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The radiation crosslinked films based on PLLA/PDLA stereocomplex after TAIC absorption in supercritical carbon dioxide

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Abstract

The absorption of triallyl isocyanurate (TAIC) to equimolar stereo blends of PLLA and PDLA (sb-PLA samples) with crosslinker (TAIC) was controlled by supercritical carbon dioxide (sc-CO_2) treatment. The well-mixed sb-PLA/TAIC (sc-PLA) samples containing certain ratios of TAIC were obtained after vacuum evaporation. The sc-PLA samples were become much softer by sc-CO_2 treatment. The crosslinked sc-PLA materials with different crosslinking density were prepared by irradiation treatment at different radiation doses. Gel fraction, thermal properties and mechanical properties of crosslinked samples were investigated with different sc-PLA samples irradiated at the same radiation dose of 30 kGy and sc-PLA3 irradiated at different radiation doses. The crosslinking network inhibited crystallization, and enhanced the rigidity as well as lowered brittleness of irradiated samples. Although tensile strength and Young's modulus of sc-PLA are reduced by sc-CO_2 treatment, they are much improved by radiation crosslinking at a suitable dose and the crosslinked samples become harder and tougher. The typical crosslinked obtained from sc-PLA3 irradiated at 30 kGy reveals the best thermal stability with the improved mechanical properties.

Keywords: Stereocomplex; Radiation crosslinking; Dynamic mechanical properties

1. Introduction

Several polymer–polymer stereocomplexes that formed in mixture of two polymers with different compositions have been found in various polymer systems. However, only few stereocomplex such as poly(methyl methacrylate) (PMMA), poly(lactide) (PLA)... can be produced by enantiomers with the identical chemical composition but different steric structure (Fukushima & Kimura, 2006). Since discovery by Ikada, Jamshidi, Tsuji, and Hyon (1987), the stereocomplex between poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) have been intensively studied by preparations, structural, functional properties and applicability.

It was found that the van der Waals interaction between enantiomeric polymers was related to the stereocomplexation (Brizzolara, Cantow, Diederichs, Keller, & Domb, 1996). The degree of stereocomplexation was affected by weight ratio, preparation conditions and structural properties of polymer chains, especially by molecular weight of PLA homopolymers. The most suitable ratio of PLLA and PDLA for stereocomplex formation is 50:50, but the stereocomplex can also predominantly form without single polymer crystallization at the ratio from 40:60 to 60:40 (Ikada et al., 1987). PLA stereocomplex can be prepared from both solution and melt mixtures of homopolymers. In contrast to a large number of researches based on solution evaporation samples (Brochu, Prud'homme, Barakat, & Jérôme, 1995; Ikada et al., 1987; Tsuji, Hyon, & Ikada, 1991; Tsuji & Ikada, 1999; Urayama, Kanamori, Fukushima, & Kimura, 2003), very few studies based on melt blend samples have been reported (Furuhashi, Kimura, Yoshie,

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& Yamane, 2006; Quynh, Mitomo, & Zhao, 2006; Tsuji & Ikada, 1993). Therefore, the application of stereocomplex has not developed as expected but limited in biomedicine. In addition, the difficulties relate to removal the residual of solvents from cast-films have somewhat reduced their application even in biomedical field.

Tsuji and Ikada (1993) have reported that the complete stereocomplex favorable formed from the homopolymers with low molecular weight. For high molecular weight homopolymers, the stereocomplex formation was suppressed by the crystallization of the single polymer chains (Tsuji et al., 1991). Although homo crystals with different degree of crystallization competed with stereo crystals in blend, the equimolar stereo blends of high molecular weight PLLA and PDLA (sb-PLA) have revealed higher thermal stability and better mechanical properties compared with both homopolymers (Furuhashi et al., 2006; Tsuji & Ikada, 1999). The stereocomplex crystallization can be increased with annealing treatment (Furuhashi et al., 2006). Beside that, degree of crystallization also can be modified by blending, orientation, plasticization, supercritical carbon dioxide treatment... (Hirota, Sato, Tominaga, Asai, & Sumita, 2006; Ikada & Tsuji, 2000; Takasaki, Ito, & Kikutani, 2003). Thus, modification of sb-PLA is expected to improve the applicability of stereocomplex in particular and PLA based materials in general.

Recently, the use of supercritical fluids as processing solvents or plasticizers in polymer systems have become the focus of interest not only in academic studies but also in practical applications. It can be used to polymerization, polymer processing and extraction of the residual monomers or solvents from polymers (McHugh & Krukonis, 1994). Carbon dioxide is the most common used supercritical fluid because it is nontoxic, inexpensive and reveals an easily obtainable critical condition ($T_c = 31.1$ °C, $P_c = 7.38$ MPa) (Cooper, 2000), no harmful effect on the environment and human health. Consequently, it has been widely applied in polymer synthesis (Cooper, 2000; Hile & Pishko, 1999; Liu et al., 2002), extraction of low molecular weight compounds (Carson, Wells, & DeSimone, 2001), contaminants (Anitescu & Tavlarides, 2006) from substrate, formation of microspheres, porous fibers, foams and membranes... (Goel & Beckman, 1994; Nalawade, Picchioni, & Janssen, 2006; Tsivintzelis, Pavlidou, & Panayiotou, 2007; Xu et al., 2005)

On the other hand, the plasticization effect caused by impregnation of compressed CO_2 into polymers can also be observed in almost polymer systems (Alessi, Cortesi, Kikic, & Vecchione, 2003). For semicrystalline polymers such as PLA, the behavior became more complicated because the polymer structure was not homogenous but contained crystal–amorphous heterogeneous structures resulting in the brittle polymers. The adding of plasticizers to polymer matrix reduced their glass transition temperature (T_g), resulted in a remarkable improvement of the strain at break of polymer and changes of the physical and mechanical properties of polymers as well (Alessi et al., 2003; Jacoben & Fritz, 1999; Martin & Avérous, 2001).

During the relaxation of polymer matrix by compressed CO_2 at high pressure, the monomers or other low molecular weight compounds can be absorbed or diffused into the polymer systems. The diffusivity of solutes increased with compressed CO_2 concentration under processing. After depressurization, the polymer shrunk and the low molecular weight compounds were trapped inside (Shim & Johnston, 1991). Moreover, because the affinity of monomer or other low molecular weight compounds for polymer is higher than that of CO_2 for polymer, sc-CO_2 treatment can also be applied for absorption of various additives such as nucleation agents, crosslinkers into polymer. Similar processes have been studied for impregnation of polymer with drug in the production of controlled release device (Clough, 2001).

The molecular structure and properties of polymer can be modified by radiation treatment. It is well-known that the free radicals and transient species produces during irradiation and these free radicals and species affect on polymer through radiation degradation, crosslinking and grafting (Burillo et al., 2002; Filardo, Dispenza, Silvestri, & Spadaro, 1998; Jin, Hyon, Iwata, & Tsutsumi, 2002; Mitomo, Sasada, Nishimura, Nagasawa, & Yoshii, 2004; Nijienhuis, Grijpma, & Pennings, 1996). In the previous studies (Mitomo, Kaneda, Quynh, Nagasawa, & Yoshii, 2005; Quynh et al., 2007), we have proved that radiation crosslinking significantly improved thermal stability of PLA materials.

The radiation crosslinked materials of PLLA, PDLA with TAIC shows a very low crystallinity and the complete crosslinking structure has eliminated their crystallization and reduced their melting point. The crosslinked PLA materials become harder and more brittle. The crosslinking network can also form in the amorphous part of sb-PLA in the presence of TAIC (Quynh et al., 2006). Therefore, the simultaneous combination of radiation crosslinking and sc-CO_2 treatments may improve the heat stability together with reduce the brittleness of material met the requirements of the further applications beyond biomedicine. In this work, the sb-PLA samples were prepared from melt mixture of PLLA and PDLA. And then sc-CO_2 treatment has been applied to absorb TAIC and soften the CO_2 treated films to obtain different sc-PLA/TAIC samples. The crosslinked sc-PLA samples were prepared from sc-PLA by irradiation with different doses. The effect of sc-CO_2 treatment and crosslinking density on the properties of crosslinked sc-PLA has also investigated through concentration of crosslinker and radiation dose.

2. Experiments

2.1. sb-PLA preparation

The commercial grade PLLA (weight average molecular weight $Mw = 1.6 \times 10^5$ g/mol, polydispersity $DPI = 1.58$)

and PDLA (Mw = 2.6×10^5 g/mol, DPI = 1.52) were purchased from Mitsui Chemical Inc (Japan) and Purac Biochem Inc. (Netherlands), respectively. Melting point (T_m), crystallization (T_c) and glass transition temperature (T_g) of PLLA and PDLA in turn were 160.6, 107, 59.5 °C and 177, 109 and 60.8 °C, as measured by differential scanning calorimetry (DSC). Triallyl isocyanurate (TAIC) was purchased from Nihon Chemical Co. (Japan). Other solvents were bought from Wako Pure Chemical Ltd. (Japan).

Pure PLLA and PDLA with the same weight content were melted and mixed together in a Labo Plastomill (Toyoseiki Co.) at 10 cycle min^{-1}, 230 °C for 10 min to prepare melt L/D mixture. The mixture was hot pressed at 230 °C, 100 atm for 5 min and then cold pressed for other 5 min to form the sb-PLA films with thickness of 0.5 mm. The films were cut into samples of 30 × 50 mm for further treatments.

2.2. Supercritical carbon dioxide treatment

TAIC absorption in sb-PLA was controlled by SC-CO_2 treatment using CO_2 system (Jasco Co., Ltd, Japan) equipped with delivery pump (SCF-Get), automatic backpressure regulator (SCF-Bpg) and high pressure reactor (SUS-Ni alloy). A scheme of apparatus used for TAIC absorption is presented in Fig. 1.

The experiments were started by placing sb-PLA films in a glass vial containing TAIC solution with different volume so that surface of films can easily contact with TAIC. Then the vial was placed in reactor. The compressed CO_2 at 70 °C and 20 MPa were applied to reactor for 1 h. During treatment, TAIC was absorbed to the films. After that, CO_2 treated PLA samples (sc-PLA) were obtained by quickly depressurization. The compressed CO_2 and dissolved TAIC can impregnate to the polymer at different degree. Therefore, the sc-PLA films were dried under vacuum at 50 °C for 3 days to remove CO_2 residues. The polymer matrix relaxes with supercritical CO_2 at the same fraction because compressed CO_2 were homogenous distributed in reactor. However, an insignificant amount of CO_2 can be retained in polymer due to their affinity with polymer, while most compressed CO_2 were removed by vacuum evaporation. The amount of TAIC absorbed in sb-PLA/TAIC samples was determined by the weight gain of initial sb-PLA using the expression,

$$\text{Absorbed TAIC}(\%) = 100 \times (W_t - W_i)/W_i \quad (1)$$

where W_i, W_t are weight of sb-PLA before and after sc-CO_2 treatment.

The different sc-PLA samples were observed with scanning electron microscopy (Hitachi SEMEDX, Type N) after Au coating with ion coater as presented in previous report (Quynh et al., 2007).

2.3. Electron beam irradiation treatment and gel fraction of irradiated samples

The CO_2 treated samples were hot-sealed in polyethylene bag under vacuum then irradiated at room temperature in air by electron beams (EPS-750 kV) at various radiation doses with the same dose rate of 10 kGy by pass. The obtained crosslinked sc-PLA samples were used for further measurements.

Gel fraction of crosslinked sc-PLA samples were measured by dissolving them in chloroform at 90 °C in close vial because of the low solubility of sb-PLA in chloroform at room temperature (Tsuji, 2000). Gel fraction was measured by the amount of insoluble material using the following equation,

$$\text{Gel fraction}(\%) = (W_g/W_0) \times 100 \quad (2)$$

where W_0 is initial weight (dry), W_g is the remaining weight (dry gel component) of the crosslinked sample after dissolving in chloroform at 90 °C for 1 h.

Degree of swelling (volume ratio of absorbed solvent to dry gel sample) is calculated using the following equation,

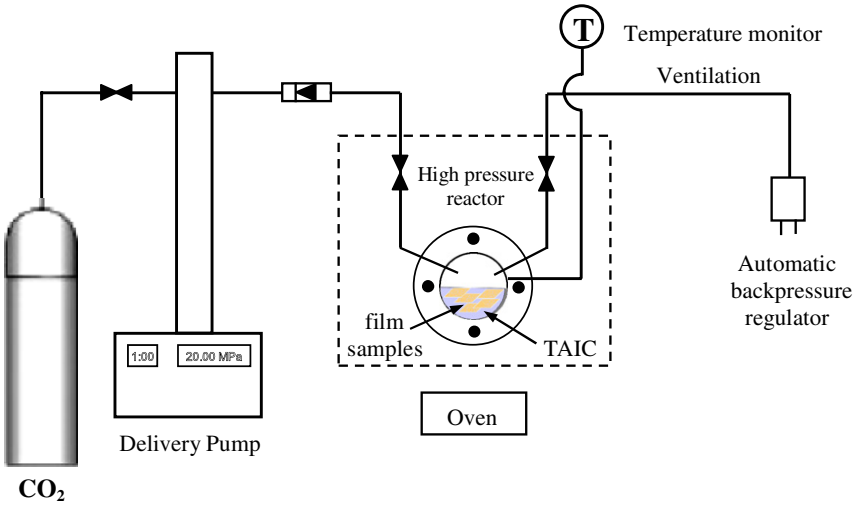

Fig. 1. A schematic diagram of experiment apparatus for TAIC absorption in sb-PLA samples.

$$\text{Degree of swelling} = [(W_s - W_g)/W_g](\rho_p/\rho_{CHCl_3}) \quad (3)$$

where W_g is the weight of dry gel component in the cross-linked sample, W_s is the weight of gel component swollen in chloroform at room temperature for 48 h in chloroform and $\rho_p/\rho_{CHCl_3} = 0.838$.

2.4. Measurements

Wide angle X-ray diffraction (WAXD) patterns of the irradiated sc-PLA samples were determined by X-ray diffractometer RINT-2200 (Rigaku, Japan) equipped a CuKα radiation source and operated at 40 kV and 20 mA at ambient conditions. Samples were scanned at scan rate of $2° \text{ min}^{-1}$ under diffraction angle 2θ from 5° to 30°.

The melting (T_m), crystallization (T_c), glass transition temperature (T_g) and enthalpy of melting (ΔH_m) of all samples were determined with a differential scanning calorimeter (Shimazu DSC-60 thermal analyzer) under nitrogen atmosphere with indium as a reference sample. About 3 mg of polymer was placed on aluminum pan for sampling. The samples were heated from RT to 250 °C, and then cooled down to 30 °C at the same heating rate of 10 °C/min. The second run was also performed to evaluate thermal degradation.

Thermomechanical analyzer (Shimadzu TMA-50) was used for evaluation of heat stability. A film 5 mm × 4 mm × 0.5 mm (thickness) in size was fixed to the sample holder under a constant load of 5.0 g (i.e., initial stress is about 24.5 kPa), then heated up from 20 to 250 °C with a heating rate of 10 °C/min under a nitrogen flow of 50 ml/min. The elongation of film was recorded against the temperature.

The mechanical properties of films were measured at room temperature using tensile tester (Tensilon, Toyo Baldwin, Japan) with crosshead speed of 2 mm/min. The sample was cut into strip of 40 mm × 10 mm dimension. The length of sample between two gages was kept constant at 20 mm.

The dynamic mechanical properties were measured with dynamic mechanical analyzer DMS 6100 C (Seiko Instruments Inc., Japan). Sample with 20 mm × 10 mm × 0.5 mm in dimension was measured at constant frequency. The storage modulus (E') and loss modulus (E'') were recorded as a function of temperature from 20 to 250 °C at 2 °C/min in air.

3. Results and discussions

3.1. TAIC absorption and structure of CO_2 treated samples

The absorption of sb-PLA with TAIC in supercritical carbon dioxide are affected by treatment conditions and structure of constituents. At the same conditions, the absorbed TAIC ratio increases with initial volume of TAIC added to reactor. Several attempts were made to obtain the reproductive values. In this experiment, the sc-PLA1, sc-PLA2, sc-PLA3, sc-PLA4 and sc-PLA5 were obtained with absorbed TAIC content of 4%, 6%, 8%, 10% and 12%, respectively. Fig. 2 shows the SEM photographs of surface structure of sb-PLA film before and after CO_2 treatment.

SEM images show that the free spaces were formed in CO_2 treated-films because of CO_2 were removed during depressurization and vacuum evaporation. The uniformity of the sc-PLA films decreases with increasing of the

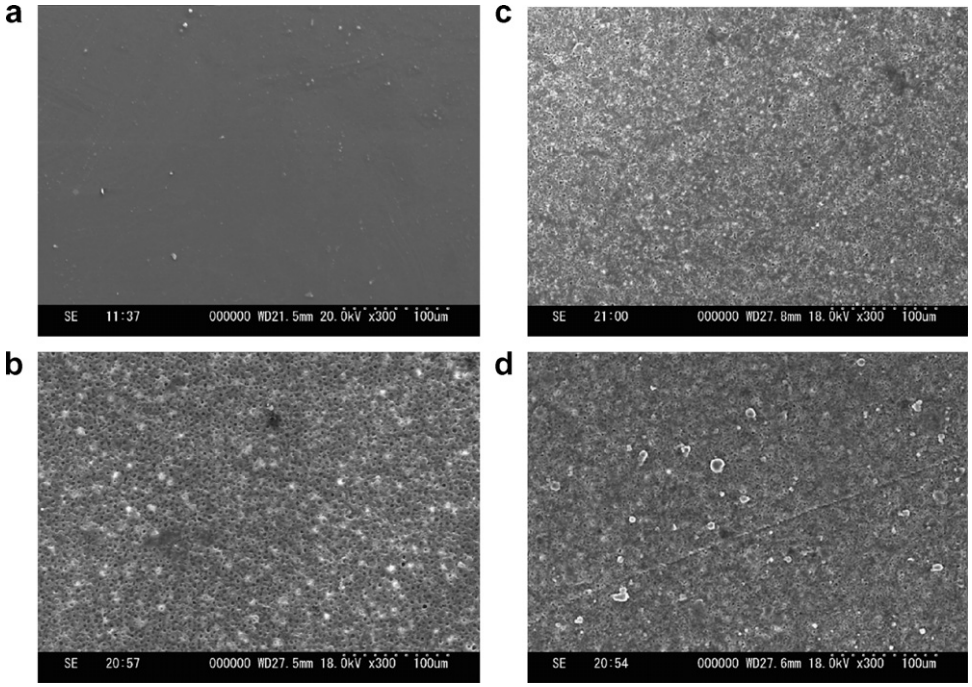

Fig. 2. SEM photographs of sb-PLA (a), sc-PLA without TAIC (b), sc-PLA with 4% (c) and 10% (d) of absorbed TAIC.

absorbed TAIC content suggested that amount of CO_2 impregnated into polymer matrix decreases by increasing of the absorbed TAIC content. The voids formed by CO_2 treatment eliminate the stress stored in the films and then more or less influence on the thermal and mechanical properties of CO_2 treated samples (Xu et al., 2005). These photographs also reveal that different absorbed TAIC contents caused different changes on the structure of sc-PLA samples. Moreover, the absorbed TAIC content and radiation dose may determine the properties of radiation crosslinked sc-PLA samples.

3.2. Crosslinking behavior of irradiated sc-PLA films

The crosslinking formed in sc-PLA films by irradiation, and the crosslinking density was represented by gel fraction. During irradiation treatment, the intramolecular and intermolecular crosslinking network of polymer chains and crosslinker can form in polymer system as explained in previous reports (Mitomo et al., 2005; Quynh et al., 2007) resulted in the gel formation. Gels formed in all irradiated sc-PLA samples but an insignificant gel fraction can be observed in non-irradiated ones. Fig. 3 shows gel fraction as a function of radiation dose. As proved in our previous studies (Mitomo et al., 2005), the crosslinking structures only form in amorphous region. Thus, the complete crosslinking, i.e., 100% gel could not obtain because the sc-PLA were low crystallinity but not the entire amorphous materials after crystallization by sc-CO_2 treatment.

Gel fraction of all crosslinked samples quickly increases with radiation dose and it seems to saturate at dose higher than 30 kGy. Although maximum gel fraction obtained in sc-PLA3 irradiated at 30 kGy, there are no significant differences between the gel fractions of crosslinked samples irradiated at 30 and 50 kGy. Therefore, the dose of 30 kGy was chosen as the most suitable radiation dose for radiation induced crosslinking of sc-PLA to reduce the irradiation cost.

At the same radiation dose, the gel fractions of crosslinked samples increased with TAIC content, but they reduced in samples containing TAIC over 10% (sc-PLA4 & sc-PLA5). This may be caused by decreasing the amount of polymer in samples when TAIC increases. The increasing of the number of monomer radicals and the decreasing of the number of polymer radicals resulted in a significant number of TAIC radicals could not take part in crosslinking network with polymer chains, though they can linked with each other. However, the radiation effects are very complicated in PLA stereo blend and they required the specific measurements such as electron spin resonance. In this study, together with gel behavior, the thermal analyses and mechanical measurements were carried out for the crosslinked samples and discussed with the absorbed TAIC content and radiation dose.

3.3. Thermal analyses for crosslinked sc-PLA samples

Fig. 4 shows DSC heating curves of initial sb-PLA and the different sc-PLA samples irradiated at the same radiation dose of 30 kGy. There are no exothermic peak can be observed in DSC thermograms of sc-PLA. After irradiation, only one endothermic peak corresponding to T_m(h) of homo crystals can be observed whereas the endothermic peak corresponding to T_m(s) of stereo crystals were significantly reduced with increasing of TAIC content. It is because the crosslinking network formed in irradiated sc-PLA films.

The crosslinking structure not only forms in amorphous region, but the imperfect crystals also can take part in this three dimensional network. The imperfect crystallites of mixture of PLLA and PDLA homopolymer chains can merge into the crosslinking networks. Although, the unmixed PLLA and PDLA chains can crystallize, the crosslinking structures formed by irradiation much inter-

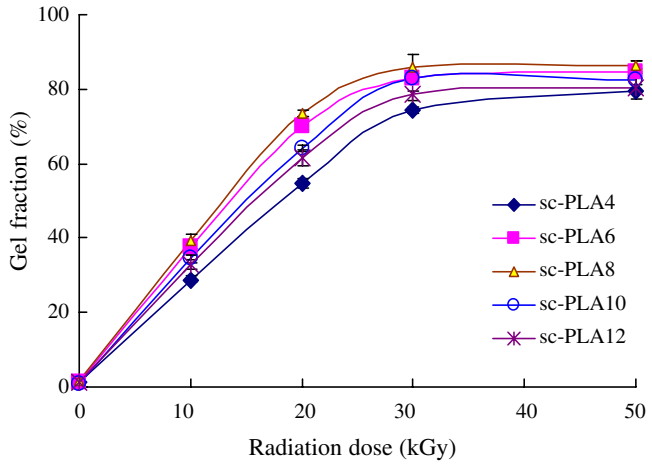

Fig. 3. Gel fraction of different crosslinked sc-PLA with different radiation doses.

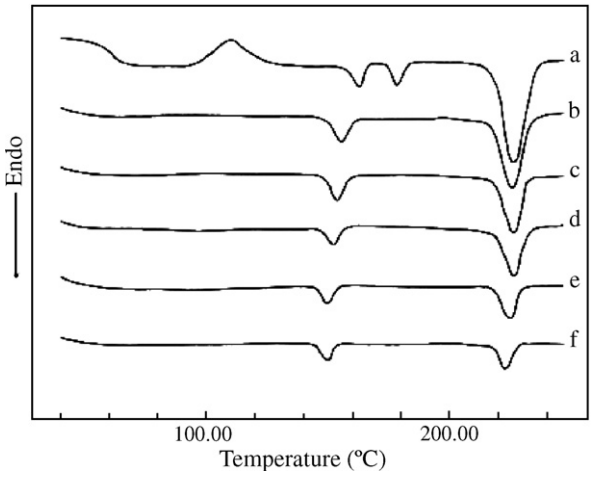

Fig. 4. DSC heating curves of sb-PLA (a) and crosslinked sc-PLA1 (b), sc-PLA2 (c), sc-PLA3 (d), sc-PLA4 (e) and sc-PLA5 (f) irradiated at 30 kGy.

fered with their crystallization, therefore their T_m shifted to lower temperature as indicated in Fig. 4.

These results are similar to DSC heating curves of crosslinked PLA (Jin et al., 2002; Mitomo et al., 2005; Quynh et al., 2007). Although, the crystallization of homo and stereo crystals still can be observed in all crosslinked sc-PLA samples, DSC of sc-PLA3 (curve (d)) shows a typical thermogram of crosslinking sample with very small melting peaks.

The WAXD patterns of different crosslinked sc-PLA samples irradiated at 30 kGy are shown in Fig. 5. All samples show the typical diffraction peaks of stereocomplex crystallites at around 12°, 20.9°, 24.2° and a peak of homo-crystallites around 18.5°. The initial PLA stereo blend show the peaks at 16° and 22.5° related to PLA homopolymers, but these peaks are not very clear for the crosslinked sc-PLA. These data also indicated that the diffraction peaks of crosslinked films reduced and the crosslinked sc-PLA showed smaller amorphous domains. The crosslinked sc-PLA3 showed the smallest diffraction peaks means that the sample almost crosslinked by irradiation at this radiation dose.

Thermomechanical analysis (TMA) of PLA stereo blend and crosslinked sc-PLA samples at the same radiation dose of 30 kGy are shown in Fig. 6 as functions of temperature. All samples start to elongate over their glass transition temperature (~60 °C) with different extension rate. Above 190 °C, PLA stereo blend (a) quickly elongates and breaks at 220 °C (around its T_m).

After pretreatment with sc-CO_2, compressed CO_2 sample (b) shows a larger extension rate over T_g. The sc-PLA rapidly elongates and breaks at around 200 °C, but thermal stability of sc-PLA were significantly improved by radiation induced crosslinking. The sc-PLA1 (c) broke at 230 °C, whereas other crosslinked samples can withstand over 250 °C. The crosslinked sc-PLA2 (d) and sc-PLA3 (e) showed the same extension rates with temperature and

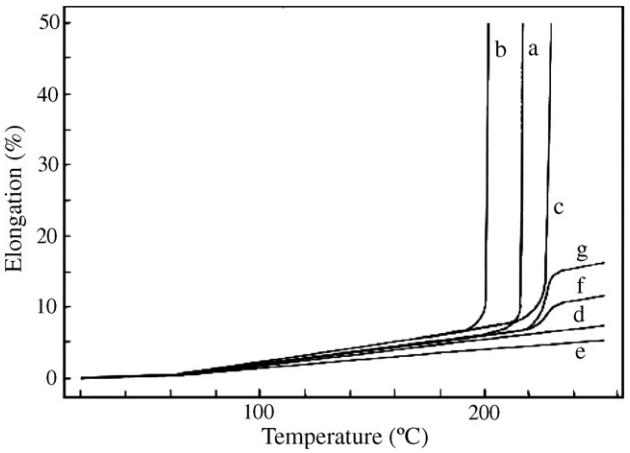

Fig. 6. TMA heating curves of sb-PLA (a), sc-PLA (b) and crosslinked sc-PLA1 (c), sc-PLA2 (d), sc-PLA3 (e), sc-PLA4 (f) and sc-PLA5 (g) irradiated at 30 kGy.

sc-PLA3 (e) showed the best thermal stability with elongation lower than 6% to 250 °C. Therefore, the absorbed TAIC of 8% by CO_2 pretreatment is regarded as the optimum content for preparation of the radiation crosslinked sc-PLA sample.

3.4. Mechanical properties of crosslinked sc-PLA films

The mechanical properties of crosslinked films were investigated by tensile test at room temperature and dynamic mechanical analysis (DMA). Figs. 7 and 8 show the stress–strain curves of different sc-PLA films irradiated at 30 kGy and sc-PLA3 irradiated at different radiation doses, respectively. Tensile strength and Young's modulus of sc-PLA reduced by CO_2 treatment, but they were significantly recovered by crosslinking structures introduced in polymer whereas their toughness still remained. Even the tensile strength of irradiated sc-PLA3 was higher compared

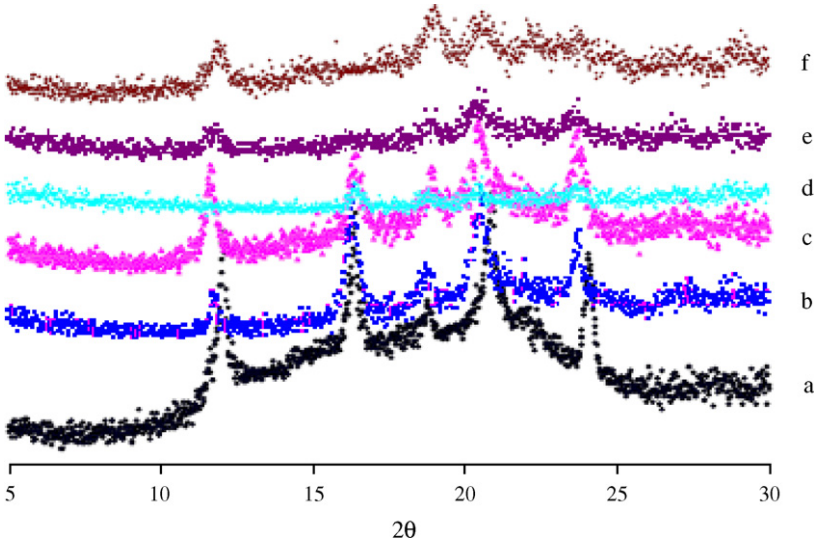

Fig. 5. WAXD patterns of sb-PLA (a) and crosslinked sc-PLA1 (b), sc-PLA2 (c), sc-PLA3 (d), sc-PLA4 (e) and sc-PLA5 (f) irradiated at 30 kGy.

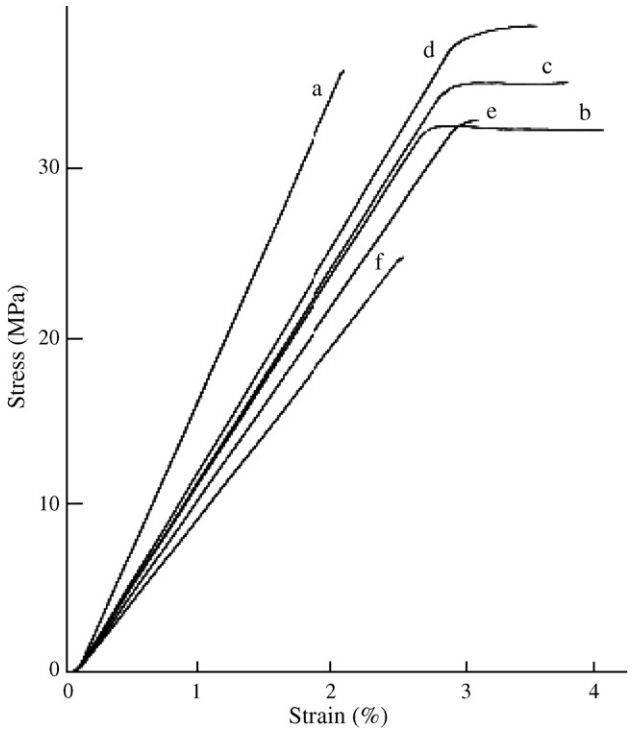

Fig. 7. Stress–strain curves of sb-PLA (a) and crosslinked sc-PLA1 (b), sc-PLA2 (c), sc-PLA3 (d), sc-PLA4 (e) and sc-PLA5 (f) irradiated at 30 kGy.

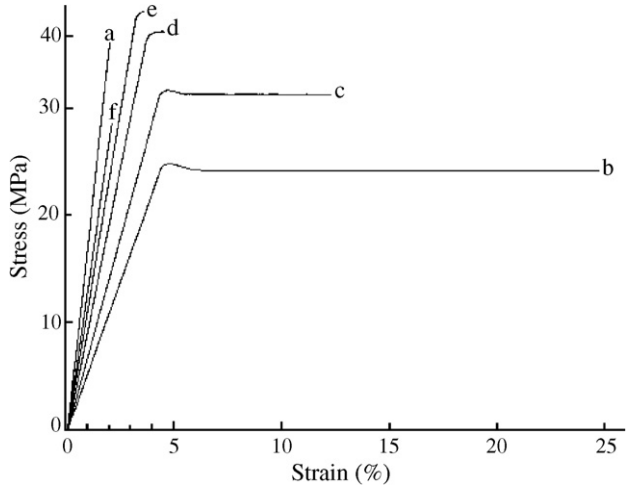

Fig. 8. Stress–strain curves of sb-PLA (a) sc-PLA3 (b) and crosslinked sc-PLA3 irradiated at 10 kGy (c), 20 kGy (d), 30 kGy (e) and 50 kGy (f).

with initial PLA stereo blend. The mechanical properties of irradiated sc-PLA4 and sc-PLA5 (with TAIC higher than 10%) did not recovered as desired. It may be due to some monomers, which are not able to take part in crosslinking network of polymer chains and they somewhat influenced on the structure of the crosslinking materials.

For crosslinked sc-PLA3 samples irradiated at 30 kGy as presented in Fig. 7, the recovery of tensile strength and Young's modulus increases, though the samples become more brittle with the increasing of radiation dose. Fig. 8 also shows that the better mechanical properties obtained with crosslinked sc-PLA3 irradiated at 20 and 30 kGy. When a high radiation dose (50 kGy) was applied, both of stress and strain have reduced. It was because the crosslinking network of shorter polymer segments that produced at high radiation dose is brittle and unstable.

The introduction of crosslinking structures made the PLA based materials become harder and more brittle as in our previous studies (Mitomo et al., 2005; Quynh et al., 2006, 2007). However, the sc-CO_2 pretreatment reduced the rigidity of materials resulted in not only tensile strength but also the strain at break of the crosslinked sc-PLA samples were significant improved.

Figs. 9 and 10 show the storage modulus of different sc-PLA samples irradiated at 30 kGy and sc-PLA3 irradiated at different radiation doses as functions of temperature, respectively. Because the change of loss modulus is similar to storage modulus, then it was not shown in these figures. Storage modulus (E') is stable at low temperature, then decrease with heating due to several thermal transitions. sb-PLA sample shows a recrystallization at around 75 °C. This may be caused by PLLA/PDLA stereo blend samples recrystallized to some extent during heating. Along with the increasing of temperature, the sb-PLA film become rubbery and soft and then broke at around 225 °C, the Tm of PLLA/PDLA stereocomplex. However, the crystallization of sc-PLA during sc-CO_2 treatment made the crosslinked sc-PLA does not crystallize at any extent as temperature rises.

As can see in Fig. 10, although the storage modulus of sc-PLA films was decreased by sc-CO_2 treatment, it was completely recovered by radiation crosslinking, even E' of crosslinked sc-PLA samples obtained at 30 kGy were still stable over 250 °C. Fig. 9 also indicated that the crosslinked sc-PLA samples at 30 kGy did not break at their T_m, even crosslinked sc-PLA3 samples can withdraw over 250 °C. These results confirmed again the best crosslinking network have been formed in sc-PLA3 irradiated at 30 kGy.

4. Conclusions

The PLA stereo blend samples with good heat stability and mechanical properties were prepared from equimolar blend of PLLA and PDLA. In order to reduce the brittleness of sb-PLA samples, these films were pretreated with supercritical carbon dioxide in presence of TAIC. The absorbed TAIC content and crystallization of sc-PLA during sc-CO_2 treatment influenced on the surface structure of CO_2 treated samples as well as the properties of crosslinked sc-PLA samples. Diffraction patterns and DSC measurements of typical crosslinked samples show the crosslinking structure have been produced not only in amorphous regions of irradiated sc-PLA, but the imperfect crystals of homopolymers can also merge into the crosslinking network. The typical crosslinked sample obtained with sc-PLA3 irradiated at 30 kGy revealed the best thermal stability.

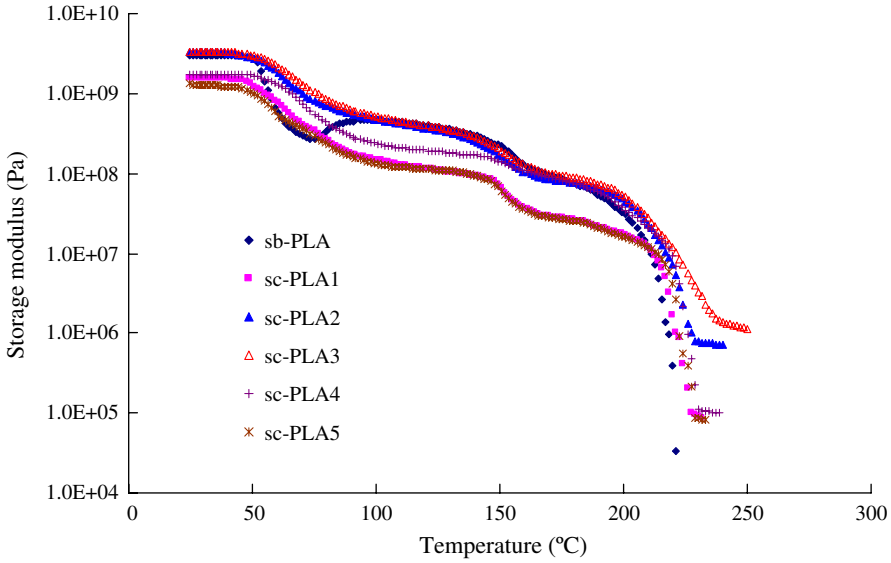

Fig. 9. Dynamic mechanical behavior of different crosslinked sb-PLA samples irradiated at 30 kGy.

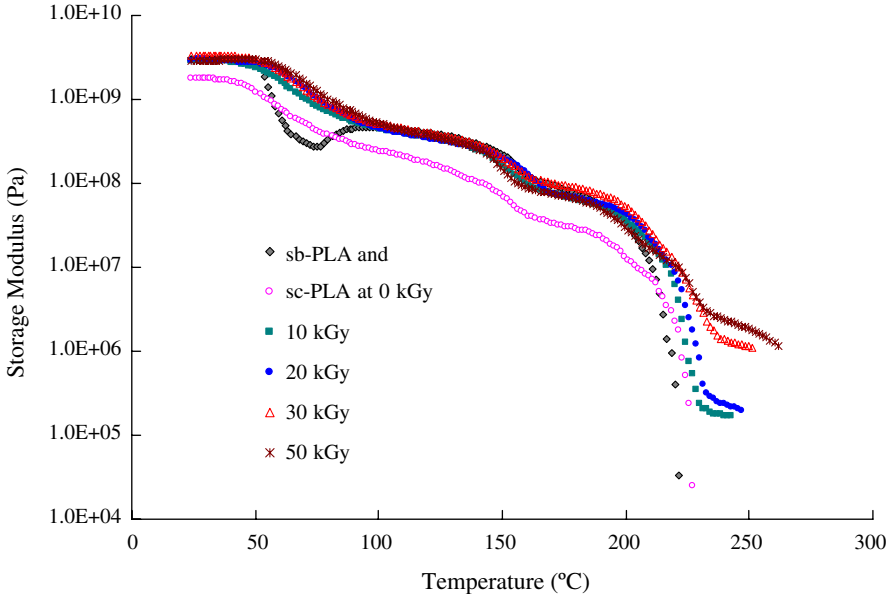

Fig. 10. Dynamic mechanical behavior of crosslinked sc-PLA3 irradiated at different radiation dose.

The brittleness of sb-PLA was much reduced by sc-CO_2 treatment. Although tensile strength and Young's modulus of sc-PLA have also been reduced by undesirable affects during CO_2 treatment, they were completely recovered by radiation crosslinking. Not only toughness but also tensile strength of irradiated sc-PLA films can significant improve by simultaneous combination of supercritical CO_2 and radiation treatments. And the sc-PLA3 irradiated at 30 kGy showed the best tensile strength with improved toughness compared with PLA stereo blend.

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