

# Compatibility of Liquid Deproteinized Natural Rubber Having Epoxy Group (LEDPNR)/Poly (L-Lactide) Blend

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**ABSTRACT:** Reaction after mixing of liquid epoxidized natural rubber/poly(L-lactide) blend was performed to enhance the compatibility of the blend. The liquid epoxidized natural rubber was prepared by epoxidation of deproteinized natural rubber with peracetic acid in latex stage followed by depolymerization with peroxide and propanal. The resulting liquid deproteinized natural rubber having epoxy group (LEDPNR) was mixed with poly(L-lactide) (PLLA) to investigate the compatibility of the blend through differential scanning calorimetry, optical light microscopy, and NMR spectroscopy. After heating the blend at 473 K for 20 min, glass transition temperature

( $T_g$ ) of LEDPNR in LEDPNR/PLLA blend increased from 251 to 259 K, while  $T_g$  and melting temperature ( $T_m$ ) of PLLA decreased from 337 to 332 K and 450 to 445 K, respectively, suggesting that the compatibility of LEDPNR/PLLA blend was enhanced by a reaction between the epoxy group of LEDPNR and the ester group of PLLA. The reaction was proved by high-resolution solid-state  $^{13}\text{C}$  NMR spectroscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 393–399, 2008

**Key words:** compatibility; natural rubber; epoxy group; poly(L-lactide); blend; NMR measurement

## INTRODUCTION

Epoxidized natural rubber (ENR) has been recognized to be a reactive elastomer having epoxy group, which is made from natural rubber.<sup>1–4</sup> It may accomplish not only high reactivity but also outstanding mechanical properties of natural rubber.<sup>5</sup> Thus, ENR may be useful for reaction after mixing with other polymers. The reaction may enhance compatibility of the blend of ENR with the polymers, since it produces block and graft copolymers as a compatibilizer. For instance, for a blend of ENR with poly(L-lactide) (PLLA), we may consider a reaction between the epoxy group of ENR with the ester group of PLLA, based upon the previous work.<sup>6</sup>

PLLA is a biodegradable polymer whose biodegradation takes place just after immersing it into hot water as a trigger. However, it has been known to be difficult to use PLLA in industry due to its inferior properties such as brittle and rigid in nature. Thus, PLLA has to be mixed with a biodegradable soft material such as ENR to improve the nature from brittle to tough.<sup>7–10</sup> Since PLLA is immiscible with ENR, the reaction after mixing must be applied

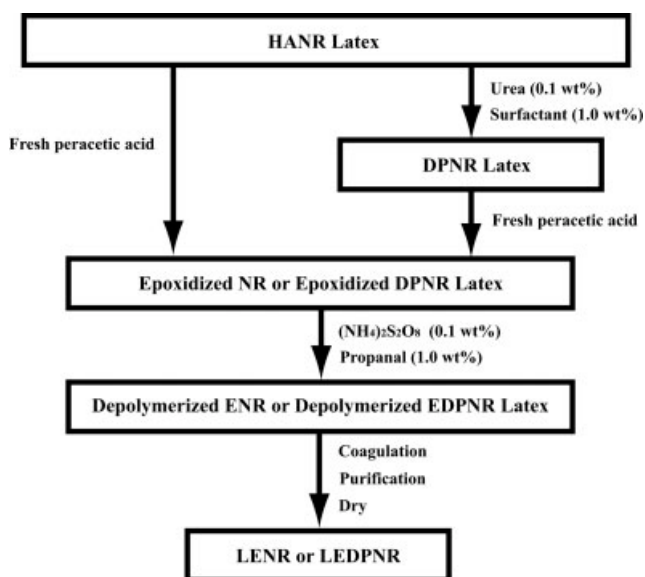
to ENR/PLLA blend to enhance its compatibility. In principle, the reaction between PLLA and ENR may produce the graft and block copolymers. However, when one uses commercial ENR, the epoxy group of ENR may not react with the ester group of PLLA due to the presence of naturally occurring proteins, which are attracted with water. To make the reaction between the epoxy group of ENR and the ester group of PLLA, it is important to remove the proteins from natural rubber.

In previous works, we proposed enzymatic deproteinization<sup>11–13</sup> and urea deproteinization<sup>14,15</sup> to remove the proteins from natural rubber. We prepared highly deproteinized natural rubber (DPNR) and hyper-deproteinized natural rubber, which contained about 0.1 wt % and 0.02 wt % proteins, respectively, being less than about 2 wt % proteins present in the untreated natural rubber. From the DPNR's, a liquid epoxidized DPNR (LEDPNR) was prepared with ammonium persulfate ( $\text{NH}_4)_2\text{S}_2\text{O}_8$  and propanal  $\text{CH}_3\text{CH}_2\text{CHO}$ , after epoxidation.<sup>16–18</sup> Thus, we expect that the epoxy group of LEDPNR may react with the ester group of PLLA.

In this work, an attempt to make the reaction after mixing between LEDPNR and PLLA was performed to enhance the compatibility of the blend of LEDPNR with PLLA. The reaction between the epoxy group of LEDPNR and the ester group of PLLA was analyzed by different scanning calorimetry (DSC), optical light microscopy (OLM), and nuclear magnetic resonance (NMR) spectroscopy.

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**Figure 1** Schematic illustration of preparation procedure for LENR and LEDPNR.

## EXPERIMENTAL

Natural rubber used in this study was commercial high ammonia natural rubber latex. Deproteinization of natural rubber was performed by incubation of the latex with 0.1 wt % urea and 1.0 wt % sodium dodecylsulfate (SDS) for an hour at room temperature followed by centrifugation.<sup>14,15</sup> The cream fraction was re-dispersed in 1.0 wt % SDS solution and it was washed twice by centrifugation to prepare DPNR latex. DPNR latex was diluted to 10% DRC and it was stabilized with 0.5–1.0 wt % SDS. After adjusting pH to 5–6 with acetic acid, the DPNR latex, pre-cooled at 283 K. The DPNR latex (100 g, 10% DRC) was epoxidized at 283 K for 90 min with peracetic acid, which was prepared by acetic anhydride and hydrogen peroxide.<sup>16–21</sup>

The depolymerization of the epoxidized DPNR (EDPNR) latex was carried out; after pH was adjusted to 9–10 with ammonia solution. The 0.1 wt % ammonium persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as a radical initiator and 1.5 wt % propanal were added into EDPNR latex. The depolymerization of the latex was carried out by incubation of the latex at 338 K for 12 h. The resulting latex was coagulated with methanol and the coagulum was dried up at 303 K for a week under reduced pressure.<sup>16–18,22</sup> The procedure to prepare the sample was schematically represented in Figure 1. PLLA used in this study was PLLA1518. The blend of LEDPNR/PLLA, LENR/PLLA at blend ratio (40/60) were prepared by precipitation of 2 w/v% chloroform solution into excess methanol and dried under reduced pressure at room temperature for a week. The procedure to prepare the blends was schematically represented in Figure 2. The reac-

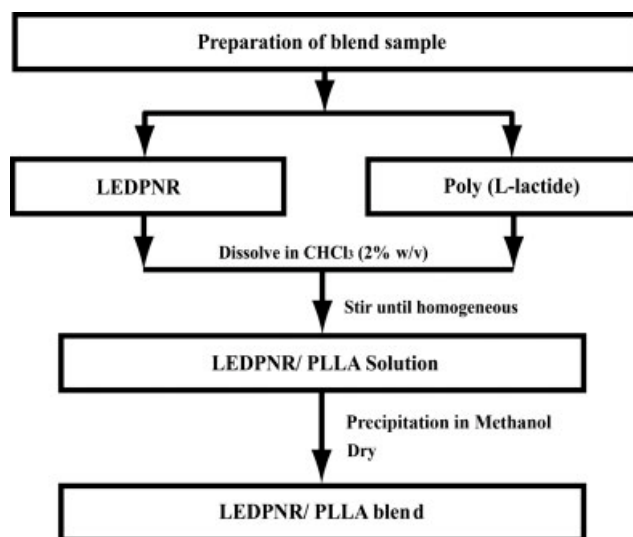
tion after mixing of the LEDPNR/PLLA blends was carried out at 473 K for 0.5–20 min.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR measurements were carried out with a JEOL-400 NMR spectrometer at the pulse repetition time of 7 s and 5 s, respectively. Morphology of LEDPNR/PLLA blend was observed by OLM, using a Nikon Eclipse E600 POL. The sample, sandwiched between two cover glasses, was placed on a heating stage (Linkam LK 600 PM) whose temperature control was maintained within 0.1 K. The sample was heated at 473 K.  $T_g$  and  $T_m$  of the blend were assessed with a Seiko Instruments Inc., DSC 220, which was calibrated with standard indium and linoleic acid before measurement. The blend packed into an aluminum pan was heated at 473 K. After the reaction, the DSC measurement was made from 153 to 523 K at a heating rate of 10 K/min. Measurements of molecular weight and molecular weight distribution of the rubber were made with a TOSOH size excluded chromatography (SEC), consisting of a TOSOH CCPD pump, a RI-8012 differential refract meter and a UV-8011 UV detector. The measurement was made at room temperature and the flow rate of the mobile phase, tetrahydrofuran (THF), was 0.5 mL/min. The molecular weights were estimated on the basis of the molecular weight of standard polystyrene.

The gel fraction was separated by centrifugation at  $11,000 \times g$  for 30 min in toluene solution. The content of gel fraction,  $C_{\text{gel}}$  was estimated as flows:

$$C_{\text{gel}} = W_{\text{gel}}/W_{\text{rubber}} \times 100\% \quad (1)$$

where  $W_{\text{gel}}$  and  $W_{\text{rubber}}$  are weight of gel fraction and rubber, respectively. Total nitrogen content was measured by Kjeldahl method as described in RRIM



**Figure 2** Schematic illustration for preparation procedure for LEDPNR/PLLA blend.

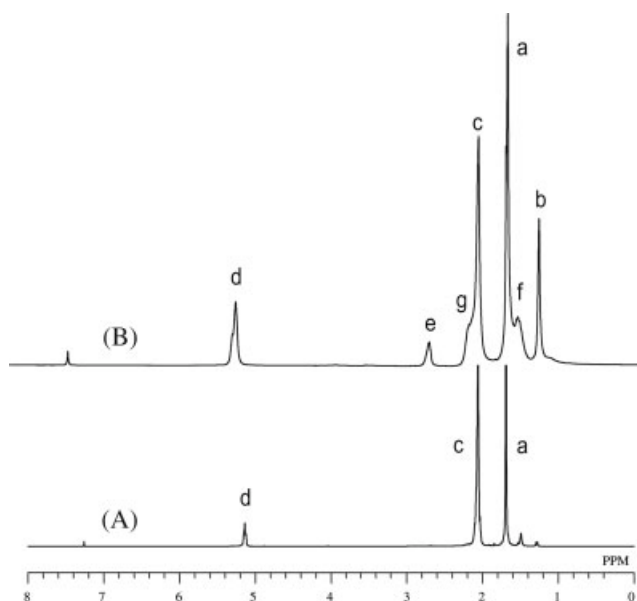
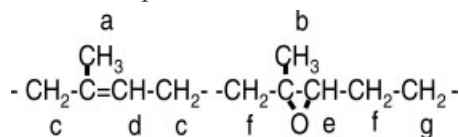


Figure 3  $^1\text{H}$  NMR spectra for (A) DPNR and (B) EDPNR.



test method B7.<sup>23</sup> Rubber sample, mixed with catalyst mixture, i.e. potassium sulphate: copper sulphate: selenium in the weight ratio of 15 : 2 : 1, was digested with concentrated  $\text{H}_2\text{SO}_4$ . The resulting solution was distilled, and the distillates were titrated with 0.005M  $\text{H}_2\text{SO}_4$  using methyl red as an indicator.

## RESULTS AND DISCUSSION

$^1\text{H}$  NMR spectra for DPNR and EDPNR are shown in Figure 3. Signals characteristic of methyl, methylene, and unsaturated methine protons of isoprene units appeared at 1.6, 2.1, and 5.1 ppm, respectively. After epoxidation of DPNR, other two signals appeared at 1.2 and 2.7 ppm, which were assigned to methyl and methine protons of the resulting epoxy group, respectively, as shown in Table I. The epoxy group content,  $X_{\text{epoxy}}$ , was, thus, estimated from intensity ratio of the signals, as follows:

$$X_{\text{epoxy}} = I_{2.7} / (I_{2.7} + I_{5.1}) \times 100\% \quad (2)$$

where  $I$  is intensity of the signals and the subscripts represent chemical shift. The estimated epoxy group content of the rubber at various amounts of freshly prepared peracetic acid and epoxidation times are shown in Figure 4. The epoxy group content was dependent upon amount of peracetic acid and time of epoxidation ( $t$ ); the higher the amount of peracetic acid, the higher was the epoxy group content. Furthermore, the epoxy group content increased abruptly up to 3 h and, then, it reached plateau. Figure 5 shows the gel content of EDPNR. The gel content was dependent upon the amount of peracetic

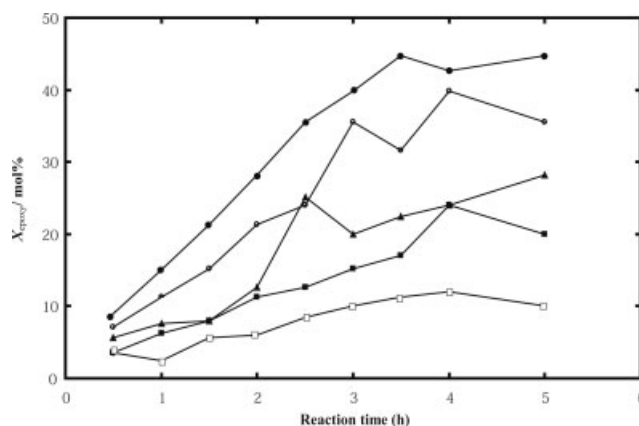


Figure 4  $X_{\text{epoxy}}$  of EDPNR versus reaction time at  $\text{CH}_3\text{COOOH}$  amount of 10 mL ( $\square$ ), 20 mL ( $\blacksquare$ ), 30 mL ( $\blacktriangle$ ), 40 mL ( $\circ$ ), and 50 mL ( $\bullet$ ), respectively.

oxy group content,  $X_{\text{epoxy}}$ , was, thus, estimated from intensity ratio of the signals, as follows:

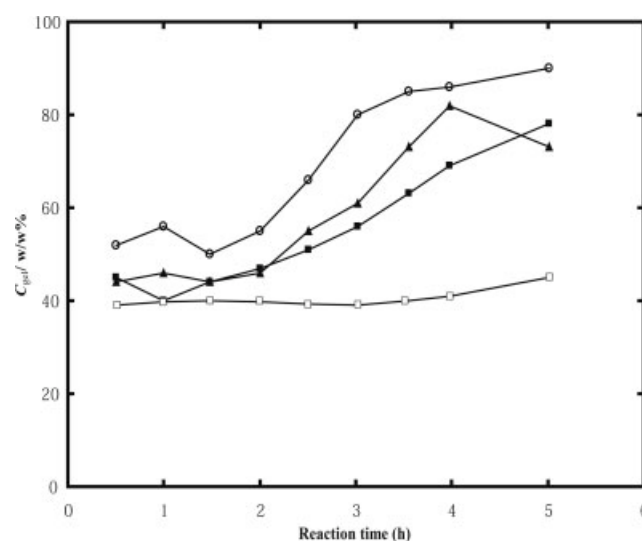


Figure 5 Gel content of EDPNR versus reaction time at  $\text{CH}_3\text{COOOH}$  amount of 10 mL ( $\square$ ), 20 mL ( $\blacksquare$ ), 30 mL ( $\blacktriangle$ ), and 40 mL ( $\circ$ ), respectively.

TABLE I  
Chemical Shifts of  $^1\text{H}$  NMR Spectra for DPNR and EDPNR

Signals	Chemical shifts (ppm)	DPNR	EDPNR
a	1.6	$\text{CH}_3(-\text{C}=\text{C}-)$	
b	1.2		$\text{CH}_3(-\text{O}-\text{C}-)$
c	2.1	$-\text{CH}_2-$	$-\text{CH}_2-$
d	5.1	$-\text{CH}(-\text{C}=\text{C}-)$	
e	2.7		$-\text{CH}$ Oxiran
f	1.5		$-\text{CH}_2-$

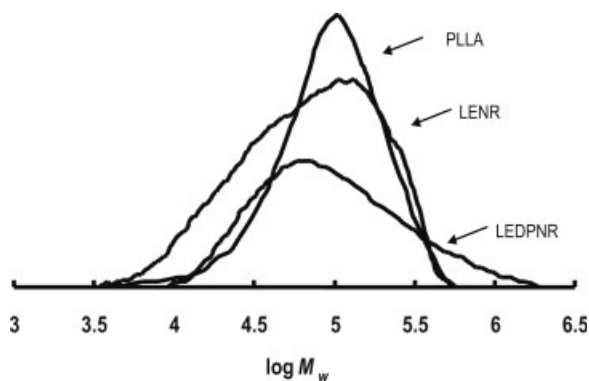


Figure 6 SEC curves for LENR, LEDPNR, and PLLA.

acid, as in the case of epoxy group content. However, the gel content was almost independent of the time of epoxidation until 2 h and then it increased linearly. The increase in gel content may be attributed to side reactions that occur during epoxidation. As the result, a suitable time of epoxidation for DPNR was determined to be 3 h. Since EDPNR contained the significant amount of gel fraction, in order to reduce the amount of gel fraction, it was degraded with ammonium persulfate to prepare LEDPNR, before mixing with PLLA.

After depolymerization, LENR and LEDPNR were thoroughly soluble in toluene, THF, and chloroform, so that the rubber was subjected to SEC measurement. Figure 6 shows a typical SEC curve for depolymerized ENR and depolymerized EDPNR together with PLLA. Average molecular weights for depolymerized ENR, depolymerized EDPNR and PLLA were estimated on the basis of the molecular weight of standard polystyrene. The estimated values of weight average molecular weight,  $M_w$ , number average molecular weight,  $M_n$ , and polydispersity,  $M_w/M_n$ , are tabulated in Table II, together with the epoxy group content.

Figure 7 shows DSC thermograms for LENR, LEDPNR, and PLLA. Glass transition temperature,  $T_g$  was estimated to be a point of inflection in glass transition. The values of  $T_g$  and  $T_m$  are shown in Tables III and IV. The  $T_g$  of LEDPNR was quite similar to that of LENR, perhaps due to similar  $X_{\text{epoxy}}$ ,  $M_w$ ,  $M_w/M_n$ . On the other hand, for PLLA, the  $T_g$  and  $T_m$  were 337 K and 450 K, respectively.  $T_g$  of PLLA was higher than that of LEDPNR and LENR, as is clearly seen in Table III. The  $T_g$  of LENR,  $T_g$  of

TABLE II  
Characteristics of LENR, LEDPNR, and PLLA

Specimens	$M_w/10^5$	$M_n/10^4$	$M_w/M_n$	$X_{\text{epoxy}}/\text{mol } \%$
LENR	1.01	4.08	2.49	43.1
LEDPNR	1.53	5.99	2.56	43.5
PLLA	1.20	7.1	1.69	

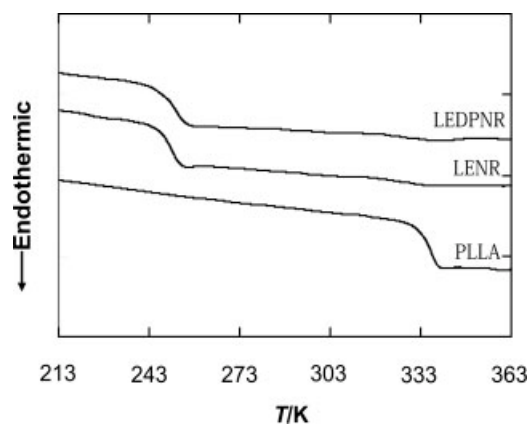


Figure 7 DSC thermograms for LENR, LEDPNR, and PLLA.

PLLA, and  $T_m$  of PLLA in the blends were almost independent of the reaction time. This suggests that little reaction occurs between LENR and PLLA. In contrast, as shown in Table IV, the  $T_g$  of LEDPNR in the LEDPNR/PLLA blend was dependent upon the reaction time; the higher was  $T_g$  of LEDPNR in the blends, i.e.  $T_g = 251\text{--}259$  K. Furthermore,  $T_g$  and  $T_m$  of PLLA in the blends decreased significantly:  $T_g = 337\text{--}332$  K,  $T_m = 450\text{--}445$  K. Since  $T_m$  depression is a function of composition, the PLLA phase may contain a small amount of LEDPNR while the LEDPNR phase may contain a small amount of PLLA, after reaction at 473 K. Figure 8 shows DSC thermograms of LEDPNR/PLLA blend, which was reacted at 473 K for 0.5–20 min. The  $T_g$  was clearly shown in the thermograms. The changes in  $T_g$  and  $T_m$  may be attributed to reaction between epoxy group of LEDPNR and carboxyl group of PLLA, which is explained to be due to the removal of proteins.

Figure 9 shows the phase contrast micrographs for LEDPNR/PLLA blend, which was reacted at 473 K for 0–20 min. In the micrographs (a)–(c), the island–matrix morphology was shown clearly. However, in the micrographs (d)–(g), interface between island

TABLE III  
 $T_g$  and  $T_m$  of LENR/PLLA Blend after Reacted at 473 K for 0.5–20 min

Specimens	Reaction time (min)	LENR $T_g$ (K)	PLLA $T_g$ (K)	PLLA $T_m$ (K)
LENR	–	250	–	–
PLLA	–	–	337	450
LENR/PLLA0	0	251	334	448
LENR/PLLA1	0.5	250	335	448
LENR/PLLA2	1	250	335	448
LENR/PLLA3	3	250	335	448
LENR/PLLA4	5	250	335	448
LENR/PLLA5	10	251	335	448
LENR/PLLA6	20	250	334	447

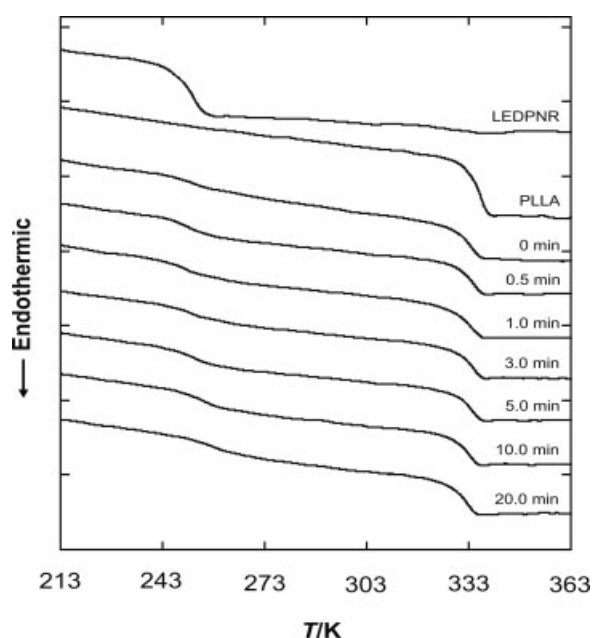


**TABLE IV**  
 $T_g$  and  $T_m$  of LEDPNR/PLLA Blend after Reacted  
 at 473 K for 0.5–20 min

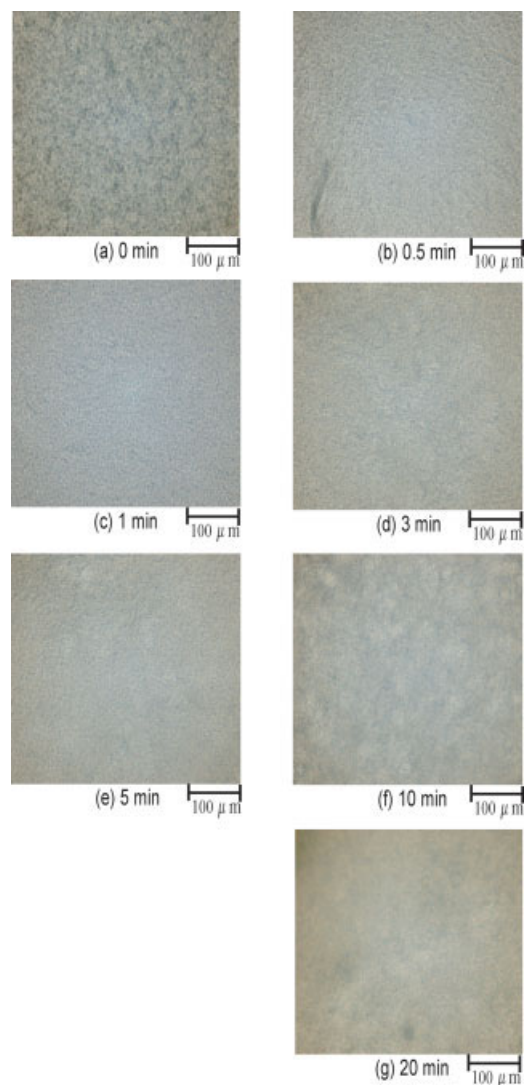
Specimens	Reaction time (min)	LEDPNR $T_g$ (K)	PLLA $T_g$ (K)	PLLA $T_m$ (K)
LEDPNR	–	251	–	–
PLLA	–	–	337	450
LEDPNR/PLLA0	0	252	334	449
LEDPNR/PLLA1	0.5	251	335	448
LEDPNR/PLLA2	1	251	334	448
LEDPNR/PLLA3	3	251	335	448
LEDPNR/PLLA4	5	254	333	447
LEDPNR/PLLA5	10	257	333	446
LEDPNR/PLLA6	20	259	332	445

and matrix was unclear after annealing for more than 3 min. Additionally, the pictures for LENR/ PLLA and LEDPNR/PLLA at 473 K for 0–20 min are shown in Figure 10. In the micrographs for LENR/ PLLA (a), (b), the island–matrix morphology was shown clearly even after heating at 473 K for 20 min. In contrast, in the micrographs for LEDPNR/PLLA, (c), (d), the interface between island and matrix was unclear after reacted at 473 K for 20 min. This may be explained to be due to the formation of the graft copolymer as a compatibilizer, i.e. LEDPNR-*graft*-PLLA. The possible reaction between LEDPNR and PLLA is shown in Figure 11.

The  $^{13}\text{C}$  NMR spectra for LEDPNR/PLLA and LENR/PLLA blends reacted at 473 K for 20 min are shown in Figure 12. In the  $^{13}\text{C}$  NMR spectrum for LEDPNR/PLLA blend, a new signal appeared at 73.5 ppm after reaction at 473 K for 20 min. This



**Figure 8** DSC thermograms for LEDPNR/PLLA blend reacted at 473 K for 0–20 min.

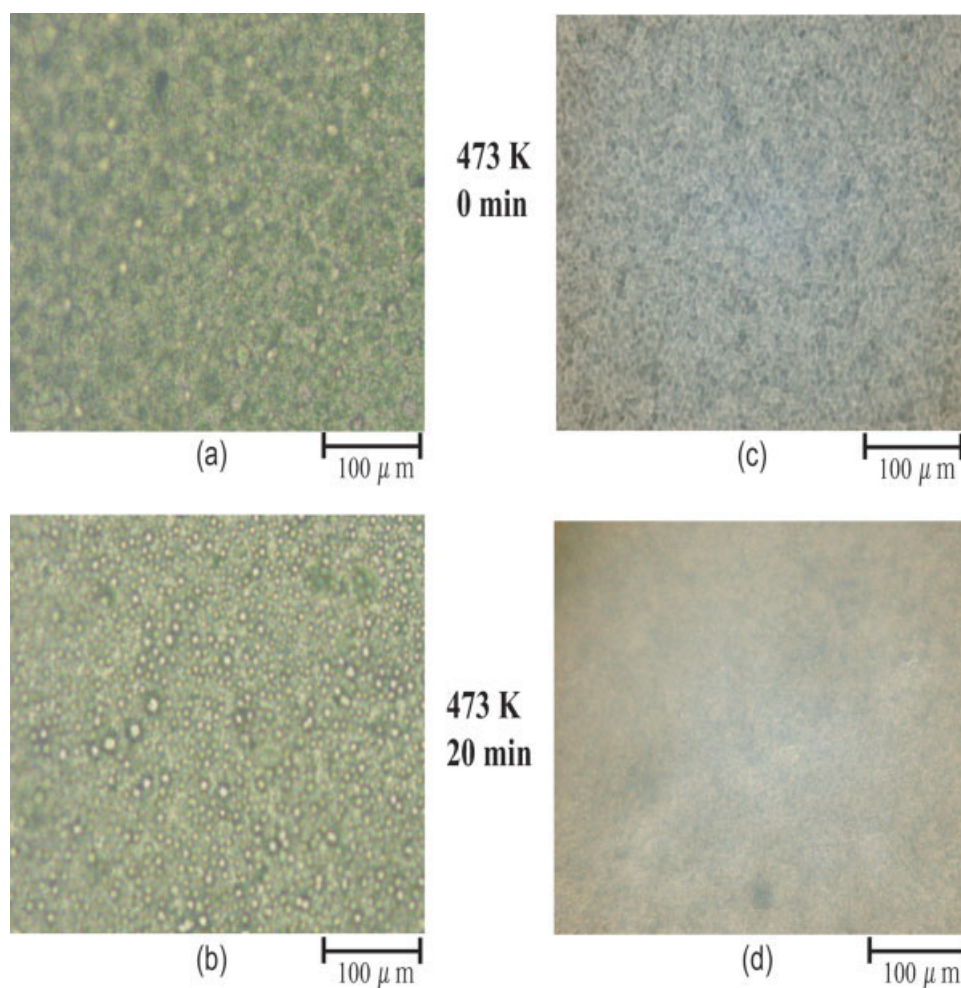


**Figure 9** Phase contrast micrographs for LEDPNR/PLLA blend reacted at 473 K for 0–20 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

was assigned to the ester linkage formed between the epoxy group and the ester group, according to Furst method.<sup>24</sup> This is a supporting evidence that the reaction occurs between the epoxy group of LEDPNR and the ester group of PLLA at 473 K. In contrast, in the  $^{13}\text{C}$  NMR spectrum for LENR/PLLA blend, no signal appeared at 73.5 ppm, after reaction at 473 K for 20 min. This may be attributed to side reaction, since LENR contains significant amount of proteins which are attracted with water.

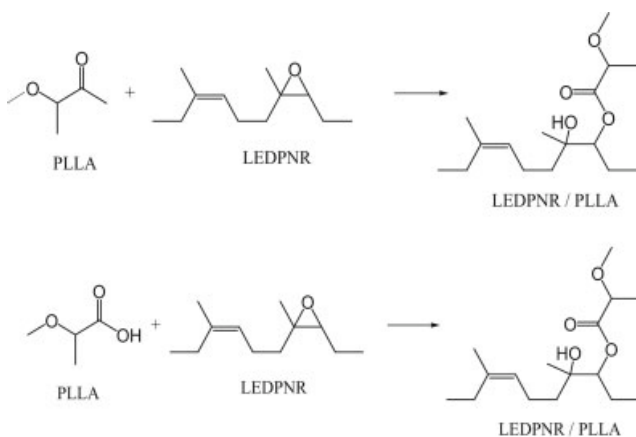
## CONCLUSION

A suitable time of epoxidation for DPNR was determined to be 3 h. The EDPNR was degraded with ammonium persulfate to prepare LEDPNR. The

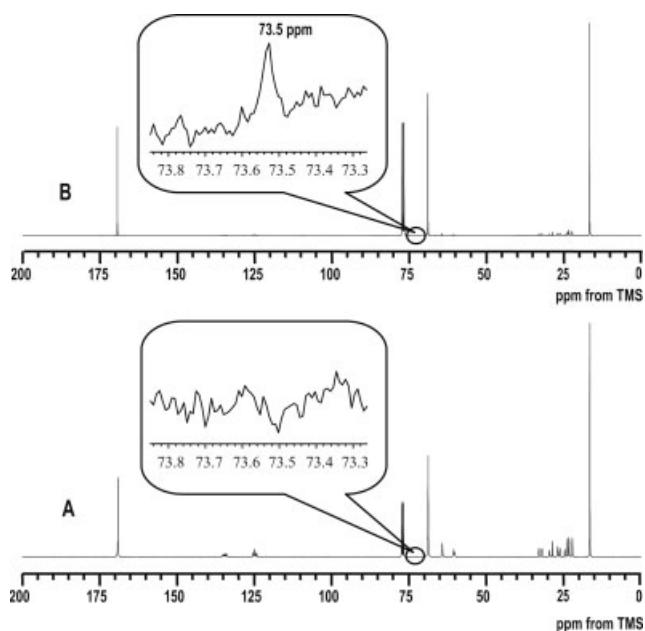


**Figure 10** Phase contrast micrographs for LENR/PLLA and LEDP NR/PLLA blends reacted at 473 K for 0 and 20 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

LEDP NR was used for the reaction after mixing with PLLA. The compatibility of the blend was enhanced after reaction. It is concluded that the reaction occurs between the epoxy group of LEDP NR



**Figure 11** The possible reaction between LEDP NR and PLLA.



**Figure 12**  $^{13}\text{C}$  NMR spectra for (A) LENR/PLLA and (B) LEDP NR/PLLA blends reacted at 473 K for 20 min.

and the ester group of PLLA in solid state due to the removal of proteins from the rubber to enhance the compatibility of the blend.

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