The chain extender content and NCO/OH ratio flexibly tune the properties of natural rubber-based waterborne polyurethanes

Anuwat Saetung,[1] Phathanyaphon Tsupphayakorn-ake,[1] Tulyapong Tulyapituk,[1] Nitinart Saetung,[2] Pranee Phinyocheep,[3] Jean-François Pilard[4]

[1]Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani campus, Pattani 94000, Thailand
[2]Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[3]Faculty of Science, Department of Chemistry, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand
[4]Département Méthodologie et Synthèse, Équipe Méthodologie en Synthèse des Polymères, Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Université du Maine, Faculté des Sciences, Avenue Olivier Messiaen, 72085, Le Mans, Cedex 9, France
Correspondence to: A. Saetung (E-mail: sanuwat@bunga.pn.psu.ac.th)

ABSTRACT: The effects of chain extender content (ethylene diamine, EDA) and NCO/OH ratio on the properties of natural rubber-based waterborne polyurethanes (WPUs) were investigated experimentally. The particle size of WPU increased significantly with the NCO/OH ratio, in the presence of the EDA chain extender, while it was unaffected by the EDA content. The water uptake of WPU film increased with the EDA content, while the swelling in various solvents decreased. In a thermal analysis, the second decomposition stage of a WPU film increased with the EDA content and with the NCO/OH ratio that also positively affected the dynamic mechanical and mechanical properties. These factors in WPU films had no the effect on the T_g. The stress–strain curves clearly showed the change in WPU films from soft elastomeric materials to ductile and hard plastics. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42505.

INTRODUCTION

Polyurethanes play a vital role in many industries, such as those producing footwear, ships, and automobiles, as well as in the construction business. They appear in various very surprising forms, and their use is continuously increasing.[1] Waterborne polyurethanes (WPUs) are binary colloid systems, in which the polyurethane particles containing ionic or nonionic groups are dispersed in an aqueous continuous medium.[2–4] Since the late 1960s, WPUs have been commercially important and have increasingly replaced solvent-based polyurethanes in the market.[3] Among the important advantages over solvent-based polyurethanes are reduced environmental concerns regarding the volatile organic compounds (VOCs) that pollute and cause health problems. Other advantages are nonflammability and economic competitiveness. However, the main advantage of the WPUs may be the performance that in many applications is comparable to or better than of the solvent-based polyurethanes.[2,3,5–8] The WPUs are widely applied as coatings, on substrates such as wood, leather, plastics, and metals for automotives, and are used in printing inks.[6,9]

The polyurethanes, such as polyether or polyester, are mostly synthesized from various isocyanates with petroleum based polyols, with the inclusion of polydiene diols that act as soft segments in the structure.[10] However, the cost of fossil fuels has typically increased, and there have been concerns about depleting the petroleum oil reserves, and also environmental concerns about toxic waste or climate warming; these factors encourage a transition to renewable raw materials.[11] These aspects have motivated increasing research on alternative renewable raw materials in the manufacture of polymers. The natural polyols are important candidates as they are abundant, renewable, cheap, and environmentally friendly. Castor oil[12–14] and other (modified) vegetable oils[7,15–17] have been used to prepare various forms of polyurethane, such as waterborne, foams, films, and adhesives. Recently, Lu and Larock[18] prepared novel polyurethane dispersions based on modified soybean oils (MSOLs), with the OH functionalities of MSOLs ranging from 2.4 to as high as 4.0. The dispersed particle size, as well as the structure, thermophysical, and mechanical properties of the resulting polyurethane films, containing 50−60 wt % of bio-renewable

Table I. General Properties of Hydroxyl Telechelic Natural Rubber

Precursors	T_g (°C)	$\overline{Mn}_{NMR}$ (g mol^{-1})	$\overline{Mn}_{SEC}$ (g mol^{-1})	PDI	$\overline{fn}_{(OH)}$	Appearance
HTNR3500	−64	3500	3800	2.04	2	Yellowish, viscous liquid

MSOL, depend strongly on the polyol functionality and the hard segment content. In that study, the cross-link density of the polyurethanes increased significantly with the OH functionality of the MSOLs, whereas the hydrogen bond interactions increased with the hard segment content. Thus, it is possible to synthesize vegetable oil-based materials ranging from elastomeric polymers to ductile plastics, and further on to rigid plastics.

Rubber trees are important economic plants in the South-East Asia, and Thailand leads the global exports of natural rubber with its about 200,000 kgs in 2013.[19] Natural rubber is an abundant renewable natural polymer with unique strength and elastic properties, so it has been exploited in many applications since Mr. Goodyear revealed the vulcanization reaction. Chemically it is composed of cis-1,4-polyisoprene units. The rich double bonds on its polymer backbone provide a great opportunity for easy chemical modifications to produce polyols.

During the past decade, our laboratory has successfully modified natural rubber, with controlled molecular weight and functionalities, to polyols labeled hydroxytelechelic natural rubber (HTNR). The HTNR has further been variously modified with epoxidation, hydrogenation,[20] amination,[21,22] etc. These modified HTNRs have been consistently explored as starting materials for various types of polyurethane; for example, antibacterial film,[11] foam,[20,23] waterborne,[24] (Table I) elastomers,[10] and biodegrable polymers.[25] In prior work, we have synthesized a new natural rubber-based WPU by prepolymer technique. The effects of interior emulsifier content, molecular weight, and HTNR and its modified structure on the physical and thermal properties were investigated.

A chain extender is an important additive in the polyurethane formulation. Its structure (linear or aromatic), functionalities, and reactive groups (amine or hydroxyl groups) affect the properties of polyurethane. Kebir et al.[10] reported the influences of chain extender types and contents on the properties of polyurethane films based on a new hydroxytelechelic cis-1,4-polyisoprene (HTPI). They concluded that the material properties of polyurethane films depend on the nature and content of chain extender, and on the isocyanates. Thermosetting materials were obtained with isocyanates, or with chain extenders possessing

functionality higher than 2. Thermoplastic materials were obtained when the molar ratio of chain extender and HTPI was 2. However, elastomeric behavior was obtained without the chain extender. Ligadas and coworkers[26] studied the effects of 1,3-propanediol content on the properties of poly(ether urethane) network, formed from epoxidized methyl-oleate-based polyether polyol and L-lysine diisocyanates. The chain extender, through increasing the hard segments, controlled the physical, mechanical, and degradation properties of these polymers.

However, there is no prior report on the effects of chain extender content and NCO/OH ratio on natural rubber-based WPU. Therefore, we investigated experimentally the influences of chain extender content and the NCO/OH ratio, as well as the NCO/OH ratio at a constant EDA content, on the physical properties of WPU. The mechanical, thermal, morphological, water absorption, and swelling properties were determined for WPU films.

EXPERIMENTAL

Materials
Toluene diisocyanates (TDI), dimethylol propionic acid (DMPA), 2-butanone or methyl ethyl ketone (MEK), dibutyltin dilaurate (DBTL), and triethylamine (TEA) were purchased from Sigma-Aldrich. Toluene and tetrahydrofuran (THF) were obtained from LabScan. All chemicals were used as received.

Syntheses
Hydroxyl telechelic natural rubber (HTNR) was prepared from carbonyl telechelic natural rubber (CTNR) as described previously.[20,23] Their chemical structures are shown in Figure 1.

Synthesis of Waterborne Polyurethane
All samples were synthesized by the prepolymer mixing technique that is schematically illustrated in Figure 2, following methodology described previously,[24] and the synthesis formulations are shown in Table II. Briefly, DBTL was added in an amount equal to 0.5 wt % of the total solids. An amount of TEA that was 5% in excess of the DPMA content was then added. The WPU was synthesized in a 100 mL round-bottomed, four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. The reaction
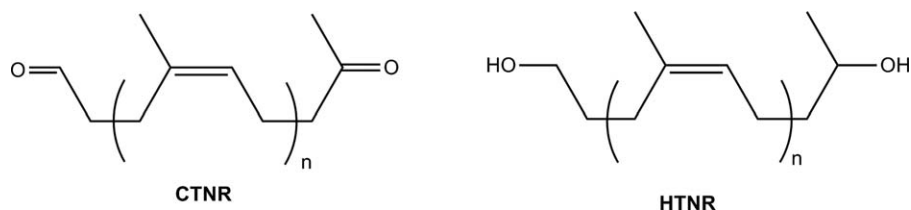
Figure 1. Chemical structure of telechelic natural rubbers.
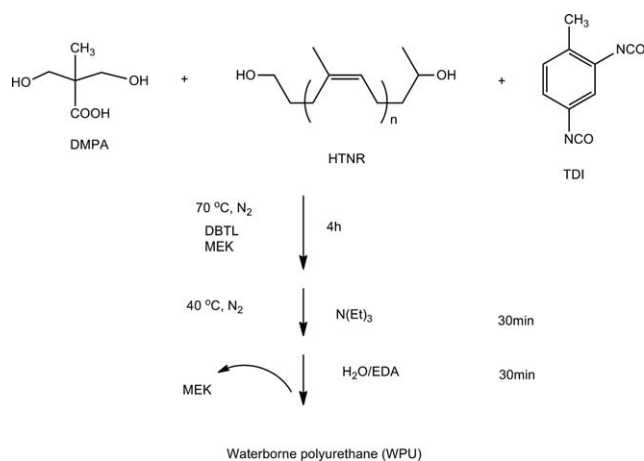
Figure 2. Synthesis of WPU.

temperature was controlled by a constant temperature oil bath. The HTNR, DMPA, and DBTL were weighed and transferred into the reactor flask. The mixture was adjusted to 40 wt % by adding MEK, then heated to 70°C under nitrogen atmosphere and held for 20 min. Then TDI was added dropwise into the flask, and allowed to react at 70°C under nitrogen atmosphere for 4 h. The prepolymer was allowed to cool to 40°C. Then the carboxylic acid groups in DMPA were

neutralized with TEA. The mixture was stirred for a further 30 min to ensure that neutralization was complete. The next step was dispersion as follows. The ionomeric prepolymer was dispersed by adding desired amounts of deionized water and ethylene diamine (EDA) while stirring vigorously, and stirring was continued for 30 min. Finally, the MEK was evaporated to obtain the WPU. All the samples were desired to 20% wt.

Film Preparation

The WPU films were prepared by casting each dispersion in a polypropylene mold without a releasing agent. The films were allowed to dry at room temperature for 2 days, and were kept under 50°C for 7 days before testing.

Analyses

FT-IR. The FT-IR spectra were recorded on a Nicolet Avatar 370 DTGS FT-IR spectrometer across the range 4000–500 cm^{-1}, equipped with a diamond attenuated total reflection (ATR) device and controlled by OMNIC software.

Particle Size. The particle size distributions of the aqueous WPU dispersions were measured with a laser particle size analyzer, model Beckman Coulter LS 230 by Coulter LTD. Each sample was diluted with deionized water to 10% concentration before testing, without any filtering or ultrasonic treatment.

Table II. Formulation of Waterborne Polyurethanes

Samples	TDI (mole)	HTNR (mole)	EDA (mole)	NCO/OH
WPU3	1.0	1.0	0.0	1.0/1.0
WPU5	1.5	1.0	0.5	1.0/1.0
WPU7	2.0	1.0	1.0	1.0/1.0
WPU9	2.5	1.0	1.5	1.0/1.0
WPU11	3.0	1.0	2.0	1.0/1.0
WPU30	1.5	1.0	0.0	1.5/1.0
WPU31	2.0	1.0	0.0	2.0/1.0
WPU32	2.5	1.0	1.0	2.5/1.0
WPU33	3.0	1.0	1.0	3.0/1.0

DMPA = 5.6%; TEA = 1.05 mole of DMPA; Controlled TSC = 20%.

Table III. Results of EDA Contents or NCO/OH Ratios on TSC, pH, and Particle Size of WPU

| Samples	EDA (mol)	NCO/OH	Appearances	TSC (%)	pH	Average particle size (nm)
WPU3	0.0	1.0/1.0	Milky blue	20	7.01	79 ± 29
WPU5	0.5	1.0/1.0	Light yellowish	22	8.94	80 ± 31
WPU7	1.0	1.0/1.0	Light yellowish	20	9.00	88 ± 42
WPU9	1.5	1.0/1.0	Light yellowish, viscous	22	8.98	76 ± 39
WPU11	2.0	1.0/1.0	Light brown, high viscous	24	8.92	75 ± 40
WPU30	0.0	1.5/1.0	Milky	23	8.97	88 ± 51
WPU31	0.0	2.0/1.0	Milky	19	8.67	86 ± 52
WPU32	1.0	2.5/1.0	Milky	21	9.16	143 ± 50
WPU33	1.0	3.0/1.0	Milky/partially precipitate	11	8.86	Nonstable
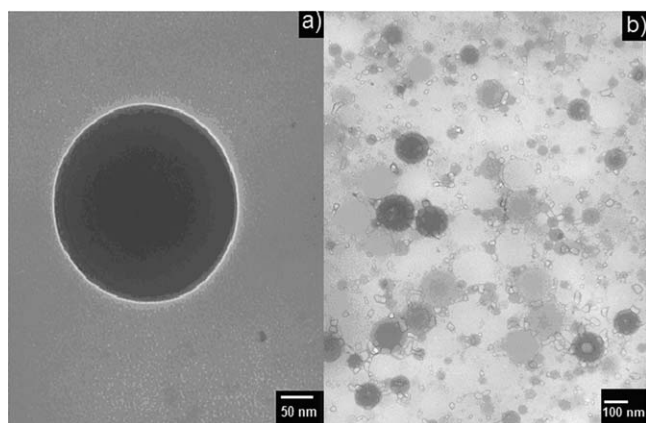
Figure 3. TEM images of WPU3: (a) 100 K and (b) 50 K.

Morphology of WPU. The morphology of WPU was observed on a transmission electron microscope (TEM), model JEOL JEM-2010. The sample was diluted with deionized water to 0.05%. One drop of the diluted dispersion was placed on the coated side of a 200-mesh nickel grid in a petri dish, and stained with 2% osmium tetraoxide. After drying, the sample was imaged by TEM.

Tensile Properties. The sample films were preformed following ISO 37 with Type 2 die. The tensile properties of each WPU film were tested using Hounsfield model H 10KS, from Hounsfield test equipment LTD. It was equipped with a 100 N load cell, and the grips included a laser sensor for

determining the elongation. The cross-head speed was set at 100 mm min^{-1}.

Water Absorption. The water absorption measurement was carried out by immersing a 10 × 10 × 1 mm WPU film sample in distilled water at 20°C. After immersion, the water on the sample surfaces was wiped off with tissue paper, and then the sample was weighed. The absorption percentage ($W(\%)$) was calculated as follows:

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

where W_s is the weight of the immersion treated film and W_0 is the weight of the original film.

Swelling. Swelling properties were assessed with solvents (THF, MEK, and toluene) by using 16-mm-diameter circular WPU film samples. Each sample was immersed in a solvent for 24 h, and the diameter of the swollen specimen was then determined. The swelling behavior was quantified from the original and swollen diameters.

Thermal Properties. TGA analysis was performed on a Perkin-Elmer (model STA 6000) using Pyrist software. The heating rate was 10°C min^{-1} from room temperature to 600°C, under nitrogen atmosphere with a 90 mL min^{-1} flush flow rate. The starting weight of each sample was about 10 mg.

DSC analysis was performed on a DSC7 (Perkin Elmer, USA). Aluminum pans containing 10–15 mg of sample were heated from −100 to 100°C under nitrogen atmosphere. The heating rate was 10°C/min. The first heating run was carried out to
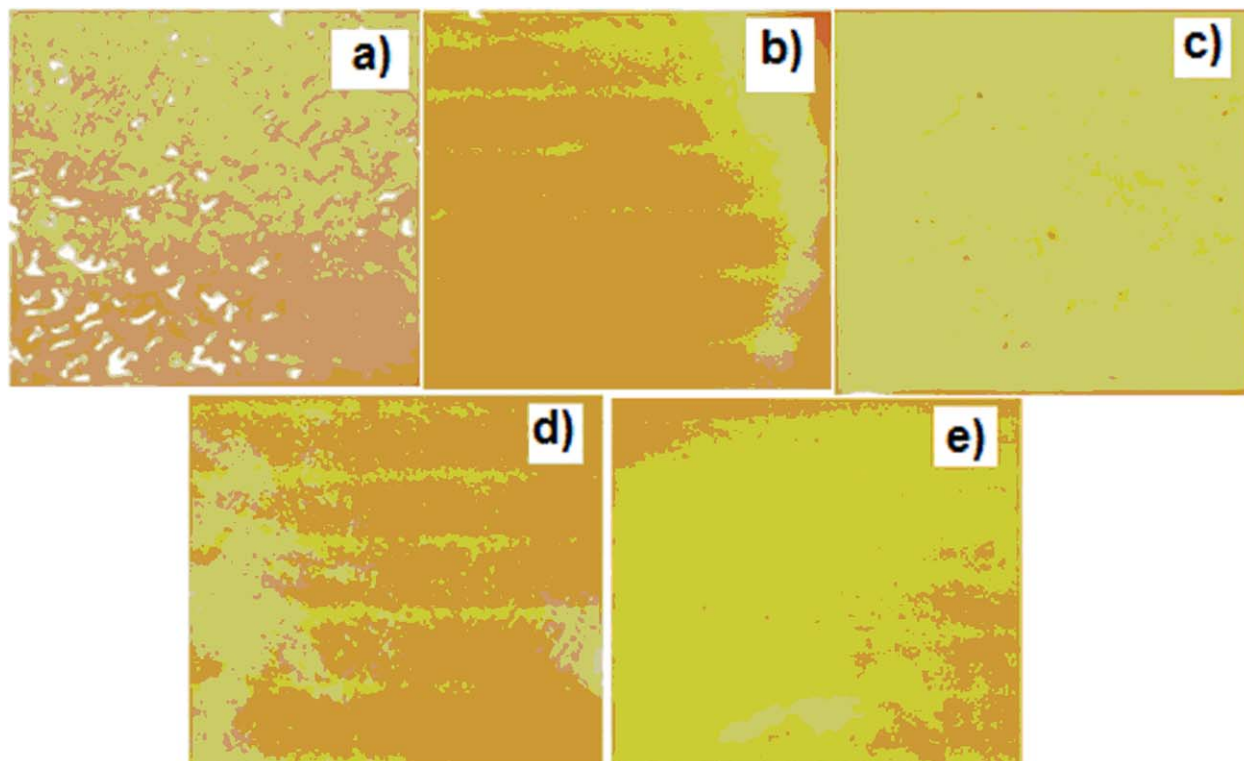

Figure 4. Appearance of WPU films: (a) WPU3, (b) WPU5, (c) WPU7, (d) WPU9, and (e) WPU11. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
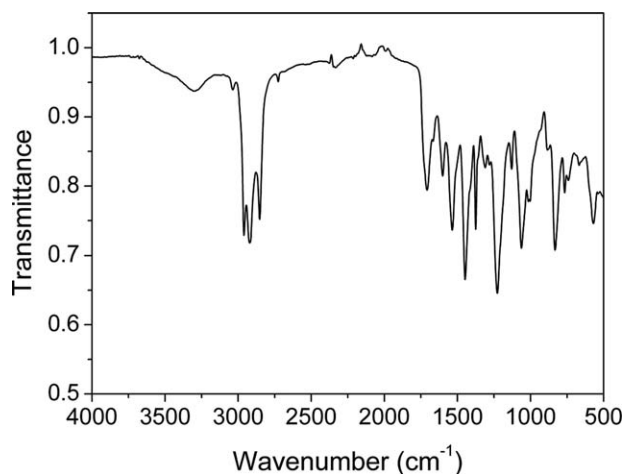
Figure 5. FT-IR spectrum of WPU3 film.

remove the thermal history of the samples. From the second heating run, the glass transition temperature (T_g) of the polyurethanes was obtained.

Dynamic mechanical analyses of the WPU films were carried out by DMTA (Rheometric Scientific DMTA V, USA) in tensile mode at a frequency of 1 Hz and 0.01% strain with a heating rate of 3°C/min by scanning the WPU films from −100 to 150°C. Tensile storage modulus (E'), loss modulus, and the loss factor (tan δ or tan delta) as the quotient of loss and storage, E''/E'. E' and E'' characterize the elastic and viscous components of a viscoelastic material under deformation.

RESULTS AND DISCUSSION

In the experiments to assess effects of chain extender content, at a constant 1/1 NCO/OH ratio, the WPU samples had 5.6% wt of the internal emulsifier, DMPA, as shown in Table II. The effects of varied EDA content on the physical properties of WPU samples, namely, particle size, pH, and TSC, are summarized in Table III. For instance, the subjective appearance of WPU3 was milky blue to slightly blue. The TEM images of these natural rubber-based WPUs at magnifications (a) 50 K and (b) 100 K are shown in Figure 3. Generally, natural rubber consists of carbon–carbon double-bonded isoprene units forming polymer chains. When the repeating units are stained by OsO$_4$, this results in a dark PU phase in the TEM images. It is clear that the WPU3 particles were round in shape and well dispersed. The particle diameter was around 100 nm, which agrees with Coulter analysis using a light scattering technique. The average particle size of all samples was not significantly influenced by the EDA content. Normally, several factors affect the particle size of a WPU; for instance, the hydrophilicity, the prepolymer viscosity, the ionic group position, the chain rigidity, and the chemical structure of soft segments.[18,27] In experiments with varying NCO/OH ratios, this ratio had a clear effect on the average particle size, especially with EDA content at 1 mole (WPU7, WPU32, and WPU33). The average particle size increased from 88 to 143 nm, and the particles partly precipitated at NCO/OH ratios of 1, 1.5, and 2, with EDA content at 1 mole. At a fixed DMPA content,

the increasing WPU particle size with the NCO/OH ratio might be mainly due to the increased viscosity of the WPU prepolymer.[18,27] According to García-Pacios et al.,[28] it is revealed that the polycarbonate of hexanediol-based WPU dispersion with NCO/OH ratio of 1.3 showed a smaller and homogeneous particle size and by increasing the NCO/OH ratio, the particle size of the dispersion increases and the particle crowding is favored.

As the EDA content was increased from 0 to 2 mole (Table III), the WPUs became more viscous and dark in color, and film samples are shown in Figure 4. These films were yellowish, soft, and flexible.

Figure 5 shows the FT-IR (ATR technique) results for assessing the chemical structures in the WPU films. In the FT-IR spectra, the polyurethane was represented by absorption bands around 3330, 1700, and 1530 cm^{-1}, corresponding to N—H, C=O, and N—CO stretching vibrations, respectively. In addition, the absorption bands of cis−1,4 polyisoprene at 2860 cm^{-1} (C—H stretching), 1453 cm^{-1} (—CH$_2$— deformation), 1378 cm^{-1} (methyl-H deformation), and 838 cm^{-1} (=C—H out-of-plane deformation) were observed.[24] The disappearance of the
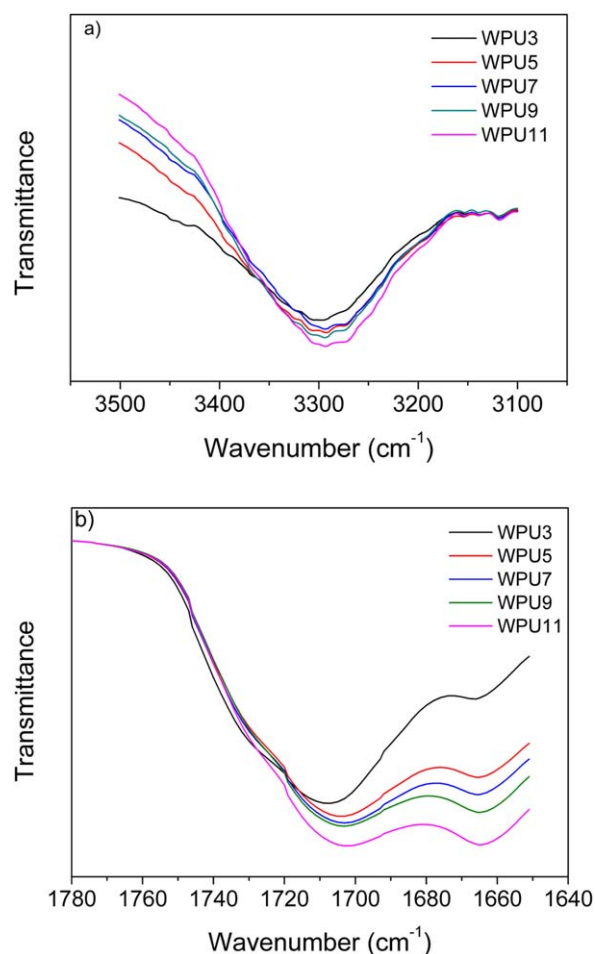

Figure 6. FT-IR spectra of WPU films with various EDA contents (0–2 mol): (a) at 3300 cm^{-1} and (b) at 1700 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
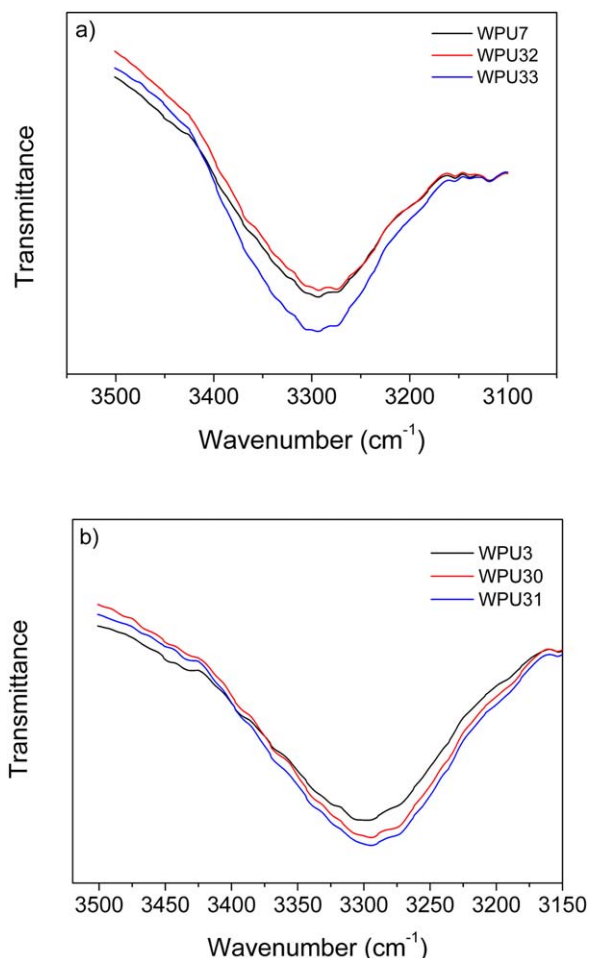
Figure 7. FT-IR spectra at 3300 cm^{-1} of WPU films with various NCO/OH ratios: (a) with EDA 1 mol and (b) without EDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2270 cm^{-1} absorption peak confirms that no residual-free NCO remained in the WPU films. These observations indicate that the synthesis of WPU from natural rubber was successful.

The physical bonding by hydrogen bonds is important to the properties of polyurethanes. These bonds occur between the N—H part of an amide group (i.e., urethane or urea) as the donor and the carbonyl group in an amide group as the acceptor. Therefore, FT-IR analysis is good for assessing these interactions in WPU films. The FT-IR spectra of WPU samples with various chain extender (EDA) contents are shown in Figure 6. These spectra indicate two important vibration regions. The first is the NH-stretching vibration around 3200–3500 cm^{-1}, and the other is the carbonyl (C—O) stretching vibration region (1700–1730 cm^{-1}). In addition, clearly the N—H bond stretching shifted to a lower wavenumber for WPU11 as compared to WPU3, due to an increased degree of association in those WPU films with a higher hard segment content.[18] In agreeing with a shift of peaks from 1710–1720 cm^{-1} to approximately 1700 cm^{-1} with the increase of hard segment for EDA extended. It might be that the stretching vibration mode of carbonyl groups became easier. Because the hard segments interrupt dipole–dipole interactions of the carbonyl groups, these groups are freed from interactions with each other. Moreover, the 1660 cm^{-1} intensity from carbonyl of urea increased with the EDA content of the WPU film samples.[26,29]

The FT-IR peak intensity at wavenumber 3300 cm^{-1} is shown for the WPU films with various NCO/OH ratios, with and without EDA, as shown in Figure 7. The intensity of N—H vibration at 3300 cm^{-1} increased with the NCO/OH ratio, in both conditions regarding EDA, because the increased isocyanate content formed more amide structures. Moreover, the N—H bond stretching vibration moved to a slightly lower frequency as NCO/OH ratio was increased, due to the increased degree of association, caused in turn by the hard segment content increase in the WPU films.

The results of tensile strength, elongation at break, and Young's modulus for the WPU films from HTNR3500 with various EDA contents and NCO/OH ratios are shown in Table IV and Figure 8. The WPU3 film was very soft and rubbery with a 1.47 MPa modulus, 0.09 MPa tensile strength, and 100% elongation at break. When the EDA content was further increased, the modulus and ultimate stress of the WPU11 sample (2 moles EDA) clearly increased, while elongation at break was not significantly affected. Those WPU films (WPU3–7) that exhibited around 100% maximum strain probably had relatively low cross-link density or highly linear structure, and the stress–strain behavior was that of a soft elastomeric polymer.[18] However, the WPU11 sample's behavior is typical of a ductile plastic with a clear yield

Table IV. T_g and Mechanical Properties of WPU Films

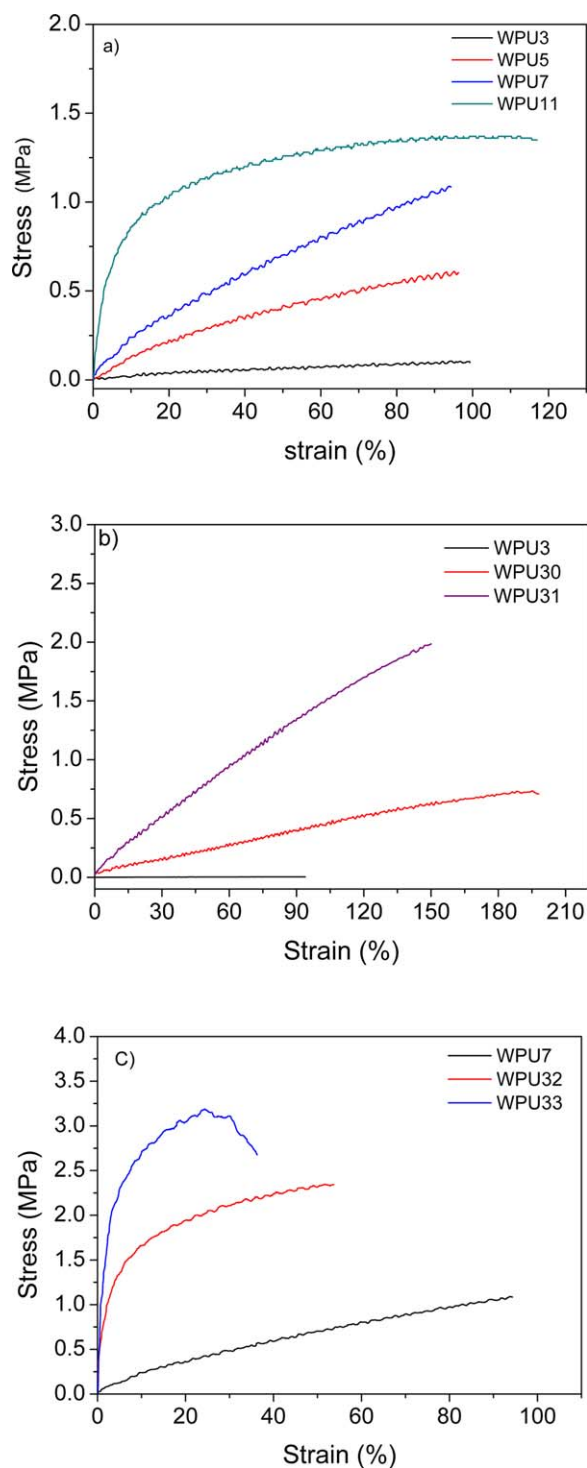| Samples	Hard segment (%)	T_g (°C)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU3	21.2	−64.1	1.47 ± 0.7	0.09 ± 0.0	100 ± 11.0
WPU5	23.4	−65.6	10.72 ± 5.5	0.60 ± 0.0	97 ± 0.2
WPU7	25.7	−64.7	11.14 ± 2.2	1.09 ± 0.2	94 ± 29.8
WPU11	29.9	−64.0	64.44 ± 0.0	1.35 ± 0.0	117 ± 42.8
WPU30	22.7	−65.3	5.91 ± 0.1	0.75 ± 0.0	200 ± 4.2
WPU31	24.2	−64.3	15.95 ± 11.5	2.00 ± 0.1	150 ± 31.2
WPU32	27.4	−66.1	143.14 ± 15.8	2.35 ± 0.1	54 ± 7.5
WPU33	28.4	−65.9	229.33 ± 0.0	3.19 ± 0.0	38 ± 0.0

Figure 8. Stress and strain curves of WPU films: (a) EDA contents, (b) NCO/OH ratios without EDA, and (c) NCO/OH ratios with EDA 1 mol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

point, and its modulus and tensile strength were approximately 43 and 135 times higher than those of the WPU3 film sample.

In addition, the WPU films without EDA content showed elastomeric polymer behavior. Their modulus and tensile strength

increased with the NCO/OH ratio: the WPU31 sample (NCO/OH = 2/1) had about 200% higher tensile properties than the WPU3 (NCO/OH = 1/1). Moreover, with NCO/OH = 2/1 and 1 mole of EDA (WPU 33), the highest modulus and tensile strength were achieved, while the elongation at break was smallish (38% ± 0). This was a relatively hard plastic with yielding behavior and strain softening. These changes in the mechanical behavior were attributed to the hard segment content. This content contributes to the interaction by hydrogen bonds in the WPU films from HTNR. It is concluded that increasing the EDA content and the NCO/OH ratio in WPU films improved the mechanical properties, and it was possible to transition from soft elastomeric materials to ductile and hard plastics.

Figure 9 shows SEM micrographs of WPU films (WPU3, WPU5, WPU11, WPU30, WPU32, and WPU33), which was revealed by a scanning electron microscope (SEM). In the series of EDA contents, the micrographs reveal that the fracture surface exhibits greater matrix tearing in WPU11 [Figure 9(c)] compared to the WPU3 [Figure 9(a)] and WPU5 [Figure 9(b)] films, respectively. The rougher surface observed in the WPU films indicates that the matrix tearing has contributed to a higher tensile strength. In addition, the NCO/OH ratio, the micrograph also shows that the fracture surface exhibits the greatest matrix tearing in WPU33 [Figure 9(f)]. This result was supported by tensile behavior. Moreover, all WPU films do not show the presence of domains. This may be due to the very small size of the domains, which are densely distributed in the HTNR matrix.[30]

The water uptake of WPU films at a constant 5.6% DMPA content is shown in Figure 10, for various EDA contents. Clearly the water uptake increased with immersion time as well as with the EDA content, which contributed to the hydrophilic blocks in the hard segments of urea and urethane groups. For example, in immersion for 7 days, the minimum 17% water uptake was with WPU3, while the maximum 45% was with WPU7. However, these water uptakes for the WPUs based on natural rubber were very low in comparison with other ionic PU films, due to the hydrophobic nature of the soft segments in our WPUs. The ionic PUs based on hydrophilic precursors have water uptakes around 1000%.[24,31]

The swelling properties of WPU films in select solvents, namely, tertrahydrofuran (THF), toluene, and methyl ethyl ketone (MEK), are shown in Table V and Figure 11. The WPU3 samples were completely dissolved in each solvent, due to the low cross-linking or the linear structure, and the nonpolar nature. In addition, toluene gave high swelling of these HTNR-based polyurethane films. However, the swelling decreased with the EDA content [Figure 11(a)] and the NCO/OH ratio [Figure 11(b)], so that for example WPU11 with 2 moles of EDA had only 100% swelling. It was expected that increasing the EDA content or the NCO/OH ratio would increase the hard segments, promoting hydrogen bonding and the formation of physical networks also by more active proton positions. With the hardest segments, WPU33 exhibited the lowest 23.8% swelling in toluene and 5.4% in MEK.
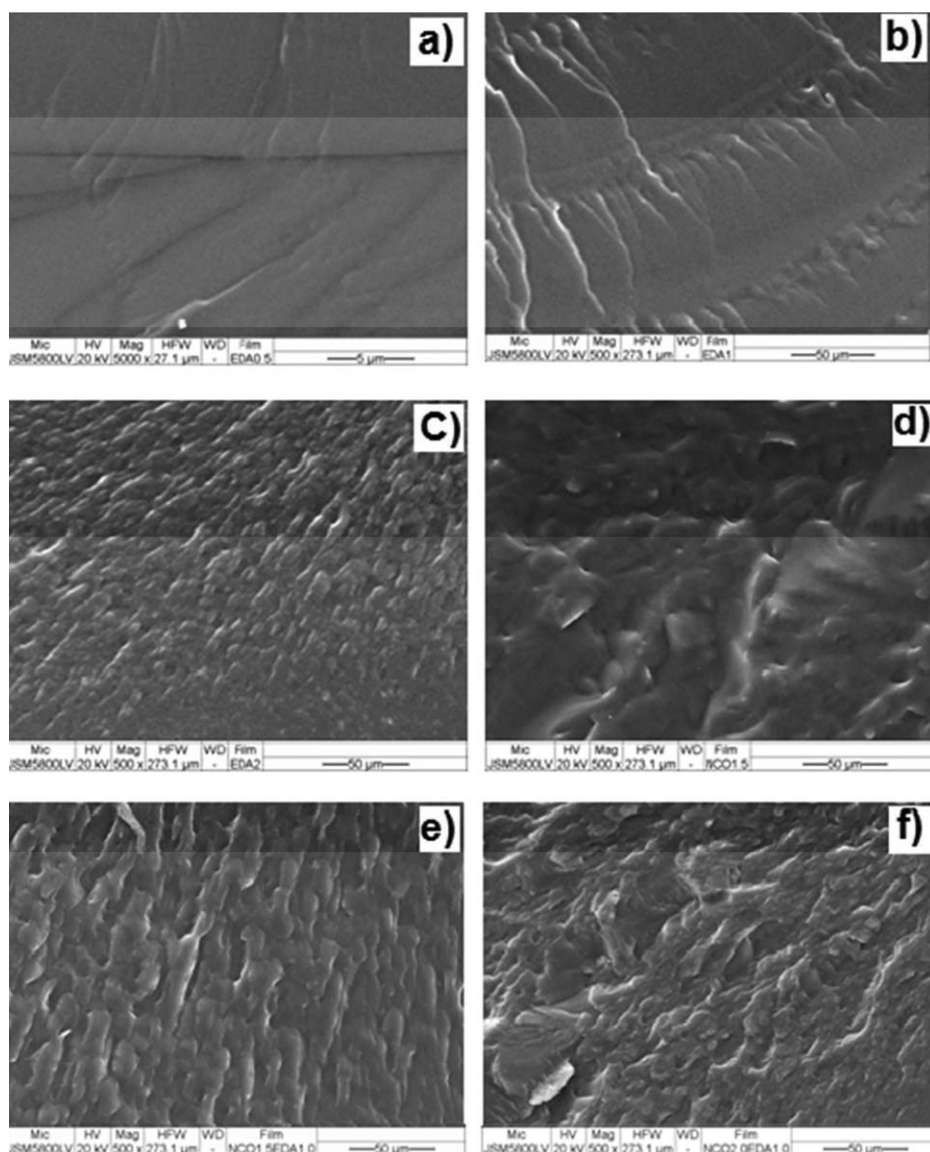
Figure 9. SEM of WPU films: (a) EDA 0.5, (b) EDA 1.0, (c) EDA 2.0, (d) EDA0/NCO1.5, (e) EDA 1.0 and NCO/OH=1.5, and (f) EDA 1.0 and NCO/OH = 2.0.

DSC is a good technique to measure a number of characteristic properties of a sample. It is possible to observe fusion and crystallization events as well as T_g. Normally, T_g of polymer is depended on a movement of backbone chains. For instance, the more chain mobility or flexibility, the lower T_g of polymer was obtained. For this work, the amount of EDA contents and the NCO/OH ratio in WPU films formulation were studied. It was widely assumed that the increasing of EDA contents or the NCO/OH ratio gave a shift to higher T_g of WPU films. However, their T_g belonged to HTNR segment and were changed slightly in the range from -64 to $-66°C$ as varying EDA contents or the NCO/OH ratio as shown in Figure 12 and Table IV. It was concluded that these factors in WPU films had no effect on the T_g for them. Therefore, WPU films improved the mechanical properties by adjustment of EDA contents (WPU3–11) or the NCO/OH ratio (WPU30–33) without an influence in T_g of WPU films. According to some literatures, for instance,

our previous work,[24] it was observed that all WPU films showed only the T_g of HTNR or soft segment when an increasing of DPMA contents, and we do not observed melting point and crystallization transitions. It was concluded that the T_g of PU was greatly depended on mobility of soft segment. Moreover, Kebir et al.[29] and Pual et al.[32] were attended to the effect of NCO/OH ratios and amount of chain extender (diols) on T_g of polyurethane materials. It was found that the T_g of PU had no influence on the NCO/OH ratios and amount of chain extender. Their films showed only the T_g. However, the T_g of WPU films were significantly influenced on modification of HTNR such as epoxidation, hydrogenation as well as a different molecular weight of HTNR due to reducing of mobility of polymer chain.

In an effort to understand the structure–property relationships, dynamic mechanical analysis was utilized to study the thermochemical properties of WPU films based on natural rubber.
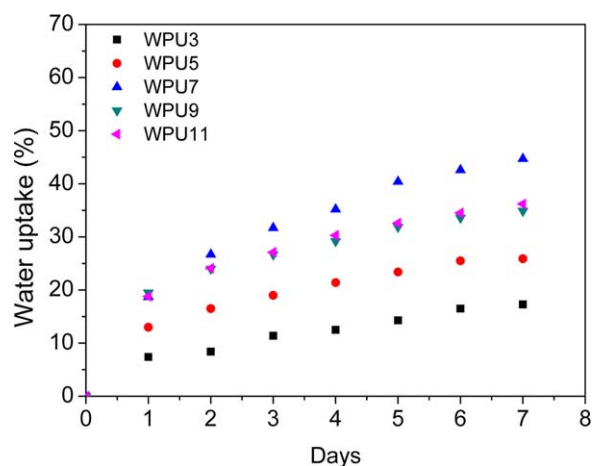
Figure 10. Water uptake of WPU films with different EDA contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMTA provides the information on the mechanical behavior and glass transition of a polymer. The temperature associated with the peak magnitude of tan delta is defined as the glass transition temperature (T_g). The storage modulus is a measurement of material stiffness.[33,34] Figure 13(a) shows the E' versus temperature plot of WPU films in the series of EDA content or the NCO/OH ratio. It was found that the WPU film at low hard segment gave the low E' at the beginning period according to Young's modulus of WPU films. While the drop in storage modulus of WPU films generally shifted to higher temperature with lower amount of hard segments, especially WPU3. It was assumed that WPU films had the effect of EDA content or the NCO/OH ratio on the molecular weight or physical cross-linking of WPU films. For instance, WPU3 (EDA 0.5 mole) film shows the most drop in storage modulus at high temperature due to low molecular weight or low physical cross-linking. Whereas the increasing of EDA contents or NCO/OH ratio, for instance, WPU11 (EDA 2 mole) film or WPU32 (EDA 1 mole

with NCO/OH = 2) shows the rubbery plateau and the resistance to flow with rising temperature due to increasing of molecular weight or physical cross-linking of WPU film. The corresponding plots of tan delta versus temperature are given in Figure 13(b). The samples show a major relaxation at about −50°C characterized by a decrease in storage modulus of at least two orders of magnitude. This is attributed to the glass transition of the HTNR segments. This T_g value is unaffected by the hard segment content, indicating that the soft segment phase is well separated.[30]

The TGA data for the WPU films from HTNR are shown in Table V and Figure 14, with various EDA contents and NCO/OH ratios. The weight loss and the characteristic temperatures were determined from the maximum of the derivative curve (T_{max}).

A three-stage thermal degradation process was observed for all the WPU films. The weight loss in the first stage at 162–197°C corresponded approximately to the ammonium salts of carboxylic parts, formed with TEA and DMPA. The second stage at 250–270°C was attributed to urethane bond breaks through the dissociation to HTNR and isocyanates, the formation of primary amines and olefins, or the formation of secondary amines, with loss of carbon dioxide from the urethane bonds. Finally, the third stage at 375–377°C relates to the decomposition of oligoisoprene.[24] The increased EDA content on comparing WPU3 and WPU11 increased the second stage weight loss from 8.8 to 22.0%. As the NCO/OH ratio increased from 1/1 to 1.5/1 and to 2/1 in WPU3, WPU30, and WPU31, respectively, the second stage degradation weight loss increased from 8.8 to 19.8%. We assume that in this thermal degradation, the urethane or urea groups of EDA, or polyols and diisocyanates, were cleaved. The results agree with prior studies of hydroxyl telechelic natural rubber (HTNR), where the thermal decomposition in the second stage increased with the NCO/OH ratio of WPU films.[29] However, the first stage weight loss was in the narrow range from 2.0 to 4.6% because the amount of DMPA was fixed at 5.6% wt.

Table V. Swelling and Thermal Properties of WPU Films

| | | | | Thermal degradation | | | | | |
| | | Swelling (%) | | First step | | Second step | | Third step | |
Code	THF	Toluene	MEK	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
WPU3	Diss.	Diss.	Diss.	163	2.0	266	8.8	377	89.1
WPU5	43.7	62.0	37.7	176	2.0	252	15.1	376	82.9
WPU7	44.0	50.0	26.7	185	2.3	250	16.4	377	81.2
WPU9	30.0	48.0	27.0	187	3.2	255	20.8	378	74.8
WPU11	27.0	31.0	16.7	194	4.6	254	22.0	375	74.6
WPU30	Diss.	76.9	16.7	180	3.2	270	18.9	376	77.8
WPU31	102.2	50.0	47.4	183	3.2	267	19.8	376	77.1
WPU32	11.6	27.0	4.3	184	3.8	258	15.7	377	80.5
WPU33	8.5	23.8	5.4	197	3.7	255	21.9	377	74.4

Diss. = dissolve.

Figure 12. DSC thermograms of WPU films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

however, these factors in WPU films had no effect on the T_g for them. For dynamic mechanical, the increasing of EDA contents or NCO/OH ratio in WPU films shows the rubbery plateau and
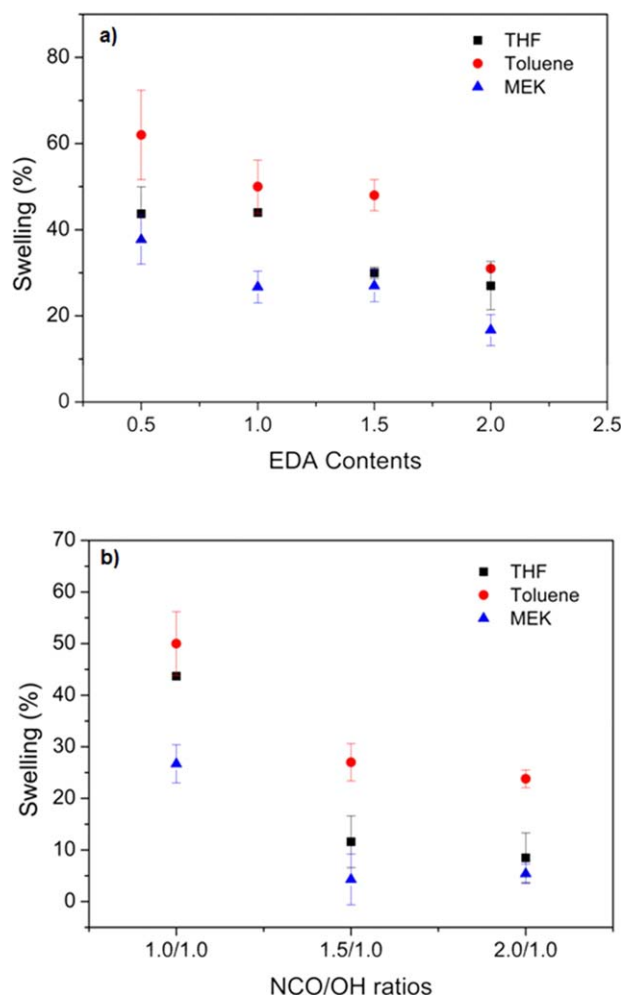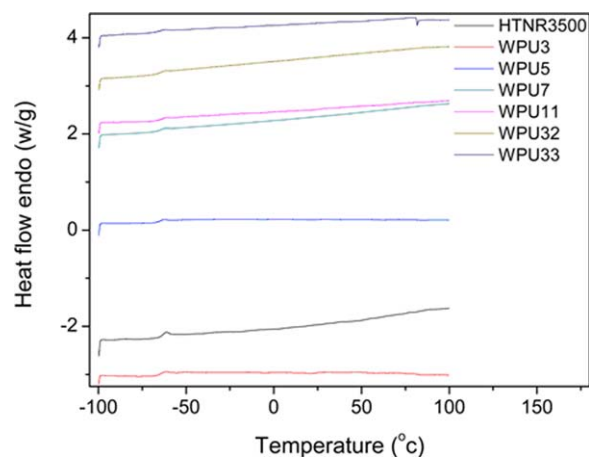

Figure 11. Swelling of WPU films: (a) EDA contents and (b) NCO/OH ratios with EDA 1 mol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this study, waterborne polyurethanes based on hydroxytelechelic natural rubber (HTNR) were successfully prepared by a prepolymer process, using various amounts of EDA, and various NCO/OH ratios with or without EDA. The particle size of the WPU was unaffected by the EDA content, but increased dramatically with the NCO/OH ratio in the presence of the EDA chain extender. The FT-IR technique was used to assess the chemical structures in the WPU films and their hydrogen bonding. The WPU33 sample with the highest hard segment content exhibited the lowest 23.8% swelling in toluene and 5.4% in MEK, whereas the WPU3 samples with the lowest hard segment content completely dissolved in all solvents tested. In mechanical properties, the WPU3 film was very soft and rubbery with 1.47 ± 0.7 MPa modulus, 0.09 ± 0.0 MPa tensile strength, and 100% elongation at break. The ratio NCO/OH = 2/1 in the presence of 1 mole EDA gave the highest modulus (233.3 ± 0.0 MPa) and tensile strength (3.19 ± 0.0 MPa) with smallish 38% elongation at break, acting like a ductile material. In thermal degradation tests, the decomposition in the second stage increased with the EDA content and the NCO/OH ratio;
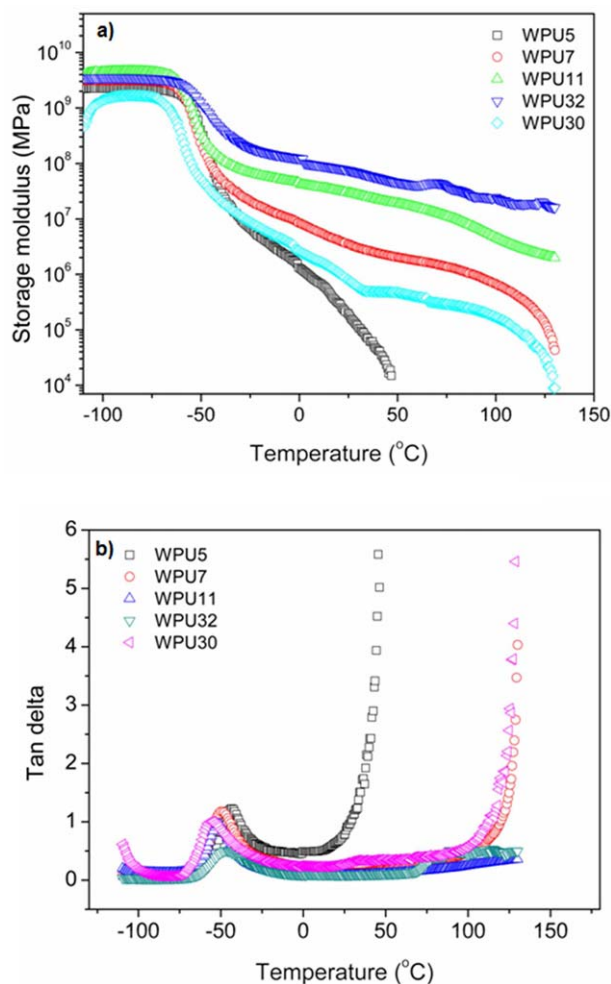

Figure 13. DTMA curve of WPU films: (a) storage modulus; (b) Tan delta. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
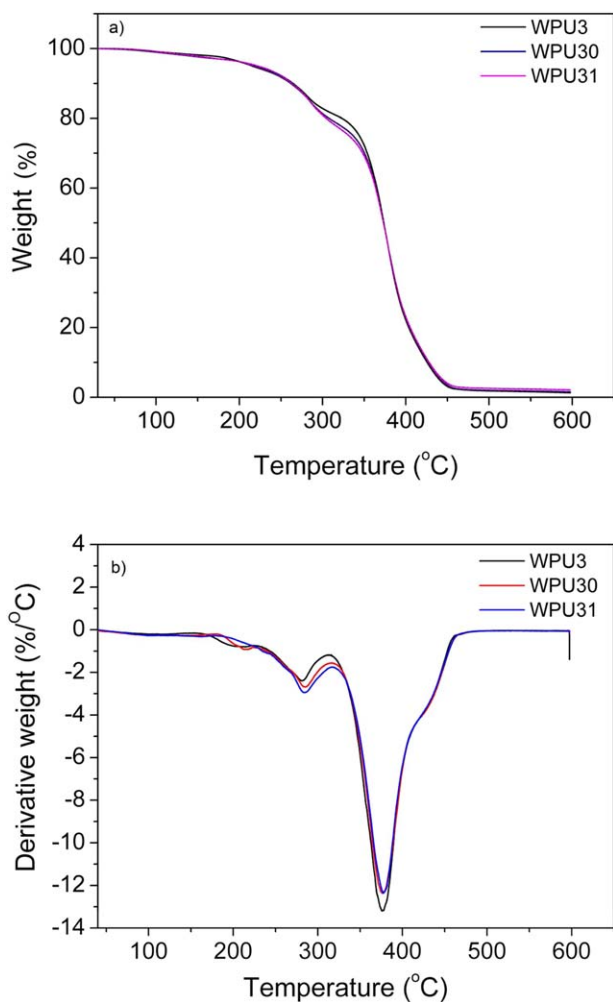
Figure 14. TGA curves of WPU films with different NCO/OH ratios without EDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the causing increased resistance to flow deformations at elevated temperatures.

The results overall suggest that new useful WPUs can be synthesized form natural rubber-based polyols, and their various properties can be adjusted in a wide range by manipulating the EDA content and the NCO/OH ratio. Natural rubber is a renewable and environmentally friendly raw material, and the new WPUs are solvent free. This combination of advantages suggests a high potential for NR based WPUs.

ACKNOWLEDGMENTS

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