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Synthesis and Characterisation of Waterborne Polyurethane Adhesives from Hydroxyl Terminated Natural Rubber

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Waterborne polyurethane adhesives (WPUAs) were synthesised by an isocyanate terminated polyurethane prepolymer process using 2,2-bis (hydroxymethyl) propionic acid (DMPA) as an internal emulsifier and chain extension by 1,4-diaminobutane. The different characteristic polyols such as hydroxyl terminated natural rubber (HT) with various number average molecular weights (Mn) at 600 (HT600) and 1000 g/mol (HT1000) and epoxidised HT (eHT) with 10 (10eHT) and 37 (37eHT) percentages of epoxidation were synthesised from natural rubber latex (NRL) for preparing the WPUA. Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) techniques were used to characterise the chemical structures. The pH value, mean particle size, viscosity, glass transition temperature (T_g), T-peel strength and lap shear strength of the WPUAs were measured. The WPUAs had pH values of about 7.80 to 8.50. The mean particle size of the WPUAs depended on the DMPA content. At higher DMPA content, a smaller mean particle size was obtained. The T_g of WPUAs exhibited the same trend values of HT and eHT. T-peel strength and lap shear strength of adhesives were measured by bonding of leather to leather. It was found that WPUA600 and WPUA1000 showed good adhesion. Thus, HT and eHT prepared from NRL can be used to prepare WPUA for the footwear industry.

Keywords: Hydroxyl terminated natural rubber; waterborne polyurethane; polyurethane dispersion

Polyurethane adhesives have advantages over other types of materials in that they have excellent low temperature resistance, low cure temperature, good flexibility, high impact strength and good wetting to a variety of substrates[1]. Polyurethane adhesives can be classified by solvent based and waterborne polyurethane. In recent years, the waterborne polyurethane adhesives (WPUAs) have been increasingly used for replacing solvent based

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adhesives in a number of application areas because the WPUAs are environmentally friendly, non-flammable and have no volatile organic components (VOC) emission. Water based systems fully contain linear polymers that are emulsified or dispersed in water. These polymers are formed by incorporating hydrophilicity into the long hydrophobic polyurethane segment using either cationic or anionic groups on or, less frequently, through the use of external emulsifiers. Consequently, they are typically blended with other dispersions without any problems and also exhibit good mechanical properties.

In the recent reports, Pérez-Limiñana *et al.*[2] found that the adhesion of WPUA to PVC increased as the internal emulsifier (2,2-bis (hydroxymethyl) propionic acid (DMPA)) content in the polyurethane ionomer decreased. The crosslinking reaction of WPUA containing high DMPA content with hexamethoxymethyl melamine gave high adhesive strength[3]. Aruna and Rohini Kumar[4] prepared waterborne poly (urethane semicarbazide) dispersions of various DMPA contents and compositions, the resulting adhesives exhibited excellent adhesion to leather and good storage stability. The published reports indicated that the application of polyurethane adhesives with various materials such as styrene–butadiene-styrene rubber (SBS)/leather[5–8], Salz leathers[9,10], styrene-butadiene rubber (SBR)/leather[5,11], bovine tanned leather/poly(vinyl chloride) (PVC)[12], split leather/microporous polyurethane film[13], leather/canvas[4], SBS[5], SBR[5,14,] PVC[2,5,15], wood[16], nylon fabrics[3], and polycarbonate/aluminum[17]. Polyurethane adhesives are also widely used in shoe and slipper manufacture or applications in the footwear industry. In the footwear industry, leathers are still the main source and most common upper material since the porous nature of leathers facilitates their adhesion bonding strength.

Relatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce polyurethane adhesives. Among the widely different polyols used, hydroxytelechelic polydiene, especially, hydroxytelechelic polyisoprene[18–20] based polyurethanes were found to present particular interest both in industry and public research in regards to their physicochemical and mechanical properties. Natural rubber (NR) is an interesting material for development to a hydroxyl terminated polymer because it can be chemically modified by using some special functional groups at the chain ends. Moreover, the molecular weight of NR can be easily controlled.

Therefore, the objective of this study was to prepare WPUA from hydroxyl terminated NR (HT), polymethylene polyphenyl polyisocyanate (PMDI) and 1,4-diaminobutane. The resulting WPUA was focused on leather applications. HT[21,22] was prepared by cleavage of the epoxide group in epoxidised NR (ENR)[23,24] and reduction of the carbonyl group in carbonyl terminated NR (CTNR). The HT was further modified by adding epoxide groups onto the HT molecular structure, designated epoxidised HT (eHT), for the preparation of WPUA. After that, the properties of WPUA and also the adhesion properties on leather were investigated.

MATERIALS AND METHODS

Materials

High ammonia concentrated natural rubber latex (HA-NRL, Yala Latex Industry Co., Ltd), terric N-10 (Huntsman), formic acid (Merck, 98%), hydrogen peroxide (Merck, 30%), periodic acid (Merck), sodium borohydride (Merck), *m*-chloroperbenzoic acid (*m*-CPBA, Fluka, 70%) were used for preparing hydroxyl terminated natural rubber (HT). WPUAs were prepared from HT, Lupranate M20S (polymethylene polyphenyl polyisocyanate: PMDI (BASF, Korea)) with a free isocyanate content of 37 weight percentage and an average functionality of 2.7, *2,2-bis* (hydroxymethyl) propionic acid (DMPA, Acros) as an internal emulsifier, triethylamine (TEA, Sigma-Aldrich) as a neutralisation reagent, and *1,4*-diaminobutane (1,4-NH, Sigma-Aldrich) as a chain extender. Tetrahydrofuran (THF), dichloromethane, methanol and acetone were used as solvent.

Methods

The chemically modified NR and WPUAs were characterised by the following methods:

Fourier transform infrared spectroscopy (FTIR). The chemically modified NR and HT were characterised by FTIR technique with an Omnic ESP Magna-IR 560 spectrometer (Nicolet, USA) in the range of 4000 to 400 cm^{-1}. The samples were dissolved in chloroform and then cast on a KBr cell.

WPUA film was characterised by ATR technique with an Equinox 55 Infrared Fourier Transform Spectrometer with 16 scans at a resolution of 4 cm^{-1} over the range between 4000 to 600 cm^{-1} and an incident angle of 45º. A germanium crystal was used for single mode ATR.

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). ^{1}H-NMR spectra of chemical modified NR and HT were recorded in a Fourier Transform NMR spectrometer 500 MHz model Unity Inova (Varian, Germany). The samples were dissolved in deuterated chloroform.

Differential scanning calorimetry (DSC). The thermal behaviour of HT, eHT and WPUAs was analysed by a Perkin Elmer model DSC7 with a heating rate of 10ºC min^{-1} from -80ºC to 40ºC under a nitrogen atmosphere. The glass transition temperature (T_g) was obtained.

OH value. OH values of HT and eHT were investigated by esterification with a phthalic mixture. Three grams of sample and 25 mL of phthalating reagent was heated at 50ºC in a reflux flask for 1 hour. After heating, it was removed from the bath and cooled to ambient temperature. 50 mL of distilled water was added into the flask and titrated with 1.0 N sodium hydroxide solution to a faint pink end point that lasted 15 s, using a few drops of phenolphthalein as an indicator[25].

pH. The pH values of WPUAs were measured at ambient temperature in pH meter of inoLab pH Lavel 1 (Germany) with pH-electrode SenTix81.

Mean particle size. The mean particle sizes of WPUAs were measured using a Beckman Coulter LS230 laser diffraction particle size analyser (USA) with a small volume module plus. A small volume of WPUA was added into a deionised water tank. The mean particle sizes were measured at room temperature.

Brookfield viscosity. The viscosities of WPUAs were measured with a Brookfield viscosity LVDV-III at ambient temperature using a spindle speed of 50 r.p.m. Spindle no. 1 was used for all products except WPUA37E for which spindle no. 3 was used.

T-peel strength and lap shear strength. The adhesive strength of WPUAs was assessed as T-peel strength and lap shear strength. The strength values of leather/WPUAs/leather joints were investigated with a Hounsfield H 10KS universal testing machine (England) with a load cell of 500 N and crosshead speed of 12.7 mm/min.

EXPERIMENTAL

Synthesis of Epoxidised Natural Rubber (ENR)

HA-NRL of 60% DRC was diluted to 20% DRC in a reaction kettle, stabilised with Terric N-10 3 p.h.r. (parts per hundred of dry rubber) and stirred overnight at room temperature to eliminate ammonia. Then, the latex was heated to 60ºC. Formic acid (0.3 mol equivalent) was added drop by drop. Hydrogen peroxide (0.3 mol equivalent) was then added. The reaction was stopped at 8 and 20 h to obtain 9% and 16% epoxide contents, respectively. ENR latex was coagulated in methanol, washed with water several times and dried in a hot air oven at 40ºC. The resulting ENR was analysed by ^{1}H-NMR technique to determine the percentage epoxide content.

Synthesis of Carbonyl Terminated Natural Rubber (CTNR)

ENR was dissolved in THF and reacted with periodic acid (1.1 mol equivalent) at 30ºC for 6 h in a reaction kettle with stirring at 300 r.p.m. Solvent was later removed from the CTNR solution by evaporation.

Synthesis of Hydroxyl Terminated Natural Rubber (HT)

Sodium borohydride (4 mol equivalent) was dissolved in THF in a reaction kettle at 30ºC and a solution of CTNR was added drop by drop. The solution was heated to 60ºC and the reaction continued for 6 hours. The solution was then cooled down to ambient temperature and hydrolysis was performed by adding cool water. THF was then evaporated from the reaction mixture under vacuum.

Synthesis of Epoxidised Hydroxyl Terminated Natural Rubber (eHT)

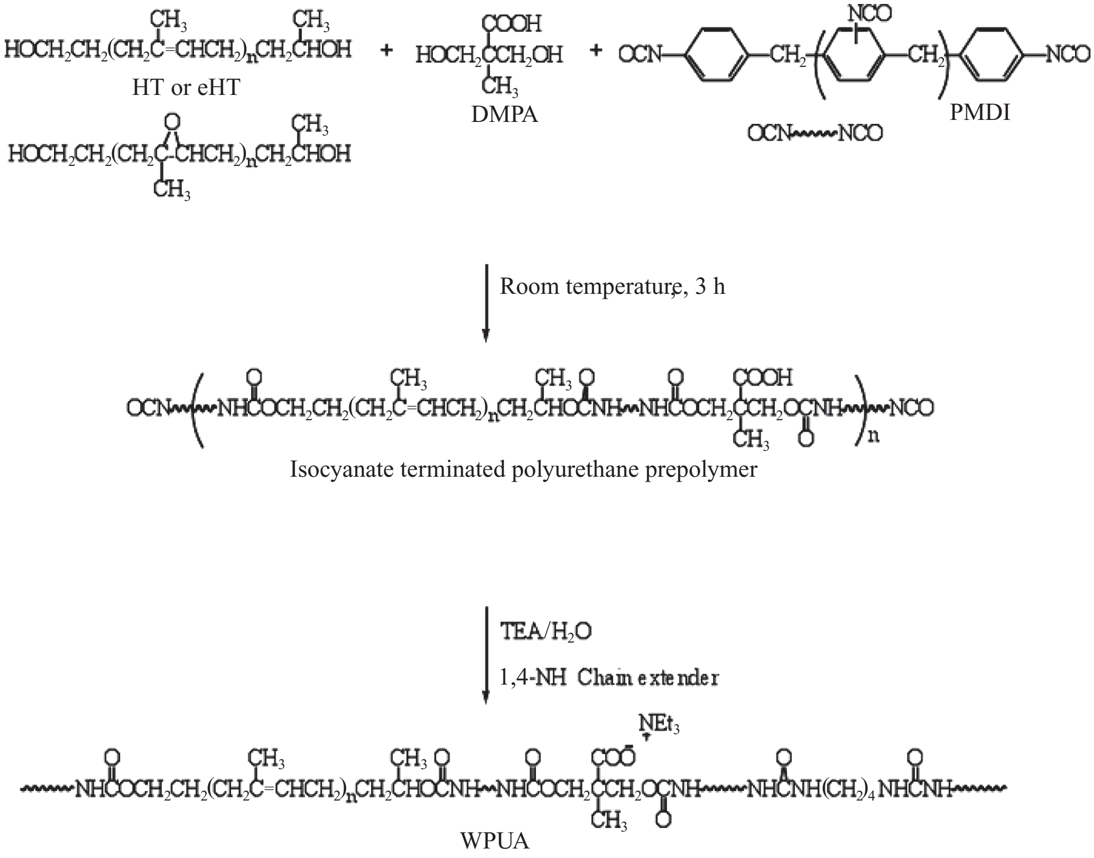
HTNR was dissolved in dichloromethane and reacted with a solution of *m*-CPBA (1 mol equivalent) in dichloromethane in a three necked round bottom flask at 0ºC for 3 hours. In this procedure, eHT was prepared at epoxide contents of 10% and 37%. After that the solvent was removed.

Synthesis of Waterborne Polyurethane Adhesives

WPUAs were prepared by a prepolymer process. PMDI was mixed with HT (M_n = 600 and 1000 g/mol) or eHT (10 and 37% of epoxide contents), DMPA and a minimum amount of acetone in a reactor with stirring at 60 r.p.m. The reaction was carried out at ambient temperature for 3 h to obtain the isocyanate terminated PU prepolymer. When the calculated free isocyanate content of prepolymer was obtained, speed of the mechanical stirrer was adjusted to 400 r.p.m. TEA, water and 1,4-NH were then added according to *Scheme 1*, followed by continuously stirring for another 30 minutes. The formulae of preparation of WPUAs are presented in *Table 1*.

Sample Preparation for Adhesion Testing

Leather was washed with detergent and water to eliminate contaminants and heated at 40ºC for 24 hours. The dimensions of the leathers were 25 × 152 × 1.4 mm (T-peel test) and 25 × 76 × 1.4 mm (lap shear test). The typical overlap was about 7.6 and 2.5 cm for T-peel and lap shear tests, respectively. The amount of adhesive used was controlled. When leather was treated with WPUA on one strip another was pasted in contact and left to dry at 80ºC for 24 hours. The adhesive joints



Scheme 1. Synthesis of WPUA.

TABLE 1. SAMPLE CODES AND MATERIAL CONTENTS OF WPUAs

Materials	Sample codes with material contents (mol equivalents)			
	WPUA600	WPUA1000	WPUA10E	WPUA37E
HT600	1.0	-	-	-
HT1000	-	1.0	-	-
10eHT	-	-	1.0	-
37eHT	-	-	-	1.0
DMPA	0.3	0.3	0.3	0.5
PMDI	1.4	1.4	1.4	1.6
1,4-NH	0.1	0.1	0.1	0.1

were kept at ambient temperature for 24 h before testing.

RESULTS AND DISCUSSION

Chemical Structure and Properties of Modified NR

HT and eHT were prepared by controlled degradation reaction through epoxidation and a selective cleavage reaction. The epoxide groups of ENR were cleaved by periodic acid in preparing CTNR. The chemical structures of ENR, CTNR, HT600 (M_n = 600 g/mol), HT1000 (M_n = 1000 g/mol), 10eHT (%epoxidation = 10) and 37eHT (% epoxidation = 37) were studied by FTIR and ^{1}H-NMR techniques, as shown in *Figures 1–4*. By FTIR technique (*Figures 1*, *2*), all spectra have the same peaks at 2860, 2960 and 1660 cm^{-1}, indicating methylene, methyl and olefin in the chemical structure of NR, respectively. ENR spectrum (*Figure 1*) shows small peaks at 1250 and 870 cm^{-1}, indicating an epoxide group. The CTNR spectrum shows a peak at 1720 cm^{-1} indicating a carbonyl group. The HT1000 spectrum shows a peak at 3360 cm^{-1} indicating a hydroxyl group. FTIR spectra of 10eHT and 37eHT show similar peaks indicating epoxide groups as the ENR spectrum. The HT600 spectrum has the same peaks when compared with the HT1000 spectrum but the peak area of alkane (2800-2900 cm^{-1}) is lower than the HT1000 since it had lower M_n.

The chemical structure of the chemically modified NR was further confirmed by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of chemically modified NR and HT (*Figures 3* and *4*) exhibited the signals from functional groups of NR, such as methyl (CH_3), methylene (CH_2) and methine protons (C=CH) at 1.67, 2.04 and 5.12 p.p.m., respectively. The epoxide methine proton signals of ENR, 10eHT and 37eHT were clearly observed at 2.70 p.p.m. The CTNR shows the characteristic signal at 9.80 p.p.m. indicative of an aldehyde group. The ^{1}H-NMR spectra of chemically modified HT (*Figure 4*) had the same signals at 3.63 p.p.m. (CH_2OH) and 3.80 p.p.m. (CHOH). The small signal at 2.70 p.p.m. (about 1% epoxiation) was observed in HT600 and HT1000. Thus, the reaction between periodic acid and ENR was incomplete. The percentages of epoxidation and M_n were calculated from integrated signals in the ^{1}H-NMR spectra[18,24].

The properties *i.e.*, M_n, T_g and OH-value of the HT and eHT are presented in *Table 2*. It was found that M_n of HT and eHT depended on the epoxide contents of ENR before preparing CTNR. The higher the epoxide contents of ENR were found, the lower M_n of HT was obtained. Also, the M_n of eHT depended on the M_n of HT. The M_n can be calculated from the integrated ^{1}H-NMR signals[18]. The Tg of 37eHT was the highest owing to the high epoxide content in eHT. This was due to the restricted movement of the chain, therefore it needed a higher temperature for relaxation. The OH-values of HT and eHT depended on M_n, and the lower the M_n was the higher OH-value was observed.

Properties of WPUA

WPUA with 40% of total solid content (TSC) was heated at 40ºC until a dried film was obtained. After that the film was characterised by ATR-FTIR spectroscopy to examine the structure of the polyurethane. In *Figure 5*, the ATR-FTIR spectrum of WPUA1000 is presented. The peaks appeared at 3330 cm^{-1} (N-H stretching) assigned to the urethane function, 1708 cm^{-1} (C=O stretching) assigned to the urethane function, 1640 cm^{-1} (C=O stretching) assigned to the urea function, 1537 cm^{-1} (N-H bending) assigned to the amine salt ($-NH_3+$), 1231 and 1067 cm^{-1} (N-CO-O asymmetric and symmetric

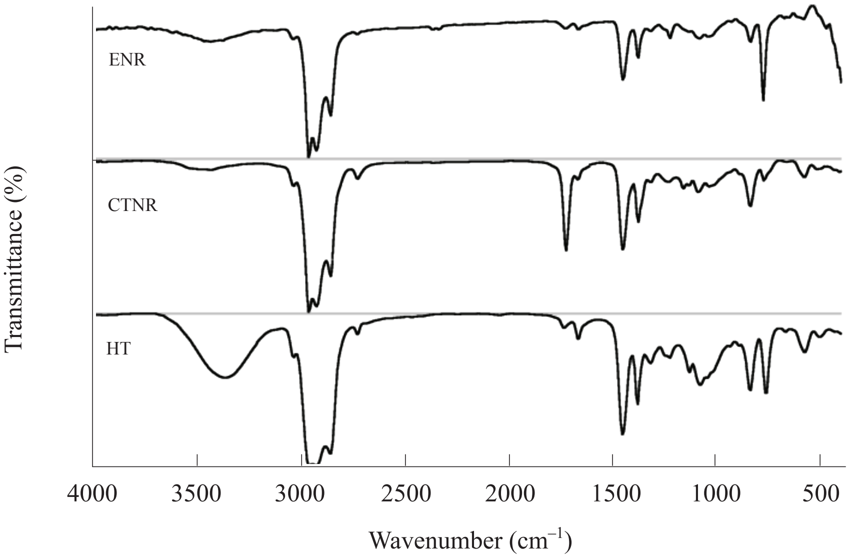


Figure 1. FTIR spectra of chemically modified NR.

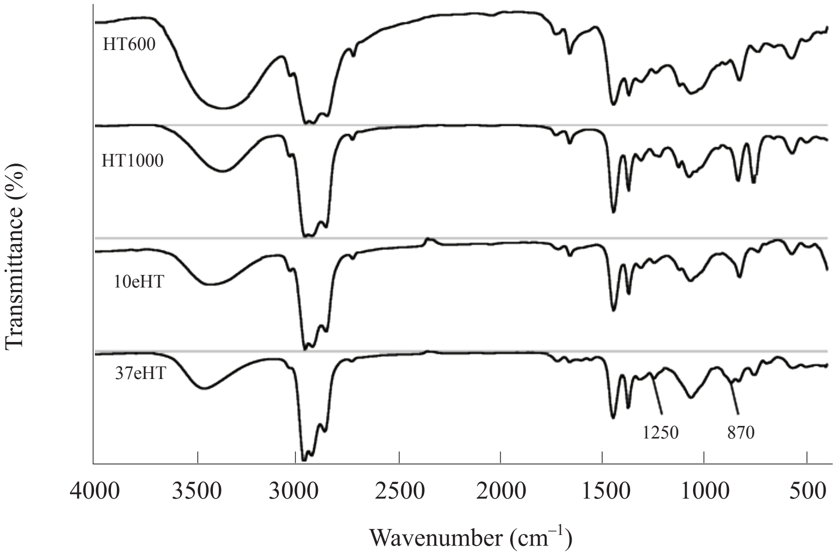


Figure 2. FTIR spectra of HT and chemically modified HT.

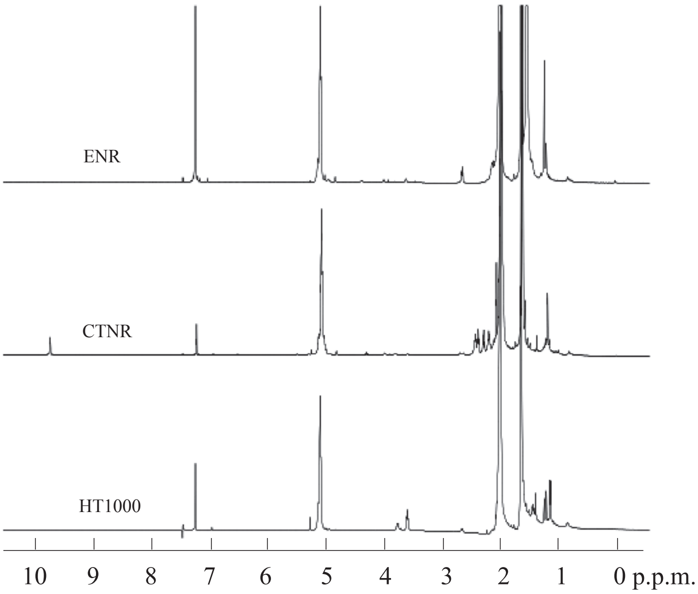


Figure 3. ^{1}H-NMR spectra of chemically modified NR.

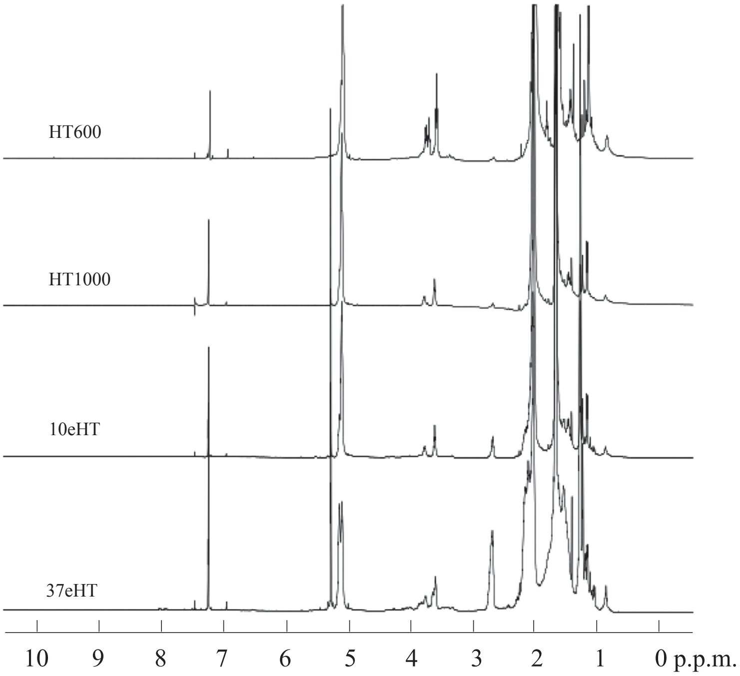


Figure 4. ^{1}H-NMR spectra of chemically modified HT.

stretching) assigned to the urethane function and 1017 cm^{-1} (C-O-C stretching) assigned to the urethane function.

The properties of WPUAs and adhesion strengths are summarised in *Table 3*. WPUAs had pH values in the range between 7.80 to 8.50 because of using excess TEA for neutralisation of the carboxylic group in DMPA.

As a result, the WPUAs were basic. WPUA37E had a higher T_g than the other materials because of the relatively higher T_g of 37eHT. The higher the epoxide contents in eHT, the higher was the observed T_g of WPUA. The particle sizes of WPUAs from HT600, HT1000 and 10eHT were larger than those of the WPUA37E. The preparation of WPUA37E used a higher amount of DMPA than the other WPUAs. Since the role of DMPA was to act as an internal emulsifier reagent, a higher DMPA content could improve dispersion of the isocyanate terminated PU prepolymer and yield a small particle size[2,4] (*Figure 6*). The viscosity of WPUAs was observed in the range of 48–113 mPa.s.

The adhesion properties of leather/WPUA/leather joints were determined from T-peel and lap shear tests as indicated in *Table 4*. WPUA600 and WPUA1000 provided higher bond strengths than those of the WPUA10E and WPUA37E. This is because cohesive failure was observed in leather/WPUA600/leather and leather/WPUA1000/leather bonding. In general, cohesive failure occurs when the bond to the substrate exceeds the internal strength of the adhesives. On the other hand, adhesive

TABLE 2. THE PROPERTIES OF HT AND eHT

Sample code	% Epoxide of ENR	% Epoxide of eHT	M_n (g/mol) from ^{1}H-NMR	T_g (ºC)	OH-value (mg KOH/g)
HT600	16	-	600 ± 100	-63	142
HT1000	9	-	1000 ± 100	-64	79
10eHT	9	10	1200 ± 100	-62	63
37eHT	9	37	1000 ± 100	-45	69

TABLE 3. THE PROPERTIES OF WPUAs AND ADHESION STRENGTH

Sample code	pH	T_g (ºC)	Particle size (in volume) (μm)	Viscosity (mPa.s)*	T-peel strength (N/mm)	Lap shear strength (N/mm^2)	Failure pattern**
WPUA600	8.20	-51	13.50	113[a]	0.89	0.32	CF
WPUA1000	8.50	-58	11.40	48	1.23	0.19	CF
WPUA10E	7.90	-51	24.00	77	0.13	0.07	AF
WPUA37E	7.80	-35	1.30	62	0.03	0.04	AF

*spindle no.1
[a] spindle no.3

**CF: cohesive failure in leather/WPUA/leather
AF: adhesive failure in leather/WPUA/leather

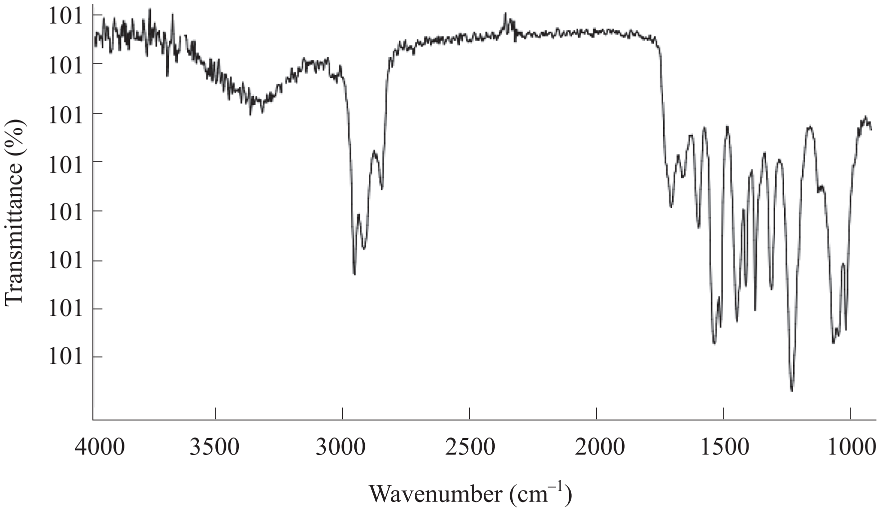


Figure 5. ATR-FTIR spectrum of WPUA1000.

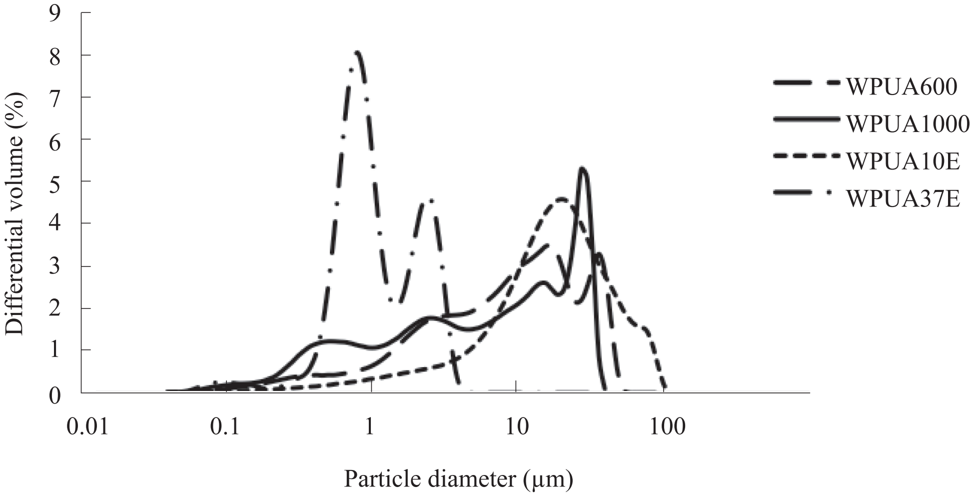


Figure 6. The particle size (in volume) of WPUAs.

failure occurs when bond to substrate is less than the internal strength of the adhesive. The T-peel strength of WPUA1000 is higher than that of WPUA600 because the soft segment of WPUA1000 chain is longer. Thus, the long chain of soft segment could react with PMDI to give a more flexible polyurethane adhesive. On the other hand, WPUA600 showed the highest lap shear strength because HT600 was a short chain polyol that was reacted with PMDI to form a more rigid polyurethane. The lowest bond strength of WPUA37E was observed since high DMPA content was used in the composition. Normally, compositions with high ionic content exhibit the lowest bond strength because the coulombic forces of attraction between counterions is the deciding factor for adhesive strength[4]. The other reason for the low bond strength of WPUA37E was that the small particle size of the dispersion allowed easy penetration into the porous leather substrate resulting in insufficient adhesive content for covering all areas. Lap shear strength and peel strength depended on the chemical structure and M_n of HT.

CONCLUSION

Chemical modification of NR to obtain HT and eHT can be achieved through the oxidative degradation of ENR in the latex phase using periodic acid. The M_n of HT depended on the epoxide content in the ENR before preparing CTNR. The higher the epoxide contents of ENR, the lower M_n of HT were obtained. The end groups of HT and eHT were verified by FTIR and ^{1}H-NMR spectroscopy. The preparation of WPUAs based on HT and eHT was investigated. It was found that an increase in DMPA content produced a decrease in the particle size. The pH values of WPUAs were basic. The mean particle size was dependent on the distribution of particle size of WPUA. The T_g of the WPUAs exhibited the same trend as the HT and eHT. Good adhesive strength on leather substrates were found for WPUA600 and WPUA1000.

The present work demonstrates the possibility of using chemically modified NR to produce a water based polyurethane which is free from organic solvents. Thus, this material could be a choice for leather applications or in the footwear industry.

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