

Quantitative Analysis for Reaction Between Epoxidized Natural Rubber and Poly (L-Lactide) Through $^1\text{H-NMR}$ Spectroscopy

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ABSTRACT: Reaction between epoxidized natural rubber and poly(L-lactide) (PLLA) was investigated quantitatively in terms of conversion of the epoxidized natural rubber. The epoxidized natural rubber was prepared by epoxidation of high ammonia natural rubber (HA-NR) or deproteinized natural rubber (DPNR) with peracetic acid followed by depolymerization with ammonium persulfate. The resulting liquid HA-NR having epoxy group (LENR) or liquid DPNR having epoxy group (LEDPNR) were subjected to heating at 473 K for 20 min, after blending with PLLA. The products were characterized through

morphology observation, DSC measurement, and $^1\text{H-NMR}$ spectroscopy. The conversions of the rubbers were estimated from intensity ratio of signals in $^1\text{H-NMR}$ spectrum for the products after removing unreacted rubber with toluene. Difference in the estimated conversion between the LENR/PLLA and LEDPNR/PLLA blends was interpreted in relation to proteins present in the rubber. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3598–3604, 2010

Key words: epoxidized natural rubber; poly(L-lactide); NMR

INTRODUCTION

Epoxy group of epoxidized natural rubber (ENR) has been recognized to be an indispensable functional group for a preparation of novel materials, since it can react with the other functional groups, such as carboxylic acid, amine, and alcohol.¹ For instance, it is possible to prepare block or graft copolymers consisting of ENR and poly (L-lactide) (PLLA) through the reaction between the epoxy group and the carboxylic acid or ester.^{2–4} The resulting copolymers may enhance a compatibility of the ENR/PLLA blend, since it exists at interface between ENR and PLLA.^{5,6} When the copolymers are formed during mixing process of ENR with PLLA, the resulting ENR/PLLA blend may exhibit a superior impact strength,⁷ due to not only an island-matrix structure consisting of matrix of rigid PLLA and dispersoid of flexible ENR but also the copolymers existing at the interface between ENR and PLLA, as in the case of poly(1,4-butylene terephtha-

late)/polycarbonate/ethylene-propylene-ethylidene norbornene-*g*-(styrene-*co*-acrylonitrile) blend.⁸ Thus, it is important to prove the formation of the compatibilizer through a quantitative analysis for the reaction.

In the previous work, preparation of ENR/poly(lactide) (PLA) blend was investigated by Okamoto et al.⁹ They reported that the Izod impact strength of PLA increased from 2.4 to 10.8 kJ/m² after blending it with ENR. The increase in the Izod impact strength was explained to be due to a formation of chemical linkages between ENR and PLA, without any evidences. However, recently, we found that proteins present in ENR prevented the reaction between ENR with PLLA,¹⁰ since the proteins were attracted with water,¹¹ which interacted with not only ENR but also PLLA. Thus, we prepared a liquid deproteinized natural rubber having epoxy group (LEDPNR).^{12–14} After the reaction of the resulting LEDPNR and PLLA at 473 K for 20 min, the formation of the chemical linkages between LEDPNR and PLLA were proved through $^{13}\text{C-NMR}$ spectroscopy.¹⁰ Furthermore, we found that few chemical linkages were formed between ENR and PLA used by Okamoto et al. Since the impact strength of the blend depends on the amount of the

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resulting compatibilizer,^{7,8,15,16} it is necessary to perform the quantitative analysis of the reaction.

The quantitative analysis is carried out with either conversion of the polymers or the amount of the resulting copolymers. For example, the conversion of LEDPNR may be estimated through ¹H-NMR measurement for LEDPNR/PLLA blend after extracting unreacted LEDPNR. However, in the ¹H-NMR spectrum for the LEDPNR/PLLA blend, signals characteristic of methyl and methine protons of PLLA at 1.6 and 5.2 ppm is overlapped with signals of LEDPNR at 1.5–1.7 and 5.1 ppm,¹⁷ which have not been assigned in the previous literature.^{18,19} Hence, the assignments of the signals of LEDPNR at 1.5–1.7 and 5.1 ppm must be performed to estimate the conversion of LEDPNR. In the previous work, we successively assigned the signals in aliphatic region of the ¹H-NMR spectrum for LEDPNR through 2D NMR spectroscopy: that is, 1.5–1.7 ppm assigned to methylene protons of epoxidized *cis*-1,4-isoprene units and methyl protons of *cis*-1,4-isoprene units, and 2.0–2.2 ppm to methylene protons of *cis*-1,4-isoprene units.²⁰ Thus, on the basis of these assignments, we may estimate the conversion of LEDPNR through ¹H-NMR spectroscopy.

In this study, to accomplish the quantitative analysis for the reactive mixing of epoxidized natural rubber with PLLA, the reaction of LEDPNR with PLLA was performed at higher temperature after mixing them as a model reaction. The characterization of the resulting blend was performed through solution state ¹H-NMR spectroscopy.

EXPERIMENTAL

PLLA was supplied from Toyota Motor Corporation. Number-average molecular weight, M_n , weight-average molecular weight, M_w , and polydispersity index, M_w/M_n , of PLLA is tabulated in Table I. Natural rubber latex used in this study was a commercial high ammonia natural rubber (HA-NR) latex (Golden Hope, Malaysia).

Deproteinization of HA-NR latex was achieved by incubation of the latex with 0.1% w/v urea (Nacalai tesque 99.5%) and 1.0% w/v sodium dodecyl sulfate (SDS) (Kishida Reagents Chemicals, 99 %) for 1 h at 303 K followed by centrifugation at $10,000 \times g$.^{21–23} Resulting cream fraction was redispersed in 1.0% w/v SDS solution to adjust 30% DRC latex, and then it was washed twice by centrifugation to prepare deproteinized natural rubber (DPNR) latex.

DPNR latex, precooled at 283 K, was subjected to epoxidation in the latex stage with fresh peracetic acid (33% v/v concentration) for 3 h. After completion of the reaction, pH of the latex was adjusted to about 9 with an ammonia solution (Nacalai tesque, 28 %). Depolymerization of the resulting epoxidized

TABLE I
 M_n , M_w , M_w/M_n , Gel Content, and T_g of DPNR, LEDPNR, LENR, and PLLA

Specimens	$M_n/10^5$ (g mol ⁻¹)	$M_w/10^5$ (g mol ⁻¹)	M_w/M_n	Gel content (% w/w)	T_g/K
PLLA	0.71	1.2	1.7	0	337
HA-NR	2.2	6.9	3.2	40.8	212
DPNR	1.8	6.9	3.9	38.7	213
LENR	0.41	1.0	2.5	0	250
LEDPNR	0.60	1.5	2.6	0	251

DPNR latex was carried out by the incubation of the latex with 0.1% w/v ammonium persulfate (Nacalai tesque, 99.5%) and 1.5% w/v propanal (Nacalai tesque, 99.5%) at 338 K for 10 h to prepare liquid epoxidized DPNR (LEDPNR) latex.^{12–14} The LEDPNR latex was coagulated with excess amount of methanol (Nacalai tesque, 99 %) followed by purification with toluene (Nacalai tesque, 99.5%) and methanol, and the coagulated LEDPNR was dried at 303 K for a week under reduced pressure.

LEDPNR/PLLA blend was prepared by dissolving the rubber and PLLA at blend ratio of 4–6 into chloroform (Nacalai tesque, 99 %), and it was followed by precipitating the sample with excess amount of methanol. The resulting LEDPNR/PLLA blend was dried under reduced pressure at room temperature for a week. The reaction of the LEDPNR/PLLA blend was carried out by heating at 473 K for 20 min.¹⁰ After completion of heating, the sample was immersed in toluene for several hours to remove unreacted rubber, and then unextracted fraction was dried under reduced pressure at room temperature for a week.

Liquid epoxidized HA-NR (LENR)/PLLA blend was prepared in same manner as the preparation of the LEDPNR/PLLA blend, except for the deproteinization process. The procedure to prepare the LEDPNR/PLLA blend and the LENR/PLLA blend is schematically represented in Figure 1.

The apparent molecular weights and molecular weight distributions of the rubbers were determined with a size exclusion chromatography system from Tosoh, with a computer-controlled dual pump, an RI-8012 differential refractive-index detector, a UV-8011 ultraviolet spectroscopy detector, and a series of three G4000H_{HR} columns (bead size 5 μm, exclusion molecular weight of 400 K for polystyrene) or a series of three G6000H_{HR} columns (bead size 5 μm, exclusion molecular weight of 4000 K for polystyrene) with 300 mm long with a 7.8 mm i.d. THF was used as an eluent, and the flow rate was 0.5 mL/min at room temperature. Standard polystyrenes were used for a calibration.

Gel content of the rubber was determined by swelling the rubber in dried toluene in the dark for

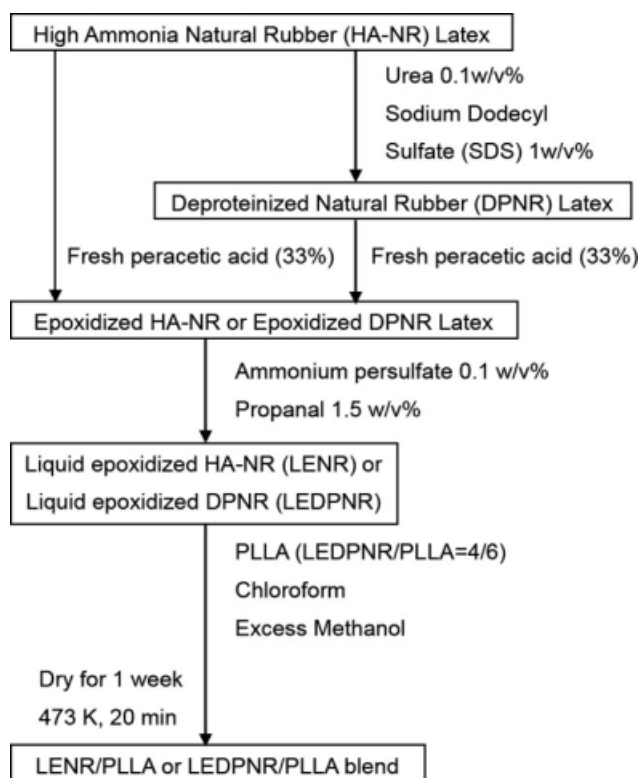


Figure 1 Schematic illustration of preparing LEDPNR/PLLA blend and LENR/PLLA blend.

a week. The gel fraction was separated by centrifugation at $10,000 \times g$ for 30 min and dried at room temperature under reduced pressure for a week. The gel content, C_{gel} , was estimated, as in the following equation:

$$C_{\text{gel}} = \frac{W_{\text{gel}}}{W_{\text{rubber}}} \times 100$$

where W_{gel} and W_{rubber} are the weight of gel fraction and the rubber, respectively.

Morphology of the LEDPNR/PLLA blend and LENR/PLLA blend were observed by optical light microscopy, using a Nikon ECLIPSE E600 POL microscope equipped with CCD Color Digital Camera Module (SONY DFW-SX900). LEDPNR/PLLA blend or LENR/PLLA blend, sandwiched between two cover glasses, were placed on a stage without temperature control. At room temperature, the photomicrograph of the samples was taken with the CCD Color Digital Camera Module.

DSC measurements of the rubbers were performed with a Seiko Instruments DSC 220 differential scanning calorimeter over the temperature range of 153–473 K at the heating rate of 10 K/min. Samples of about 10 mg were encapsulated in an aluminum pan. Glass transition temperature, T_g , of the samples was determined from a point of inflection in DSC curve.

NMR measurements were carried out with a JEOL ECA-400 NMR spectrometer operating at 399.65 MHz for ^1H . The samples were dissolved in chloroform-*d* (Nacalai tesque, 99.8%) without tetramethylsilane (TMS) to make 2% w/v solution. Chemical shifts were referred to chloroform-*d*/in. ^1H -NMR measurements were carried out at 323 K at the pulse repetition times of 7 s, the pulse width of 6.1 μs , and pulse delay of 4.24 s, respectively.

RESULTS AND DISCUSSION

Table I shows number-average molecular weight, M_n , weight-average molecular weight, M_w , polydispersity index, M_w/M_n , and gel content of PLLA, HA-NR, DPNR, LENR, and LEDPNR, respectively. HA-NR used in this work contained 40.8% w/w gel, which was ascribed to physical and chemical crosslinks due to interactions of nonrubber components, that is, proteins and phospholipids, present in the rubber.²⁴ The gel content of the rubber decreased from 40.8 to 38.7% w/w after deproteinization, reflecting the decomposition of physically crosslinking junctions.^{21,22} The remaining gel of DPNR is assigned to three dimensional networks held with the chemical crosslinking junctions, which are formed during the long term preservation of the latex, as reported in the previous article.²⁵ The gel makes it impossible to extract the rubber after the reaction with PLLA. Therefore, we degrade the rubber after epoxidation, since the gel content increases during epoxidation.¹² After the degradation, the gel was completely decomposed, and the molecular weight of the rubbers decreased to about one-fifth. The LEDPNR and LENR as a source were subjected to ^1H -NMR measurement to determine the epoxy group content.

Figure 2 shows typical ^1H -NMR spectra for DPNR, LENR, and LEDPNR. In the spectrum for DPNR, signals characteristic of methyl, methylene, and unsaturated methine protons of *cis*-1,4-isoprene unit appeared at 1.7, 2.1, and 5.1 ppm, respectively. In contrast, for LEDPNR and LENR, new signals appeared at 1.28, 1.55, 2.2, and 2.7 ppm. The signals were assigned, according to the previous work: that is, the signal at 1.28 ppm assigned to methyl protons of epoxidized *cis*-1,4-isoprene unit, the signal at 1.55 ppm to methylene protons of the epoxidized *cis*-1,4-isoprene unit, the signal at 2.2 ppm to methylene protons of the *cis*-1,4-isoprene unit, and the signal at 2.7 ppm to methine protons of the epoxidized *cis*-1,4-isoprene unit.²⁰ The epoxy group content of LEDPNR and LENR was estimated from intensity ratio of the signals at 2.7 and 5.1 ppm, as in the following equation;

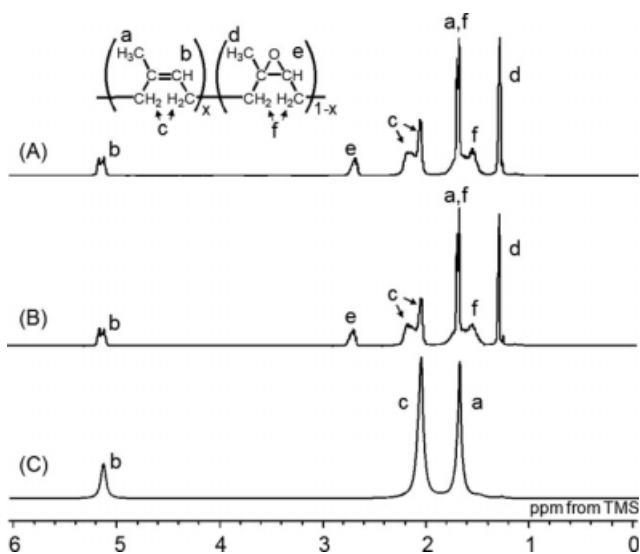


Figure 2 $^1\text{H-NMR}$ spectra for (A) LEDPNR, (B) LENR, and (C) DPNR.

$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \quad (1)$$

where I is the intensity ratio of the signals and the subscript numbers represent chemical shift (ppm). The estimated epoxy group contents of LEDPNR and LENR were 43.1 and 42.7%, respectively.

Figure 3 shows optical light micrographs for LEDPNR/PLLA and LENR/PLLA blends before and after the heating. Before the heating, conventional island-matrix structure was observed in the micrographs for the LEDPNR/PLLA and LENR/PLLA blends. After heating the LEDPNR/PLLA blend at 473 K for 20 min, the interface between the matrix of PLLA and the island of LEDPNR was found to be obscured, suggesting the formation of the compatibilizer. In contrast, for the LENR/PLLA blend, the structure was observed even after the heating. The difference in the morphology between the LEDPNR/PLLA and LENR/PLLA blends may be due to the proteins present in LENR. To confirm the reaction between LEDPNR and PLLA, DSC measurement was carried out.

Glass transition temperatures, T_g , of LEDPNR, LENR, and PLLA as a source are tabulated in Table I. The T_g of LEDPNR was confirmed to be identical to that of LENR, reflecting the similar epoxy group content and molecular weight. DSC thermograms for the LEDPNR/PLLA and LENR/PLLA blends before and after the heating are shown in Figure 4, in which the arrows represent the T_g of the blend determined as a point of the inflection of the curves. The LEDPNR/PLLA and LENR/PLLA blends showed two T_g s before the heating, due to the phase separation of the blend. Since the T_g of PLLA is

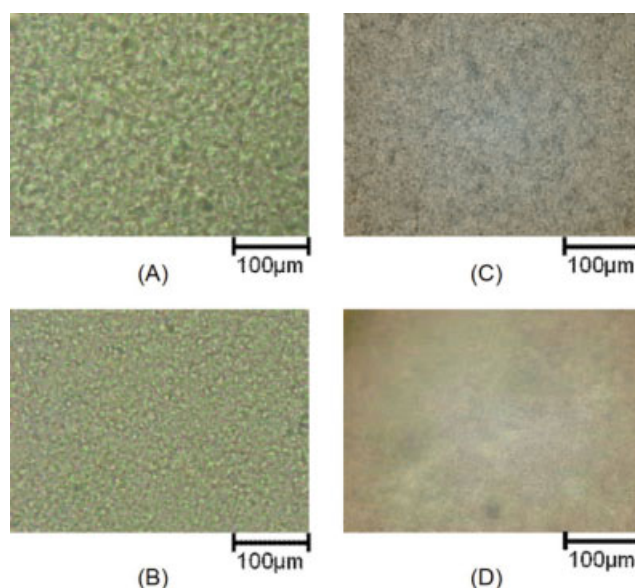


Figure 3 Morphology of (A) the LENR/PLLA blend before the heating, (B) the LENR/PLLA blend after the heating, (C) the LEDPNR/PLLA blend before the heating, and (D) the LEDPNR/PLLA blend after the heating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

higher than those of LEDPNR and LENR as shown in Table I, the lower T_g in the thermograms may represent the glass transition of LEDPNR or LENR

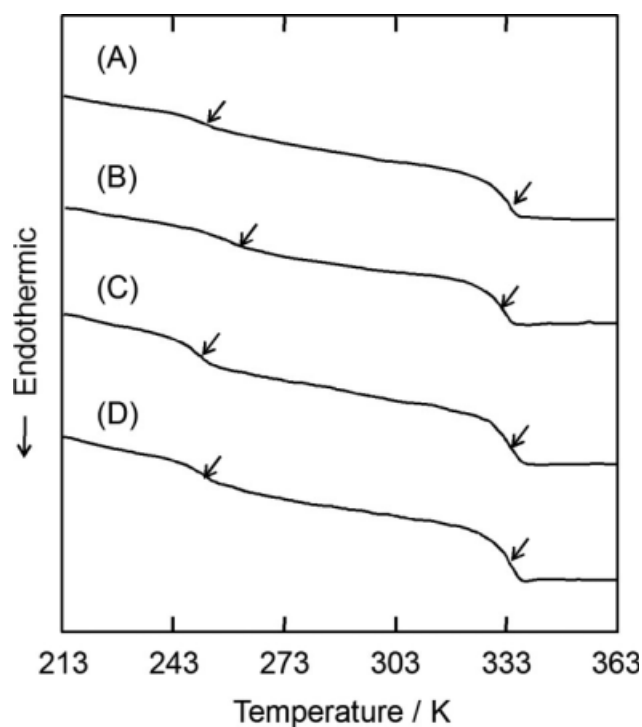


Figure 4 Typical DSC thermograms for (A) the LEDPNR/PLLA blend before the heating, (B) the LEDPNR/PLLA blend after the heating, (C) the LENR/PLLA blend before the heating, and (D) the LENR/PLLA blend after the heating.

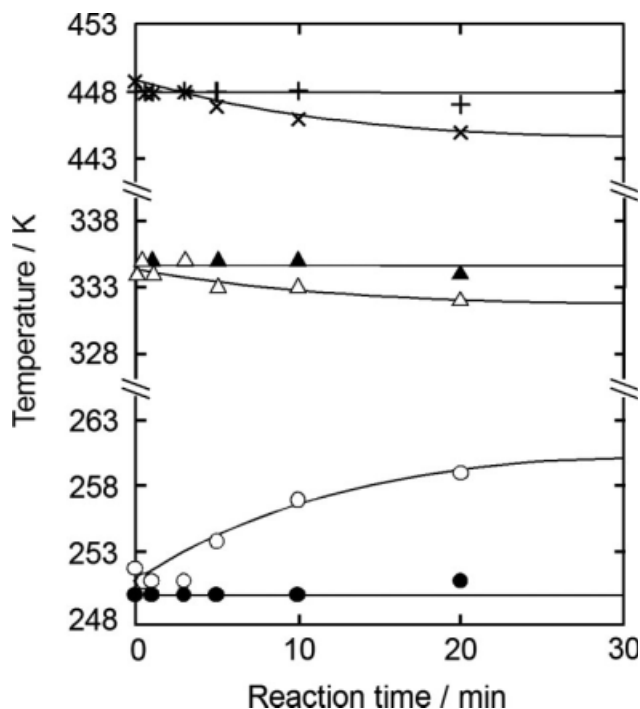


Figure 5 T_{ms} of PLLA rich phase in (x) the LEDPNR/PLLA blend and (+) the LENR/PLLA blend, T_{gs} of PLLA rich phase in (Δ) the LEDPNR/PLLA blend and (\blacktriangle) the LENR/PLLA blend, and T_{gs} of epoxidized natural rubber rich phase in (\circ) the LEDPNR/PLLA blend and (\bullet) the LENR/PLLA blend.

rich phase, and the higher T_g may represent that of PLLA rich phase. For the LEDPNR/PLLA blend, the T_g of the LEDPNR rich phase rose after the heating, whereas that of the PLLA rich phase lowered. The changes in the T_g s are explained to be due to the formation of the graft or block copolymers as a compatibilizer, which enhance the compatibility of the LEDPNR/PLLA blend. In contrast, for the LENR/PLLA blend, the T_g s of the LENR rich phase and the PLLA rich phase did not change after the heating.

To confirm the changes in T_g s, the values of T_g s and T_m s of the LEDPNR/PLLA and LENR/PLLA blends were plotted against the reaction time in Figure 5. As for the LEDPNR/PLLA blend, the value of the T_g of the LEDPNR rich phase increased from 251 to 259 K, whereas the values of the T_g and T_m of the PLLA rich phase decreased from 334 K and 449 K to 332 K and 445 K, respectively, after the reaction for 20 min. In contrast, the values of the T_g s and T_m of the LENR/PLLA blend did not change. This suggests that the reaction between the epoxy group of epoxidized natural rubber and PLLA may occur after removal of the proteins from natural rubber.

The conversion of LEDPNR may be estimated from the intensity ratio of the signals in $^1\text{H-NMR}$ spectrum after removing the unreacted LEDPNR, as in the following equation;

Conversion (%)

$$= \frac{I_{\text{LEDPNR, after extraction}}/I_{\text{PLLA}}}{I_{\text{LEDPNR, before extraction}}/I_{\text{PLLA}}} \times 100 \quad (2)$$

where I is the intensity ratio of the signals and subscript represents the materials. To estimate the conversion based upon the eq. (2), $^1\text{H-NMR}$ measurement was carried out. Figure 6 shows typical $^1\text{H-NMR}$ spectrum for the LEDPNR/PLLA blend, together with that of PLLA. In the spectrum for PLLA, methyl and methine protons of PLLA appeared at 1.6 and 5.2 ppm. After blending PLLA with LEDPNR, the signals of PLLA were confirmed to overlap with those of LEDPNR. Therefore, the I_{LEDPNR} and the I_{PLLA} in the eq. (2) were estimated from the intensity ratio of the signals, as in the following equations;

$$I_{\text{LEDPNR}} = I_e + I_h = I_e + \frac{1 - X_{\text{epoxy}}}{X_{\text{epoxy}}} \times I_e \quad (3)$$

$$I_{\text{PLLA}} = I_a = I_{a,c,h} - I_c - I_h$$

$$= I_{a,c,h} - \frac{3}{4}I_e - \frac{1 - X_{\text{epoxy}}}{X_{\text{epoxy}}} \times I_e \quad (4)$$

where X_{epoxy} is the estimated epoxy group content of the rubber, I is the intensity ratio of the signals, and subscript alphabets represent the assignment of the signals marked in Figure 6. To estimate the conversion of LEDPNR according to the equations, almost all unreacted LEDPNR must be removed. Therefore, to confirm the removal of the unreacted rubber, a ratio, $I_{\text{LEDPNR}}/I_{\text{PLLA}}$, was plotted against extraction time, together with that of LENR to PLLA in the LENR/PLLA blend, that is, $I_{\text{LENR}}/I_{\text{PLLA}}$, which was estimated in same manner as the $I_{\text{LEDPNR}}/I_{\text{PLLA}}$.

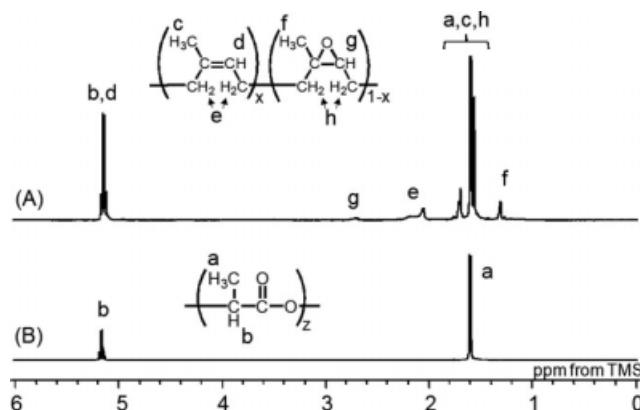


Figure 6 Typical $^1\text{H-NMR}$ spectra for (A) the LEDPNR/PLLA blend and (B) PLLA.

Figure 7 shows extraction curves for the unheated LEDPNR/PLLA blend, the heated LEDPNR/PLLA blend, and the heated LENR/PLLA blend, in which the $I_{\text{LEDPNR}}/I_{\text{PLLA}}$ and $I_{\text{LENR}}/I_{\text{PLLA}}$ were estimated by using the eq. (3) and (4). As for the unheated LEDPNR/PLLA blend, the $I_{\text{LEDPNR}}/I_{\text{PLLA}}$ reduced to 0.02 after the extraction of the blend with toluene for 36 h. This demonstrates that the block or graft copolymers consisting of LEDPNR and PLLA were not formed without heating. Therefore, the heated LEDPNR/PLLA and LENR/PLLA blends were extracted with toluene for 36 h. After the extraction for 36 h, the $I_{\text{LEDPNR}}/I_{\text{PLLA}}$ for the heated LEDPNR/PLLA blend decreased to 0.15 and reached plateau, whereas the $I_{\text{LENR}}/I_{\text{PLLA}}$ for the heated LENR/PLLA blend reduced to 0.03. This is a strong evidence of the formation of the block or graft copolymers in the heated LEDPNR/PLLA blend. In contrast, for the heated LENR/PLLA blend, it is obvious that less reaction occurred between LENR and PLLA, since the value of the $I_{\text{LENR}}/I_{\text{PLLA}}$ after the extraction for 36 h was similar to that of the unheated LEDPNR/PLLA blend.

The amount of the reacted epoxidized natural rubber was quantitatively estimated through $^1\text{H-NMR}$ spectroscopy. Thus, the conversions of the epoxidized natural rubbers were estimated through the eqs. (2)–(4). The estimated conversions of the epoxidized natural rubbers were tabulated in Table II. The conversion for the LEDPNR/PLLA blend was higher than that for the LENR/PLLA blend.

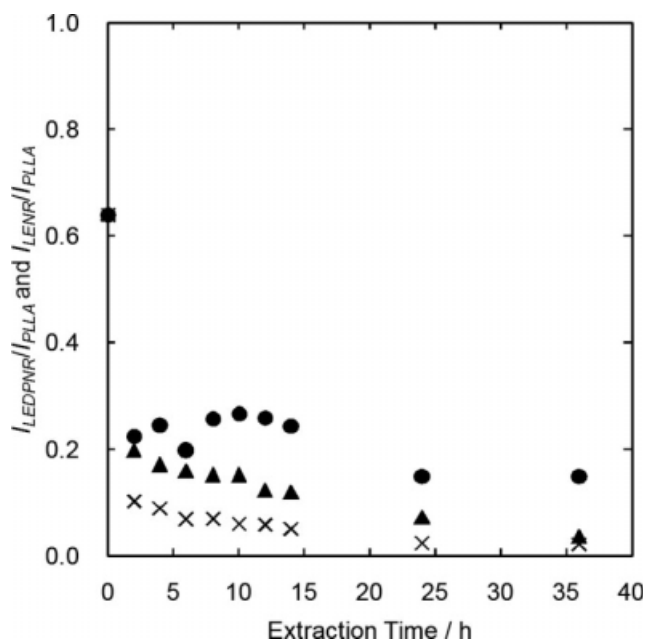


Figure 7 Extraction time versus (\times) $I_{\text{LEDPNR}}/I_{\text{PLLA}}$ for the unheated LEDPNR/PLLA blend, (\bullet) $I_{\text{LEDPNR}}/I_{\text{PLLA}}$ for the heated LEDPNR/PLLA blend, and (\blacktriangle) $I_{\text{LENR}}/I_{\text{PLLA}}$ for the heated LENR/PLLA blend.

TABLE II
Conversion of Epoxidized Natural Rubber

	Unheated LEDPNR/ PLLA	Heated LEDPNR/ PLLA	Heated LENR/ PLLA
Conversion (%)	3.5	23.4	5.8

The lower conversion of LENR/PLLA blend may be attributed to the proteins present in LENR, since the proteins were reported to prevent the chemical reactions of natural rubber in the previous work.^{10,26} Consequently, through the quantitative analysis established in this work, the deproteinization of natural rubber was proved to be necessary for the reaction between the epoxy group of epoxidized natural rubber with PLLA.

CONCLUSIONS

Quantitative analysis of the reaction between LEDPNR and PLLA was established through $^1\text{H-NMR}$ spectroscopy. From the morphology observation and DSC measurement, compatibility of the LEDPNR/PLLA blend was found to be enhanced by the reaction at 473 K for 20 min, whereas that of the LENR/PLLA blend was not enhanced. The estimated conversions of LEDPNR and LENR were 23 and 6%, respectively, which is rationally consistent with the results from the morphology observation and the DSC measurement. It is concluded that the removal of the proteins from natural rubber is necessary for the reaction between the epoxy group of epoxidized natural rubber and PLLA.

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