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Enhancement of molecular weight reduction of natural rubber in triphasic CO_2/toluene/H_2O systems with hydrogen peroxide for preparation of biobased polyurethanes

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Abstract: Molecular weight reduction of natural rubber (NR) with hydrogen peroxide (H_2O_2) oxidizing agent is limited in biphasic water-toluene systems that is attributed to mass transfer. In this work, CO_2 was applied to the (aqueous H_2O_2)-(toluene-NR) systems with the objective of improving reaction efficiency. Experiments were performed on the reaction system with CO_2 at 12 MPa and at reaction temperatures and times of 60°C–80°C and 1 h–10 h to evaluate the reaction kinetics. CO_2 could enhance the NR molecular weight reduction by lowering the activation energy (from 121 $kJ \cdot mol^{-1}$ to 38 $kJ \cdot mol^{-1}$). The role of CO_2 in the reaction system seems to be the formation of oxidative peroxycarbonic acid intermediate and promotion of mass transport due to the reduction in the toluene-NR viscosity and interfacial tension. The epoxidized liquid NRs ($\bar{M}_n = 4.9 \times 10^3$ $g \cdot mol^{-1}$) obtained from NR molecular weight reduction was further processed to prepare hydroxyl telechelic NR ($\bar{M}_n = 1.0 \times 10^3$ $g \cdot mol^{-1}$) and biobased polyurethane.

Keywords: activation energy; chemical degradation; depolymerization; HTNR.

Abbreviations and symbols

Abbreviations

CTNR	carbonyl telechelic natural rubber
CXL	CO_2-expanded liquid
ELNR	epoxidized liquid natural rubber
H_2O_2	hydrogen peroxide
HTNR	hydroxyl telechelic natural rubber
NR	natural rubber
PDI	polydispersity index ($\bar{M}_w/\bar{M}_n$)
phr	parts per hundred rubber
PU	polyurethane

Symbols

$DP_n(t_0)$	degree of polymerization at beginning $t=0$, according to Eq. (5)
$DP_n(t)$	degree of polymerization at the reaction time t, according to Eq. (5)
E_a	activation energy
k	rate constant
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
t	reaction time

1 Introduction

Polyurethane is a commodity plastic that has been used in many applications such as building and construction, thermal insulations, transportations, sport equipment, and footwear due to its desirable lightweight, excellent thermal insulating and mechanical properties [1–7]. In the chemical structures of polyurethane, urethane repeating units are produced by the reaction of isocyanates and polyols, which contain hydroxyl groups at the chain ends [5, 6].

Nowadays, polyols are readily derived from biomass feedstocks (e.g. natural rubber (NR) and vegetable oil) [7–13]. NR is one of the most well-known polymers that can be functionalized into biobased polyols [14–16] due to its structure that contains unsaturated bonds. Scheme 1 shows a four-step reaction pathway for preparing biobased polyurethane from NR that includes three intermediates: epoxidized liquid natural rubber (ELNR), carbonyl telechelic natural rubber (CTNR), and hydroxyl

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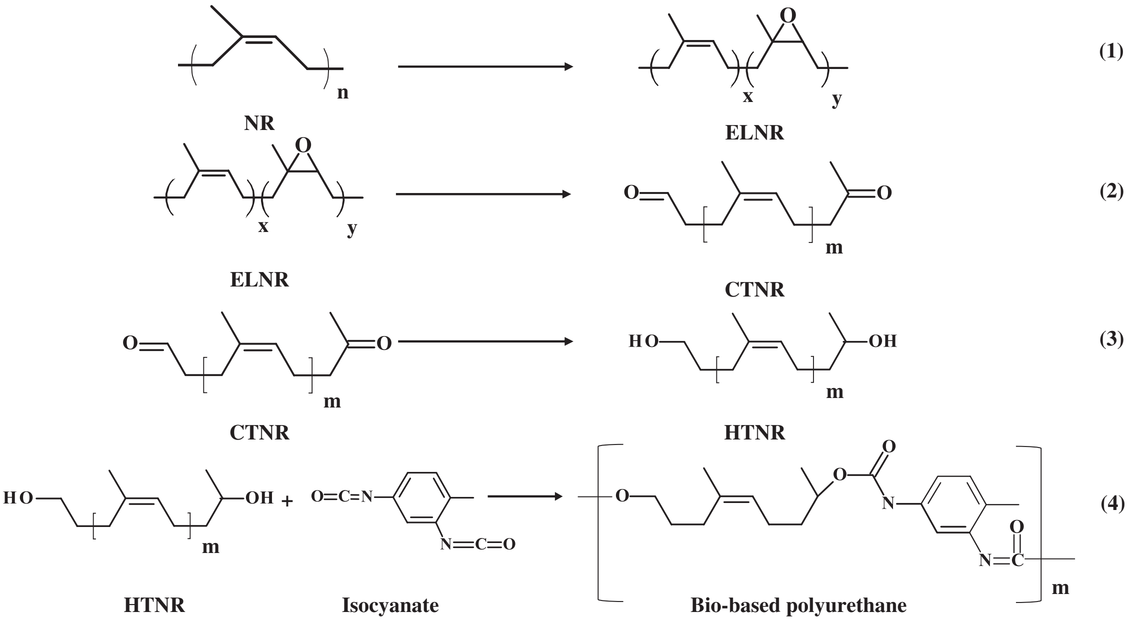

Scheme 1: Reaction pathways for preparing biobased polyurethane from NR including three intermediates as ELNR, CTNR, and HTNR.

telechelic natural rubber (HTNR). However, the use of virgin NR in Scheme 1 yields non-uniform properties of the resulting biobased polyurethanes due to the broad and high molecular weight of the natural polymer [4, 10]. To produce suitable polymeric materials, it is necessary to reduce the molecular weight of virgin NR before preparing biobased polyurethane.

In the chemical degradation process, oxidizing agents (e.g. hydrogen peroxide [15, 17, 18], periodic acid [16, 19], potassium persulfate [20, 21], and diphenyl disulfide [22–24]) were used for molecular weight reduction. Among these oxidizing agents, hydrogen peroxide (H_2O_2) is preferable due to its environmentally friendly characteristic [25, 26]. However, H_2O_2 is typically supplied in an aqueous solution with water up to 70 wt.%, while NR is only soluble in organic phases (e.g. toluene or xylene solvents). Thus, the NR molecular weight reduction with H_2O_2 as an oxidizing agent is limited due to the mass transfer of H_2O_2 from the aqueous phase into the organic phase in the biphasic aqueous-organic systems.

The use of CO_2 in CO_2-expanded liquid (CXL) reaction systems is a promising technique for green and sustainable processes [27–30] because it allows one to adjust both polarity and transport properties by altering pressure and temperature. In the triphasic CO_2/organic solvent/H_2O systems with H_2O_2, the addition of CO_2 can (i) promote the formation of oxidative peroxycarbonic acid intermediate by the reaction of CO_2 and H_2O_2 [31–33] and (ii) promote the solubility of small molecules in the organic phase (e.g. H_2, O_2, and oxidizing agent) [23, 24, 34] by lowering the viscosity and interfacial tension of the biphasic aqueous-organic systems [35]. The peroxycarbonic acid intermediate can be used as an effective oxidative agent in the epoxidation of olefins in the biphasic systems reported in literature [36–39]. Thus, chemical degradation in the triphasic CO_2/toluene/H_2O systems with H_2O_2 could improve the efficiency of the NR molecular weight reduction.

The first objective of this work is to study the enhancement of NR molecular weight reduction in triphasic systems of CO_2/toluene/H_2O using H_2O_2 as an oxidizing agent and toluene as an organic solvent for NR dissolution. The second objective of this work is to prepare biobased polyurethane obtained from the NR molecular weight-modified polymers. A comparative study on the NR molecular weight reduction in biphasic water-toluene systems without the addition of CO_2 was made as a basis for assessing the results. Reactions were performed to evaluate the activation energy at a constant CO_2 pressure of 12 MPa. Gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FT-IR), and proton nuclear magnetic resonance (^{1}H-NMR) analyses were used to analyze the products.

2 Materials and methods

2.1 Materials

Virgin NR STR-5L (Standard Thai Test Rubber) with dirt less than 5% was used as received without further purification. Liquid CO_2

(purity ≥ 99.95%) was supplied by United Industrial Gases (Thailand). Hydrogen peroxide (H_2O_2) with a purity of 30 wt.% was obtained from Fluka Chemical. Toluene, methanol (AR grade), tetrahydrofuran (AR grade), and chloroform (HPLC grade) were purchased from RCI Labscan Co. (Thailand). Periodic acid (H_5IO_6) and sodium borohydride ($NaBH_4$) were purchased from ACS Reagent Chemical Co. Dibutyltindilaurate (DBTDL) as a catalyst was obtained from Air Products and Chemicals, and toluene diisocyanate (TDI) from IRPC Public Company Limited (Thailand) was used in the preparation of biobased polyurethanes.

2.2 NR molecular weight reduction

NR molecular weight reduction was performed in the presence of CO_2 at a constant pressure of 12 MPa over a temperature range of 60°C–80°C and at reaction times of 1 h–10 h using H_2O_2 concentrations of 10–30 parts per hundred rubber (phr). These conditions were adopted from the literature that did not consider experiments in the presence of CO_2 [15, 17, 37].

In the experimental apparatus (Figure 1), a solution of NR (1% w/v in toluene) of 5 ml was loaded into a high-pressure vessel (15 ml, Taiatsu Techno/Japan SUS316) and mixed with H_2O_2 using a magnetic stirrer (550 rpm, $g \approx 9.98 \text{ m} \cdot \text{s}^{-2}$). The high-pressure vessel was then placed in a water bath at a constant temperature of 60°C. The residual air inside the vessel was subsequently flushed out with CO_2 from the cylinder. CO_2 was delivered into the high-pressure vessel by a syringe pump (ISCO 260D, USA) until the pressure inside the vessel rose to 12 MPa. CO_2 was then discharged from the vessel after reaching the reaction time. Comparative experiments on NR molecular weight reduction using similar conditions were made without the addition of CO_2. The obtained ELNR products in both cases were analyzed with GPC, FT-IR, and ^{1}H-NMR techniques.

2.3 Preparation of biobased polyurethane

ELNRs obtained from the NR molecular weight reduction were subsequently functionalized to CTNR and HTNR as shown in Scheme 1. CTNR was prepared by adding 1.1 mol equivalent of periodic acid (H_5IO_6) to 0.4 mol · l^{-1} of the ELNR solutions [Eq. (2), Scheme 1]. The solutions were stirred at a rotational speed of 720 rpm at 60°C for 6 h in a glass reactor with a magnetic stirrer. The CTNR product was neutralized with sodium hydrogen carbonate and sodium chloride.

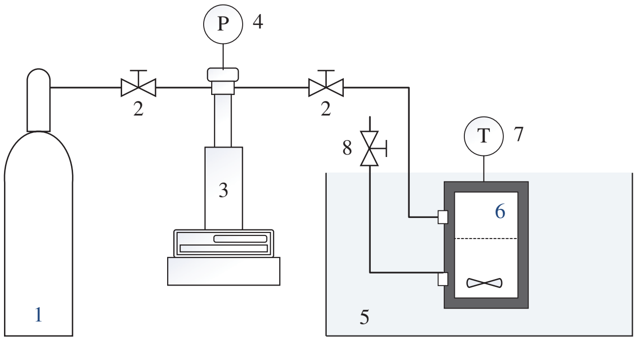

Figure 1: Apparatus for chemical degradation of NR using H_2O_2 as an oxidizing agent in the presence of CO_2. (1) CO_2 cylinder, (2) valves, (3) syringe pump, (4) pressure gauge, (5) water bath, (6) high-pressure vessel, (7) thermocouple, and (8) relief valve.

Subsequently, the resulting CTNR was functionalized to the HTNR solution by adding excess sodium borohydride (5 mol equivalent) at 60°C for 6 h [Eq. (3), Scheme 1]. The obtained HTNR product was then hydrolyzed with 10 ml of cool water, purified by a sodium chloride solution, and dehydrated by magnesium sulfate. The molecular weight and functional groups of the obtained HTNR were analyzed by GPC, FT-IR, and ^{1}H-NMR.

The HTNR was then used as a raw material for preparing HTNR-based polyurethane by a one-shot method [14, 15] [Eq. (4), Scheme 1]. A solution of HTNR in THF at a concentration of 0.5% (w/v) was mixed with dibutyltindilaurate (DBTDL) as a catalyst at a [DBTL]/[OH] ratio of 0.045, before adding isocyanate into the mixture at a [NCO]/[OH] ratio of 1.2 at 60°C. After stirring for 20 min, the resulting HTNR-based polyurethanes were cast onto an aluminum substrate and then cured at 40°C for 48 h. The functional groups of HTNR-based polyurethanes were analyzed with FT-IR.

2.4 Analysis methods

Gel permeation chromatography (GPC): The number-average molecular weight ($\bar{M}_n$), weight-averaged molecular weight ($\bar{M}_w$), and polydispersity index (PDI, $\bar{M}_w/\bar{M}_n$) of the samples were characterized by GPC. Before the measurements, the GPC apparatus was calibrated using 0.1% (w/v) polystyrene standard solutions (PS, molecular weights of 30–900 kg · mol^{-1}) in chloroform. The sample was prepared as a 0.1% (w/v) chloroform solution filtered through a 0.2-μm Teflon (Millex) filter. The GPC system had an HPLC pump (Spectra System, model P2000), a GPC column (Shodex, GPC KF-80M with two columns), and a UV-Vis detector at a fixed wavelength (λ) of 254 nm (Lab Alliance, model 201, USA). Chloroform (HPLC) was used as the mobile phase, and the flow rate of the mobile phase was 1 ml · min^{-1} in the column maintained at 40°C. A sample (20 μl) was injected into the column in the measurements.

FT-IR and ^{1}H-NMR: The functional groups in the chemical structure of NR, ELNR, CTNR, HTNR, and PU were analyzed using FT-IR and ^{1}H-NMR. A dried sample was mixed with potassium bromide tablets and then dried at 60°C for 2 h to remove moisture. The FT-IR spectra were taken in transmission mode with an FT-IR spectrometer (Thermo-Nicolet Avatar 360 Multi Bounce, USA). Each sample was dissolved in chloroform-d ($CDCl_3$), and tetramethylsilane (TMS) was used as the internal standard solution. The ^{1}H-NMR spectra were measured with an^{1}H-NMR spectrometer (Bruker, 300 MHz, USA).

3 Kinetic studies

The rate constant (k) and activation energy (E_a) were estimated for assessing the enhancement of NR molecular weight reduction by CO_2. The rate constants were estimated from second-order reaction equations as follows [21, 40–42]:

$$\left[\frac{1}{DP_{\mathrm{n(t)}}}-\frac{1}{DP_{\mathrm{n(t_0)}}}\right]=kt \qquad (5)$$

$$DP_{\mathrm{n(t)}}=\frac{\overline{M}_{\mathrm{n}}}{M_0} \qquad (6)$$

where $DP_{\mathrm{n(t)}}$ and $DP_{\mathrm{n(t_0)}}$ are the degree of depolymerization at the reaction time t and the beginning $t=0$, respectively. The $\overline{M}_{\mathrm{n}}$ and M_0 are the number-average molecular weight of NR and repeating unit of isoprene (68 g · mol^{-1}). The E_a was determined by the Arrhenius equation as follows:

$$\ln(k)=\frac{-E_{\mathrm{a}}}{R}\left(\frac{1}{\mathrm{T}}\right)+\ln(A) \qquad (7)$$

where A is the frequency of collisions in the correct orientation, and R is the universal gas constant.

4 Results and discussion

4.1 NR molecular weight reduction

Figure 2A–C and Table 1 show molecular weight reduction in terms of $\overline{M}_{\mathrm{n}}$ values of ELNR with CO_2 and without CO_2. With an increase in reaction time (Figure 2A–C), the $\overline{M}_{\mathrm{n}}$ values of ELNR in both cases tended to decrease exponentially during the first two hours and then gradually

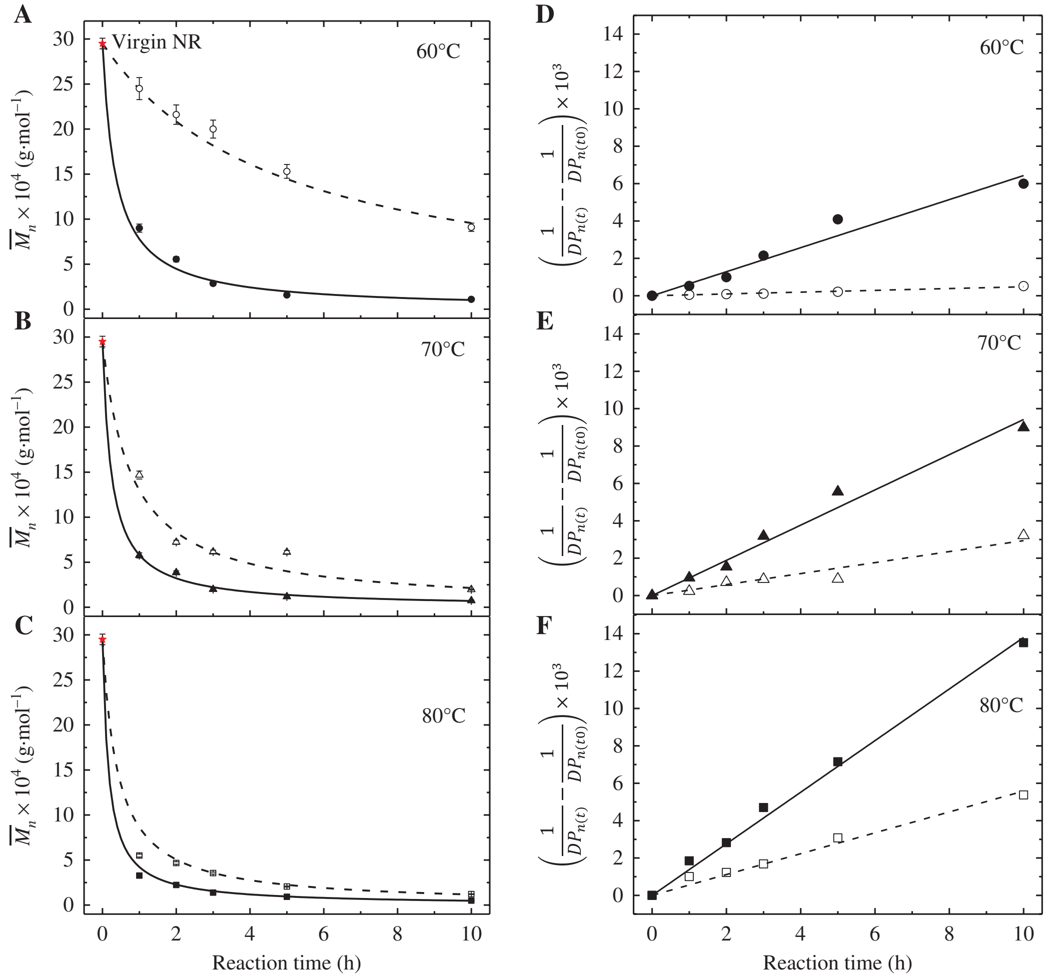

Figure 2: Number-average molecular weight ($\overline{M}_{\mathrm{n}}$) and reciprocal degree of depolymerization ($1/DP_{\mathrm{n(t)}}$) of ELNR obtained from NR molecular weight reduction using H_2O_2 in the presence (filled symbols) and in the absence (unfilled symbols) of CO_2 as a function of reaction time at 60°C (A and D), 70°C (B and E), and 80°C (C and F). Conditions were performed at a constant pressure of 12 MPa and constant H_2O_2 concentration of 20 phr. (A–C) Lines were calculated by Eq. (5) with rate constants (k) in Table 2. (D–F) Lines were obtained by fitting with Eq. (5) using $\overline{M}_{\mathrm{n}}$ values in Table 1.

Table 1: Number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$), PDI ($\bar{M}_w/\bar{M}_n$), and degree of polymerization[a] (DP_n) of ELNR obtained from molecular weight reduction of NR using H_2O_2 with CO_2 at a pressure of 12 MPa and without CO_2 for a constant H_2O_2 concentration of 20 phr.

Temperature (°C)	Time (h)	With CO_2				Without CO_2			
		$\bar{M}_w \times 10^4$ ($g \cdot mol^{-1}$)	$\bar{M}_n \times 10^4$ ($g \cdot mol^{-1}$)	PDI (–)	$DP_n \times 10^3$ (–)	$\bar{M}_w \times 10^4$ ($g \cdot mol^{-1}$)	$\bar{M}_n \times 10^4$ ($g \cdot mol^{-1}$)	PDI (–)	$DP_n \times 10^3$ (–)
60	1	44.83	9.00	4.98	4.34	101.64	24.54	4.14	3.61
	2	22.64	5.55	4.08	1.32	77.72	21.64	3.59	3.18
	3	7.87	2.86	2.75	0.82	62.34	20.03	3.11	2.95
	5	3.30	1.57	2.10	0.42	50.57	15.34	3.30	2.26
	10	2.02	1.09	1.85	0.23	26.76	9.10	2.94	1.34
70	1	17.68	5.76	3.07	0.85	66.44	14.68	4.53	2.16
	2	9.38	3.85	2.44	0.57	25.59	7.23	3.54	1.06
	3	4.65	1.99	2.33	0.29	21.17	6.15	3.44	0.91
	5	2.55	1.18	2.17	0.17	16.84	6.11	2.76	0.90
	10	1.65	0.74	2.24	0.11	4.73	1.97	2.40	0.29
80	1	7.26	3.28	2.22	0.48	19.29	5.50	3.51	0.81
	2	4.59	2.23	2.06	0.33	10.06	4.67	2.15	0.69
	3	3.22	1.38	2.34	0.20	7.14	3.55	2.01	0.52
	5	1.92	0.92	1.97	0.14	5.12	2.06	2.49	0.30
	10	1.05	0.49	2.12	0.07	3.59	1.21	2.95	0.18

[a] Degree of polymerization (DP_n), according to Eq. (6).

plateaued. Trends in decrease of $\bar{M}_n$ values of ELNR with CO_2 (Figure 2A–C) were larger than those without CO_2, especially at low temperature.

Trends of NR molecular weight reduction (Figure 2A–C) in both cases were similar to the second-order reaction rate of depolymerization [Eq. (5)]. The k [Eq. (5)] and E_a [Eq. (7)] were calculated from the $\bar{M}_n$ values (Table 1). Figure 2D–F shows a linear relationship between degree of depolymerization ($1/DP_{n(t)}$) and reaction time, according to Eq. (5). The rate constants for NR molecular weight reduction were estimated from the slopes in Figure 2D–F and are tabulated in Table 2. The k values for chemical degradation in both cases (Table 2) showed an increase with temperature, while the k values for experiments made in the presence of CO_2 were higher than those in the absence of CO_2.

The E_a can be determined from the slopes in Figure 3, according to Eq. (7). The E_a value for molecular weight reduction in the presence of CO_2 with H_2O_2 was 38 $kJ \cdot mol^{-1}$, which was lower than that in the absence of CO_2 (121 $kJ \cdot mol^{-1}$) or methods in the literature such as chemical degradation with other potassium persulfate oxidizing agent (77 $kJ \cdot mol^{-1}$) [21] and thermal decomposition of NR (203 $kJ \cdot mol^{-1}$) [43]. Due to lower oxidative activity, E_a value from chemical degradation with H_2O_2 was lower than that from potassium persulfate, however, combination of H_2O_2 with CO_2 allowed more effective than that using potassium persulfate.

Table 2: Rate constants (k) of chemical degradation of NR with CO_2 at a pressure of 12 MPa and without of CO_2 at a constant H_2O_2 concentration of 20 phr.

Temperature (°C)	With CO_2		Without CO_2	
	k (min^{-1})	R^2	k (min^{-1})	R^2
60	1.07×10^{-5}	0.96	8.00×10^{-7}	0.99
70	1.57×10^{-5}	0.98	4.90×10^{-6}	0.93
80	2.30×10^{-5}	0.99	9.30×10^{-6}	0.98

R^2, coefficient of determination for fitting with Eq. (5) as shown in Figure 2D–F.

Figure 4 shows a proposed process for NR molecular weight reduction in triphasic CO_2/organic/H_2O systems. The triphasic systems (Figure 4) include the CO_2 phase, the aqueous phase containing H_2O_2 solution, and the organic phase of NR solution in toluene solvent. As CO_2 can be soluble in both aqueous and organic phases, CO_2 can cause (i) the formation of peroxycarbonic acid in the aqueous phase by the reaction of CO_2 and H_2O_2, as reported in the literature [32, 33, 36, 37] and (ii) the promotion of the mass transfer of H_2O_2 to react with NR in the organic phase due to a reduction in viscosity in the organic phase, as reported in the literature [44–47], and interfacial tension between the aqueous and organic phases according to the molecular dynamics simulation [35].

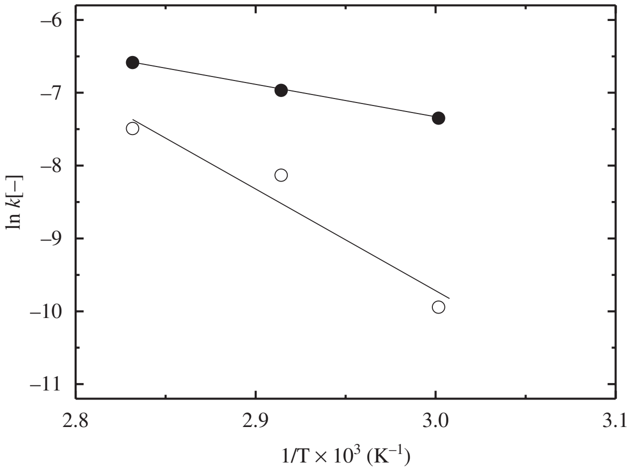

Figure 3: Plot of rate constant (*k*) with inverse temperature (1/T) used to determine E_a [Eq. (6)] of molecular weight reduction using H_2O_2 in the presence of CO_2 (filled symbols, $R^2=0.99$) and absence of CO_2 (unfilled symbols, $R^2=0.94$) over a temperature range of 60–80°C, a constant H_2O_2 concentration of 20 phr, and at a constant pressure of 12 MPa.

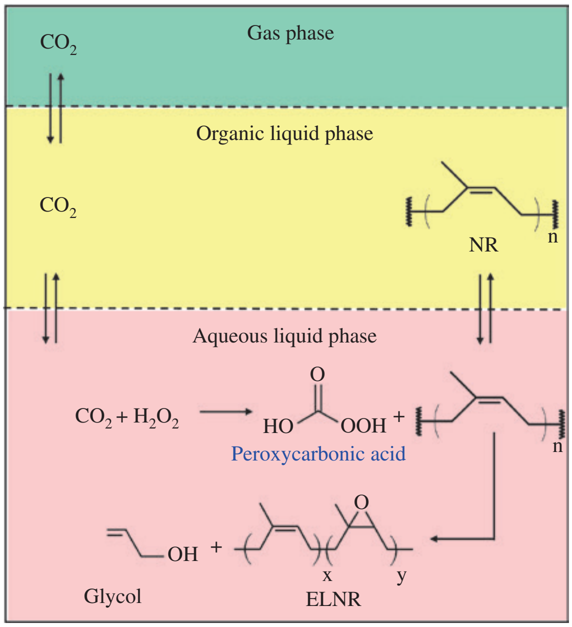

Figure 4: Proposed molecular weight reduction of NR in triphasic CO_2/toluene/H_2O systems using H_2O_2 with CO_2 to produce ELNR. The organic phase contains NR solutions in toluene solvent. The aqueous phase contains H_2O_2 and peroxycarbonic acid intermediate.

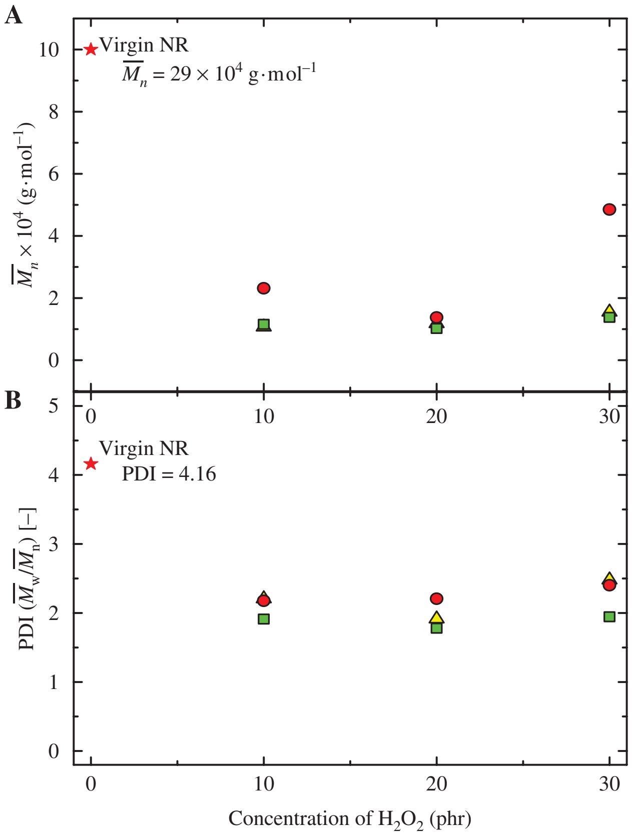

Figure 5: Concentration dependence of H_2O_2 in the unit of phr on (A) the number-averaged molecular weight ($\bar{M}_n$) and (B) PDI ($\bar{M}_w/\bar{M}_n$) of virgin NR (★) and ELNRs obtained from molecular weight reductions of NR using H_2O_2 in the presence of CO_2 at a constant pressure of 12 MPa, a constant temperature of 60°C (●), 70°C (△), and 80°C (■) for 5 h.

To elucidate the effect of peroxycarbonic acid formation on NR molecular weight reduction, the NR molecular weight reduction was carried out in the H_2O-CO_2 system without the addition of H_2O_2. The $\bar{M}_w$ and PDI values of the NR obtained in the H_2O-CO_2 system (50°C, 12 MPa, and 5 h) were 8.3×10^5 $g\cdot mol^{-1}$ and 3.4, respectively. The NR molecular weight reduction in the H_2O-CO_2 system was less effective than that with the addition of H_2O_2, according to the higher $\bar{M}_w$ values (Table 1) obtained with CO_2. These results were consistent with studies on epoxidation of cyclohexene in H_2O-CO_2 systems [48] in that no reaction occurred.

The reason for the lack of reaction in the H_2O-CO_2 system without the addition of H_2O_2 could be due to unsuitable conditions such as pH for epoxidation because pH higher than 7 is generally required for epoxidation reactions [32, 48]. However, the reaction of CO_2 with H_2O can generate carbonic acid (pH ≈ 3–4) [31] in the H_2O-CO_2 systems, while the pH values in the aqueous solution with the addition of H_2O_2 in the presence or absence of CO_2 are typically higher than 7 [32, 33].

CO_2 can reduce the viscosity of organic solvents [44–47] and polymer solutions [49–51], while the effect of viscosity reduction is negligible in aqueous solutions [52]. Thus, the main reasons for efficient NR molecular weight

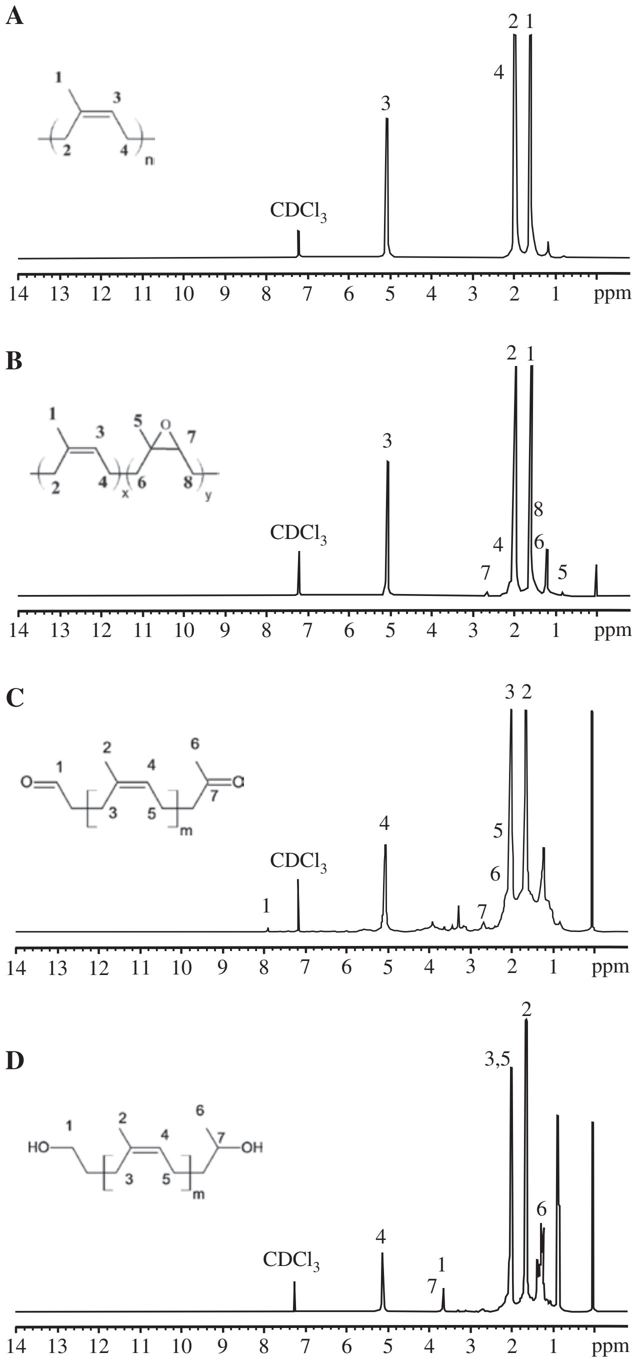

Figure 6: ^{1}H-NMR spectra of (A) virgin NR, (B) ELNR obtained from molecular weight reduction using H_2O_2 with CO_2 at a constant pressure of 12 MPa, a constant temperature of 80°C, and a constant H_2O_2 concentration of 20 phr, (C) CTNR, and (D) HTNR.

reduction in the triphasic systems with H_2O_2 as the oxidizing agent can be thought of as (i) the formation of oxidative peroxycarbonic acid intermediate that synergically reduces the NR molecular weight along with H_2O_2 and (ii) the promotion of mass transport as CO_2 can reduce both organic solution viscosity and interfacial tension that would enhance the degradation reaction and increase in the O_2 transport.

The addition of H_2O_2 up to 30 phr (Figure 5) caused an increase in $\bar{M}_n$ and polydispersity index due to an excess amount of the oxidative agent that promoted retrogressive repolymerization among the free radical chain ends [21, 53]. Therefore, the chemical degradation using H_2O_2 at 20 phr in the presence of CO_2 was used to prepare the ELNR, and the biobased polyurethane as shown in Scheme 1 is discussed in the following section.

4.2 Chemical structures of NR from molecular weight reduction

The chemical structures of the ELNR obtained from NR molecular reduction were characterized with ^{1}H-NMR and FT-IR (Figures 6 and 7). The ^{1}H-NMR spectra of both the NR and ELNR (Figure 6A and B) showed the olefinic proton of *cis*-1,4-polyisopren unit at 5.10 ppm, the methyl proton at 1.67 ppm, and the methylene proton at 2.16 ppm next to the C=C bond. After the molecular weight reduction, small signals of the ELNR (Figure 6B) were detected from the methine proton adjacent to the epoxide ring at 2.70 ppm and the methyl group (-CH_3) adjacent to the epoxide unit at 1.30 ppm. The epoxide content of the ELNR was estimated from methods in the literature [16, 17, 54] by considering the integration areas of signals of 2.70 and 5.10 ppm and determined to be 5.7%. Figure 7 shows the FT-IR spectra of the NR and ELNR that exhibited the C=C stretching of polyisoprene at 1665 cm^{-1}. The ELNR (Figure 7) showed a weak signal of the epoxide ring (C-O-C) at 870 cm^{-1}. The

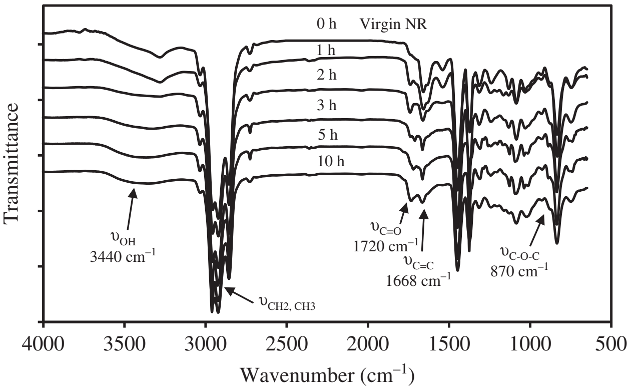

Figure 7: FT-IR spectra of virgin NR and ELNR obtained from NR molecular weight reduction using H_2O_2 in the presence of CO_2 at a constant pressure of 12 MPa, a constant temperature of 80°C, and a constant H_2O_2 concentration of 20 phr for 10 h.

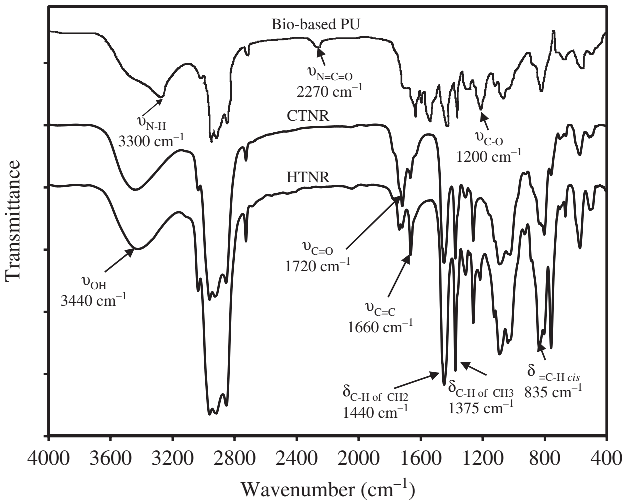

Figure 8: FT-IR spectra of CTNR, HTNR, and biobased polyurethane.

^{1}H-NMR and FT-IR results obtained in this work were in accordance with the literature [16, 17, 19].

4.3 Preparation of biobased polyurethane

The obtained ELNR was functionalized to CTNR and HTNR [Scheme 1, Eqs. (2) and (3)]. The chemical structures of CTNR and HTNR were confirmed by FT-IR and ^{1}H-NMR (Figures 6 and 8). The FT-IR spectra of the C=O stretching of CTNR at 1720 cm^{-1} (Figure 8) were observed, which were consistent with the ^{1}H-NMR results (Figure 6C) wherein there appeared new peaks for the aldehyde proton (at 9.80 ppm), the methylic proton in the ketone end groups (at 2.13 ppm), and the CH_2 in the α and β terminal carbonyl (-CH_2) groups (between 2.20 and 2.60 ppm).

The FT-IR spectra of the OH stretching in the HTNR at 3440 cm^{-1} (Figure 8) were consistent with ^{1}H-NMR results (Figure 6D) as they showed the appearance of new peaks for methylic protons adjacent to a secondary alcohol (at 1.20 ppm) and two peaks corresponding to CH (3.80 ppm) and CH_2 (3.68 ppm) adjacent to alcohol groups at the chain ends. Thus, the FT-IR and ^{1}H-NMR results showed that the hydroxyl functional groups were located at the chain ends of the HTNR.

The functionality of the HTNR was estimated by an ^{1}H-NMR method reported in the literature [15]. The HTNR obtained in this work had two functionalities, indicating that there are two hydroxyl groups at the chain end of the HTNR structure so that the prepared HTNR material can be used for preparing the biobased polyurethane. The biobased polyurethane synthesized from the HTNR was confirmed by FT-IR analysis (Figure 8) that exhibited absorption wavenumbers of 3300 cm^{-1} for N-H stretching and 1720 cm^{-1} for C=O stretching.

5 Conclusion

High-pressure (12 MPa) CO_2 improves the efficiency of NR molecular weight reduction in water-toluene biphasic systems with hydrogen peroxide as the oxidizing agent. The role of CO_2 in the reaction system seems to be to improve mass transport in the toluene phase and to enhance the oxidation rate through H_2O_2 transport and formation of peroxycarbonic acid intermediate. CO_2 lowers the activation energy for the NR molecular weight reduction using H_2O_2 oxidation by a factor of about three in the water-toluene-NR reaction system. The ELNR obtained a molecular weight reduction that can be used subsequently to prepare biobased polyurethane.

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