

UV-curing Behaviors and Mechanical Properties of UV-cured Polylactic Acid (PLA)*¹

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ABSTRACT

UV curing was introduced via a chemical treatment by adding small amounts of a hexafunctional acrylic monomer and a photoinitiator to improve the mechanical properties of PLA. This study also employed a semi-interpenetrated structured polymer network through the process of UV-curing. The UV curing behaviors were investigated using FTIR-ATR spectroscopy and gel fraction determination. Also, the tensile strength was investigated with different hexafunctional acrylic monomer contents and UV doses. The results showed that the crosslinking of UV-induced chemically treated PLA started at a low content of hexafunctional acrylic monomer, resulting in a significant improvement of the mechanical properties compared to those of neat PLA due to crosslinking.

Keywords : polylactic acid (PLA), UV curing, chemical crosslinking, hexafunctional acrylic monomer, mechanical properties, semi-IPN structure

1. INTRODUCTION

Poly(lactic acid) (PLA) has attracted the attention of both industry and research institutions. It is a biopolymer whose properties are comparable to those of commercial plastics such as poly(ethylene terephthalate) (PET)[1]. PLA production is derived from annually renewable resources such as corn starch, cassava starch or sugarcane. PLA exhibits the useful properties of biodegradability, transparency and processability

[2-5]. However, its poor heat stability and mechanical properties limited its applications[6-8]. Many technologies, such as annealing, the addition of nucleating agents[9-12], the formation of composites with fiber or nanoparticles[13-16], chain extensions[17,18] and the introduction of crosslinking structures have been shown to be effective for enhancing the heat stability or mechanical properties of PLA materials[19].

Photo-induced reactions consist of polymerization as introduced by ultra-violet (UV) light, visible light, an electron beam (EB) or a laser.

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Photopolymerization science and technology has acquired a considerable amount of attention due to its various industrial applications, such as inks, coatings, photoresists and pressure-sensitive adhesives (PSAs)[20-22]. Among the various methods of photo-curing, UV-curing systems are widely used due to their various advantages, such as their rapid production rate in a small work area, lower processing costs, high chemical stability, high dimensional stability and solvent-free curing at ambient temperatures [23]. Interpenetrating polymer networks (IPNs) are the subject of much current research because IPNs have a range of possible technological applications. IPNs can be briefly defined as a combination of two incompatible polymer networks with at least one synthesized and/or crosslinked in the presence of the other. The selection of different systems, such as polymerization by a combination of radical and cationic mechanisms, is used to prevent the copolymerization and grafting reactions that may occur between the two polymer networks[24]. Moreover, the kinetics and properties of multifunctional acrylates which are crosslinked quickly by radical and cationic polymerizations have been investigated[25,26].

The main objective of this study is to improve and modify film produced from PLA by adding a hexafunctional monomer to enhance the mechanical properties of PLA. The UV-curing behaviors are investigated using FTIR-ATR spectroscopy and gel fraction determination. Also, the tensile strength was investigated with different hexafunctional acrylic monomer contents and UV doses.

2. EXPERIMENTAL

2.1. Materials

The commercially available polylactic acid

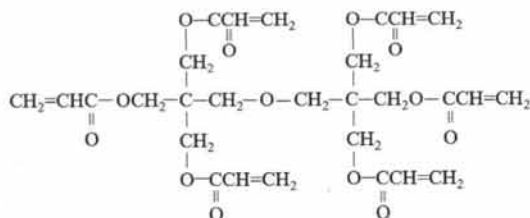


Fig. 1. Chemical structure of the dipentaerythritol hexacrylate (DPHA).



Fig. 2. Cleavage of hydroxydimethyl acetophenone as a photoinitiator in the presence of UV light[27].

(PLA) (NatureWorks, PLA 2002D) with a density of 1.24 g/m³ was purchased from Nature Works LLC. Dipentaerythritol hexacrylate (DPHA, Miwon Specialty Chemical, Republic of Korea) was used as the hexafunctional monomer. Fig. 1 shows the chemical structure of DPHA, which has six C=C double bonds. 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Miwon Specialty Chemical, Republic of Korea) was the photoinitiator, as shown in Fig. 2.

2.2. Preparation of UV-cured PLA Film

UV-curable PLA was prepared by blending melted PLA, a photoinitiator and a hexafunctional acrylic monomer. It was coated onto polyester (PET) release films and then cured using conveyor-belt-type UV-curing equipment with a 100 J/s high-pressure mercury lamp (main wavelength : 365 nm). The UV doses were measured using an IL 390C Light Bug UV radiometer (International Light, USA). Despite the low molecular weight, the hexafunctional monomer could be photopolymerized after a UV dose to form semi-IPN structures (Fig. 3). The cured PLA films were weighed and im-

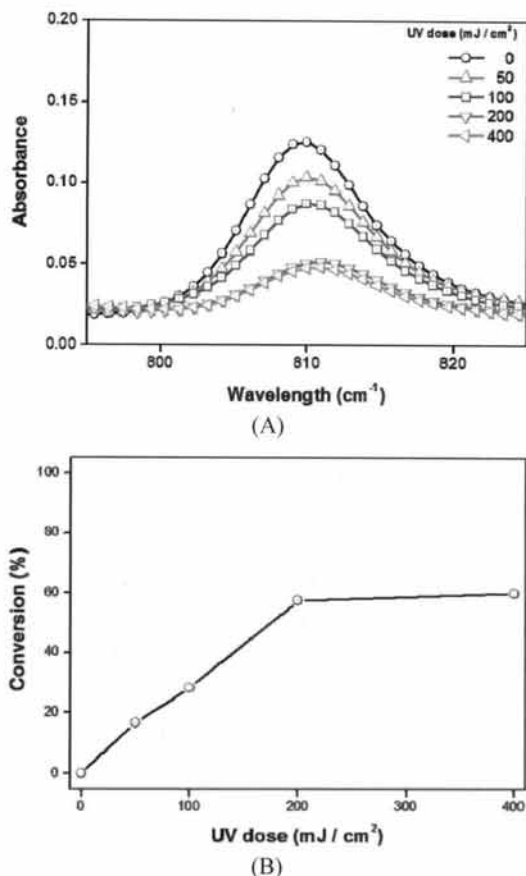


Fig. 3. FTIR-ATR spectra of UV-curable PLA films with different UV doses (A) and changes in the concentration of C=C bonds as a function of the dose (from 0 to 400) for UV-curable PLA films with 3 phr DPHA in PLA (B).

mersed in toluene for 3 days at 50°C and then screened and dried at room temperature to a constant weight. The gel fraction of the samples was calculated using the following equation:

$$\text{Gel fraction (\%)} = W_t / W_0 \times 100 \quad (1)$$

In this equation, W_0 and W_t are the PLA film weights before and after immersion, respectively. The gel content provides information on the degree of crosslinking.

2.3. Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR)

The IR spectra were obtained using a Jasco FTIR-6100 (Japan) equipped with an attenuated total reflectance (ATR) accessory. In order to obtain the IR spectra of UV-curable PLA film, the cured PLA films were cut into $0.5 \times 0.5 \text{ cm}^2$ pieces. The ATR crystal was diamond and its refractive index at $1,000 \text{ cm}^{-1}$ was 2.4 with a transmission range of $4,000$ to 650 cm^{-1} . The resolution of the recorded spectra was 4 cm^{-1} . The curing behavior of the UV-curable PLA film was analyzed by observing the changes in the deformation of the C=C bonds at 810 cm^{-1} . Also, all FTIR-ATR spectra were modified by means of baseline correction.

2.4. Mechanical Properties

The tensile test was done according to ASTM D638-08 with a texture analyzer (Micro Stable Systems, TA-XT2i) at a crosshead speed of 5 mm/min and room temperature. Five specimens were measured to determine the value and the deviations.

3. RESULTS and DISCUSSION

3.1. UV-curing Behavior of PLA Films

3.1.1. FTIR-ATR Spectroscopy

DPHA, whose structural formula given in Fig. 1, has been shown to be one of the most effective crosslinking agents for PLA. The double bonds in DPHA can be easily broken to produce monomer radicals and then combine with the polymer radicals to form a crosslinking network. The UV-curing kinetics of the photo-induced crosslinking was observed by means of FTIR-ATR spectroscopy, as shown in Fig. 3.

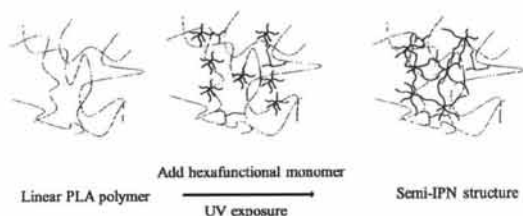


Fig. 4. Process of producing a semi-IPN structure in UV-cured PLA.

After photoinitiation by UV irradiation at a specific wavelength, the functional monomers began to polymerize, after which they formed a crosslinked structure. The curing behavior of the functional monomers can be explained through the use of FTIR-ATR, as the C=C twisting vibration in these functional monomers participates in the crosslinking reaction. These double bonds have a plane conformation, but UV irradiation deforms them into an out-of-plane conformation[25]. After the reaction between the C=C bonds of DPHA through radical polymerization, it formed a semi-IPN structure, as shown in Fig. 4. Therefore, the kinetic profile can be explained by the evaluation of the absorption band at 810 cm^{-1} . The characteristic signal used for calculation was at 810 cm^{-1} and then was integrated to determine the decrease in the concentration of the C=C bonds as a function of the UV dose. The concentration of the C=C bonds as a function of the UV dose was calculated using the following equation:

Conversion of UV-cured group (%) =

$$\frac{(A_{810})_0 - (A_{810})_t}{(A_{810})_0} \times 100$$

Here, $(A_{810})_0$ is the IR absorbance at 810 cm^{-1} before UV irradiation and the $(A_{810})_t$ is the IR absorbance at 810 cm^{-1} after UV irradiation. Fig. 3(A) shows the FTIR-ATR spectra at 810 cm^{-1} . These spectra were collected at different

UV doses (ranging from 0 to 400). It can be observed that the characteristic signal at 810 cm^{-1} gradually decreased with an increase in the UV dose. Integration of the characteristic signals is shown in Fig. 3 (A). The change in the concentration profile is apparent in Fig. 3(B). The UV dose for optimal crosslinking is approximately 200 mJ/cm^2 . Beyond this point, only a minor change in the C=C concentration can be observed. UV light has the potential to decompose the C=C bonds in a polymer or monomer, but the conversion in this case was not 100%. The remaining C=C bonds may remain unreacted after the action of the photoinitiator as they are trapped in the crosslinked polymer network[21].

3.1.2. Gel Fraction

To determine the degree of UV curing, the gel content was calculated by measuring the insoluble material that was left behind[28]. The amount of gel phase that was measured is defined as the number of both the crosslinked molecules as well as highly entangled and coiled polymer molecules. In the latter case, crosslinking occurs only through entanglement. Moreover, it is not truly a polymeric network, which usually consists of interconnected polymeric molecules. Therefore, the gel phase can vary due to a change in the polymer molecular weight[25,26] or with an increase in the crosslinking density. In this study, only UV-induced crosslinking should affect the amount of the gel phase, as the initiator concentration, the temperature, and the humidity profiles were equal for all samples. A similar increase in the gel phase amount was also identified in our previous study, where the crosslinking of polymer molecules was induced by an addition of a multifunctional acrylic monomer in the polymerization phase[30]. Not only the molecular weight but also the crosslinking density can be considered as the most important

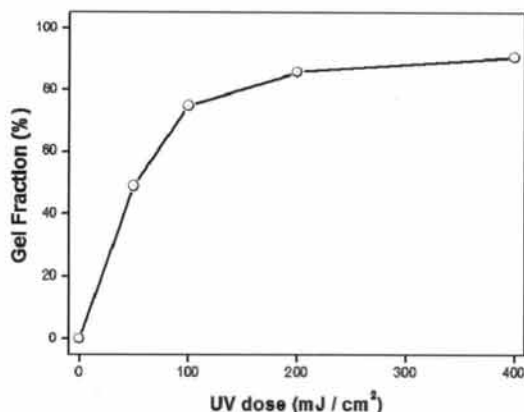


Fig. 5. Gel fraction of chemically crosslinked PLA films with 3 phr DPHA in PLA as a function of the UV dose.

factors related to the adhesion property. Moreover, the mobility of polymer molecules is strongly reduced by the chemical bond in the polymer structure[31].

Fig. 5 clearly shows that the gel fraction increased with an increase in the UV dose. The gel content indicated nearly 90% after a dose of 200, which was relatively stable compared to the other samples. This shows that a UV dose of 200 mJ/cm² offers a higher probability of forming entanglements and crosslinked structures between polymers.

3.2. Mechanical Properties

The tensile properties of pure PLA and the crosslinked PLA samples are shown in Fig. 6. The introduction of crosslinked structure into PLA results in an increase in the tensile strength and a decrease in the degree of elongation upon breakage, as shown in Fig. 6(A). This can be attributed to the crosslinked structure, which stiffened the PLA. Also, the increase in the gel fraction and crosslink density made the crosslinked PLA more brittle. In the strain-stress

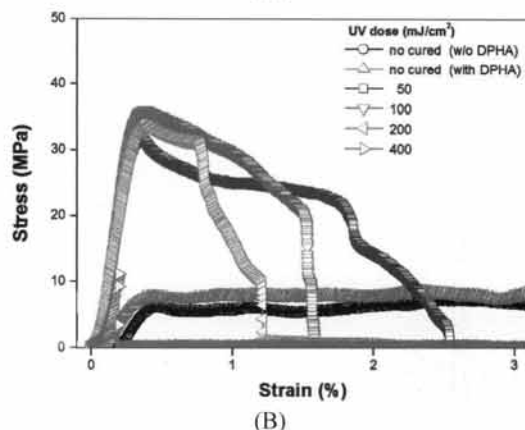
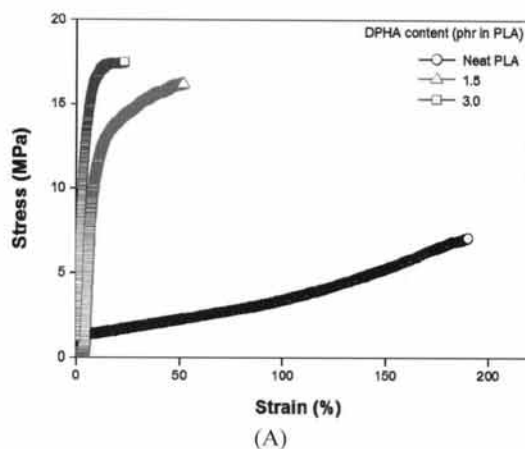


Fig. 6. Strain-stress curve of chemically crosslinked PLA films; effect of (A) the DPHA content (phr in PLA) and (B) UV dose.

curves with different UV doses shown in Fig. 6(B), the area clearly decreases with an increase in the UV dose. This result indicates that the fibrillation was not only affected by the UV dose but that area of the strain-stress curve also decreased.

4. CONCLUSION

UV-cured crosslinking structures can be effectively introduced in PLA by adding a small amount of DPHA. The UV-curing behavior and

mechanical properties of chemically crosslinked PLA were investigated by FTIR-ATR, the gel fraction, and by the crosslink density. The tensile strength improved with the introduction of a crosslinking structure. However, a highly cross-linked structure may present a problem to be overcome. This can be investigated in future work.

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