

# Synthesis, Characteristic, and Properties of Waterborne Polyurethane Based on Natural Rubber

Anuwat Saetung,<sup>1,2</sup> Lalita Kaenhin,<sup>3</sup> Pairote Klinpituksa,<sup>3,4</sup> Adisai Rungvichaniwat,<sup>2,3</sup> Tulyapong Tulyapitak,<sup>2</sup> Summa Munleh,<sup>2</sup> Irène Campistron,<sup>1</sup> Jean-François Pilard<sup>1</sup>

<sup>1</sup>L.C.O.M. Chimie des Polymères (UCO2M, UMR CNRS 6011), Université du Maine, Avenue Olivier Messiaen, 72085, Le Mans Cedex 9 France

<sup>2</sup>Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

<sup>3</sup>Center of Excellence in Natural Rubber Technology, Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

<sup>4</sup>Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

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**ABSTRACT:** A series of new waterborne polyurethanes (WPU) was successfully prepared by prepolymer process from renewable source, hydroxytelechelic natural rubber (HTNR), with different amounts of DMPA (1.6–8.4 wt %), different molecular weights (1000–4000 g mol<sup>-1</sup>), and different levels of epoxide (0%–20%) of HTNR. It was found that the urethane conversions of prepolymer were over 80% as calculated by FTIR technique. The resulting HTNR2000-based WPU exhibit a uniform particle size, which decreases from 420- to 83-nm diameters with an increase in the amount of DMPA from 2.9 to 6.6 wt %. The particle size also decreases with an increase of soft segment or with an increase of epoxide content. They are

well stable more over 6 months and without a significant difference in particle size compared with starting of them. Chemical structure of WPU films was confirmed by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR. Molecular weight and polydispersity were determined by SEC. In addition, thermal and water uptake properties were investigated. The experimental results reveal that the DMPA content, molecular weight of HTNR, and epoxide content play an important key role in water uptake and thermal properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2742–2752, 2012

**Key words:** telechelic; natural rubber; waterborne polyurethane; polyurethane dispersion; oligoisoprenes

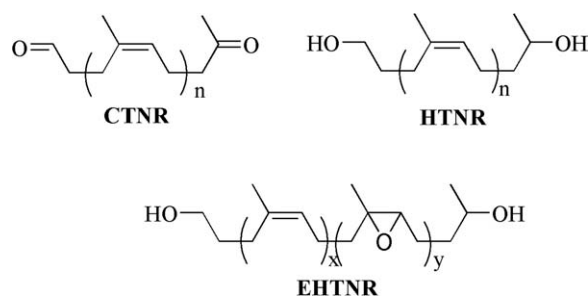
## INTRODUCTION

Polyurethane is all around and is playing a vital role in many industrial applications ranging from shipbuilding to footwear and construction to automobile in an astonishing variety of forms,<sup>1</sup> i.e., foams, elastomers, adhesives, and dispersions.<sup>1–10</sup> The increasing importance of waterborne polyurethanes (WPU) or dispersion processes has started on the market since early 1970s.<sup>11,12</sup> It is well known that its advantage is no or little solvent use leading to non-toxic and nonflammable coating with low volatile organic compounds (VOCs).<sup>11</sup> In addition, it is also cheaper in cost aspect and easier to handle than the conventional solvent based.<sup>13,14</sup> WPU has been performed in a wide range of commercial applications,

including adhesives and coatings for various substrates.<sup>15,16</sup> Among the various types of polyols, which normally are synthesized from products of petroleum oil, used to synthesize WPU, polyether,<sup>16–18</sup> polyester,<sup>19–21</sup> or hydroxytelechelic polydienes<sup>15,22–24</sup> are generally used as soft segment in polyurethane structure. However, in the trend of increasing price and exhausting day over day of petroleum oil as well as environmental concerns (toxic waste or climate warming), a change from petroleum products with renewable sources is necessary for replacement development into the future.<sup>5,10</sup> For these reasons, many researchers are increasingly devoting their attention and effort to the possibility using of renewable sources as potential raw materials for the manufacture of polymers.<sup>5,10</sup> Recently, Lu et al. successfully prepared WPUs based on castor oil<sup>25</sup> and modified rapeseed oil.<sup>26</sup> Larock and coworkers also reported the successful synthesis of a new WPUs and urethane–acrylic hybrid latex based on modified soybean oil.<sup>10,27,28</sup> In this aspect, natural rubber (NR) is also an interesting and attractable renewable source to represent a potential material for synthesis of functional precursors of a wide range of

Correspondence to: A. Saetung (sanuwat@bunga.pn.psu.ac.th) or J.-F. Pilard (jean-francois.pilard@univ-lemans.fr).

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**Scheme 1** Chemical structure of telechelic natural rubbers.

polymers. It can be chemically modified in either latex phase, solvent phase, biphasic systems, or solid phase owing to the double bonds on the polymeric backbone.<sup>29</sup> In addition, it is well known that its mechanical and physical properties are accepted and applied in many areas such as automobile, footwear, and adhesive products.<sup>30,31</sup> During the last decade, our research group has focused on selective degradation of synthetic *cis*-1,4-polyisoprene and NR using well-controlled oxidative chain cleavage reaction leading to new carbonyl telechelic *cis*-1,4-polyisoprene.<sup>32–34</sup> The chemical modifications of carbonyl end groups and carbon–carbon double bonds at various ratios have also led to the development of new hydroxyl and amino telechelic *cis*-1,4-polyisoprenes.<sup>33–35</sup> In addition, our group has successfully prepared new materials from these precursors i.e., polyurethane films,<sup>6,36</sup> polyurea films,<sup>36</sup> and polyurethane flexible foam.<sup>2,3</sup> We also investigated their interesting properties such as mechanical,<sup>2,3,35</sup> biological,<sup>5</sup> thermal,<sup>3,35,37</sup> and acoustic properties.<sup>3</sup> Considering the literatures of NR-based polyurethanes, the preparation of NR-based WPU gives a possibility to investigate new WPUs and to study its interesting properties. Moreover, this type of WPU has never been reported in the review literatures before. In this work, a series of WPUs based on precursors from NR with average molecular weight ranging from 1000 to 4000 g mol<sup>-1</sup> and with different epoxide levels on backbone chain ranging from 0% to 20% have been prepared. The effect of internal emul-

sifier contents, average molecular weights as well as epoxide contents on the synthesis, chemical structure, water uptake, and thermal properties of resulting NR-based WPU and cast films have been investigated.

## EXPERIMENTAL

### Materials

Hexamethylene diisocyanates purchased from Merck, France. Dimethylol propionic acid (DMPA), 2-butanone or methyl ethyl ketone (MEK), dibutyltin dilaurate (DBTL) and triethylamine (TEA) were purchased from Sigma-aldrich, France. They were used without further purifications.

### Syntheses

#### Synthesis of telechelic natural rubber

Hydroxytelechelic NR (HTNR) and epoxidized HTNR (EHTNR) were prepared from carbonyl telechelic NR (CTNR) according to a methodology previously described.<sup>2,5,32,36</sup> Their chemical structures and general properties were shown in Scheme 1 and Table I, respectively.

#### Synthesis of waterborne polyurethane

All samples were synthesized by prepolymer mixing technique with a constant NCO/OH equivalent molar ratio of 1 : 1 as shown in Scheme 2. The formulations for the WPU synthesis are showed in Table II. The amount of DBTL equal to 0.5 wt % was added to all samples. The amount of TEA equal to 5 wt % excess of DPMA content was added. The WPUs were synthesized in a 100-mL round-bottomed, four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. Reaction temperature was controlled using constant temperature oil bath. The HTNR, DMPA, and DBTL were weighed and added into the reactor. The concentration of mixtures was controlled at 40 wt % by adding MEK. The mixtures were heated to

**TABLE I**  
General Properties of Hydroxyl Telechelic Natural Rubber

Precursors	$T_g$ (°C)	$\overline{M}_n^{\text{NMR}}$ <sup>a</sup> (g mol <sup>-1</sup> )	$\overline{M}_n^{\text{SEC}}$ <sup>b</sup> (g mol <sup>-1</sup> )	PDI	$\overline{f}n_{\text{(OH)}}$	Appearance
HTNR1000	-57	1000	1100	2.12	2	Yellow, viscous
HTNR2000	-61	2000	1900	1.96	2	Yellow, viscous
HTNR4000	-62	4000	3800	2.04	2	Yellow, viscous
10%EHTNR2000	-55	2000	1900	1.96	2	Yellow, viscous
20%EHTNR2000	-48	2000	1900	1.96	2	Yellow, viscous

<sup>a</sup> Calculation from Refs. <sup>2</sup> and <sup>6</sup>  $((I5.1/I3.8) \times 68) + 104$ .

<sup>b</sup> Calculation from Refs. <sup>2</sup> and <sup>6</sup>  $\overline{M}_n^{\text{SEC}} \times \text{Benoit factor (0.67)}$ .



**TABLE III**  
**WPUs Properties**

Code	Conv. <sup>a</sup> (%)	Stability	Appearance	Properties	
				Particle size (nm) (PDI) <sup>b</sup>	
				1 Month	6 Months
WPU1	83	Unstable	Solid	ND <sup>c</sup> >	ND
WPU2	84	Stable	Milky	ND	420(0.25)
WPU3	92	Stable	Milky	ND	213(0.24)
WPU4	82	Stable	Milky blue	149(0.10)	146(0.10)
WPU5	87	Stable	Milky blue	120(0.21)	122(0.20)
WPU6	80	Stable	Milky blue	87(0.20)	83(0.21)
WPU7	80	Stable	Milky blue	100(0.40)	97(0.42)
WPU8	81	Stable	Milky blue	ND	300(0.20)
WPU9	88	Stable	Milky blue	ND	160(0.15)
WPU10	90	Stable	Milky blue	ND	120(0.50)
WPU11	83	Stable	Milky blue	ND	140(0.10)
WPU12	82	Stable	Milky blue	ND	150(0.20)
WPU13	80	Stable	Milky blue	ND	126(0.10)

<sup>a</sup> Conversion (%) at 4 h.

<sup>b</sup> Polydispersity.

<sup>c</sup> ND: not determined.

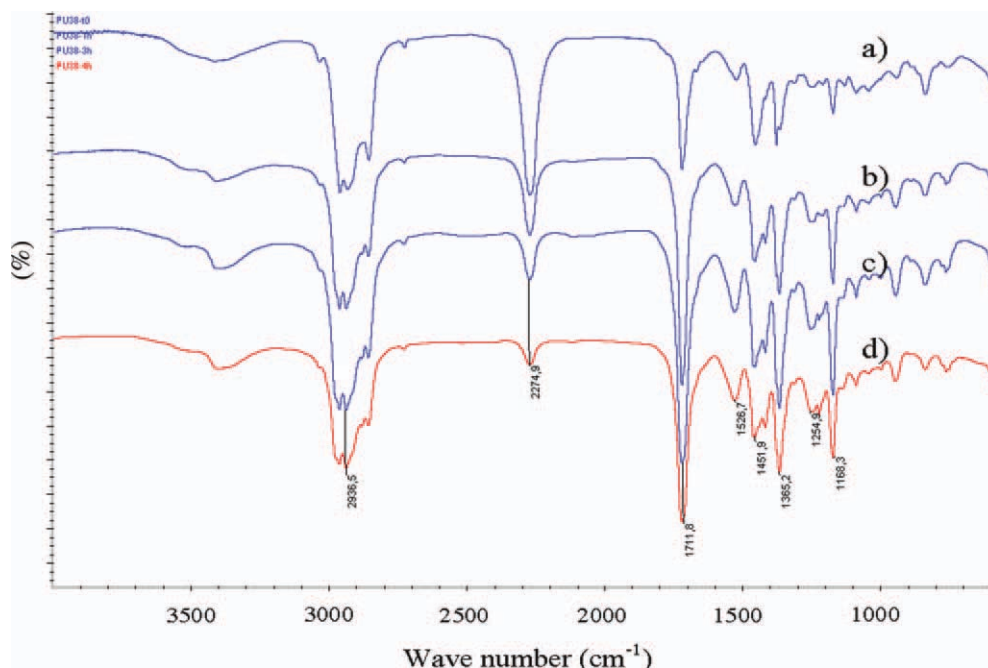
#### Size exclusion chromatography

Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a Spectra SYSTEM AS 1000 autosampler, with a Guard column (Polymer Laboratories, PL gel 5  $\mu$ m Guard column, 50 mm  $\times$  7.5 mm) followed by two columns (Polymer Laboratories, 2PL gel 5  $\mu$ m MIXED-D columns, 2  $\times$  300  $\times$  7.5) and with a Spectra SYSTEM RI-150 detector. The eluant used was tetrahydrofu-

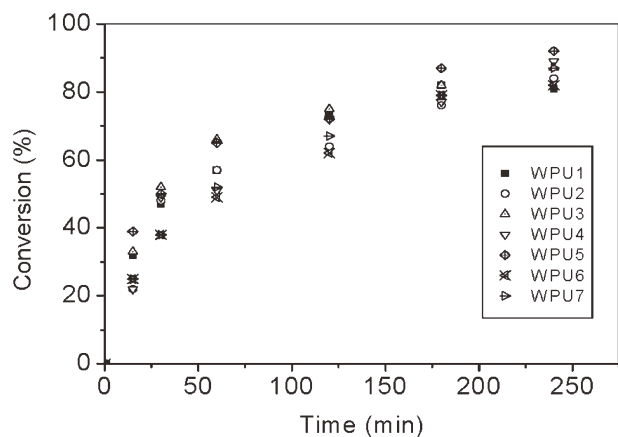
ran (THF) at a flow rate of 1 mL min<sup>-1</sup> at 35°C. Polystyrene standards (580–483  $\times$  10<sup>3</sup> g mol<sup>-1</sup>) were used to calibrate the SEC.

#### Particle size measurements

Particle sizes and particle size distributions of the WPU were measured with dynamic light scattering (Zetasizer nanoZS, Malvern) at 25°C after an equilibration time of 2 min. Measurements from a single



**Figure 1** FTIR spectra of the prepolymer of WPU5 at various times: (a) 0 h, (b) 1 h, (c) 3 h, and (d) 4 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 2** Conversion of prepolymer of WPUs at various reaction time.

angle ( $173^\circ$  backscattering) were recorded, and the data were processed using the CONTIN analysis method. The samples were diluted with deionized water to the concentration of 0.5% before testing without filtering and ultrasonic treating.

#### Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments (DSC Q 100) with a heating rate of  $10^\circ\text{C min}^{-1}$  in a range of  $-80^\circ\text{C}$  to  $150^\circ\text{C}$  under nitrogen atmosphere at a flow rate of  $50\text{ mL min}^{-1}$ . The sample weight was about 5 mg. Calibration was achieved by using indium as a reference material.

#### Thermogravimetric analyzer

Thermogravimetric analysis (TGA) was performed on a TA Instruments (TGA Q 100) with a heating rate of  $10^\circ\text{C min}^{-1}$  from room temperature to  $600^\circ\text{C}$  under nitrogen atmosphere at a flow rate  $90\text{ mL min}^{-1}$ . The sample weight was about 10 mg.

#### Water resistance behaviors

The water-swelling measurements were carried out by immersing the cast PU films  $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$  in distilled water at  $20^\circ\text{C}$ . The films was taken out and wiped off water on surface of film with tissue paper followed by immediate weighing of the swollen film. The swelling percentage  $W$  (%) was calculated by dividing the increase in weight by the original weight of the dried PU film, which is shown as:

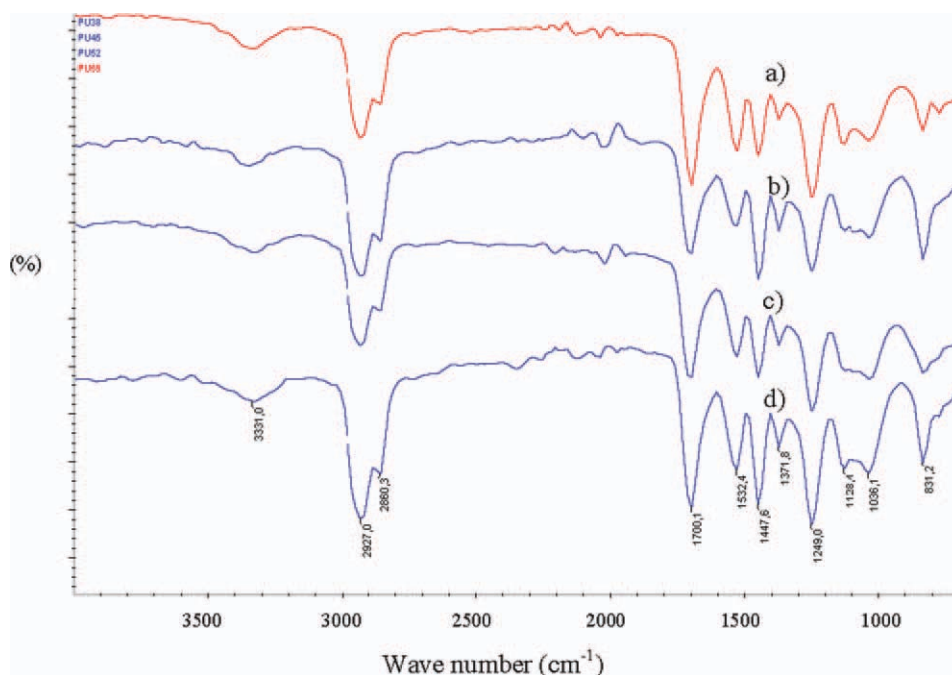
$$W\{(\%) = \frac{W_s - W_0}{W_0} \times 100 \quad (2)$$

where  $W_s$  is the weight of the swollen film, and  $W_0$  is the weight of the original dry film.

## RESULTS AND DISCUSSIONS

### Synthesis of waterborne polyurethane

All anionic WPUs were synthesized by prepolymer technique in MEK medium. During 4 h, the reaction of diisocyanates and OH-compound was monitored



**Figure 3** FTIR spectra of WPU film samples: (a) WPU8, (b) WPU11, (c) WPU12, and (d) WPU5. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)]

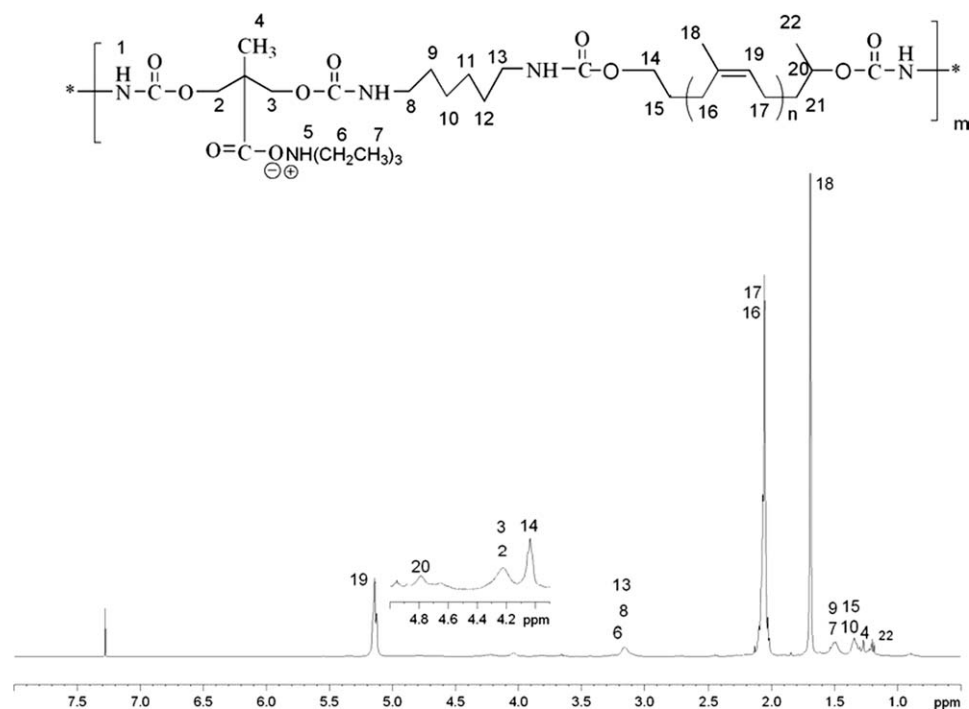


Figure 4 <sup>1</sup>H-NMR of WPU film (WPU5).

by FTIR technique. It was found that the absorption of NCO peak was decreased as reaction time increases. However, the prepolymer still shows the slightly residue NCO compound absorption at 4 h. The reaction of diisocyanates and OH compounds

was calculated in terms of the conversion (%) as shown in Table III and Figure 2. It was observed that the reaction conversions of all prepolymers of WPUs were increased with an increase of the reaction time, and their conversions were over 80% at 4 h.

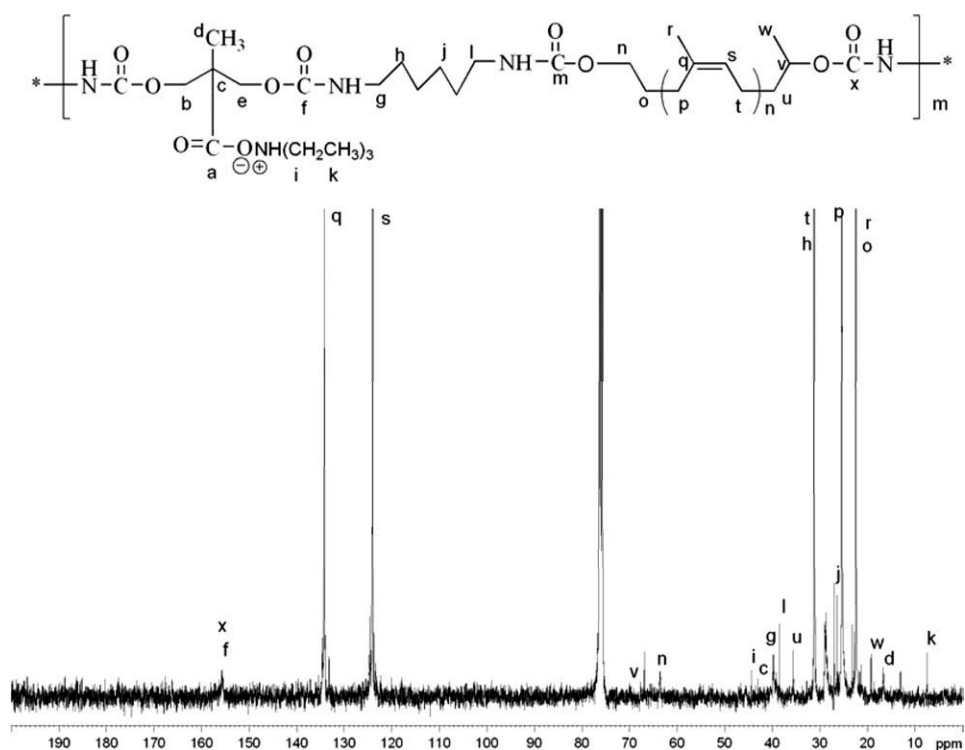


Figure 5 <sup>13</sup>C-NMR of WPU film (WPU5).

**TABLE IV**  
Samples of Average Molecular Weight and Polydispersity (PDI) of WPU Films at 4.2 wt % DMPA

WPU films	Precursors	$\overline{M}_n$	$\overline{M}_w$	$\overline{DP}_n^a$	PDI
WPU8	HTNR1000	5900	16,300	5	2.78
WPU4	HTNR2000	8900	22,200	4	2.48
WPU11	HTNR4000	16,000	44,400	4	2.79

<sup>a</sup> Degree of polymerization =  $(\overline{M}_n / (\text{HTNR} + \text{HDI} + \text{DMPA}))$ .

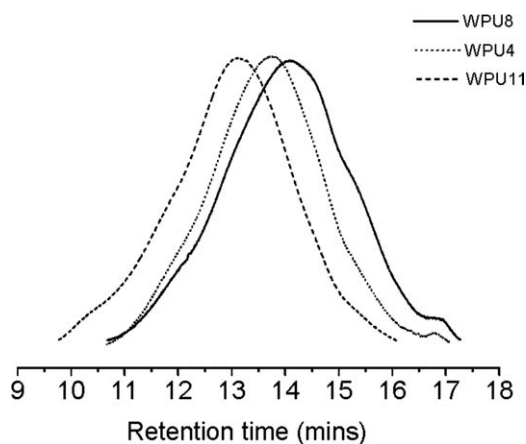
### Chemical structure of WPU films

#### FTIR

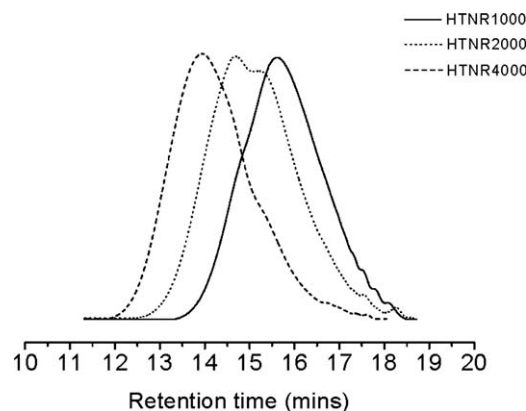
The chemical structures of WPU films were characterized by FTIR (ATR technique) and NMR analysis. The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530  $\text{cm}^{-1}$ , which correspond to  $N-H$ ,  $C=O$ , and  $N-CO$  stretching vibrations, respectively.<sup>6,36</sup> In addition, the absorption bands of *cis*-1,4 polyisoprene at 2860  $\text{cm}^{-1}$  ( $C-H$  stretching), 1453  $\text{cm}^{-1}$  ( $-CH_2-$  deformation), 1378  $\text{cm}^{-1}$  (methyl  $C-H$  deformation), and 838  $\text{cm}^{-1}$  ( $=C-H$  out-of-plane deformation) were observed.<sup>38,39</sup> The disappearance of absorption peak at 2270  $\text{cm}^{-1}$  confirms that there was no residual-free NCO in WPU films.

#### NMR

The sample of <sup>1</sup>H-NMR spectrum of WPU film (WPU5) in Figure 4 shows the presence of signal at 5.12 ppm assigned to the olefinic proton of *cis*-1,4-polyisoprenic structure. The signals of methyl and methylene proton next to carbon-carbon double bonds were observed at 1.67 and 2.09 ppm, respectively. The two new signals at 4.75 and 4.05 ppm corresponding to  $CH-$  and  $-CH_2$  adjacent to urethane groups were found. The other signals at 4.20



**Figure 6** Overlaid SEC traces of WPU films.



**Figure 7** Overlaid SEC traces of HTNR with different molecular weights.

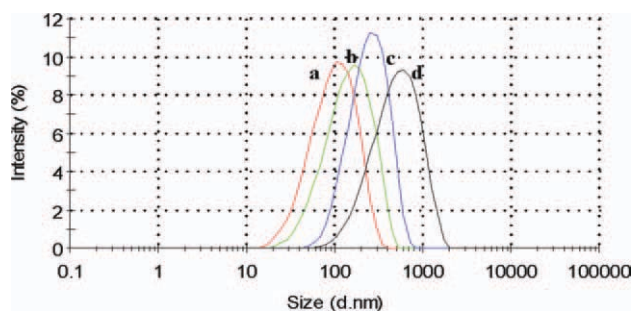
and 1.27 ppm adjacent to urethane groups were assigned to methylene and methyl proton of DMPA structure, respectively. The signals of ammonium carboxylate salt group are also observed at 3.28 and 1.56 ppm corresponding to methylene and methyl protons, respectively. The polyurethane structure was further confirmed by the <sup>13</sup>C-NMR in Figure 5, which reveals the two small peaks at 70 and 63 ppm corresponding to  $CH$  and  $CH_2$  of HTNR adjacent to urethane groups. In addition, the peak at 157 ppm corresponding to carbon atom of urethane group was also observed.

#### SEC

The molecular weights of WPU films based on different molecular weights HTNR (from 1000 to 4000  $\text{g mol}^{-1}$ ) were analyzed. It was found that the WPU films had number average molecular weights of 5900, 8900, and 16,000  $\text{g mol}^{-1}$  and polydispersity index of 2.78, 2.48, and 2.79 respectively, as determined by SEC as shown in Table IV. The overlaid SEC traces of these WPU films is also presented in Figure 6. It shows a shift of the SEC chromatograms toward earlier retention times corresponding to higher molecular weight when the molecular weight of HTNR increases as shown in Table I and Figure 7. However, the low molecular weight of WPU films or low degree of polymerization was obtained (Table IV) because of no chain extension step by chain extender in this system. Fortunately, they can be improved by an increase in degree of chain extension, i.e., an adding or an increasing of chain extender in the system.<sup>14,40</sup>

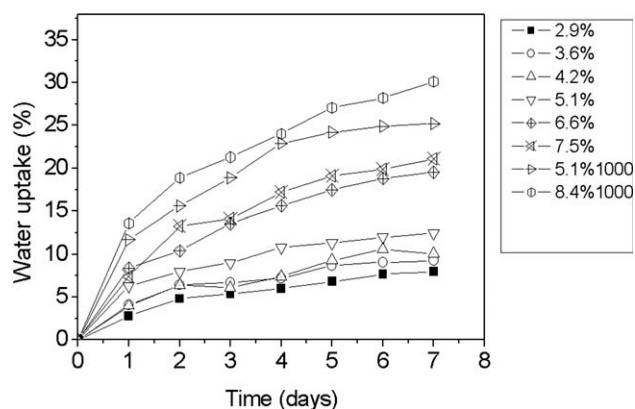
#### Particle size

For these samples, the NCO/OH equivalent mole ratio as 1 : 1 was kept constant in formulations based on HTNR2000 and was synthesized by prepolymer



**Figure 8** Particles size distribution of WPU samples (a) WPU6, (b) WPU5, (c) WPU3, and (d) WPU2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

process following in Scheme 2. The influence of DMPA contents on the particles size of the WPU1–WPU7 and particle size distribution of WPU samples is shown in Table III and Figure 8, respectively. DMPA content was varied from 1.6 to 7.5 wt % for WPU1 to WPU7 (Table II). It was found that the sample WPU1 containing DMPA content 1.6 wt % (0.25 mol) was unable to prepare in dispersion form. It was coagulated immediately after adding deionized water because of hydrophobic nature of precursor and inadequate ionic groups in hydrocarbon chains. However, others samples containing higher contents of DMPA (2.9–7.5 wt %) were still stable after keeping for 6 months. Moreover, their particle sizes were still in the same range after storage for 6 months. The particle size decreased significantly from 420 to 97 nm with an increase in the DMPA content from 2.9 to 7.5 wt %. This can be explained by the introduction of carboxylic groups ( $-\text{COOH}$ ) into hydrophobic polyurethane backbone and then their complete neutralization with TEA to form a ionic groups (ammonium carboxylate salt,  $-\text{COO}(\text{HN}^+(\text{C}_2\text{H}_5)_3)$ , which will enhance the polymer solubility in aqueous phase. Therefore, with increasing of the amount of these ionic groups, each particle in the dispersion is surrounded by a thin layer of water because of the presence of hydrophilic groups on the surface of the particles.<sup>17</sup> The molecular weight of HTNR also affected the particle size of WPUs as shown in Table III. The particle size decreased significantly from 300 to 140 nm with an increase of the molecular weight of HTNR from 1000 to 4000  $\text{g mol}^{-1}$ . This is consistent with results published by other researchers.<sup>11,15,41,42</sup> The increased flexibility of the soft segment results in decreasing particle size because the polyurethane chains lose their rigidity and strength not only from their fractional increase in weight but also from the reduced number of urethane linkages, which with the diisocyanates form the hard domains. With the same reasons, it can be explained that the increase of epoxide groups on backbone molecule of

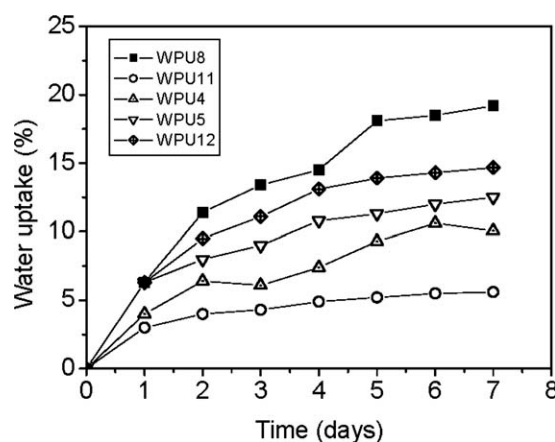


**Figure 9** Water uptake of WPU films with various DMPA content versus immerse time.

HTNR2000 affected the particle size of WPU. It was shown that the particle size increased slightly from 122, 126, and 150 nm with an increase of the epoxide content of HTNR of 0%, 10%, and 20%, respectively.

### Water uptake

The films formed after drying of WPUs at 60°C are nontacky, flexible, and light-yellowish to yellow. The water uptake of WPU films for the various DMPA content is represented in Figure 9. It was clearly observed that the water uptake of WPU films increased with immerse time and gave a slight change on the less 5.1 wt % DMPA contents. In addition, the result revealed that if the higher DMPA content in WPU films were added, the higher water uptake of their films were obtained because of the enhancement of hydrophilic ionic group from DMPA moieties and urethane groups.<sup>16</sup> For example, the series of WPU based on HTNR2000, WPU2 was the minimum water uptake (8%) while that of WPU7 was the maximum (20%) during 7 days.



**Figure 10** Water uptake of WPU films based on different WPU versus immerse time.



TABLE V  
Thermal Properties of WPU Films

Samples	DMPA (%)	$T_g$ (°C)	Thermal degradation					
			First step		Second step		Third step	
			Weight loss (%)	$T_{max}$ (°C)	Weight loss (%)	$T_{max}$ (°C)	Weight loss (%)	$T_{max}$ (°C)
WPU1	1.6	-60	4.5	256.7	17.9	322.1	76.8	374.8
WPU2	2.9	-60	5.8	259.8	18.9	305.8	74.6	376.0
WPU3	3.6	-59	6.0	259.1	19.2	311.8	73.7	374.8
WPU4	4.2	-60	7.7	263.4	19.9	308.2	71.5	374.2
WPU5	5.1	-60	9.5	257.9	20.8	314.2	68.7	377.8
WPU6	6.6	-60	10.7	260.4	21.4	305.8	67.2	374.8
WPU7	7.5	-59	11.5	264.6	23.0	312.4	63.4	376.6
WPU8	4.2	-53	7.7	268.2	20.4	316.0	71.1	372.9
WPU9	5.1	-54	9.8	268.8	21.0	309.4	68.4	368.4
WPU10	8.4	-53	14.5	263.4	26.1	303.9	57.2	367.5
WPU11	4.2	-63	7.0	268.2	13.2	310.6	78.9	377.6
WPU12	5.1	-46	9.4	257.3	20.9	315.4	68.9	383.1
WPU13	5.1	-51	8.3	255.5	20.7	311.2	69.8	385.0

According to Figure 10, the maximum water uptake of all WPU films is 30% for WPU10.

Figure 10 shows the water uptake based on the various molecular weights at 4.2 wt % DPMA content. An increase of water uptake was observed with a decrease of molecular weight of HTNR. The water uptake clearly increased from 6% to 19% with a decrease of the molecular weight of HTNR from 4000 to 1000 g mol<sup>-1</sup>. This is mainly due to an increase of hard segment or urethane groups. Also, an increase of the level of epoxide groups on HTNR backbone from 0% to 20% at 5.1% wt DMPA content led to a slight increase of the water uptake because of an increase of polar group on hydrophobic chain. However, WPUs based on HTNR gave very low water uptake by comparison with other ionic PUs, which are based on hydrophilic precursors (100%).<sup>22,43,44</sup> It is concluded that these WPU films based on HTNR have a good hydrophobic property.

## Thermal analysis

### TGA

TGA data for the WPU films from HTNRs with different contents of DMPA, different molecular weights of HTNR, and different epoxide contents of HTNR are shown in Table V. Weight loss and characteristic temperatures were determined from the maximum of the derived curve ( $T_{max}$ ).

A three-stage loss thermal degradation was observed for all WPU films. The first stage degradation at 256°C–269°C corresponds to the approximate content of weight loss of the ammonium salt of carboxylic parts formed with TEA and DMPA. The second stage at 304°C–322°C can be attributed to urethane bond breaks that occur through the dissociation to HTNR and isocyanates, the formation of primary amines and olefins, or the formation of

secondary amines, which results in the loss of carbon dioxide from the urethane bond.<sup>45</sup> Finally, stage at 368°C–383°C relates to the decomposition of structure of oligoisoprene. We observed that the increased DMPA contents in sample WPU1–WPU7 led to an increased first stage weight loss. Their degradations were assumed that the cleavage of TEA ionic groups and breakage of the urethane bonds reacted of DMPA and diisocyanates were occurred (Figs. 11 and 12). The results agreed with the previous work,<sup>46</sup> which studied on hydroxyl telechelic polybutadiene (HTPB) in which the thermal decompositions in first step of film polyurethane dispersion were increased with an increase of DMPA and TEA contents.

For the WPU films based on HTNR with different molecular weights, the temperature of weight loss due to decomposition of urethane bonds increases with a decrease of molecular weight of soft segment (NR) or an increase in hard segment. It was

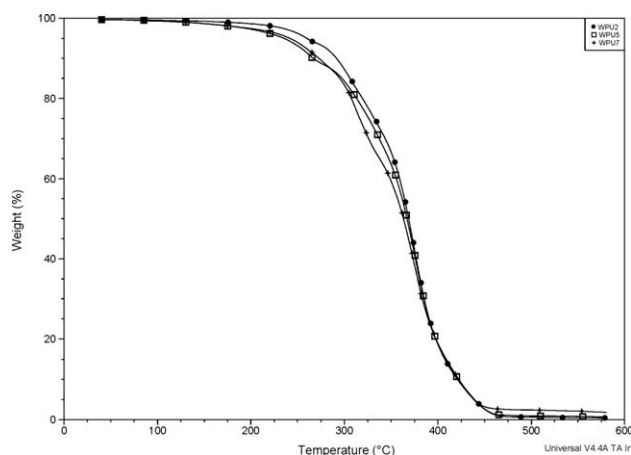
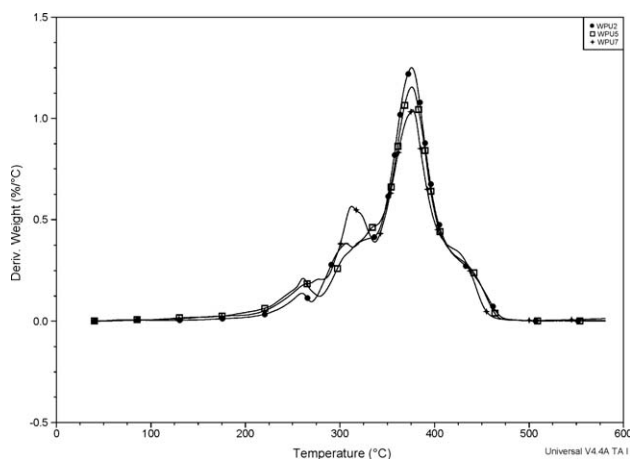


Figure 11 TGA thermogram of WPU films: (○) WPU2, (□) WPU5, and (×) WPU7.



**Figure 12** DTGA thermogram of WPU films: (○) WPU2, (□) WPU5, and (×) WPU7.

confirmed that the weight loss of secondary stage is increased approximately of 7% from HTNR4000 to HTNR1000 at the same DMPA contents. This means that the increasing of this soft segments leads to a decrease of thermal stability in terms of weight loss (Table V). The temperature of decomposition of HTNR slightly increased from 377°C to 385°C with an increase of epoxide units on the backbone of HTNR from 0% to 20% (Table V). This gives rise to an expectation that an interaction of these polar groups was occurred.

## DSC

The glass transition temperatures ( $T_g$ ) of the WPU films are shown in Table V. We observed that all WPU films show only a glass transition temperature of soft segment, and we do not observed melting points and crystallization transitions. The glass transition temperatures of WPU films depend strongly on the epoxide content and on the molecular weight of HTNR with a variation from  $-63^\circ\text{C}$  to  $-46^\circ\text{C}$ . The  $T_g$  value increases with an increase in the epoxide content of WPU based on HTNR2000 from  $-60^\circ\text{C}$  to  $-46^\circ\text{C}$ . This is mainly due to higher backbone rigidity and higher chain interactions.

In addition, the influence of molecular weight of HTNR (1000, 2000, and 4000  $\text{g mol}^{-1}$ ) on  $T_g$  of WPU films was also examined, which is presented in Table V. It was found that the  $T_g$  value decreases from  $-53^\circ\text{C}$  to  $-63^\circ\text{C}$  with an increase in the molecular weight from 1000 to 4000  $\text{g mol}^{-1}$ . This increase can be attributed to the less restricted mobility of the polymer chain as a result of the lower degree of hydrogen bonding between the hard segments and the soft segments.<sup>3,10,47</sup> For the case of the increasing DPMA content in WPU-based HTNR2000, the  $T_g$  values are constantly  $\sim -60^\circ\text{C}$  with an increase in

content of DMPA from 1.6 to 7.5 wt % as given in Table V. This indicated that the phase mixing of soft segment with hard segment was almost not occurred.<sup>16</sup>

## CONCLUSIONS

WPU based on HTNR were successfully prepared by prepolymer process with various amounts of DMPA, different molecular weights, and epoxide contents of HTNR. The particle size of WPU dramatically decreases when an amount of DMPA was increased from 2.6 to 6.6 wt % or molecular weight of HTNR was increased from 1000 to 4000  $\text{g mol}^{-1}$ . However, the particle size of WPU slightly increased with an increase of epoxide content of precursors from 0% to 20%. The water uptake of WPU-based films increased with an increase of DMPA content, hard segment, and epoxide content. The WPU film based on HTNR4000 exhibited the lowest water uptake at 4 wt % DMPA content. In first stage, decomposition of WPU films was increased with an increase of DMPA content. The glass transition temperature ( $T_g$ ) of WPU films was increased with an increase of epoxide content or a decrease of molecular weight of HTNR. However, the increasing of DMPA content had no affect on  $T_g$  of WPU films.

NR-based polyols has a potential to develop a synthesis of new WPUs based on renewable source and has been motivated by environmental considerations, i.e., replacement of petroleum-based products, and use of solvent-free products.

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