decreased to 36.2% by 37.2% with increasing the gel fraction from null to 83.1%. Therefore the photocrosslinked samples showed that the crosslinking has been produced not only in amorphous region but also in the crystalline region merging into the crosslinking network. The photoinitiator may be penetrated into the crystalline region by the sublimation when formed to film. Unsurprisingly, the loss of crystallinity had sig-

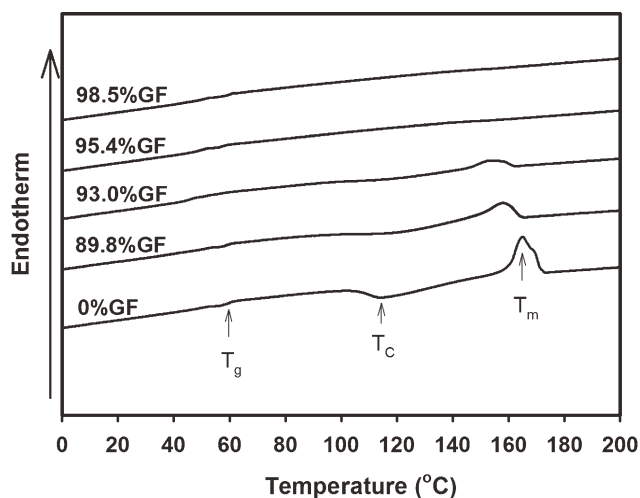


Figure 5. DSC heating curves of crosslinked PLA depending on the gel fraction.

nificant influence on the thermal properties such as melting temperature and heat of fusion.

Thermal Properties

DSC parameters of the crosslinked PLA were given in Table IV and Figure 5. Three peaks of pristine PLA (0% GF) corresponded to the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of PLA. While the T_g slightly increased because of the introduction of crosslinking structure in PLA samples. Both T_c and T_m of the crosslinked PLA samples shifted to higher temperatures and finally disappeared with increasing gel fraction, which may be caused

Table III. XRD Data of the Crosslinked PLA Films

Condition					
BP content (% mol/repeat unit)	UV energy (J/cm ²)	% GF	2θ (°)	d (Å)	Crystallinity (%)
0	0	-	19.6 (16.9)	4.5 (5.2)	32.2 (73.4)
2.0	100	74.3 (57.3)	17.2 (16.8)	5.1 (5.3)	8.8 (56.5)
2.0	160	93.0 (77.2)	17.0 (16.6)	5.2 (5.3)	6.5 (43.8)
3.6	160	98.5 (83.1)	16.6 (16.4)	5.4 (5.4)	- (36.2)

Parenthesis indicates the properties of the annealed at 90°C for 60 min PLA before UV irradiation.

Table IV. DSC Data of the Crosslinked PLA Gels

% GF	T_g (°C)	T_c (°C)	T_m (°C)	H_m (J/g)	DSC crystallinity (%)
0	57.7	114.1 (-25.1 J/g) ^a	164.8	34.9	25.8
38.4	55.9	-	157.2	22.8	16.8
74.3	56.4	-	154.2	12.4	9.1
89.8	57.1	-	157.8	10.8	8.0
93.0	56.6	-	153.1	9.3	6.8
95.4	56.3	-	-	-	-
98.5	57.1	-	-	-	-

^aParenthesis indicates the enthalpy of recrystallization.

Table V. TGA Data of Crosslinked PLA Films

% GF	Residue			DTGA (°C)	Char (%)
	T_5	T_{50}	T_{95}		
0	283.6	380.4	403.3	389.5	0.3
38.4	330.3	384.2	405.6	392.4	0.4
74.3	332.4	385.2	407.3	394.5	0.7
89.8	327.8	384.4	404.6	391.9	0.7
93.0	338.8	385.9	408.9	395.9	0.7
95.4	339.0	386.9	408.9	396.0	0.7
98.5	339.6	387.2	409.8	397.2	0.7

by the mobility restriction of the crosslinked polymer chains. The decreases of T_m and ΔH_m have been also reported in the crosslinking of PLA using electron beam and γ -ray radiation,^{17–23} even though they did not disappear. As expected the PLA chains were crosslinked not only in the amorphous region but also in the crystallites. The polymer network with high crosslinking density can suppress the molecular motion necessary for crystallization and melting. The DSC crystallinity of the crosslinked samples decreased from 25.8% to null, which is fully amorphous. Therefore photocrosslinking of PLA can be called to crystal crosslinking as proved by XRD and DSC data, which can be distinguished from conventional amorphous crosslinking. The crystal crosslinking could make the thermoplastic PLA into a new thermosettable polymer.

The thermal degradation behavior of the crosslinked PLA determined by thermogravimetric analysis under nitrogen atmosphere was shown in Table V and Figure 6. While maximum peak of decomposition temperature of untreated PLA originally appeared at 389.5°C, the crystal crosslinking increased the peak temperature significantly up to 397.2°C by 7.7°C. The increased char residue at 550°C was attributed to the crosslink in the polymer structure but the content of the carbonaceous char did not increase above 0.7%. The higher thermal stability may be attributed to the network structure of the crosslinked PLA,

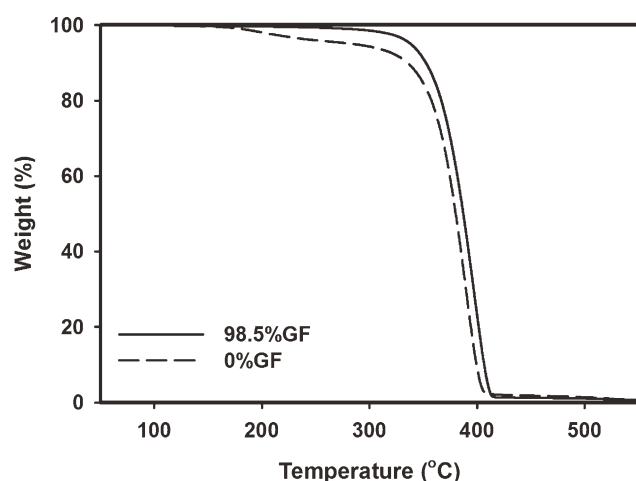


Figure 6. TGA curves of crosslinked PLA films depending on the gel fraction.

Table VI. The Mechanical Properties of Untreated and Crosslinked PLA Films

%GF	Tensile strength (MPa)	Modulus (GPa)	Strain (%)	Toughness (MPa)
0	48.1 ± 1.1	1.8 ± 0.1	3.9 ± 0.5	67.2
38.4	53.9 ± 0.9	1.9 ± 0.1	3.3 ± 0.2	69.2
74.3	62.7 ± 0.9	2.1 ± 0.1	2.9 ± 0.3	71.8
89.8	67.1 ± 1.2	2.2 ± 0.1	2.8 ± 0.4	79.6
91.6	68.0 ± 2.1	2.4 ± 0.1	2.7 ± 0.4	81.4
93.0	70.7 ± 0.9	2.5 ± 0.1	2.4 ± 0.5	83.2
95.4	75.4 ± 0.9	2.9 ± 0.1	1.9 ± 0.5	82.7
98.5	81.1 ± 0.7	3.1 ± 0.2	1.6 ± 0.4	82.3

which can be easily degraded to carbon-rich char. The improvement of thermal stability may also be due to the polymer networks with high crosslink density in the crosslinked PLA, which can modify and retard pyrolysis pathways.¹⁸ While the photocrosslinking may be enough to increase the solvent insolubility and melting property, but the crosslinked samples still have ester groups weak to the thermal degradation, which cannot necessarily increase pyrolytic resistance with increasing crosslinking.

Mechanical Properties

The mechanical properties of the untreated and crosslinked PLA films were shown in Table VI and Figure 7. The introduction of crosslink structure into PLA resulted in the increase in tensile modulus and the decrease in elongation at break. It may be resulted from the crosslinking structure which became harder and more brittle with increasing crosslinking density similar to the thermal treatment or radiation.^{16,20,21} The photocrosslinking increased both tensile strength and modulus as much as 70% with a little less decrease in elongation at break. Unexpectedly the toughness of the crosslinked PLA also increased by 22.5%.

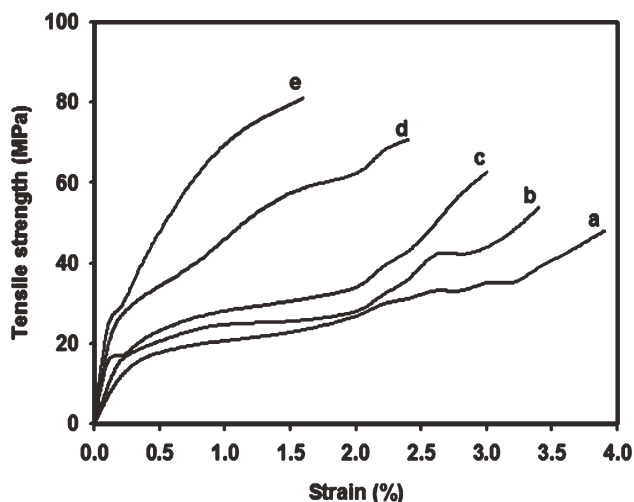


Figure 7. The mechanical properties of crosslinked PLA depending on the gel fraction of (a) 0%, (b) 38.4%, (c) 74.3%, (d) 93.0%, and (e) 98.5%.

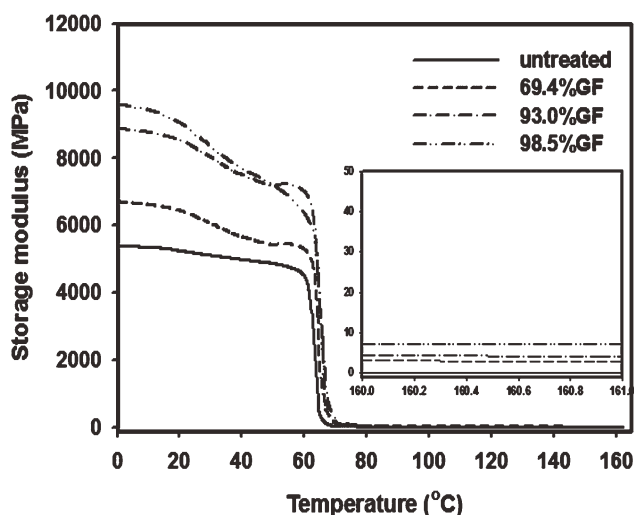


Figure 8. Storage modulus of untreated and crosslinked PLA films depending on the gel fraction.

Previously the crosslinking studies under ionized beam irradiation reported improvement in both tensile strength and modulus by 20%, resulting in decreased toughness.^{11,12,14} The mechanical properties depended on the distance between crosslink points as well as characteristics of the crosslinked polymer segments produced by the UV irradiation. The stress of the crosslinked PLA quickly increased so that the irradiated samples become tougher and more brittle with an increase in crosslinking density. Therefore the crystal crosslinking by the present photocrosslinking system is more efficient compared with conventional amorphous crosslinkings in terms of significant improvements in their thermal and mechanical properties.

Figure 8 shows storage moduli of the untreated and crosslinked PLA samples as a function of temperature. The storage moduli of the crosslinked samples increased from 5.4 to 9.6 GPa at 0°C and the crosslinked PLA can store more energy elastically during deformation than the pristine PLA, which can be explained by the reduced chain mobility of the crosslinked structure. The glass transition temperature (T_g) of PLA films can be obtained by the peak of $\tan \delta$. As expected from DSC analysis, the T_g of crosslinked PLA films increased significantly from 67.9 to 70.5°C by 2.6°C (Table II). This may be again caused by the highly crosslinked PLA network by crystal crosslinking which more effectively inhibited the segmental mobility of PLA during the heating. Therefore the melting-free and more resilient PLA films can be obtained by the crystal crosslinking.

CONCLUSIONS

Press-molded PLA films containing benzophenone can be continuously photocrosslinked under ambient UV irradiation. Maximum gel fraction of 98.5% can be achieved by adjusting UV energy and photoinitiator concentration. From NMR analysis, the photocrosslinking may be resulted from the recombination between primary and tertiary carbon radicals by the hydrogen abstraction of the PLA by the excited benzophenone. With the increasing crosslinking, glass transition temperature (DMA) increased progressively. Also both recrystallization and melting

temperatures disappeared and the spacing between the planes increased, which became a new thermosettable PLA. The photocrosslinking occurred not only in amorphous region but also in the crystalline region. Tensile strength, tensile modulus and tensile toughness all enhanced compared with the pristine PLA. The thermal stability of the crosslinked polymers remarkably improved as shown by increase in peak decomposition temperatures as much as 7.7°C. Therefore the crystal photocrosslinking of the PLA may be a very simple crosslinking process without chemical crosslinkers compared with the conventional amorphous crosslinking methods. The crystal crosslinking may apply to widen the application areas of the biodegradable polymer by taking advantage of higher toughness and melting-free property.

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