รายงานวิจัยฉบับสมบูรณ์

โครงการ การเตรียมและสมบัติของน้ำยางไฮบริดชนิดใหม่จากน้ำยางพอลิยูริเทนเตรียมจากยางธรรมชาติและไวนิลพอลิเมอร์โดยผ่านกระบวนการพอลิเมอร์ไรซ์เซชันแบบอิมัลชัน

โดย...นายอนุวัติ แซ่ตั้ง...

กรกฎาคม 2557

สัญญาเลขที่ MRG 5580108

รายงานวิจัยฉบับสมบูรณ์

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

Abstract

A series of new waterborne polyurethane (WPU)/acrylic hybrid dispersion were successfully synthesized by the emulsion polymerization of acrylic monomers (methyl methacrylate or butyl acrylate and methyl methacrylate) in the presence of a hydroxytelechelic natural rubber (HTNR) based waterborne PU using potassium persulfate as an initiator. The WPU dispersion was synthesized by a polyaddition reaction of diisocyanate (Toluene diisocyanates or Hexamehtylene diisocyanates) and a HTNR. The effect of chain extender content and the ratio of NCO/OH in formulations on WPU and their film properties were studied. It was revealed that the HTNR based WPU are stable and exhibit the improvement of mechanical properties of WPU films with an increasing of chain extender content or NCO/OH ratio. However, the WPU based on EHTNR3000 are unstable. The resulting hybrid latexes, containing 10-50 wt % WPU based on HTNR as a renewable resource, are good stable. The morphology of hybrid latex was revealed by transmittance electronic microscopy. The chemical structure, physical, thermal, and mechanical properties of the resulting hybrid latex films have been investigated by Fourier transform infrared spectroscopy, swelling properties and water absorption, TGA, and tensile testing, respectively. In addition, the hybrid film based on HDI gave a lighter yellowish color than that of TDI. Grafting copolymerization of the acrylic monomers onto the linear PU chain occurs during the emulsion polymerization, leading to a significant increase in the physical, thermal and mechanical properties of the resulting hybrid latexes. This work represents new environmentally friendly hybrid materials based on renewable source by a new preparation for coating applications.

บทคัดย่อ

ชุดน้ำยางไฮบริดชนิดใหม่จากน้ำยางพอลิยูริเทนร่วมกับอะคริลิคสามารถสังเคราะห์อย่างประสบความสำเร็จโดยอาศัยเทคนิคพอลิเมอร์ไรซเซชันแบบอิมัลชันของอะคริลิคมอนอเมอร์ (เมทิลเมทาคริเลทหรือเมทิลเมทาคริเลทร่วมกับบิวทิลอะคริเลท) กับน้ำยางพอลิยูริเทนที่เตรียมจากยางธรรมชาติน้ำหนักโมเลกุลต่ำที่มีหมู่ปลายเป็นหมู่ไฮดรอกซิล (hydroxytelechelic natural rubber (HTNR)) โดยใช้โพแทสเซียมเปอร์ซัลเฟตเป็นสารริเริ่ม น้ำยางพอลิยูริเทนสังเคราะห์โดยผ่านปฏิกิริยาการเติมของไดไอโซไซยาเนต (โทลูอีน ไดไอโซไซยาเนตหรือ เอกซะเมทิลลีนไดไฮโซไซยาเนต) และ ยางธรรมชาติน้ำหนักโมเลกุลต่ำที่มีหมู่ปลายเป็นหมู่ไฮดรอกซิล ศึกษาปัจจัยของปริมาณสารขยายสายโซ่ และอัตราส่วนของ NCO/OH ในส่วนประกอบของน้ำยางพอลิยูริเทนต่อสมบัติของน้ำยางและฟิล์ม พบว่าน้ำยางพอลิยูริเทนจาก HTNR มีความเสถียรและแสดงให้เห็นถึงสมบัติเชิงกลที่ดีขึ้นเมื่อเพิ่มปริมาณสารขยายสายโซ่ หรืออัตราส่วนของ NCO/OH อย่างไรก็ตามน้ำยางพอลิยูริเทนที่เตรียมจากอิพอกไซด์ยางธรรมชาติน้ำหนักโมเลกุล 3000 ที่มีหมู่ปลายเป็นหมู่ไฮดรอกซิล (Epoxide hydroxytelechelic natural rubber, EHTNR) ไม่มีความเสถียร ผลการทดลองของน้ำยางไฮบริดน้ำยางพอลิยูริเทนที่สัดส่วน 10-50% ซึ่งเตรียมจาก HTNR ซึ่งเป็นแหล่งผลิตที่เกิดทดแทน พบว่ามีความเสถียร สัณฐานวิทยาของน้ำยางไฮบริดได้จากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน โครงสร้างทางเคมี สมบัติเชิงกายภาพ เชิงความร้อน และเชิงกลของแผ่นฟิล์มจากน้ำยางไฮบริดวิเคราะห์โดยเทคนิค Fourier transform infrared spectroscopy สมบัติการบวมพองและการดูดซับน้ำ เทคนิควิเคราะห์ความเสถียรต่อความร้อน และการทดสอบแรงดึง ตามลำดับ นอกจากนี้ แผ่นฟิล์มจากน้ำยางไฮบริดที่เตรียมจาก เอกซาเมทิลลีนไดไฮโซไซยาเนต ให้สีเหลืองที่อ่อนกว่าแผ่นฟิล์มจากโทลูอีน ไดไอโซไซยาเนต การโคพอลิเมอร์ไรซ์แบบกราฟต์ของมอนอเมอร์อะคริลิคบนสายโซ่พอลิยูริเทนที่เป็นเส้นตรงเกิดขึ้นในระหว่างการพอลิเมอร์ไรซ์เซชันแบบอิมัลชัน นำไปสู่การเพิ่มขึ้นของสมบัติกายภาพ เชิงความร้อน และเชิงกลของแผ่นฟิล์มจากน้ำยางไฮบริดอย่างมีนัยสำคัญ งานวิจัยนี้แสดงให้เห็นถึงวัสดุที่เป็นมิตรกับสิ่งแวดล้อมแบบใหม่ที่เตรียมมาแหล่งผลิตที่สามารถเกิดทดแทนได้โดยวิธีการเตรียมแบบใหม่เพื่อประยุกต์ใช้ในงานเคลือบ

เอกสารแนบหมายเลข 2

Abstract

A series of new waterborne polyurethane (WPU)/acrylic hybrid dispersion were successfully synthesized by the emulsion polymerization of acrylic monomers (methyl methacrylate or butyl acrylate and methyl methacrylate) in the presence of a hydroxytelechelic natural rubber (HTNR) based waterborne PU using potassium persulfate as an initiator. The WPU dispersion was synthesized by a polyaddition reaction of diisocyanate (toluene diisocyanates, TDI or hexamehtylene diisocyanates, HDI) and a HTNR. The effect of chain extender content and the ratio of NCO/OH in formulations on WPU and their film properties were studied. It was revealed that the HTNR based WPU are stable and exhibit the improvement of mechanical properties of WPU films with an increasing of chain extender content or NCO/OH ratio. However, the WPU based on EHTNR are unstable. The resulting hybrid latexes, containing 10-50 wt % WPU based on HTNR as a renewable resource, are good stable. The morphology of hybrid latex was revealed by transmittance electronic microscopy. The chemical structure, physical, thermal, and mechanical properties of the resulting hybrid latex films have been investigated by Fourier transform infrared spectroscopy, swelling properties and water absorption, TGA, and tensile testing, respectively. In addition, the hybrid film based on HDI gave a lighter yellowish color than that of TDI. Grafting copolymerization of the acrylic monomers onto the linear PU chain occurs during the emulsion polymerization, leading to a significant increase in the physical, thermal and mechanical properties of the resulting hybrid latexes. This work represents new environmentally friendly hybrid materials based on renewable source by a new preparation for coating applications.

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Project Code : MRG 5580108
(รหัสโครงการ)

Project Title : Preparation and properties of a new hybrid latex from a natural rubber based waterborne polyurethane and vinyl polymer *via* emulsion polymerization
(ชื่อโครงการ) การเตรียมและสมบัติของน้ำยางไฮบริดชนิดใหม่จากน้ำยางพอลิยูริเทนเตรียมจากยางธรรมชาติและไวนิลพอลิเมอร์โดยผ่านกระบวนการพอลิเมอร์ไรซ์เซชันแบบอิมัลชัน

Investigator : Mr. Anuwat Saetung
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Project Period : 2 years (July 2012 - July 2014)
(ระยะเวลาโครงการ)

1. Objective

1.1 To prepare and modify natural rubber to be polyols (HTNR and EHTNR)

1.2 To synthesize waterborne polyurethane based on HTNR and EHTNR

1.3 To synthesize hybrid waterborne polyurethane with vinyl monomers

1.4 To study the physico-mechanical properties of the synthesized hybrid film

2. Experimental parts

2.1 Preparation of hydroxyltelechelic natural rubber (HTNR) and epoxidized hydroxyltelechelic natural rubber

The hydroxytelechelic natural rubbers with different molecular weights (1000-4000 g/mol) and different ratios of epoxidation (approximately 0 - 30% epoxidation) were prepared from carbonyl telechelic natural rubber (CTNR) according to a methodology described in our previous work as shown in figure 1. Briefly, the first reaction is epoxidation preformed by generated *in situ* of formic acid and hydrogen peroxide in natural rubber latex. The second reaction is degradation of epoxidized natural rubber by periodic acid in THF solution. The final reaction is reduction reaction of CTNR by $NaBH_4$ in THF to obtain HTNR. The HTNR can be continuously modified in isoprene units by epoxidation reaction with *m*-chloroperbenzoic acid in dichloromethane to form epoxidized natural rubber (EHTNR). Both precursors (HTNR and EHTNR) obtained will be used as starting precursors for preparation of waterborne PU.

The chemical structure and molecular weight of these precursors are analyzed by ^{1}H-NMR technique. The thermal properties of these precursors are characterized by TGA and DSC.

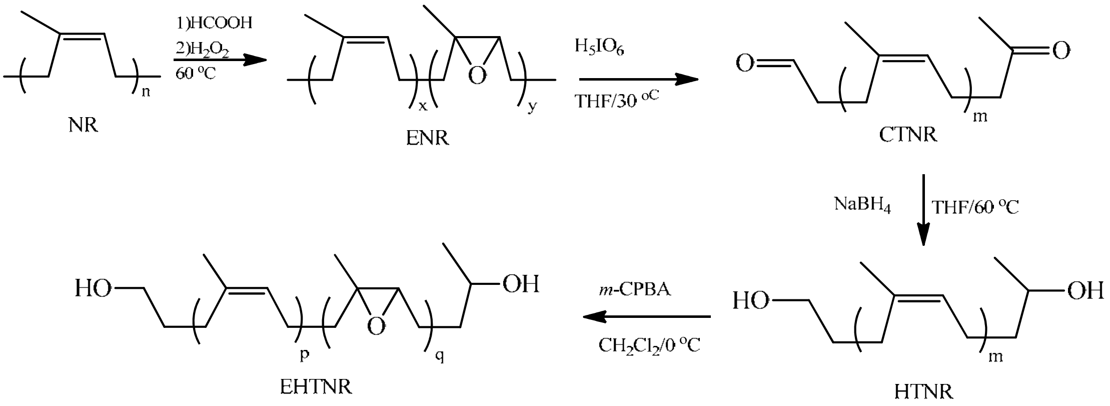


Figure 1. Preparation of HTNR and EHTNR

2.2 Synthesis of waterborne polyurethane based on HTNR and EHTNR

The waterborne polyurethane was prepared according to a methodology described in our previous work. Briefly, the synthesis of anionic waterborne polyurethane is performed by prepolymer technique as shown in below:

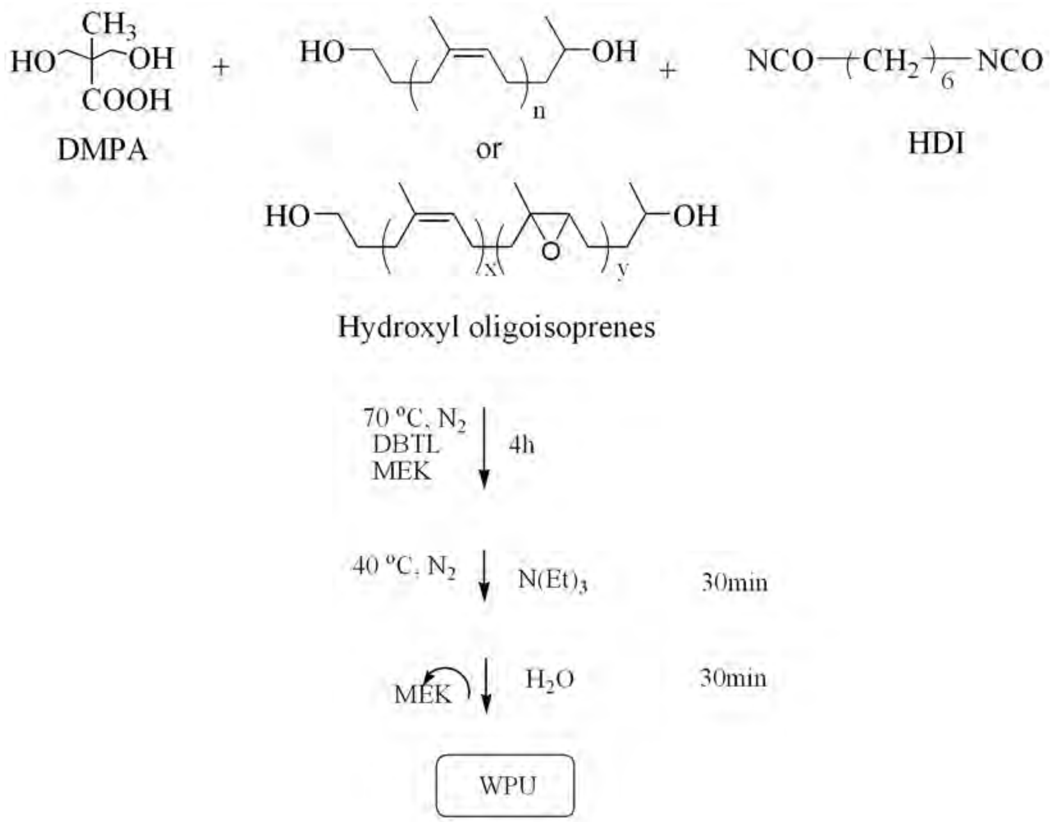


Figure 2. Preparation of waterborne polyurethane (WPU)

The chemical composition are also studied i.e., content and type of chain extender, diisocyanates. These WPUs are also measured by particle size, pH, stability, and total solid content. In addition, the physico-mechanical properties of these WPU films are measured i.e., tensile properties, swell resistance in water and solvent, thermal properties.

2.3 Synthesis of hybrid latex from HTNR and EHTNR based waterborne polyurethane and vinyl polymers

The desired amount of vinyl monomer was added to the WPU dispersion. The reactants were stirred under nitrogen gas at room temperature for 2 h, and then bring to the polymerization temperature of 80^{o} C for 4 h to obtain the hybrid emulsion, using potassium persulphate (0.5 wt% on vinyl monomers).

During the polymerization approximately 5 g portions of the emulsion are taken out by a syringe at intervals and injected into a petri dish containing 0.5% hydroquinone solution in an ice bath. Monomer conversion was determined gravimetrically from these samples.

The weight ratio of the WPU and vinyl monomers from 100:0 to 90:10, 80:20, 70:30, 60:40, 50:50 and 40:60, series of WPU/vinyl monomer hybrid latexes are synthesized. The hybrid latex is also measured by total solid content, particle size, pH, stability, and morphology. In addition, the physico-mechanical properties of these hybrid films are measured i.e., tensile properties, swell resistance in water and solvent, thermal properties. Their chemical structures are also characterized by FT-IR technique.

3. Results and discussions

3.1 Preparation of natural rubber polyols (HTNR and EHTNR)

The natural rubber polyol (Hydroxytelechelic natural rubber, HTNR) was prepared by the controlled molecular weight and modified natural rubber via three step chemical reaction as following epoxidation, degradation and reduction, respectively. Briefly, the epoxidized natural rubber (ENR) was prepared by *in situ* generated peroxide from hydrogen peroxide and formic acid ($[H_2O_2]/[HCOOH] = 1$) at 60 ^{o}C for 1.3 h. The dried ENR was then well dissolved in THF and degraded with periodic acid [epoxdie unit]/[periodic acid] = 1.1) at 30 ^{o}C for 6 h. The degraded liquid natural rubber or carbonyltelechelic natural rubber (CTNR) was obtained. Finally, it was treated by $NaBH_4$ at 60 ^{o}C for 6 h and then hydrolysis. The hydroxytelechelic natural rubber was obtained and used as starting materials in the next experiment (waterborne polyurethane).

The chemical structure and molecular weight of natural rubber polyols was characterized with ^{1}H-NMR. All samples were dissolved by *d*-Chloroform, $CDCl_3$. The spectra in Figure 6 were consisted of ENR, CTNR and HTNR, respectively. The ^{1}H-NMR spectrum of ENR shows the presence of signals at 5.12 and 2.70 ppm assigned to the olefinic proton of *cis*-1,4-polyisoprenic structure and the methane proton adjacent to the epoxide ring, respectively. The signals of methyl and methylene groups adjacent to the epoxide unit were observed at 1.26 and 2.16 ppm respectively. The positions at 1.67 and 2.09 ppm show the signals of methyl and methylene protons next to the carbon-carbon double bonds. These were no other signals indicating the formation of secondary units resulting from secondary reaction such as epoxide ring opening at 3.4 ppm (signal proton adjacent to hydroxyl group) and 3.90 ppm (proton at furan unit). It can be confirmed that the obtained epoxidized natural rubber have no side reaction. It was found that the obtained epoxidized natural rubber has 3 % mole epoxide of ENR corresponding to the reaction 1.30 h, respectively.

The degradation of epoxidized natural rubber was performed by an accurate amount of periodic acid according to epoxide amount in THF at 30 ^{o}C for 6 h. These isolated degradation products were yellowish viscous liquids. The apparent viscosity of the degradation products after cleavage reaction of 3% ENR and the yields (%) of degradation reactions of natural rubber chains were more than 80%. Its chemical structure was confirmed in Figure 3. It shows the complete disappearance of oxirane structure and the appearance of the novel peaks corresponding to an aldehyde proton at 9.80 ppm, other peaks corresponding to a CH_2 in α and β of carbonyl terminal functional between 2.20 and 2.60 ppm and the peak of methylic protons in ketone end group at 2.13 ppm.

In final step, the modification of CTNR was then performed to transform carbonyl groups to hydroxyl groups at chain-ends by reduction with sodium borohydried in THF. Its structure was revealed by NMR spectra in Figure 7. It shows that the ethylenic proton (5.12 ppm) is unchanged and the complete disappearance of both peaks of aldehyde proton at 9.80 ppm and methylic proton in ketone end group at 2.13 ppm as well as the peak of CH_2 in α and β of terminal carbonyl functions between 2.20 and 2.60 ppm. We observed the novel peak of methylic protons adjacent to secondary alcohol at 1.20 ppm and two peaks corresponding to $C\mathit{H}$ (3.80 ppm) and $C\mathit{H}_2$ (3.68 ppm) adjacent to alcohol groups at the chain-ends. The integrations of the signal of proton at 3.8 adjacent to secondary alcohol ($I_{C\boldsymbol{H}OH}$) and the signal of ethylenic proton ($I_{C=C\boldsymbol{H}}$) was allowed to calculate the average molecular weight of telechelic oligomers according to below equation. The *Mn* of HTNR were 3000 g mol^{-1} for degradation of 3% epoxidized natural rubbers.

$$Mn\ (\text{HTNR}) = \left(\frac{I_{3.80}}{I_{5.10}}\right) \times 68 + 104$$

FT-IR spectrum in Figure 3 confirmed the structure of the obtained oligoisoprene by the presence of a strong peak of hydroxyl group at 3500 cm^{-1} and by the absence of the peak of carbonyl group at 1720 cm^{-1}

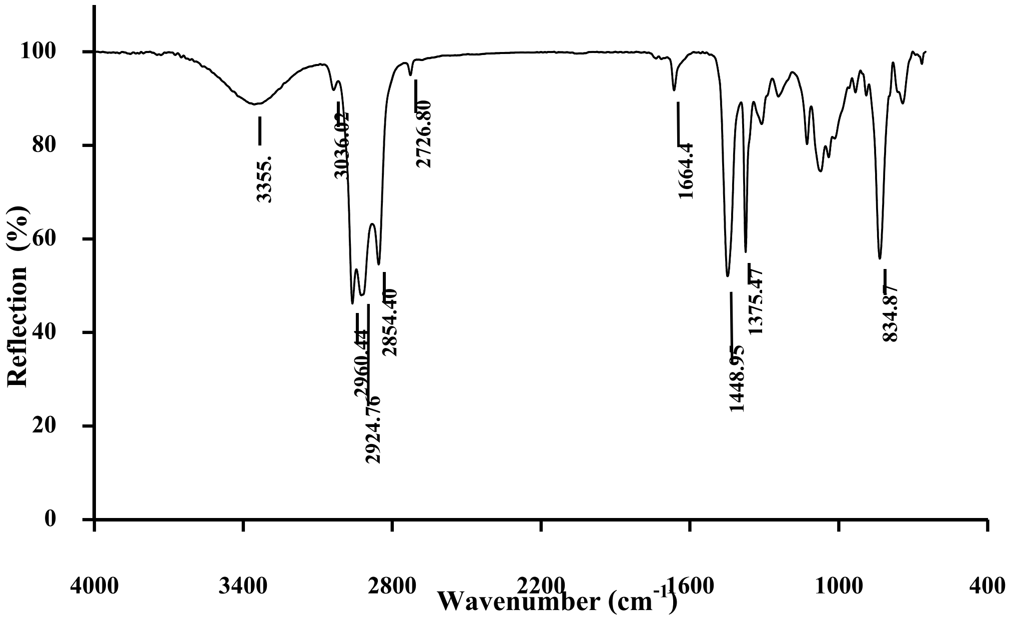


Figure 3. FT-TR spectrum of hydroxyltelechelic natural rubber (HTNR)

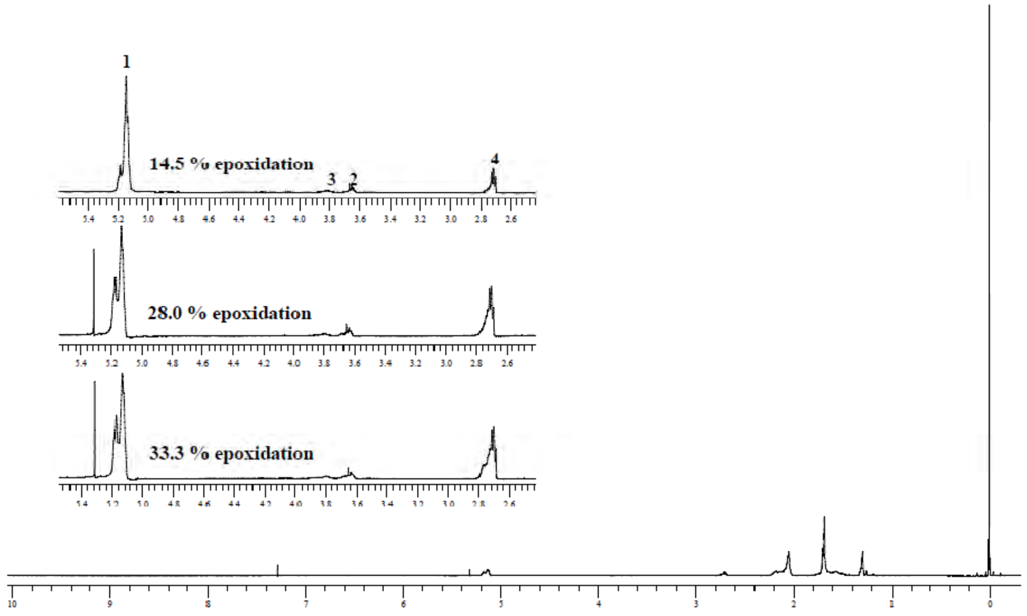


Figure 4. ^{1}H-NMR spectra of epoxidized hydroxyltelechelic natural rubber (EHTNR)

In addition, HTNR were also modified by epoxidation reaction to prepare different epoxide content from 0 to 30 %mole to obtain a epoxide units on HTNR chain. These reaction shows in Figure 1. It was found that a important signal at 2.7 ppm corresponding to proton adjacent to carbon-carbon double bonds was observed and this signal was more intensive with increasing amount of *m*-chloroperbenzoic acid. That was confirmed that the epoxide units were on HTNR chains. The three epoxide content of HTNR such as 14.5, 28.0 and 33.5% mole, respectively were obtained as shown in Figure 4.

3.2 Preparation of waterborne polyurethane (WPU)

The waterborne polyurethane was prepared by prepolymer technique and kept the ratio of NCO:OH was controlled at 1:1 as shown in Figure 2. These polyurethane films were prepared by casting on Teflon mould and kept at 60 °C for 24 h. These films continuously were kept in room temperature for 7 days before testing. For this work, we would like to study the effect of chain extender and the ratio of NCO/OH in WPU3000 based on TDI on their properties.

1. Effect of ethylenediamine content and NCO/OH ratio

Table 1. Results of EDA content on TSC, pH and particle size of WPU3000

Samples	EDA (mol)	Appearance	TSC(%)	pH	Particle size(nm)
WPU3	0.00	Milky blue	20	7.01	79±30
WPU4	0.25	Light yellowish	21	8.86	85±40
WPU5	0.5	Yellowish	22	8.94	80±30
WPU6	0.75	Yellowish	19	8.78	80±30
WPU7	1.00	Yellowish	20	9.00	88±40
WPU8	1.25	Light yellowish, viscous	21	9.02	81±40
WPU9	1.50	Light yellowish, viscous	22	8.98	76±40
WPU10	1.75	Light yellowish, viscous	20	9.02	79±80
WPU11	2.00	Light brown, high viscous	34	8.92	75±40

The WPU3000s were studied on the effect of EDA content on physical properties as shown in Table 1. It shows that the increasing of EDA content gave the physical of latex changed from milky (0 mol) to milky appearance (2 mol) and gave more high viscosity due to an effect of hard segment in polyurethane structure. The stability of latex for 3 months was quite stable however; these dispersions from EDA 1 mole to EDA 2 mol had some precipitation. In addition, their films were easier peel off from a mould but more darkness yellowish with increasing EDA content.

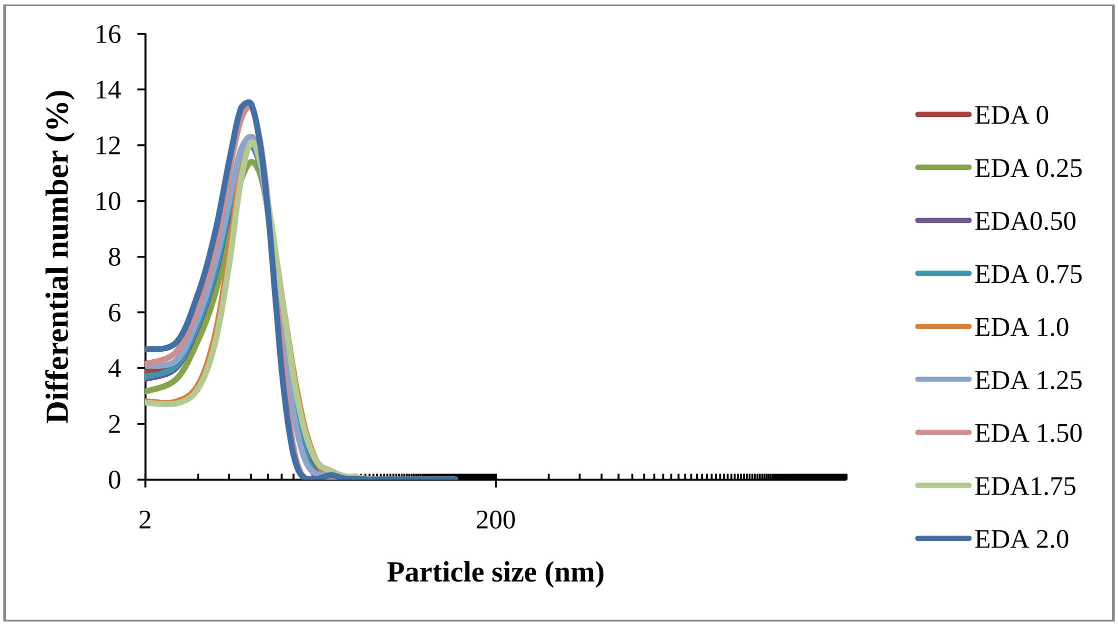


Figure 5. Results of particle size of WPU3000 with various EDA contents

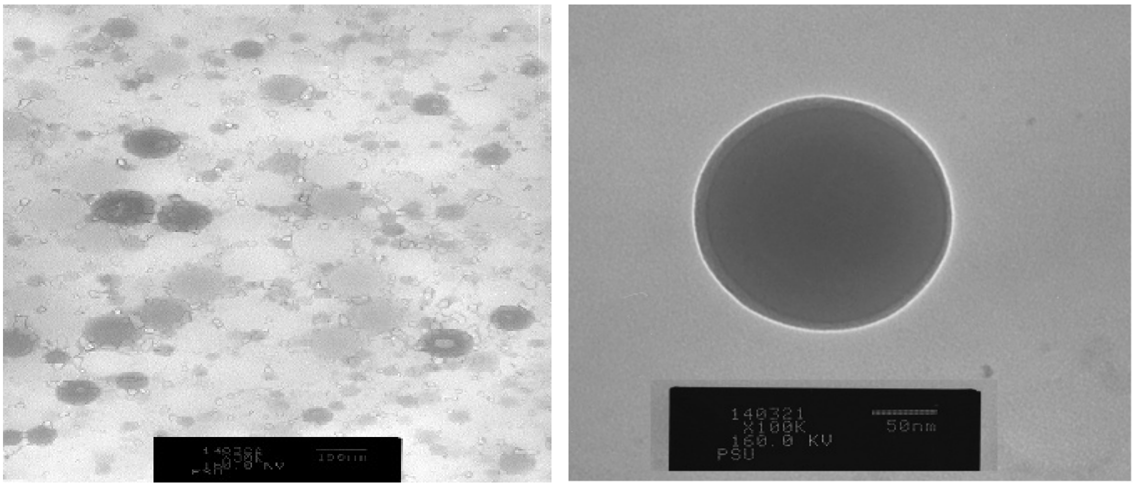


Figure 6. TEM image of particle size of WPU3 a) 50K and b) 100K

In Figure 6 shows sample of TEM images of WPU3 at the magnification 100K and 50K, respectively. The particle was stain with OsO_4 solution. It was clearly seen that the shape of particle size of WPU3 is round and well distributed in the dispersion.

Table 2. Result of the ratio of NCO/OH on TSC, pH and particle size of WPU3000

Samples	NCO/OH	EDA (mole)	Appearance	TSC (%)	pH	Particle size(nm)
WPU3	1.00	0	Milky blue	20	7.01	79±30
WPU13	1.25	0	Milky	20	8.83	82±40
WPU30	1.50	0	Milky	23	8.97	88±50
WPU15	1.75	0	Milky	20	8.44	84±40
WPU31	2.00	0	Milky	19	8.67	86±50
WPU32	2.5	1	Milky	21	9.16	143±50
WPU33	3.0	1	Milky/partially precipitate	11	8.86	Non-stable

For the ratio of NCO/OH series, they had a clearly effect on average particle size, especially, in the case of increasing of NCO/OH with fixing EDA content at 1 mole (WPU7, WPU32 and WPU33). The average particle size increase from 88 to 143 nm and partially precipitate for the ratio of NCO/OH equal to 1, 1.5 and 2, respectively at fixing EDA at 1 mole (Table 2 and Figure 7). It was explained that with the same content of DMPA, the increase in particle size for the resulting WPU with different NCO/OH ratio in this study is mainly due to occurrence of higher crosslink in the WPU.

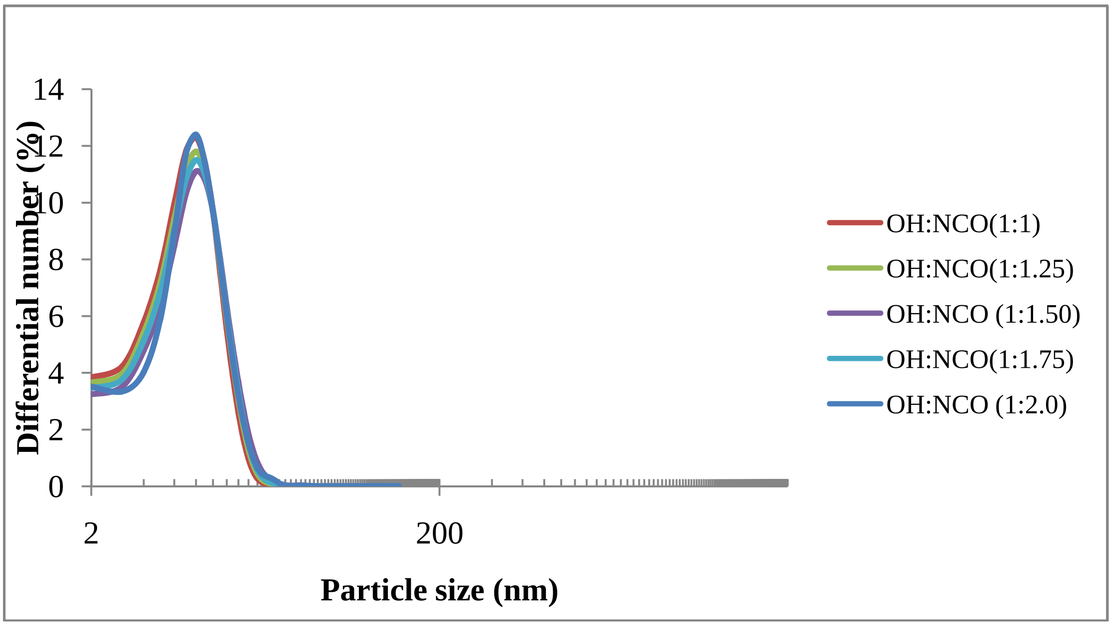


Figure 7. Results of particle size of WPU3000 with various ratios of NCO/OH (without chain extender)

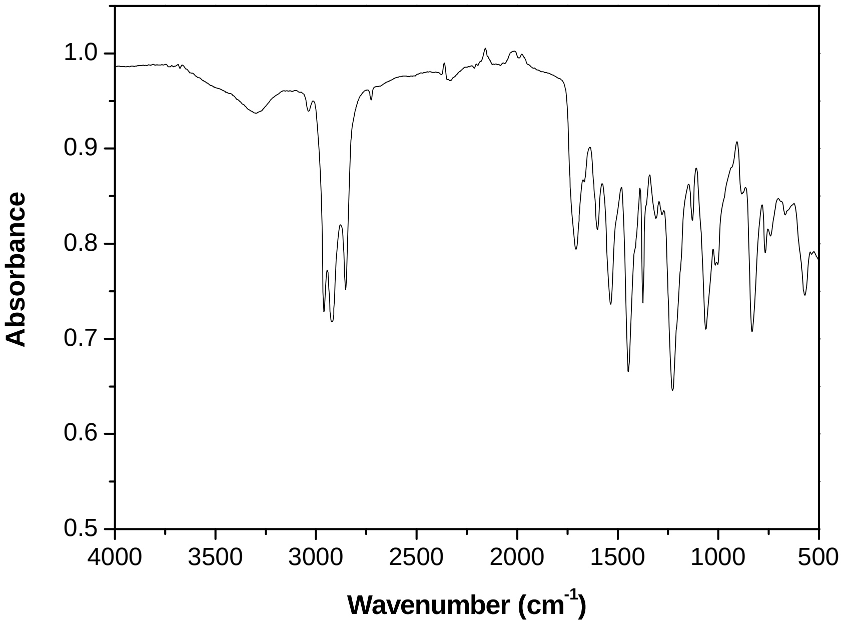


Figure 8. FT-IR spectrum sample of waterborne polyurethane (WPU3)

Figure 8, shows that the chemical structures of WPU films were characterized by FTIR (ATR technique). The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530 cm^{-1}, which correspond 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 absorption peak at 2270 cm^{-1} confirms that there was no residual-free NCO in WPU films. It was summarized that the synthesis of waterborne polyurethane based on natural rubber was well-achieve.

Figure 9-10, shows that the chemical structures of WPU films were characterized by FTIR (ATR technique). The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530 cm^{-1}, which correspond 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. The disappearance of absorption peak at 2270 cm^{-1} confirms that there was no residual-free NCO in WPU films. Moreover, the intensity of the –N-H vibration region around at

3300 cm^{-1} is higher for WPU films with higher a NCO/OH ratio or EDA content. This suggests more urethane linkages.

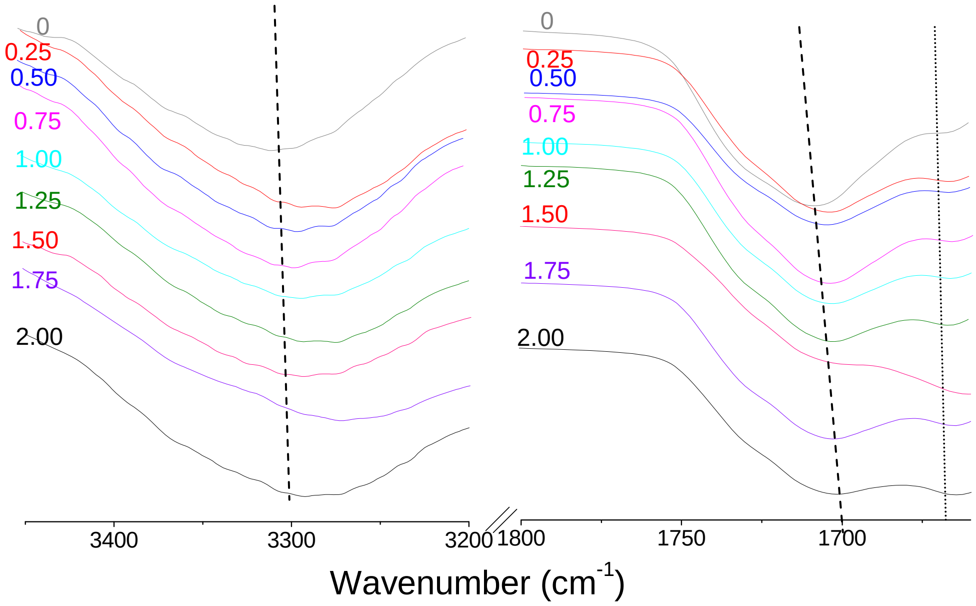


Figure 9. FT-IR spectra of WPU3000 films with various EDA contents

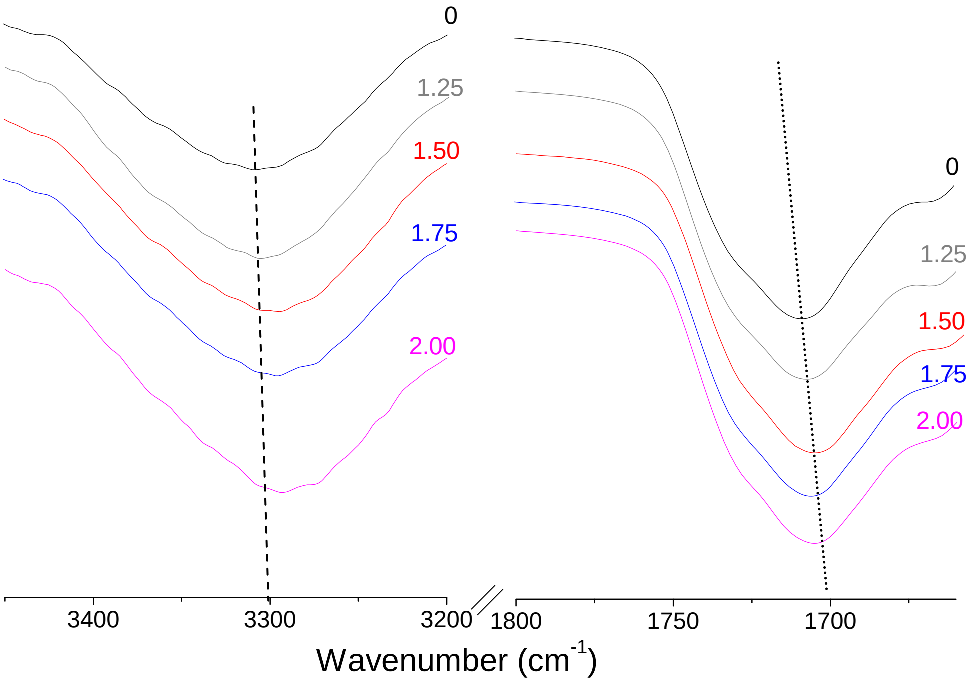
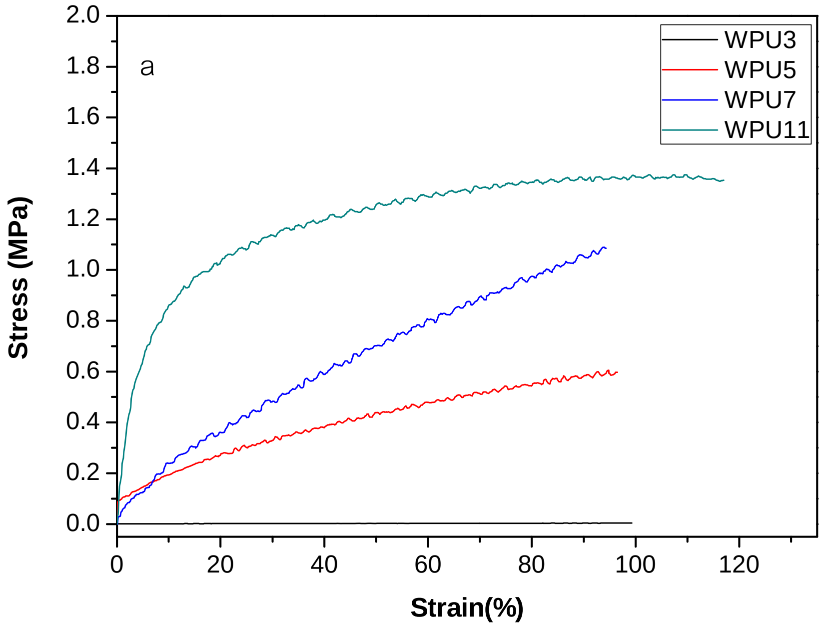


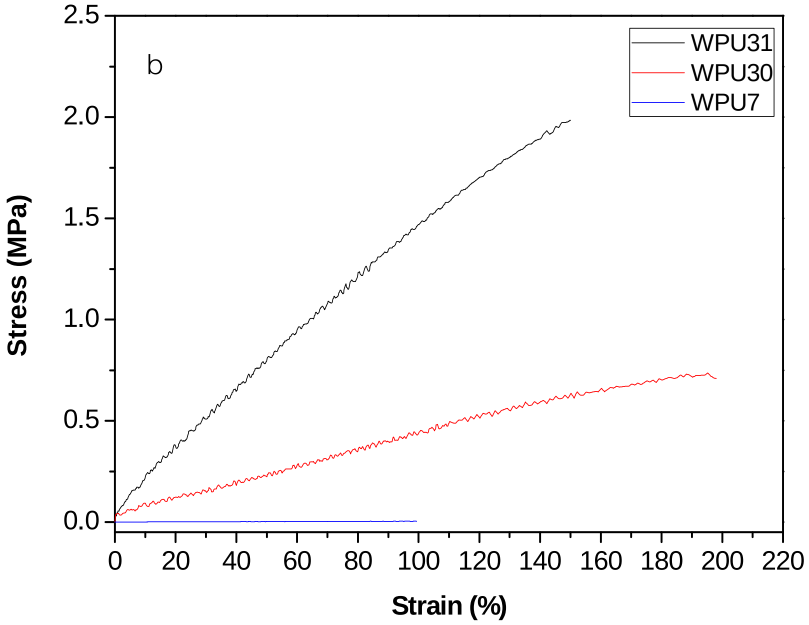
Figure 10. FT-IR spectra of WPU3000 films with various ratios of NCO/OH

In agree with a shift of peaks from 1710–1730 cm^{-1} to approximately 1700 cm^{-1} with the increase of hard segment content for EDA-extended one suggests that stretching vibration mode of carbonyl group becomes easier because the rigid hard segment interrupts dipole–dipole interaction among carbonyl groups, thus freeing each carbonyl group from interaction with the neighboring groups. In addition, the intensity of carbonyl of urea region around at 1640 cm^{-1} is higher for WPU films with an increase of EDA content.

Table 3. Mechanical properties of EDA content and NCO/OH ratio on properties

Samples	Hard segment (%)	Young 's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU3	21.2	1.47±0.7	0.09±0.0	100±11.0
WPU5	23.4	10.72±5.5	0.60±0.0	97±0.2
WPU7	25.7	11.14±2.2	1.09±0.2	94±29.8
WPU11	29.9	64.44±0.0	1.35±0.0	117±42.8
WPU30	22.7	5.91±0.1	0.75±0.0	200±4.2
WPU31	24.2	15.95±11.5	2.0±0.1	150±31.2
WPU32	27.4	143.14±15.8	2.35±0.1	54±7.5
WPU33	28.4	229.33±0.0	3.19±0.0	38±0.0





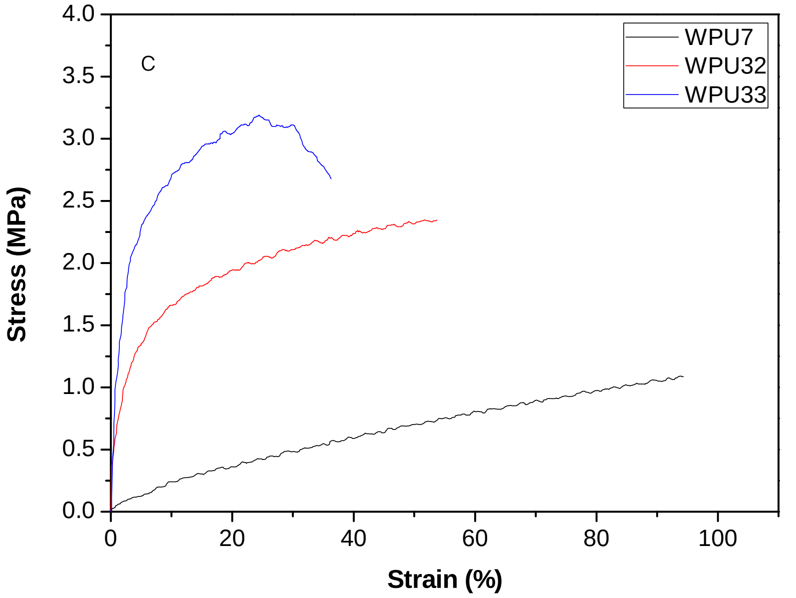


Figure 11. Stress and strain curve of WPU a) EDA content, b) NCO/OH without EDA and c) NCO/OH with EDA 1 mole

Table 3 summarized tensile strength, elongation at break and young's modulus of WPU films from HTNR3500 with various EDA contents, the ratio of NCO/OH with and without EDA 1 mole, and tensile stress-strain curve are shown in Figure 11. The WPU3 film shows a very soft rubbery modulus of 1.47 MPa, tensile strength of 0.09 MPa, and elongation at break of 100 %

(Table 3). When the EDA content in WPU formula is further increased, the modulus and ultimate stress of the resulting WPU11 (EDA 2 mole) clearly increase but they had been no significantly effected on elongation at break.

We found that among WPU films (WPU3-7) exhibit a strain of around 100% due to their relatively low crosslink density. This behavior is similar to the tensile test behavior of a soft elastomeric polymer. However, the WPU11 film shows behavior that is typical of a ductile plastic with a clear yield point and shows a modulus and a tensile strength that are approximately 43 and 135 time higher, respectively than those of WPU3 film. In addition, the NCO/OH ratio without EDA series in WPU films show behavior of elastomeric polymer. Their modulus and tensile strength increase with an increase of the NCO/OH ratio, for instant, the WPU31 film (NCO/OH =2/1) gave a tensile properties higher than that of WPU3 film (NCO/OH = 1/1) around over 200%. Moreover, the NCO/OH at 2/1 in presence of EDA 1 mole (WPU 33) shows the highest modulus and tensile strength with relatively smaller elongation at break (38% ± 0) in all WPU films. It results in a relatively hard plastic, which shows yielding behavior, followed by strain softening. It was described that these changes in the mechanical behavior are a result of the increase in the hard segments content led to increase the interaction by hydrogen bonding from the part of hard segment in the resulting WPU films from the HTNR.

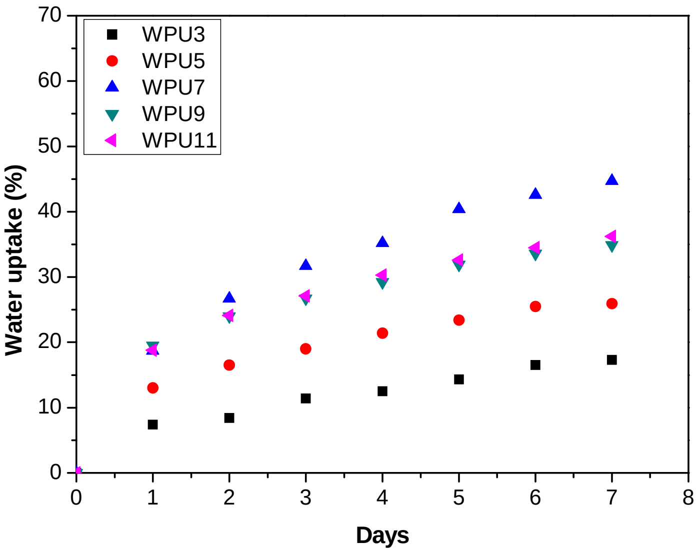


Figure 12. Water uptake of WPU films with different EDA content

Table 4. Swelling and thermal properties of WPU films

Code	Swelling (%)			Thermal degradation					
	THF	Toluene	MEK	First step		Second step		Third step	
				*T*max (^{o}C)	Weight loss (%)	*T*max (^{o}C)	Weight loss (%)	*T*max (^{o}C)	Weight loss (%)
WPU3	*Sol.*	*Sol.*	*Sol.*	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	*Sol.*	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

The films formed after drying of WPUs at 60°C are non-tacky, flexible, and yellowish. The water uptake of WPU films for the various EDA content with constant of DMPA content at 5.6% is represented in Figure 4. It was clearly observed that the water uptake of WPU films increased with immerse time. In addition, the result revealed that the higher EDA content in WPU films were added, the higher water uptake of their films were obtained because of the enhancement of hydrophilic block from hard segment of urea and urethane groups. For example, the series of WPU3, without EDA, was the minimum water uptake (17%) while that of WPU7 was the maximum (45%) during 7 days.

The swelling properties of WPU films in some solvents such as tertrahydrofuran (THF), toluene, and methyl ethyl ketone (MEK) was shown in Figure 13 and Table 4. It was observed that the WPU3 film was completely dissolved in each solvent due to low crosslink, non polar and linear structure. In addition, the toluene was a good solvent to swell of these polyurethane film based HTNR in all conditions. However, the swelling of WPU films was decreased with increasing the EDA content and the NCO/OH ratio, for instant the WPU films with increase in the EDA content from EDA 0.5 mole (WPU5) to EDA 2 mole (WPU11) indicating that the percentage of swelling decrease to 100%. As it was expect that the content of EDA and NOC/OH ratio are increased, the obtained polyurethane with higher hard segment has a greater opportunity to form hydrogen bonding or physical networks because it has more active proton positions than a lower hard segment. The highest hard segment, WPU33, exhibits a lowest swell of 23.8% in toluene and 5.4 % in MEK.

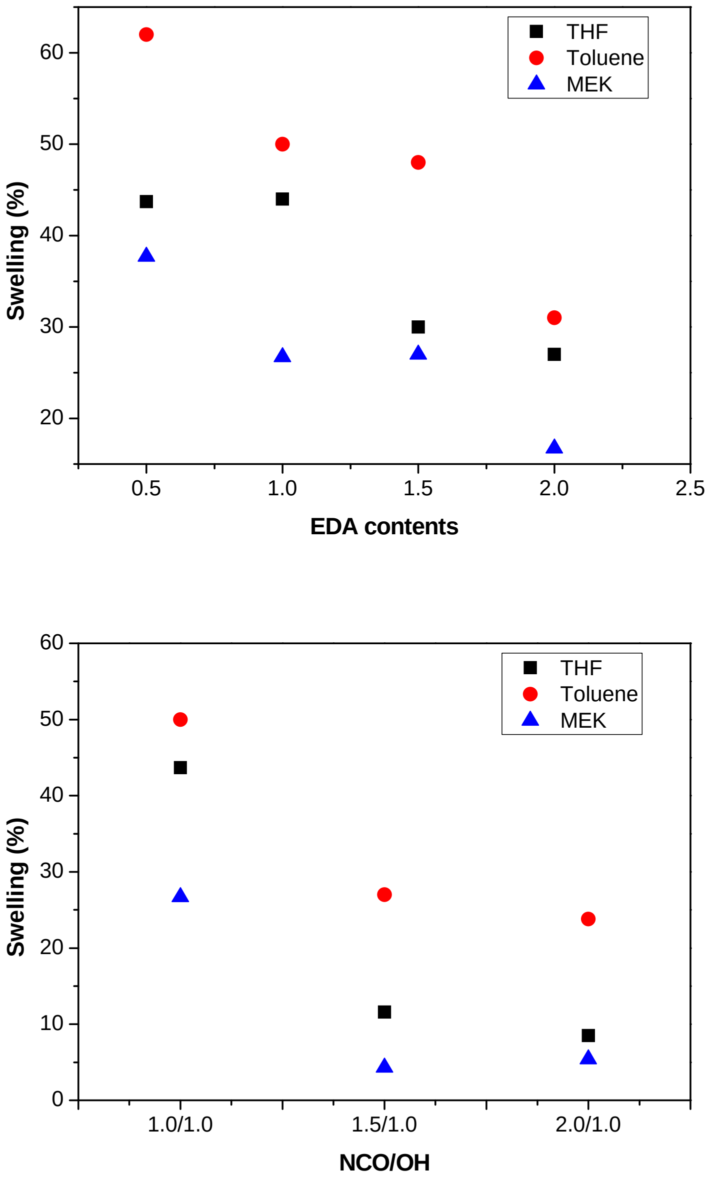
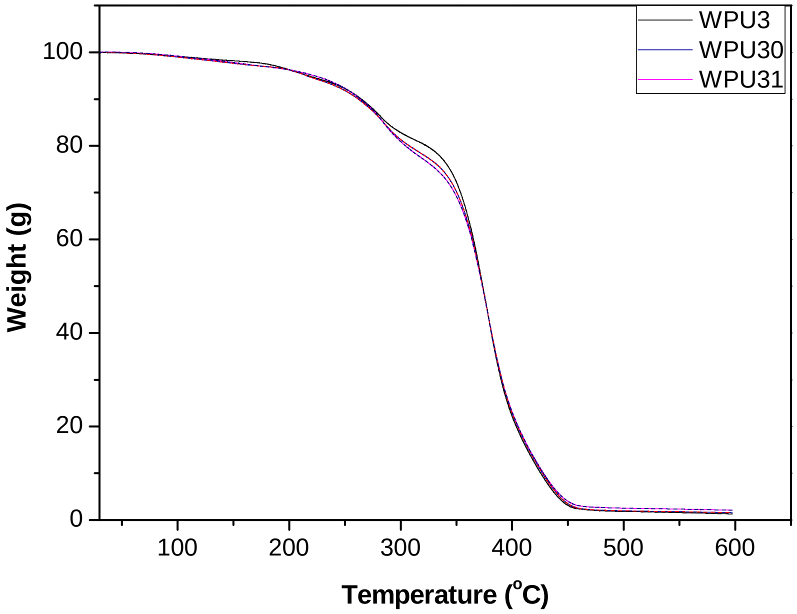


Figure 13. Swelling of WPU films a) EDA content and b) NCO/OH ratio with EDA 1 mole



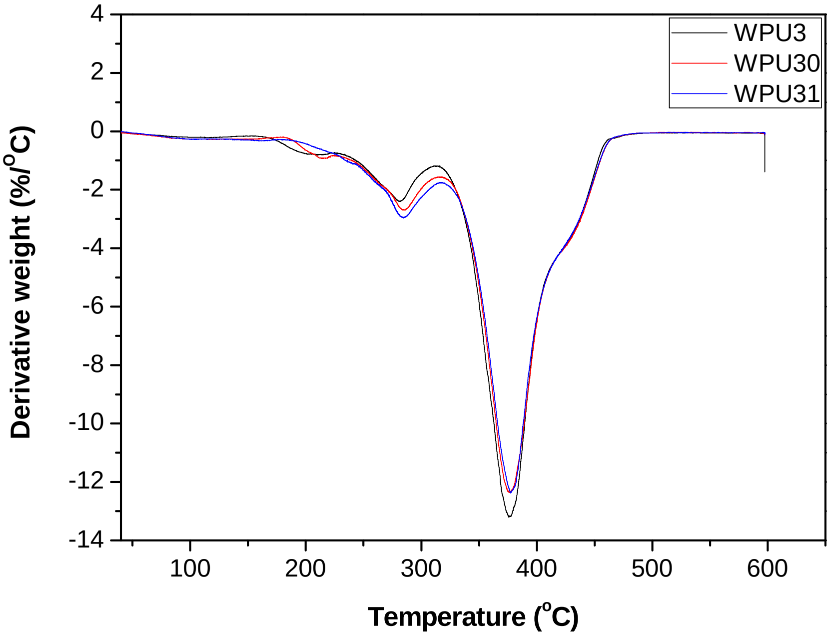


Figure 14. TGA curve of WPU films from HTNR with different the ratio of NCO/OH without EDA

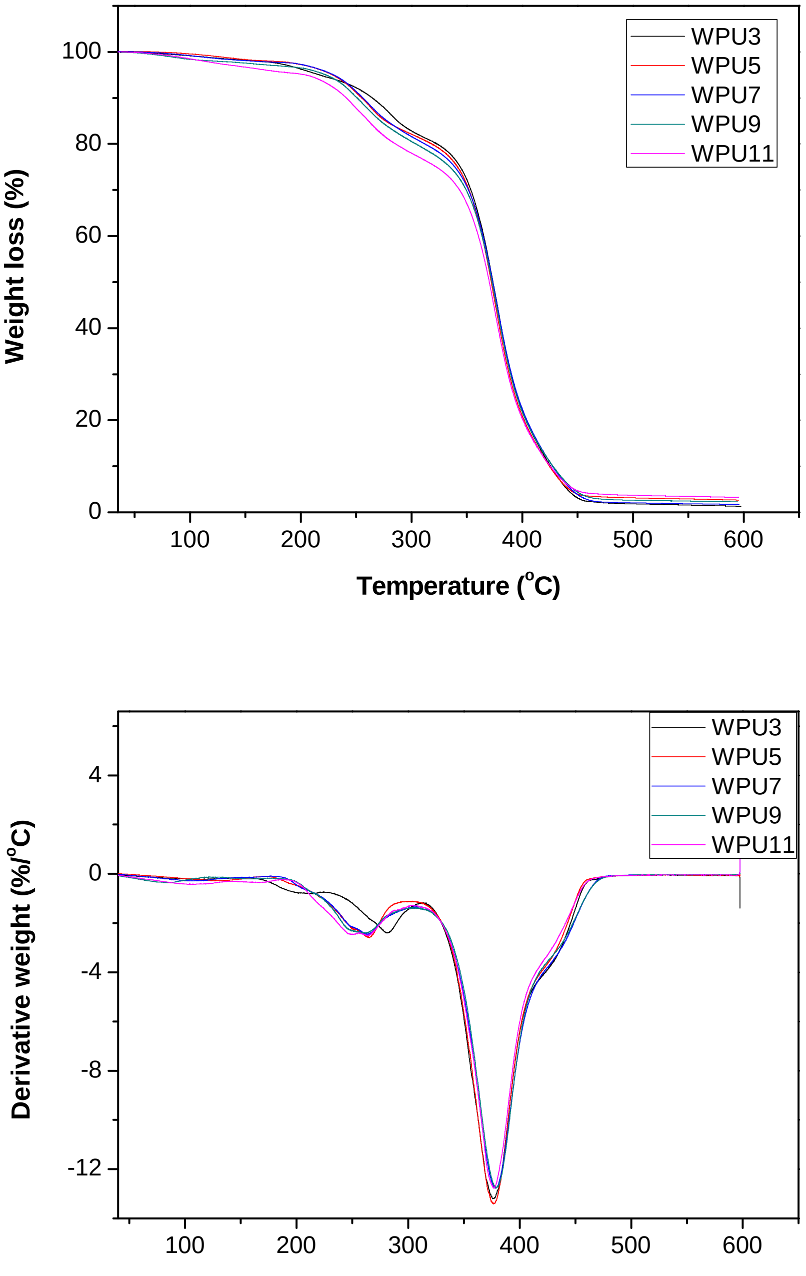


Figure 15. TGA curve of WPU films from HTNR with different EDA contents

A three-stage loss thermal degradation was observed for all WPU films (Figure 14 and 15). The first stage degradation at 162°C–197 °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 250°C–270 °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. Finally, stage at 375 °C–377 °C relates to the decomposition of structure of oligoisoprene. We observed that the increased EDA contents in sample for WPU3–WPU11 led to an increased second step of weight loss from 8.8 to 22.0 percent of weight loss, respectively. The results of the increased ratio of NCO/OH in WPU films with NCO/OH from 1/1 to 2/1 (WPU3, WPU30, WPU31) also show an increasing of the second step degradation from 8.8 to 19.8 percent of weight loss. Their degradations were assumed that the cleavage of urethane or urea groups of EDA or polyol and diisocyanates were occurred (Figure 14 and 15). The results is agreement with the previous work, which studied on hydroxyl telechelic polybutadiene (HTPI) in which the thermal decompositions in second step of film polyurethane dispersion were increased with an increase of NCO/OH ratio. However, the first step of weight loss of all WPU films was slightly changed from 2.0 to 4.6 percent of weight loss due to fixing the amount of DMPA at 5.6%wt.

2. Effect of epoxidation of HTNR

Table 5. Properties of WPU based on EHTNR

Samples	Epoxidation (%)	Properties				
		TSC	pH	Stability	Appearance	Particle size (nm)
WPU3	0	21.2	7.3	Stable	Milky	80±36
WPU97	10	17.4	8.4	Partially precipitated	Milky	738±548
WPU99	20	20.8	8.2	Precipitated	Milky	769±403
WPU100	30	10.1	7.8	Precipitated	Milky	859±539

In the epoxidation series based waterborne polyurethane (WPU97, 99 and 100) was studied. It was found that the stability of WPU based on epoxidized HTNR was lower than that of HTNR. They had a precipitation in a few days. In addition, the particle size of WPU based epoxidized HTNR was increased with increasing of the epoxidation level for instant from 0.738 to 0.859 of WPU97(10%EHTNR) to WPU100(30%EHTNR). It might be to the hydrophilic effects of EHTNR while some water was dropped in the system, the prepolymer of polyurethane was changed phase from solvent system to aqueous systems or dispersion form. Therefore, the poxidation series based WPU was not to be later prepared graft copolymerization with vinyl monomers.

3.3 Preparation of waterborne polyurethane (WPU) grafted vinyl monomer

The WPU-g-(MMA/Bu-ac (60/40)) hybrid with various the ratios of WPU and MMA/Bu-ac as 100:0, 30/70, 50/50, 70/30 and 0:100 based on HTNR3000 and TDI and DMPA 5.6% were studied. The results of WPU-g-(MMA/Bu-ac (60/40)) hybrid properties and their mechanical and physical properties show in Table 6 and Table 7, respectively.

3.3.1 Preparation of waterborne (WPU) grafted (MMA/Bu-ac (60/40)) monomers

Table 6. Results of WPU-g-(MMA/Bu-ac (60/40)) hybrid with various WPU/vinyl monomer ratio

Type of vinyl monomer	WPU:MMA/ Bu-ac ratio	Properties				
		Conversion (%)	GE[b] (%)	Stability[c]	Appearance	Particle size(nm) $\bar{X}$±S.D. (>1month)
MMA/Bu-ac (60/40)	0:100	79.67	4.66±0.78	Stable	Transparent	80±13
	30:70	96.51	33.63±1.18	Stable	Light brown	117±31
	50:50	89.62	42.47±0.76	Stable	Light brown	127±26
	70:30	94.89	36.67±2.48	Stable	Light brown	139±30
	100:0	-	66.41±3.50	Stable	Milky blue	90±30

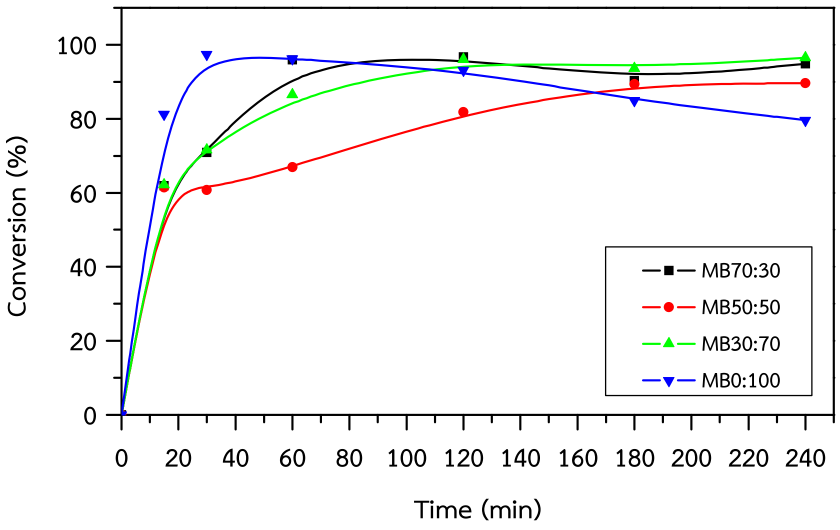


Figure 16. Conversions (%) and reaction time of WPU-g-MMA/Bu-ac (60/40) hybrid

Figure 16 shows the vinyl monomer conversion of graft copolymerization on WPU (WPU- g-(MMA/BU-ac)) with various the ratios of WPU/(MMA/Bu-ac). It was found that the MB0:100 or P(MMA/Bu-ac) was the fastest and highest conversion during 30 min of reaction time (more than 90%). However, the conversion of hybrid dispersion was slowly in the starting reaction time due to the steric effect, but their conversion was around up to 90% for 4h.

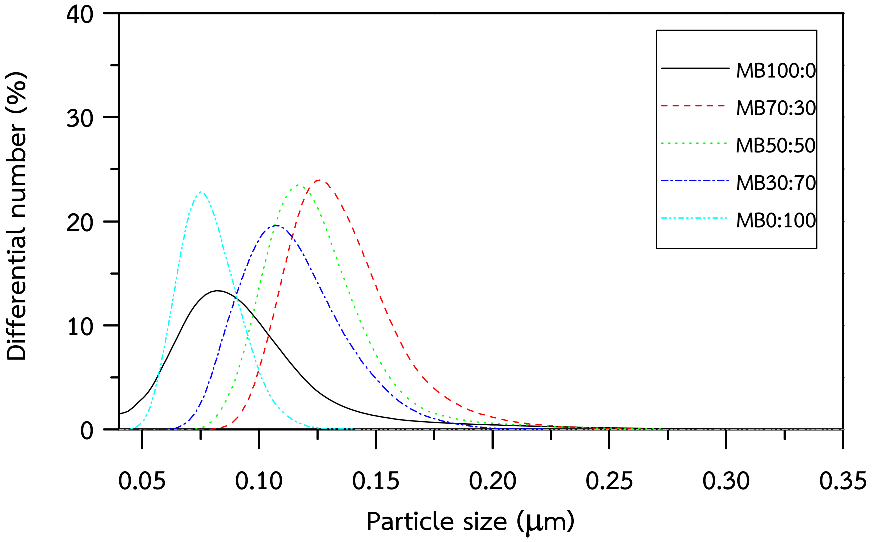


Figure 17. Particle size of WPU-g-(MMA/Bu-ac (60/40)) hybrid with various vinyl monomer ratio

Figure 17 shows the particle size of WPU- g-(MMA/BU-ac) hybrid films with various the ratios of WPU/(MMA/Bu-ac). It was found that the particle size of WPU was increased after grafted with vinyl monomer for instant, from 90 nm of MB0:100 to 139 nm of MB70:30. In addition, the particle size of hybrid dispersion was decreased with increasing of the (MMA/BU-ac) ratio.

Table 7. Result on the influence of WPU/(MMA/Bu-ac (60:40)) ratio on WPU-g-(MMA/BU-ac) hybrid films properties

Properties	**WPU: MMA/Bu-ac ratio**				
	0:100	**30:70**	**50:50**	**70:30**	**100:0**
Appearance	W/F	DB/F	DB/F	DB/F	Y/S
Tensile strength (MPa)	4.59±0.65	2.03±0.07	2.64±0.07	0.33±0.02	0.09±0.02
Elongation at break (%)	388.60±25.41	87.30±16.12	271±11.03	353.00±37.64	93.90±11.03
Swelling properties (%)					
Tetrahydrofuran (THF)	CD	87.50±0.00	100±0.00	75.00±0.00	CD
Toluene	CD	19.40±4.65	83.90±4.56	25.00±0.00	CD
Methyl ethyl ketone (MEK)	CD	58.80±3.56	61.30±0.00	18.80±8.84	CD
Water Absorption 14 days (%)	130.74±7.34	91.70±6.01	49.98±9.89	46.01±3.81	17.10±1.09

[b] (Color/Feature): W (White), DB (Dark brown), Y (Yellow), S (Sticky), F (Flexible) CD: Completely dissolved

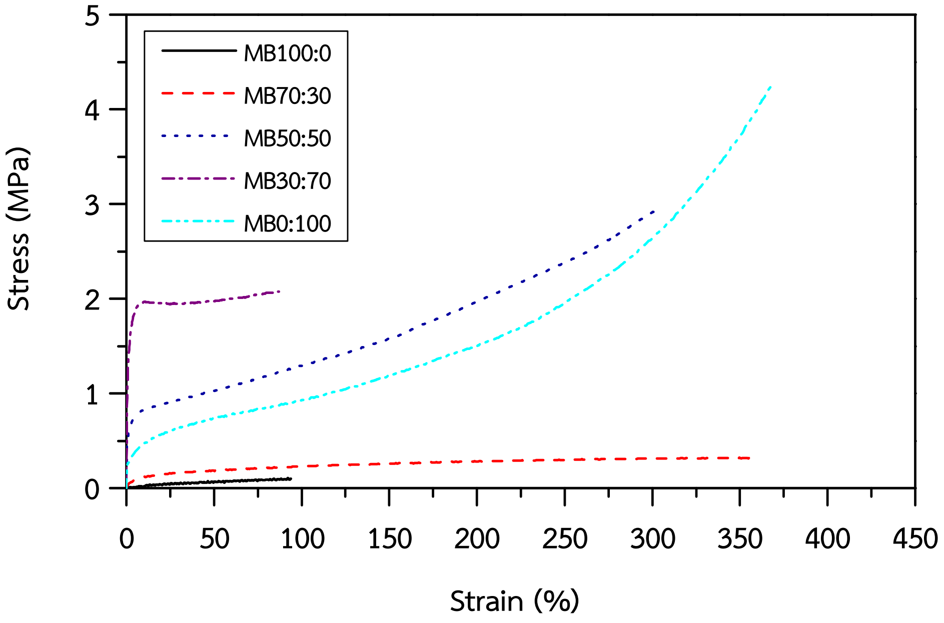


Figure 18. Stress-strain curve of WPU-g-(MMA/BU-ac) hybrid films

Figure 18 shows the tensile properties of WPU- g-(MMA/BU-ac) hybrid films with various the ratios of WPU/(MMA/Bu-ac). It was found that the WPU3 (MB100:0) film was the lowest tensile strength whereas the P(MMA/Bu-ac) (MB0:100) film was the highest tensile strength. In addition, the tensile properties of hybrid films had a tread to increase the tensile strength of films with increasing of the vinyl monomer (MMA/Bu-ac) ratio in hybrid films.

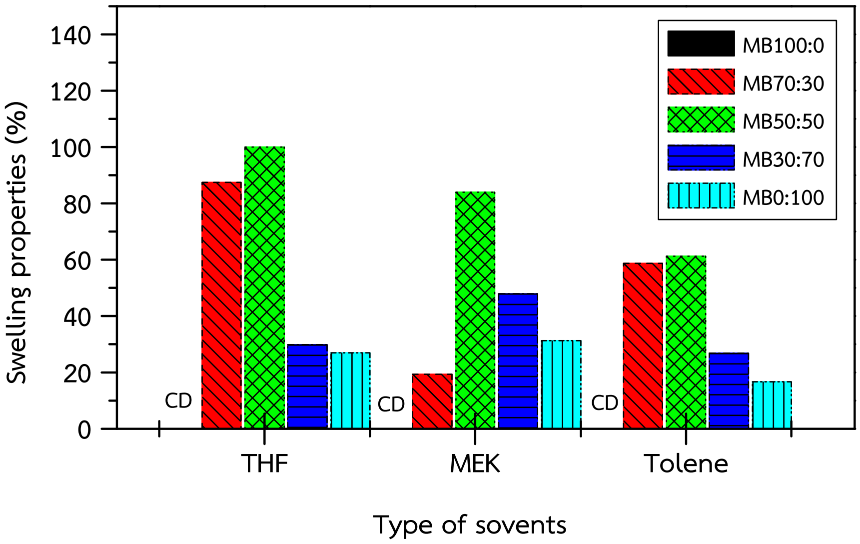


Figure 19. Swelling properties of WPU-g-(MMA/BU-ac) hybrid films

Figure 19 shows the swelling properties of WPU- g-(MMA/BU-ac) hybrid films with various the ratios of WPU/(MMA/Bu-ac). It was found that the WPU3 (MB100:0) film was completely dissolved while the poly(MMA/Bu-ac) (MB0:100) film was the best in solvent resistance. Because the nature of solvent is non-polar solvent led to dissolve the WPU film acted as more hydrophobic nature. Whereas the P(MMA/Bu-ac) (MB0:100) film is polar polymer led to non-dissolve, just swelling. In addition, the swell properties of hybrid films had a tread to reduce the swelling of films with increasing of the vinyl monomer (MMA/Bu-ac) ratio in hybrid films.

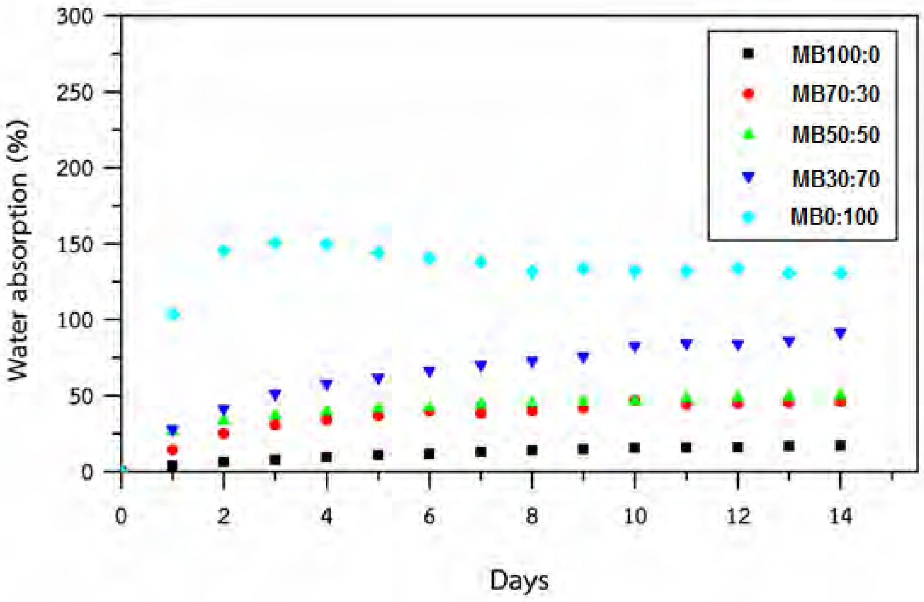


Figure 20. Water uptake of WPU-g-(MMA/BU-ac) hybrid films

Figure 20 shows the water uptake of WPU- g-(MMA/BU-ac) hybrid films with various the ratios of WPU/(MMA/Bu-ac). It was found that the WPU3 (MB100:0) film was the lowest water uptake (17%) while the P(MMA/Bu-ac) (MB0:100) film was the highest water uptake (130%). In addition, the water uptake of hybrid films was increased with increasing of the vinyl monomer (MMA/Bu-ac) ratio in hybrid films due to increasing of hydrophilic monomer in hybrid films.

3.3.2 Preparation of waterborne (WPU) grafted MMA monomers

Table 8. Results on the influence of WPU/MMA ratio on hybrid latexes properties with controlled WPU based on HTNR3000 g/mole and TDI at NCO/OH ratio 1.00/1.00 and DMPA 5.6% wt.

Type of Vinyl monomer	WPU	WPU:MMA ratio	Properties						
			TSC[a] (%)	pH	Conversion (%)	GE[b] (%)	Stability[c]	Appearance[d]	Particle size (nm) >1 month $\overline{X}$±S.D.
MMA	HTNR 3000 TDI	100:0	20.07	7.01	ND	ND	Stable	Milky blue	90±30
		90:10	27.36	4.97	93.88	92.26±9.71	Stable	Dark brown	219±90
		70:30	25.76	5.47	69.66	64.69±5.86	Stable	Light brown	216±106
		65:35	20.00	5.16	82.27	44.31±0.67	Stable	Light brown	82±62
		55:45	18.37	5.36	75.26	35.49±4.13	Stable	Light brown	78±33
		50:50	18.23	4.81	92.26	24.94±3.88	Stable	Light brown	108±113
		0:100	23.50	1.68	76.22	0.14±0.00	Stable	Transparent	68±30

[a] Total solid contents, [b] Grafting efficiency, [c,d] 1 month, ND: Not determined

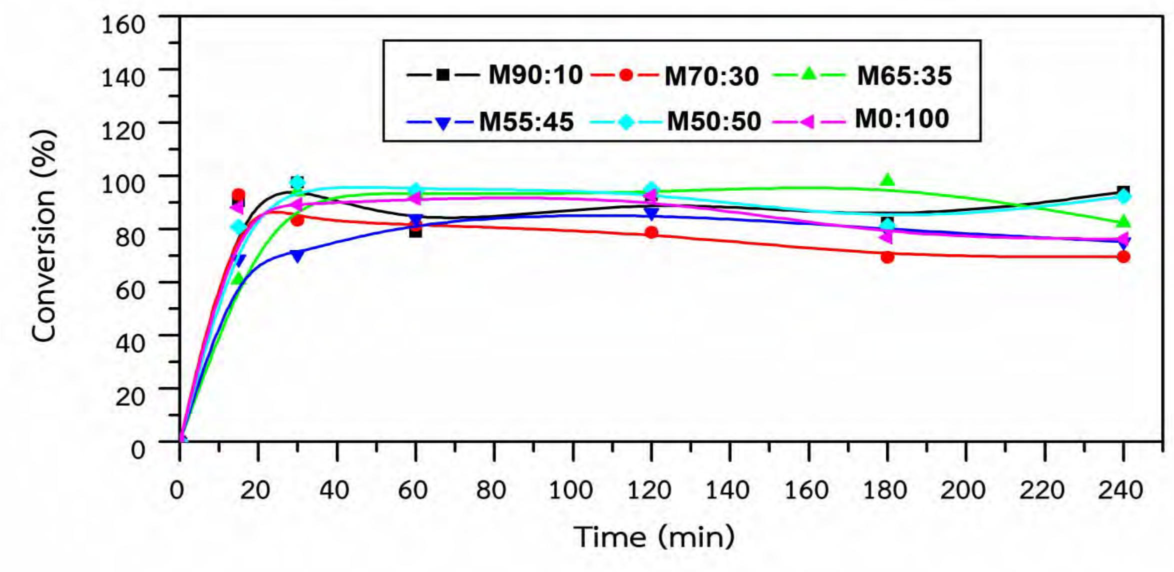


Figure 21. Conversion (%) of WPU-g-MMA hybrid

Figure 21 shows the MMA monomer conversion of graft copolymerization on WPU particle (WPU- g-MMA) with various the ratios of WPU/MMA. It was found that all hybrid latexes were high conversion up to 80% during 30 min of reaction time, except the hybrid latex of M55:45 was lowest conversion around 70% at the same time, whereas the pure PMMA had only a percentage of conversion at 76% for 4h.

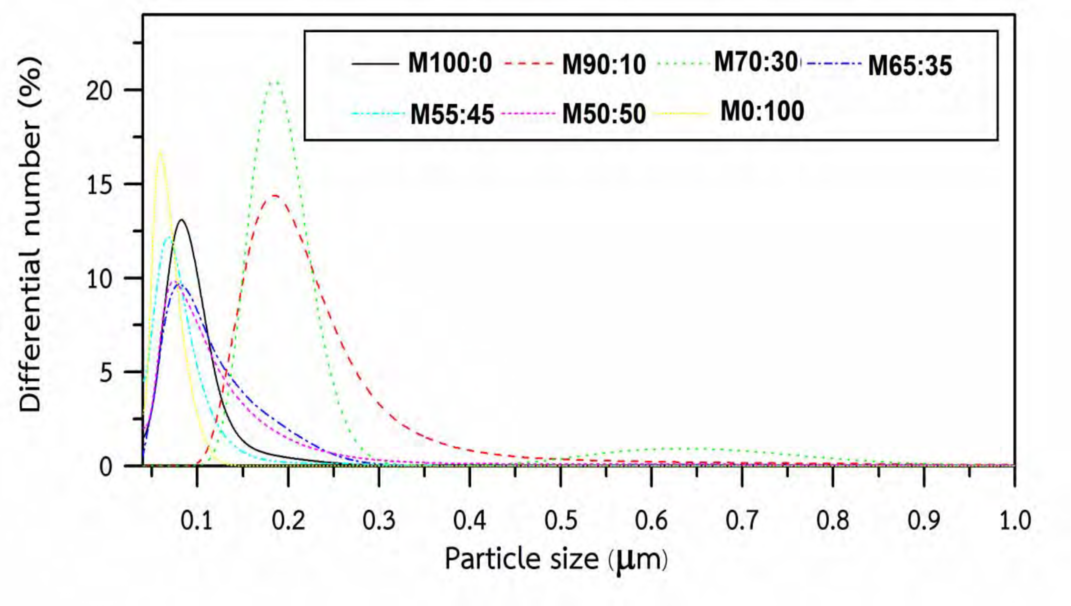


Figure 22. Particle size of WPU-g-MMA hybrid with various vinyl monomer ratios

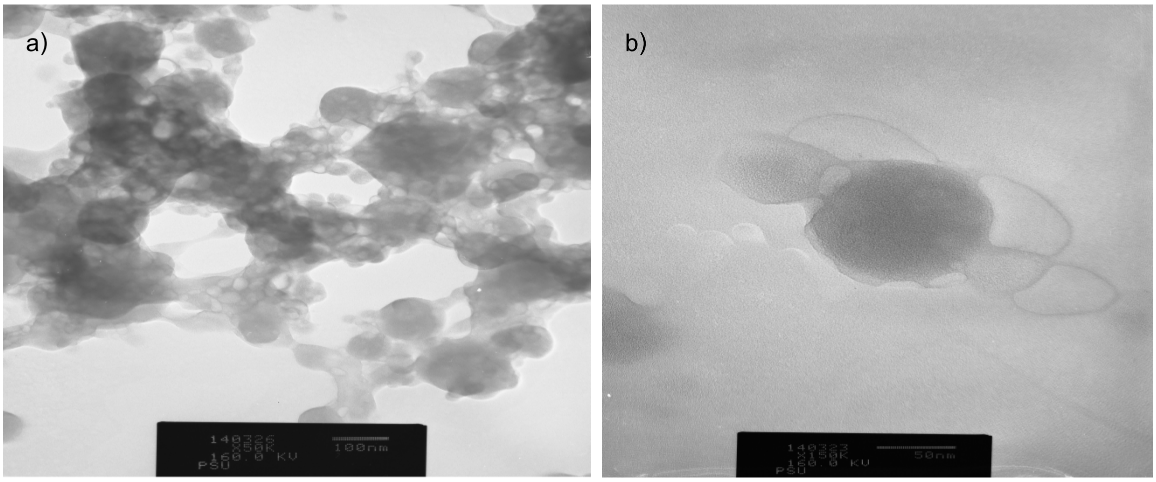


Figure 23 TEM of WPU-g-MMA (65:35) hybrid a) 50K b)150k

Figure 22 present particle size and particle distribution of hybrid latexes. It was showed that the pure PMMA latex is the smallest particle size (68 nm) and narrow particle distribution whereas the pure WPU is bigger particle size (90nm) and board particle distribution. However, the hybrid latexes from both polymers via emulsion polymerization had a trend to increase a particle size and particle distribution with an increasing of WPU ratio in the hybrid latex, for instant, WPU/MMA (90:10) hybrid of 219 nm, WPU/MMA(65:35) hybrid of 82 nm.

The particle of hybrid latex (WPU/MMA65:35) was revealed by TEM as shown in Figure 23. It was found that the particle of hybrid has 2 parts which are difference form. The one part is a spherical shape and dark region assumed that is a particle of WPU and another one is a long chain shape and light region assume that is a chain of MMA. It could be conclude that the WPU/MMA hybrid was successfully synthesized via emulsion polymerization technique.

Table 9. Result on the influence of WPU/(MMA) ratio on WPU-g-(MMA/) hybrid films properties

Properties	**WPU:MMA ratio**						
	100:0	**90:10**	**70:30**	**65:35**	**55:45**	**50:50**	**0:100**
Appearance[a]	Y/S	DB/VS	DB/F	DB/F	DB/F	LB/CR	T/CR
Mechanical properties							
Tensile strength (MPa)	0.09±0.02	ND	0.27±0.04	1.44±0.15	2.13±0.00	ND	ND
Elongation at break (%)	93.90±11.03	ND	472.50±71.13	9.98±3.92	6.01±0.00	ND	ND
Swelling properties (%)							
Tetrahydrofuran (THF)	CD	ND	146.90±4.42	115.60±30.94	103.10±22.10	ND	ND
Methyl ethyl ketone (MEK)	CD	ND	30.50±0.71	71.90±4.42	59.40±4.42	ND	ND
Toluene	CD	ND	125.00±0.00	96.90±13.26	96.90±4.42	ND	ND
Water Absorption, 14 days (%)	17.01±1.09	ND	112.90±17.48	23.37±6.62	0.93±0.50	ND	ND

[a] Color/Feature: Y (Yellow), LB (Light brown), DB (Dark brown), T (Transparent), VS (Very sticky), S (Sticky), F (Flexible), R (Rigid), CR (Cracked rigid)

CD: Completely dissolved

ND: Not determined

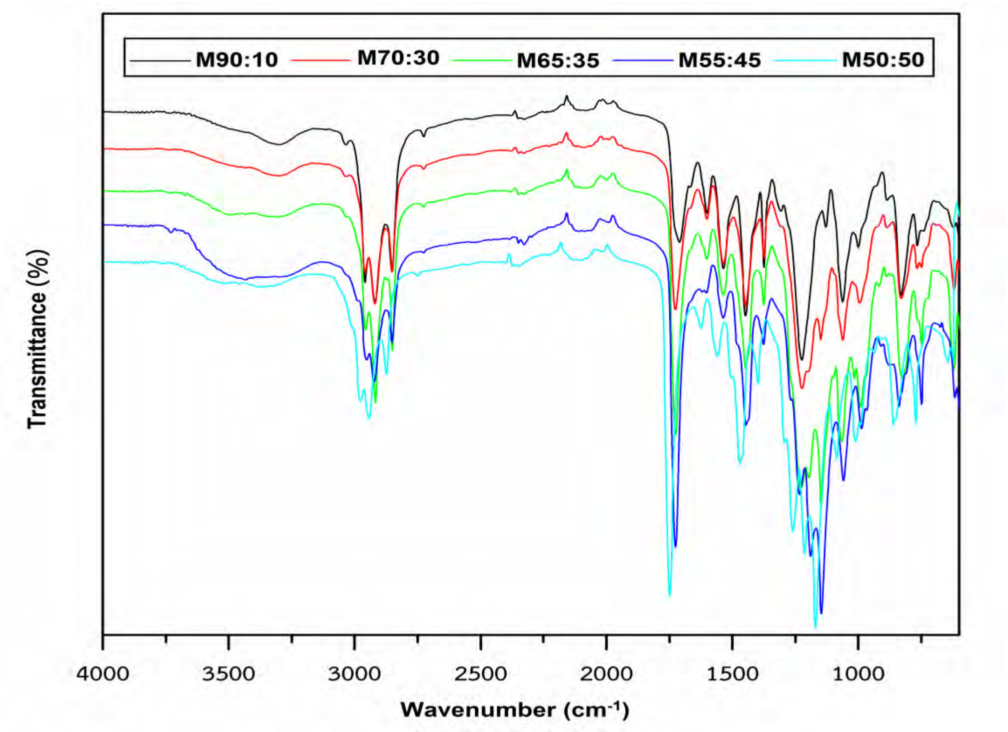


Figure 24. FT-IR spectra of WPU-g-MMA hybrid films

Figure 24, shows that the chemical structures of WPU/MMA hybrid films was characterized by FTIR (ATR technique). The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530 cm^{-1}, which correspond 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. The disappearance of absorption peak at 2270 cm^{-1} confirms that there was no residual-free NCO in WPU films. The other absorbance represented a vibration of functional groups on PMMA structure at around 1750 could be assigned to C=O stretching of the esters. The absorption bands at 1271, 1240 cm^{-1} and 1189, 1141 cm^{-1} could be assigned to C–O and C–O–C stretching, respectively.

It was summarized that the synthesis of hybrid natural rubber based waterborne polyurethane grafted methyl methacrylate was well-achieve.

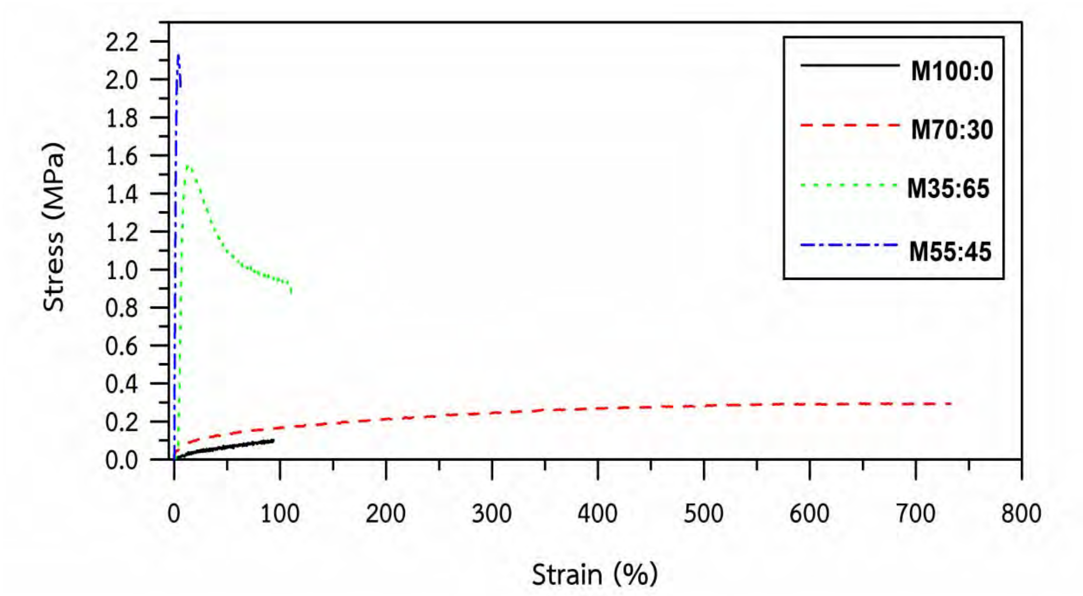


Figure 25. Tensile properties of WPU-g-MMA hybrid films

Figure 25 shows the tensile properties of WPU- g-MMA hybrid films with various the ratios of WPU/MMA. It was found that the WPU3 (M100:0) was the lowest tensile strength whereas the PMMA (M0:100) was the highest tensile strength and was the lowest elongation at break. It shows behavior like as brittle plastic. In addition, the tensile properties of hybrid films had a tread to increase the tensile strength of films with increasing of the vinyl monomer MMA ratio in hybrid films.

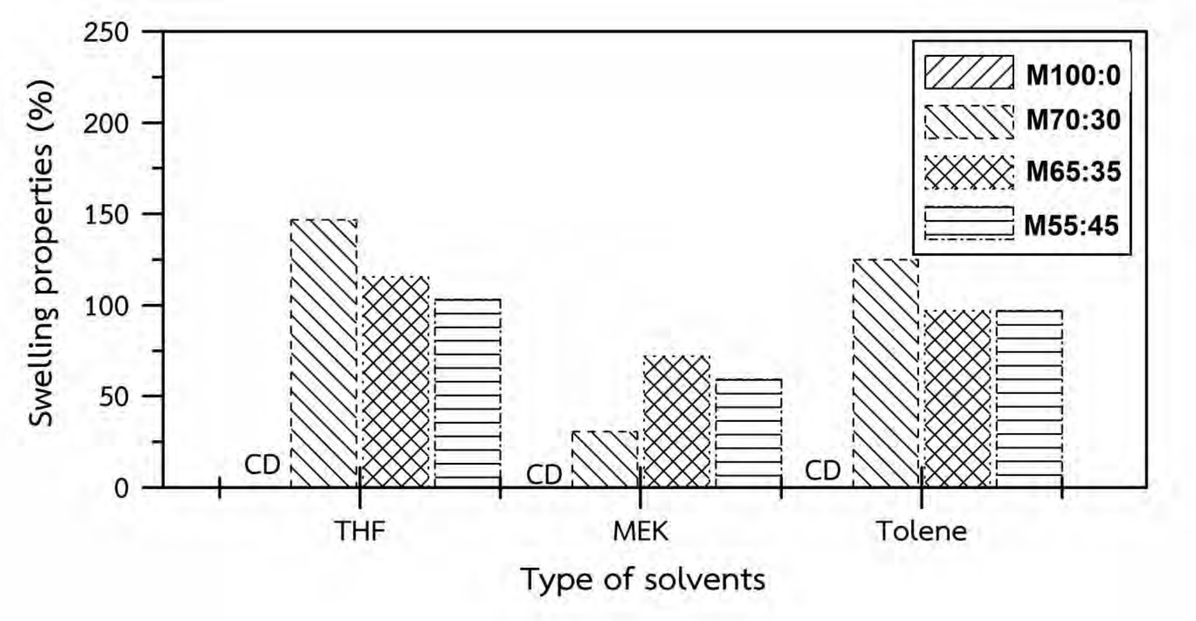


Figure 26. Swelling properties of WPU-g-MMA hybrid films

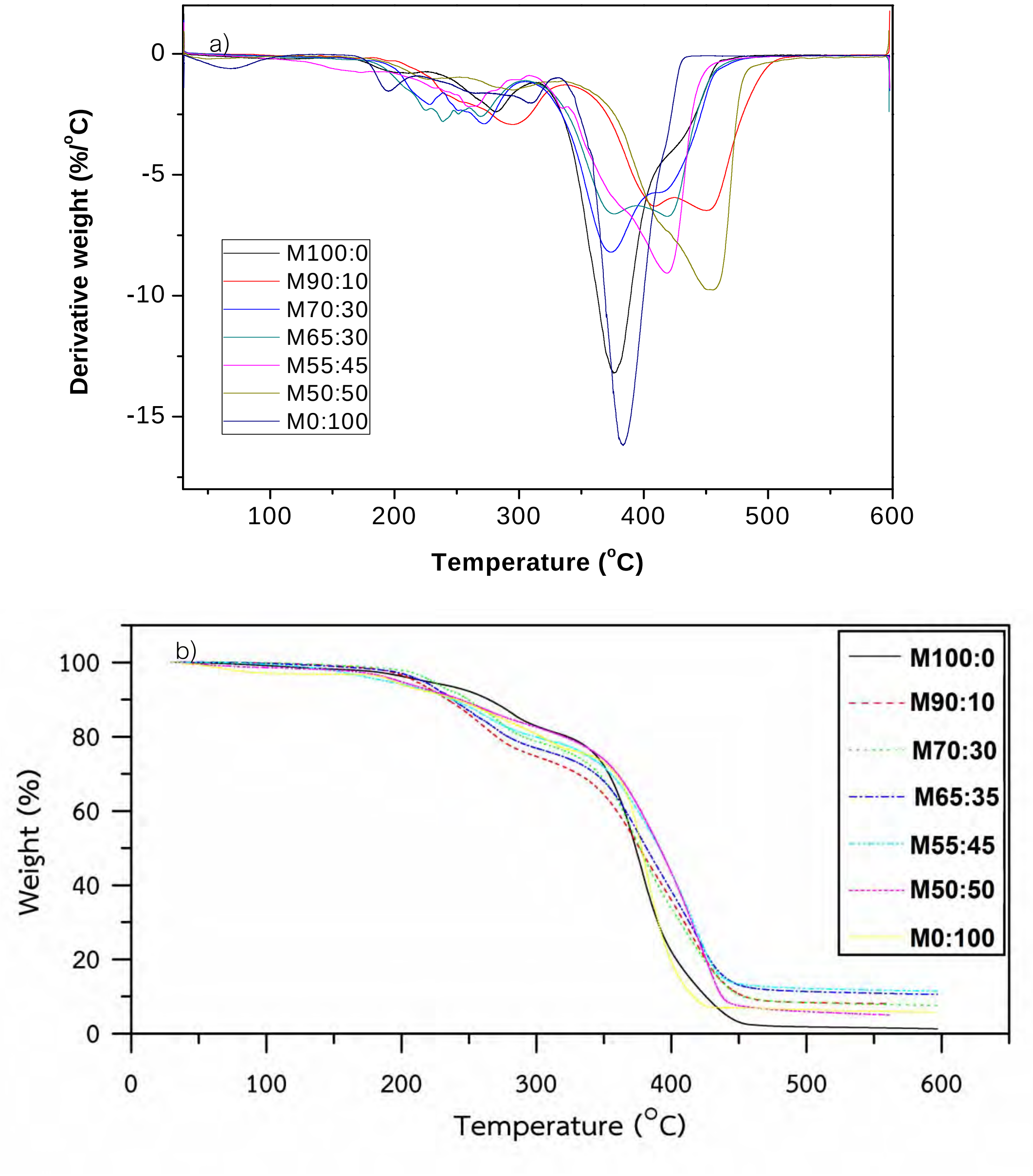


Figure 27. TGA diagrams of WPU-g-MMA hybrid films a) Derivative weight (%/°C) b) Weight (%)

Figure 26 shows the swelling properties of WPU- g-MMA hybrid films with various the ratios of WPU/MMA. It was found that the WPU3 (M100:0) was completely dissolved while the hybrid film of WPU/MMA (M55:45) was the best in solvent resistance (THF and Toluene), except MEK. Because the nature of solvent is non-polar solvent led to dissolve the WPU film acted as more hydrophobic nature. Whereas hybrid film with increasing MMA ratio is more polar polymer led to non-dissolve, just swelling.

The three-stage loss thermal degradation was observed for all hybrid films (Figure 27). The first stage degradation at 162°C–197 °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 250°C–270 °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.

Finally, stage at 375 °C – 377 °C relates to the decomposition of structure of oligoisoprene and PMMA. We observed that the increased MMA ratio in sample for M100:0–M0:100 led to an increased second step of remaining weight from 2.0 to 15.0 percent of weight. In addition, the maximum temperature (T*max*) of the second part had a trend to improve to a higher temperature than WPU or PMMA films, for instant, the T*max* of M100:0 film (WPU) is 370 ^{o}C and T*max* of M0:100 film (PMMA) is 380 ^{o}C whereas Tmax of hybrid M50:50 film is 450 ^{o}C. The phenomenal could be explained that the higher temperature of T*max* was caused from the crosslinking effect of free radical to be form network structure during graft copolymerization and give a higher thermal stability of the hybrid film.

3.3.3 Preparation of waterborne (WPU) grafted (MMA/Bu-ac (60/40)) monomers with various type of diisocyanates and molecular weight of HTNR

Table 10. Results on the influence of $\overline{M_n}$ of HTNR and type of diisocyanates based WPU/(MMA/Bu-ac) hybrid at ratio of 70:30 at NCO/OH ratio 1.00/1.00 and DMPA 5.6% wt.

Type of isocyanate	$\overline{M_n}$ of HTNR, (g/mole)	WPU	Type of vinyl monomer	WPU: MMA/Bu-ac ratio	Properties						
					TSC[a] (%)	pH	Conversion (%)	GE[b] (%)	Stability[c]	Appearance[d]	Particle size (nm) >1 month $\bar{X}$±S.D.
TDI	1000	HTNR1000 TDI	MMA/Bu-ac (60:40)	70:30	25.04	5.11	70.65	80.45±11.70	Stable	Light brown	68±35
				100:0	19.78	7.48	ND	ND	Stable	Milky	86±85
	3000	HTNR3000 TDI		70:30	24.46	4.98	94.89	36.67±2.48	Stable	Light brown	139±30
				100:0	20.07	7.01	ND	ND	Stable	Milky blue	90±30
HDI	1000	HTNR1000 HDI		70:30	27.05	5.02	88.91	33.70±1.96	Stable	Milky	86±37
				100:0	18.87	7.56	ND	ND	Stable	Milky	60±77
	3000	HTNR3000 HDI		70:30	25.80	4.98	91.23	44.05±1.45	Stable	Milky	151±160
				100:0	21.16	7.26	ND	ND	Stable	Milky	80±36
-	-	-		0:100	26.98	1.25	79.67	4.66±0.78	Stable	Transparent	80±13

[a] Total solid contents

[b] Grafting efficiency

[c, d] 1 month

ND: Not determined

Table 11. Result on the influence of molecular weight of HTNR and type of isocyanate based WPU/(MMA/Bu-ac) hybrid films properties at ratio of 70:30 at NCO/OH ratio 1.00/1.00 and DMPA 5.6% wt.

Properties	**Type of isocyanate**								
	TDI				**HDI**				**-**
	Molecular weight of HTNR (g/mole)								
	1000		**3000**		**1000**		**3000**		**-**
	WPU								
	HTNR1000 TDI		**HTNR3000 TDI**		**HTNR1000 HDI**		**HTNR3000 HDI**		**-**
	WPU:MMA/Bu-ac ratio (%)								
	100:0	**70:30**	**100:0**	**70:30**	**100:0**	**70:30**	**100:0**	**70:30**	**0:100**
Appearance[a]	Y/S	DB/VS	Y/S	DB/F	Y/VS	LY/F	Y/VS	LY/F	W/F
Mechanical properties									
Tensile strength (MPa)	0.75±0.15	ND	0.09±0.02	0.33±0.02	ND	0.28±0.03	ND	0.17±0.01	4.59±0.65
Elongation at break (%)	64.97±11.80	ND	93.90±11.03	353.00±37.64	ND	53.50±4.20	ND	130.67±14.24	388.60±25.41
Swelling properties (%)									
Tetrahydrofuran (THF)	CD	ND	CD	75.00±0.00	ND	28.10±4.42	ND	40.60±4.42	CD
Methyl ethyl ketone (MEK)	CD	ND	CD	18.80±8.84	ND	40.60±4.42	ND	40.60±4.42	CD
Toluene	CD	ND	CD	25.00±0.00	ND	31.30±0.00	ND	43.80±8.84	CD
Water Absorption, 14 days (%)	9.24±0.29	ND	17.01±1.09	46.01±3.81	ND	56.14±1.36	ND	58.88±4.49	130.74±7.34

[a] Color/Feature:

CD: Completely dissolved

ND: Not determined

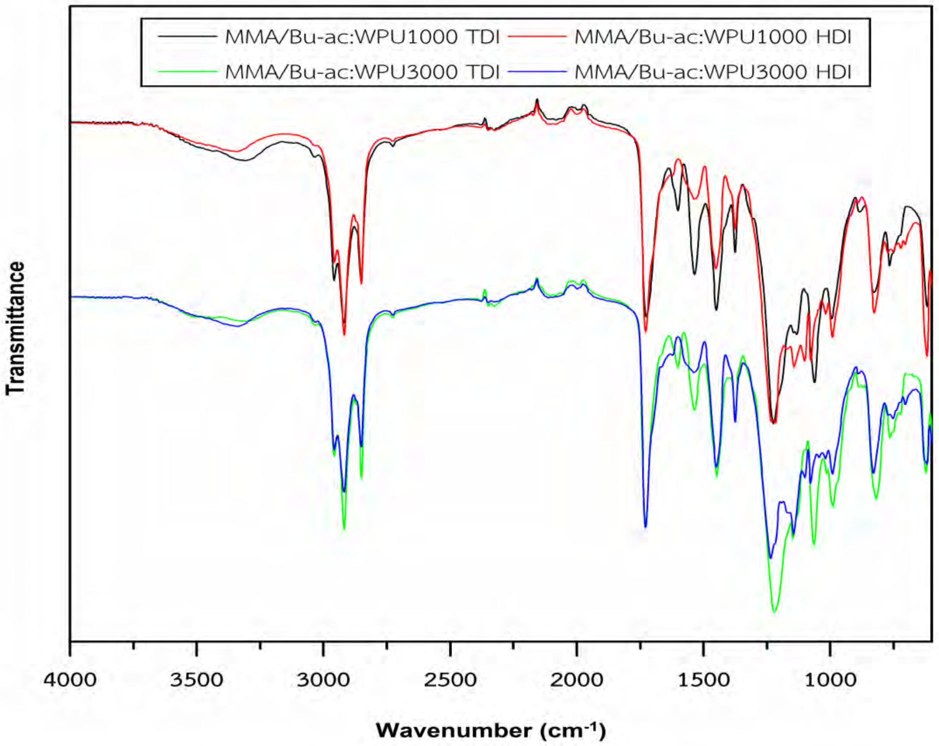


Figure 28. FT-IR spectra of WPU/(MMA/Bu-ac) hybrid films with different of molecular weight o f HTNR and type of diisocyanates

Figure 28, shows that the chemical structures of WPU/(MMA/Bu-ac) hybrid films was characterized by FTIR (ATR technique). In all WPU/(MMA/Bu-ac) hybrid both of molecular weight of HTNR and type of diisocyanates gave the same important functional groups of FT-IR spectra. The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530 cm^{-1}, which correspond 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. The disappearance of absorption peak at 2270 cm^{-1} confirms that there was no residual-free NCO in WPU films. The other absorbance represented a vibration of functional groups on P(MMA/Bu-ac) structure at around 1750 could be assigned to C=O stretching of the esters. The absorption bands at 1271, 1240 cm^{-1} and 1189, 1141 cm^{-1} could be assigned to C–O and C–O–C stretching, respectively. However, the hybrid film based on TDI show a slightly different absorption at wavenumber around 1500 cm^{-1} represented aromatic C=C stretching.

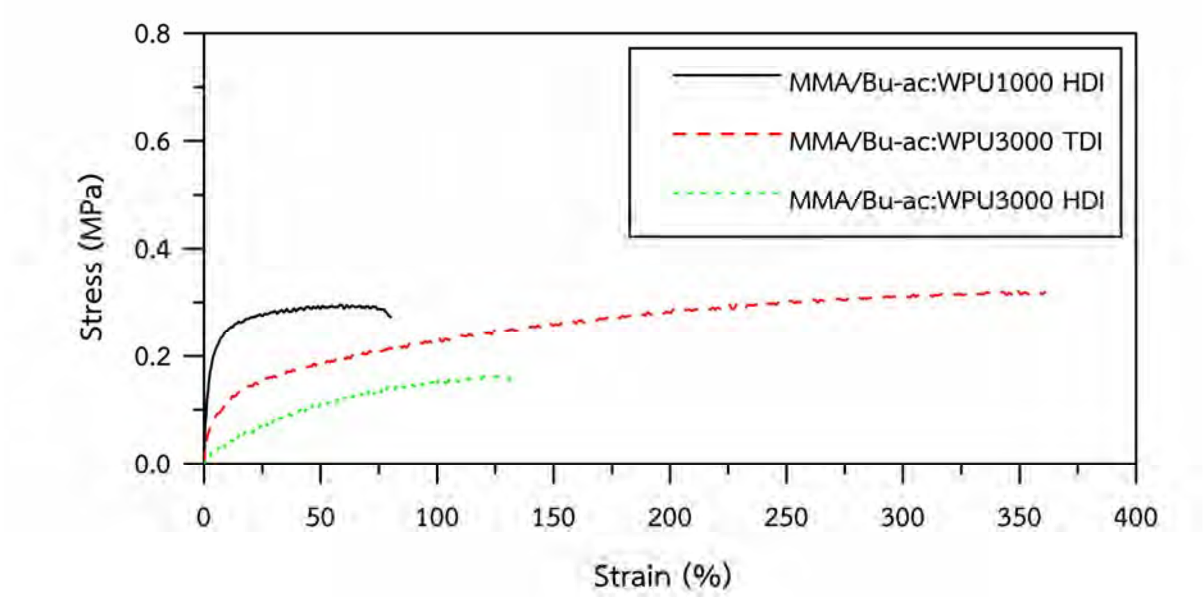


Figure 29. Stress and strain of WPU/(MMA/Bu-ac) hybrid films

Figure 29 shows the tensile properties of WPU-g-(MMA/Bu-ac) hybrid films with various the molecular weights of HTNR and type of diisocycnates. It was found that the hybrid film based on HTNR3000 and TDI gave a higher tensile strength than that of HDI due to nature of chemical structure of isocyanates. However, the both samples show behavior as elastomeric materials. Whereas the hybrid film based on HTNR1000 and HDI gave a higher tensile strength and modulus than that of HTNR3000 and show behavior as tough material due to an effect of increasing of hard segment content on polyurethane structure.

Figure 30 shows the swelling properties of WPU- g-(MMA/Bu-ac) hybrid films with various the molecular weight and type of diisocyanates. It was found that all hybrid films were swelled from 20% to 90% in all solvents. However, the hybrid films based on HTNR300 had a trend to increasingly swelling in THF (40-90%) and toluene (40-60%). Whereas the hybrid film based on HTNR1000 was less swelling for instant, around 25-30% in THF and toluene, respectively. It implied that the nature of solvent is non-polar solvent led to swell the hybrid WPU film acted as more hydrophobic nature. However, it did not clearly result in MEK solvent.

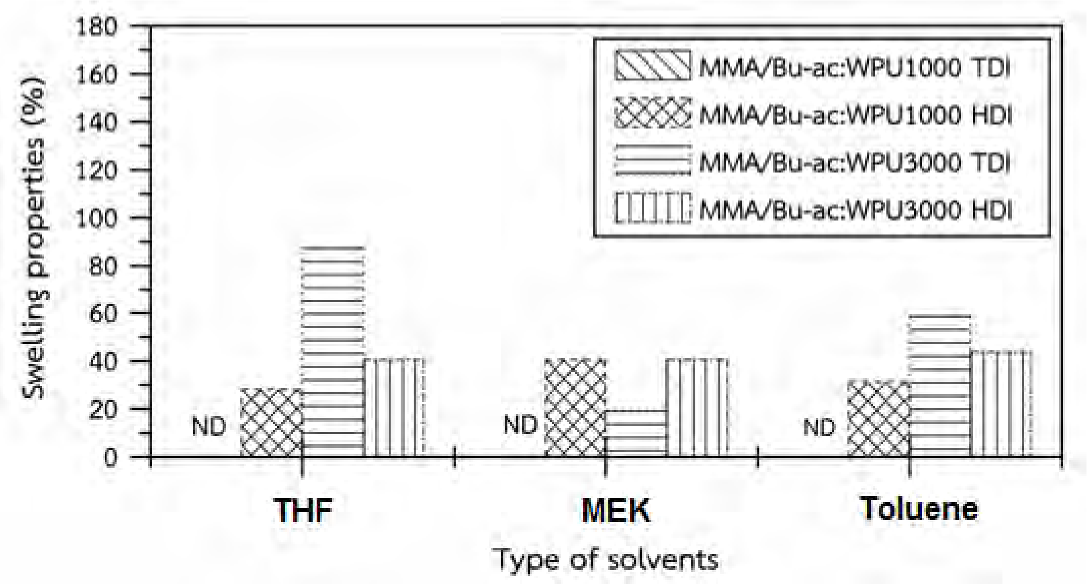


Figure 30. Swelling properties of WPU/(MMA/Bu-ac) hybrid films

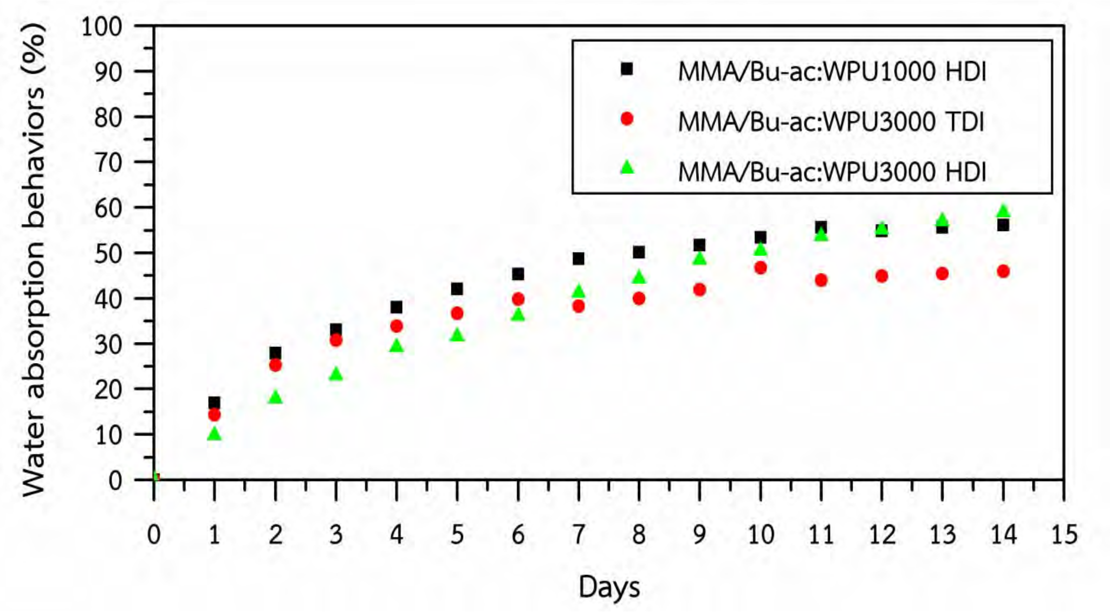
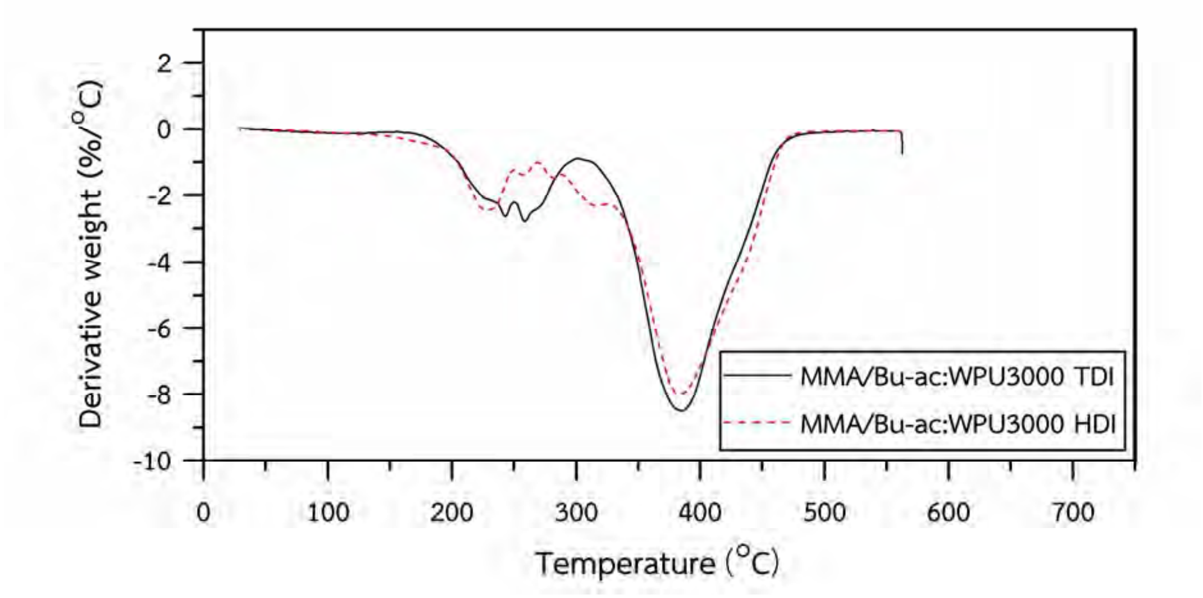


Figure 31. Water absorption of WPU/(MMA/Bu-ac) hybrid films

Figure 31 shows the water uptake of WPU- g-(MMA/BU-ac) hybrid films with various the molecular weight and type of diisocyanates. It was found that the hybrid film based on HTNR1000 gave a slightly higher water uptake and was rapidly equilibrium behavior than that of HTNR3000 due to due to nature of increasing of hydrophilic part (hard segment) in hybrid films.



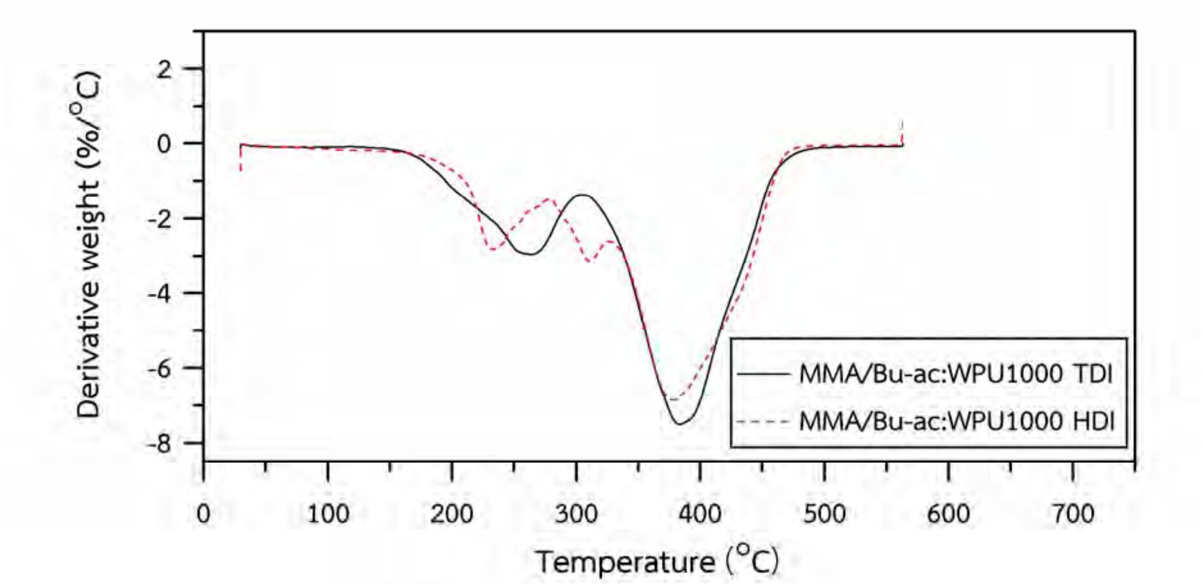
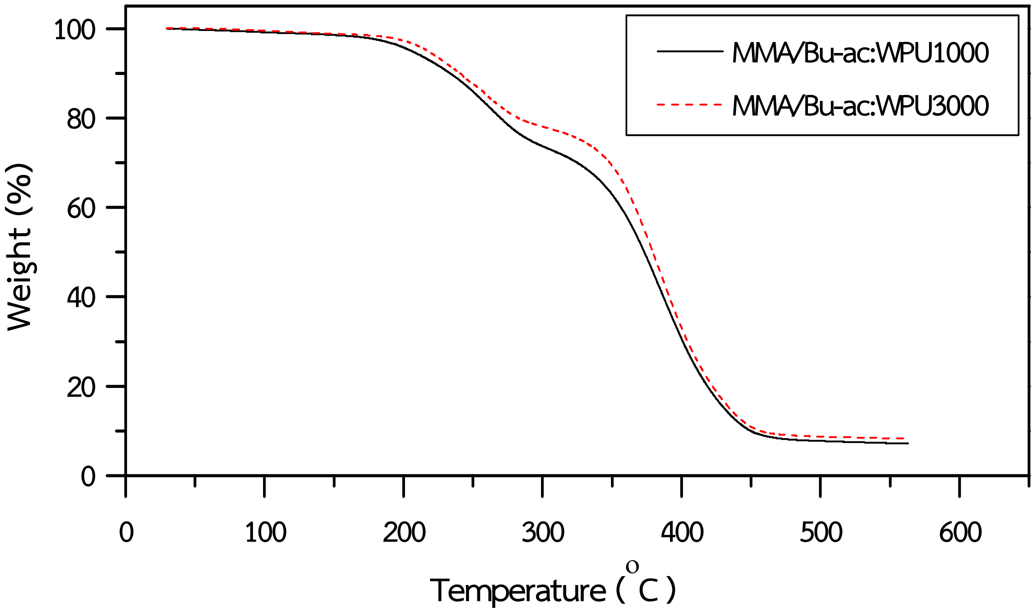


Figure 32. DTGA diagrams of WPU/(MMA/Bu-ac) hybrid films: a) HTNR3000 b) HTNR1000

TGA data for the WPUs hybrid films from MMA/Bu-ac and HTNR with different molecular weight and TDI type in (WPU/(MMA/Bu-ac)) ratio at 70:30 are shown in Figure 32. Weight and characteristic temperatures were determined from the derived curve (T_{max}). A three-stage loss thermal degradation was observed for all hybrid films. The first stage degradation at 267-270ºC corresponds to the approximate content of weight loss the ammonium salt of carboxylic parts formed with TEA and DMPA. The second stage at 315-

327°C can be attributed to urethane bond breaks that occur through the dissociation to HTNR and isocyanates, the formulation of primary amines and olefins, or the formulation of secondary amines, which results in the loss of carbon dioxide from the urethane bond. Finally, stage at 368-383°C related to the decomposition of structure of oligoisoprene and PMMA.

For the thermal stability of WPU/MMA hybrid films based on HTNR 3000 or 1000 with various types of diisocyanates (Aromatic-TDI, Aliphatic-HDI) were studied. It was found that the hybrid WPU3000 or 1000/MMA based on TDI gave a higher thermal stability at second degradation stage than that of HDI due to nature of diisocyanates structure as shown in Figure 32. For the WPU/MMA hybrid films based on HTNR different molecular weights of the same type of diisocyanates (TDI), 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 as shown in Figure 33.



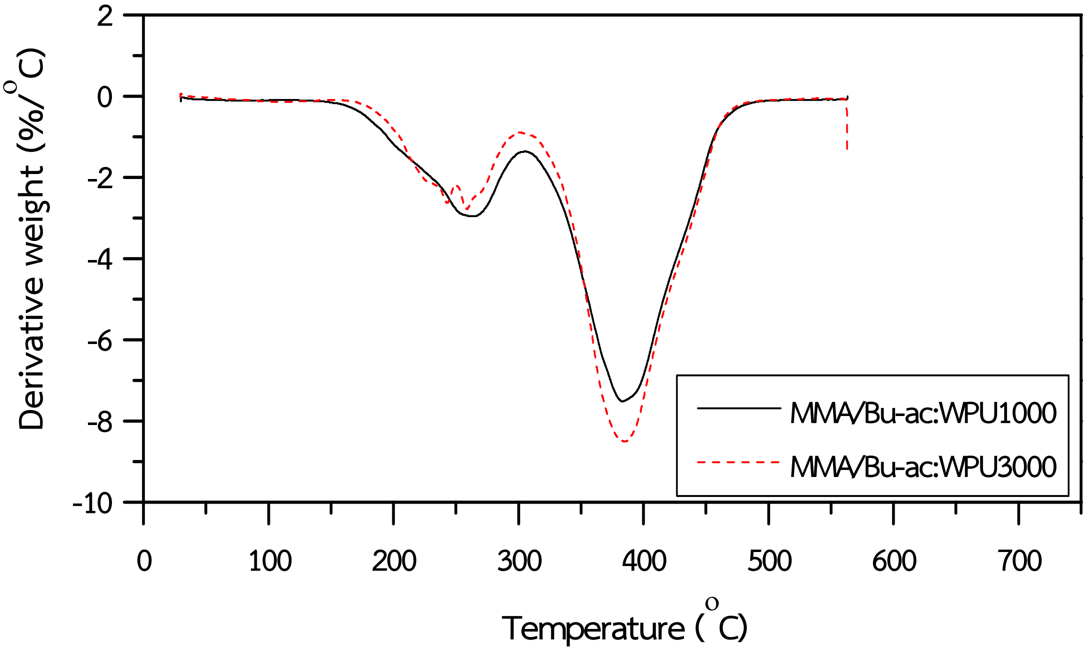


Figure 33. TGA diagram of WPU/(MMA/Bu-ac) hybrid films

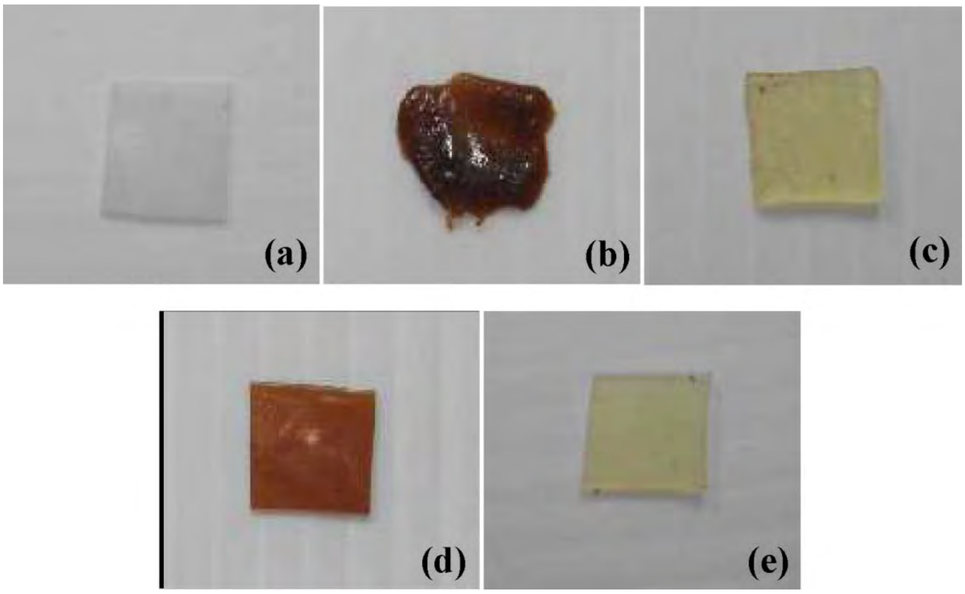


Figure 34. Appearance of WPU/(MMA/Bu-ac) hybrid films at ratio of 70/30 (a) P(MMA:Bu-ac) (b)(HTNR1000TDI) (c) (HTNR1000HDI) (d) (HTNR3000TDI) (e)(HTNR3000HDI)

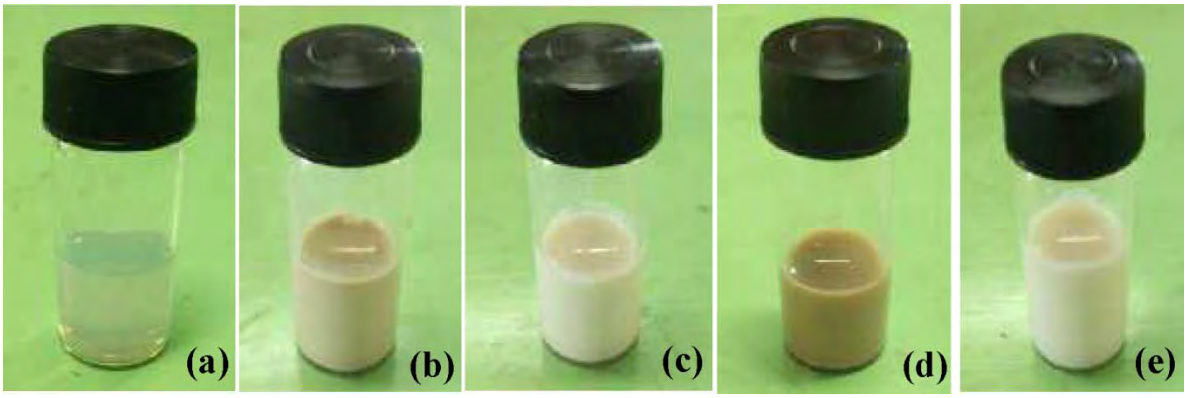


Figure 35. Appearance of WPU/(MMA/Bu-ac) hybrid latexes (a) P(MMA:Bu-ac) (b)HMB 30:70 (HTNR1000TDI) (c)HMB 30:70 (HTNR1000HDI) (e)HMB 30:70 (HTNR3000TDI) (d)HMB 30:70 (HTNR3000HDI)

Figure 34 and 35 shows the appearance of the hybrid films and hybrid dispersion. It was showed that the hybrid materials based on TDI gave a darkened brown color than that of HDI whereas the molecular weight of HTNR had no effect on appearance of materials. Therefore, the aliphatic isocycante type was used to apply on the light color polyurethane.

4. Conclusions

The WPU dispersion was well synthesized by a polyaddition reaction of diisocyanate (Toluene diisocyanates or Hexamehtylene diisocyanates) and a HTNR by prepolymer technique in the presence of DMPA as internal emulsifier. The effect of chain extender content and the ratio of NCO/OH in formulations on WPU and their film properties were studied. It was showed that all HTNR based WPU are good stable and exhibit enhanced mechanical and swelling properties of WPU films when chain extender content or NCO/OH ratio were increased. However, the WPU based on EHTNR are adequately, unstable to graft copolymerization of the acrylic monomers.

The new hybrids of natural rubber based waterborne polyurethane (WPU) grafted vinyl monomer (MMA or MMA/Bu-ac) were also successfully synthesized by emulsion technique. The resulting hybrid latexes, containing 10-50 wt % WPU based on HTNR are good stable. The morphological evidence of WPU/MMA (65:35) hybrid from transmittance electronic microscopy shows that the achievement of grafting copolymerization of the acrylic monomers onto the PU particles occurs during the emulsion polymerization, leading to a significant increase in the physical, thermal and mechanical properties of the resulting hybrid latexes. In addition, the hybrid film based on HDI gave a lighter yellowish color than that of TDI. This work represents new environmentally friendly hybrid materials based on renewable source by a new preparation for coating applications.

5. Perspectives

- Improve the mechanical properties by increasing of covalent bonding in the polyurethane matrix by UV-irradiation or vulcanization technique.
- Synthesis of surfactant-free core shell hybrid latexes HTNR based WPU and acrylic monomer

6. Keywords : Waterborne polyurethane, Natural rubber, Emulsion, Graft copolymers, Hybrid

‘

เอกสารแนบหมายเลข 3

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ (ระบุชื่อผู้แต่ง ชื่อเรื่อง ชื่อวารสาร ปี เล่มที่ เลขที่ และหน้า) หรือผลงานตามที่คาดไว้ในสัญญาโครงการ
    - Manuscript จำนวน1 ฉบับ (อยู่ระหว่างการแก้ไขของ mentor คาดว่าจะ submit ได้ในเดือนกรกฎาคม 2557) Title: Preparation and properties of waterborne polyurethane based on natural rubber: Effect of chain extender contents and the ratios of NCO and OH

    - Manuscript จำนวน 1 ฉบับ (อยู่ระหว่างการเตรียม คาดว่าจะ submit ในเดือนสิงหาคม 2557) Title: Synthesis and properties of hybrid natural rubber based waterborne polyurethane grafted methyl methacrylate (MMA): Effect of molecular weight of natural rubber polyols.

    - Manuscript จำนวน1 ฉบับ (อยู่ระหว่างการเรียบเรียงข้อมูล และวิเคราะห์ผล คาดว่าน่าจะ submit ได้ประมาณเดือนตุลาคมนี้) Title: Hybrid natural rubber based waterborne polyurethane grafted butyl acrylate/methyl methacrylate (BUA/MMA)

2. การนำผลงานวิจัยไปใช้ประโยชน์
    - เชิงวิชาการ (มีการพัฒนาการเรียนการสอน/สร้างนักวิจัยใหม่)
        - นำไปใช้ในการเรียนการสอนรายวิชาเทคโนโลยีพอลิยูริเทน สำหรับนักศึกษาระดับปริญญาตรี สาขาเทคโนโลยียาง และรายวิชาการดัดแปรโมเลกุลยางธรรมชาติสำหรับนักศึกษาบัณฑิตศึกษา สาขาเทคโนโลยีพอลิเมอร์
        - นักศึกษาระดับปริญญาโท 1 คน

3. อื่นๆ (เช่น ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ การเสนอผลงานในที่ประชุมวิชาการ หนังสือ การจดสิทธิบัตร)

39 the Congress on Science and Technology of Thailand on October 21 - 23, 2013 at BITEC, Bangkok, Thailand.

SYNTHESIS AND PROPERTIES OF HYBRID WATERBORNE POLYURETHANES – GRAFTED METHYL METHACRYLATE (MMA) ON NATURAL RUBBER POLYOLS: EFFECT OF MOLECULAR WEIGHT POLYOLS.

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Abstract: A novel waterborne polyurethanes (WPUs) has been successfully synthesized from 2, 4-toluene diisocynate (TDI), dimethylol propionic acid (DMPA) and hydroxyl telechelic natural rubber polyols (HTNR) at 1,000 and 3,000 g mol^{-1}. Then, a series of WPUs grafted copolymerization of methyl methacrylate (MMA) monomers (90 wt% WPUs and 10 wt% MMA) in the presence of WPUs, using potassium persulfate as an initiator was studies. The resulting latices, HTNR polyols as a renewable resource, have been investigated by laser particle analysis and thermogravimetric analysis. The resulting indicated that graft emulsion polymerization of a MMA onto WPUs chains occured during emulsion polymerization, leading to significate increase in the thermal stability of the miscible grafted latices. This work provides new environmentally-friendly latices from renewable resource with high performance for coating applications.

Introduction: Waterborne polyurethanes are rapidly growing segment of the polyurethane coating industry due to environmental legislations. To meet concern for health, safety and the solvent-based polyurethane have been gradually replaced by waterborne polyurethanes (WPUs). WPUs present many advantages relative to conventional solventborne polyurethanes, including low viscosity at molecular weight and good applicability. To upgrade the performance of WPU films with regard to weatherability and chemical resistance. Therefore, many efforts have been made to combine urethane and methyl methacrylate polymers in single component hybrid system through emulsion polymerization. Nowadays, the worldwide demands for replacing petroleum-derived raw materials with renewable, plant based materials in the production of polymeric materials. In this aspect, natural rubber (NR) is also an interesting and attractable renewable resource to present a potential material for synthesis of functional precursors of a wide range of polymer. In this work, a series of WPUs based on precursors from NR with average molecular weight 1,000 and 3,000 g mol^{-1} were prepared. After that, we also investigated WPUs/MMA grafted copolymerization in the weight ratio 90:10. The effect of molecular weight NR polyols on the synthesis, solvent resistance and thermal properties of resulting NR based WPUs and WPUs/MMA films have been investigated.

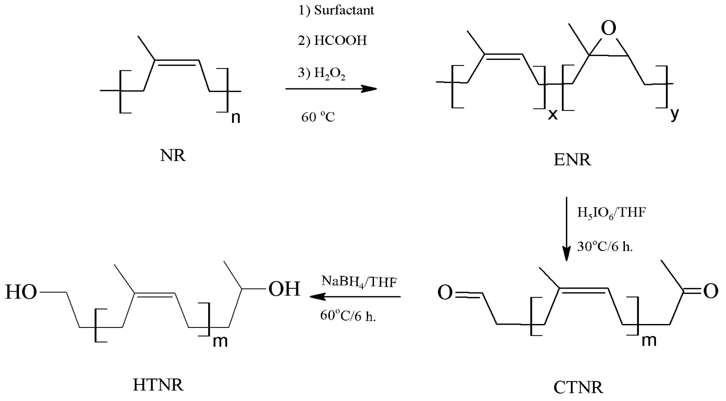
Methodology:

Materials Concentrated NR latex (Dry rubber content, DRC = 60%) was purchased from Latex Industrial, Yala, Thailand. Hydrogen peroxide (H_2O_2), sodium borohydride ($NaBH_4$), potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were purchased from Ajax Finechem. Formic acid (HCOOH) was purchased from BASF – TPC company Limited.

Periodic acid (H_5IO_6), 2,4-toluene diisocynate (TDI), dimethylol propionic acid (DMPA), triethylamine (TEA) and methyl methacrylate (MMA) were purchased from Sigma – Aldrich. 2 – butanone or Methyl ethyl ketone (MEK) was purchased from Fisher Scientific UK Limited. Hydroquinone was purchased from BDH Middle East. Teric N30 was obtained from CAMEO chemicals. Dichloromethane, Tetrahydrofuran (THF) were distilled before use.

Preparation of natural rubber polyols

Natural rubber polyols is hydroxyl telechelic NR (HTNR). It was synthesized from epoxidized NR (ENR), carbonyl telechelic NR (CTNR) via epoxidation, oxidation and reduction reaction, respectively. The reactions were performed in 2 L reactor, equipped with a mechanical stirrer, condenser, and thermometer. The preparation of ENR, CTNR and HTNR has been described in previous works in Scheme 1.[1] The general properties chemical modification of NR based HTNR as shown in Table 1.



Scheme 1. Preparation and modification of natural rubber (NR) based hydroxyl telechelic NR (HTNR)[1]

Table 1. General properties of hydroxyl telechelic natural rubber

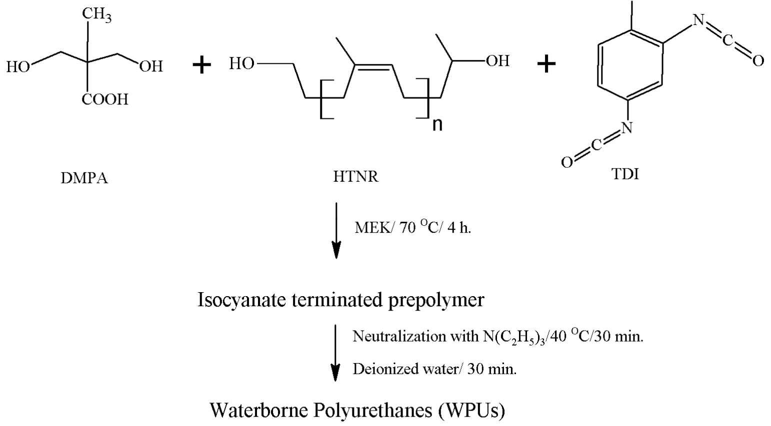
Precursors	%Epoxidation	$\bar{M}_n$ NMR (g mol^{-1})	$\bar{f}_{n(OH)}$	Appearance
HTNR 1000	6.5%	1300	2	Yellow, viscous
HTNR 3000	2.0%	3500	2	Yellow, viscous

Preparation of waterborne polyurethanes (WPUs)

The WPUs was 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 WPUs synthesis are showed in Table 2. The WPUs were synthesized in a 500 – mL reactor, equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. Reaction temperature was controlled using constant temperature oil bath. The HTNR and DMPA were weighed and added into the reactor. The reaction was carried out at 70ºC under a dry nitrogen atmosphere and then 25 g of MEK was added to reduce the viscosity of the system. After that the TDI was added dropwise into the flask and reacted continuously at 70ºC for 4 h. The prepolymer temperature was allowed to drop to 40 ºC. The carboxylic acid groups in DMPA were then neutralized by the addition of TEA. The mixture was stirred for further 30 min to ensure that neutralization was completely occurred. The next step is dispersion step. The prepolymer ionomers were dispersion by adding desired deionized water with vigorous stirring and carried out for 30 min. After that the solvent was evaporated to obtain the WPUs. All samples were controlled a solid content around 20%.[2]

Table 2. Chemical composition of the waterborne polyurethane

Sample	Chemical composition (equivalent molar ratio)			
	HTNR1000	**HTNR3000**	**DMPA(wt%)[a]**	**TDI**
WPU 1000	1.0	-	0.7 (5.6)	1.7
WPU 3000	-	1.0	1.8 (5.6)	2.8



Scheme 2. Preparation of waterborne polyurethane based on natural rubber polyols

Preparation of hybrid waterborne polyurethane grafted – methyl methacrylate (MMA)

The hybrid waterborne polyurethane was synthesized by grafted emulsion polymerization with MMA. KPS (1 g) and SDS (3 g) were dissolved in deionized water. The polymerization was carried out under nitrogen atmosphere in a 500-mL reactor, equipped condenser, stirrer and thermometer. The reaction was carried out at 70ºC under a dry nitrogen atmosphere for 4 h. During the polymerization, approximately 5 g portion of the emulsion were taken by a syringe at intervals and injected into a petri dish containing 0.5% hydroquinone solution in an ice bath.[3] Monomer conversion was determined gravimetrically from these samples. By changing the weight ratio of between WPUs and MMA from 100:0, 90:10 and 0:100, a series of WPUs/MMA hybrid latex have been successfully prepared. Films were prepared by drying the emulsions onto a teflon plate at 40ºC.

Measurements

The ^{1}H-NMR spectra were recorded on a Oxford Fourier transform spectrometer operating at 500 MHz. The samples were dissolved in $CDCl_3$, using tetramethylsilane (TMS) as an internal standard.

The particle sizes and particle size distribution of the WPU and Hybrid WPU were measured with laser particle size analyser (Beckman coulter LS 230).

Thermogravimetric analyzer (TGA) was performed on a TA Instruments (STA 6000) with a heating rate of 10 ºC min^{-1} from room temperature to 600 ºC under nitrogen atmosphere at flow rate 90 mL min^{-1}. The sample weight was about 10 mg.

Determination of percent swelling sample films with the dimension 10 mm were submerged into methyl ethyl ketone, toluene and tetrahydrofuran at room temperature for 30 min. Percent swelling was calculated as following:

$$\text{Percent swelling (\%)} = \left[\frac{\text{Linear dimension}_{\text{swelling}} - \text{Linear dimension}_{\text{initial}}}{\text{Linear dimension}_{\text{initial}}}\right] \times 100$$

Results and Discussion:

Effect of molecular weight polyols

The controlled degradation reaction of NR was performed via a two-step procedure. The first step was the epoxidation of NR which using *in situ* performic acid generated from a specific amount of formic acid and hydrogen peroxide with nonionic surfactant at 60ºC, while the second step is the selective cleavage reaction via the epoxide group of ENR dissolved in THF with periodic acid (H_5IO_6) at 30ºC, as shown in scheme 1. It was found that the degree of ENR from concentrated NR was 2.0% after1.30 h and 6.5% after 2 h. Later, the ENR solution was degraded by using a specific amount of periodic acid in THF at 30 ºC for a period of 6 h (Scheme 1). These isolated degradation products were both yellowish viscous liquids. The molecular weights obtained were:

$\bar{M}_n$ = 6,900 g mol^{-1} for the CTNR from 2.0% epoxidation

$\bar{M}_n$ = 3,400 g mol^{-1} for the CTNR from 6.5% epoxidation

The carbonyl telechelic natural rubber (CTNR) was modified into hydroxyl telechelic natural rubber (HTNR) by $NaBH_4$ as shown Scheme 1, which specifically reduces the carbonyl group (aldehyde and ketone) without affecting the vinyl bond to give a yellowish-viscous liquid as product. As expected, the $\bar{M}_n$ of oligomers could be controlled by the amount of epoxide content of ENR (Table 1) with higher epoxide content of ENR used leading to lower molecular weight oligomers being formed. Chemical modification of the polymer to demonstrate the presence of hydroxyl function groups at the chain ends was confirmed by NMR. The ^{1}H-NMR spectrum in Figure 1 shows that the signals of ENR, CTNR and HTNR have been described in previous work.[1]

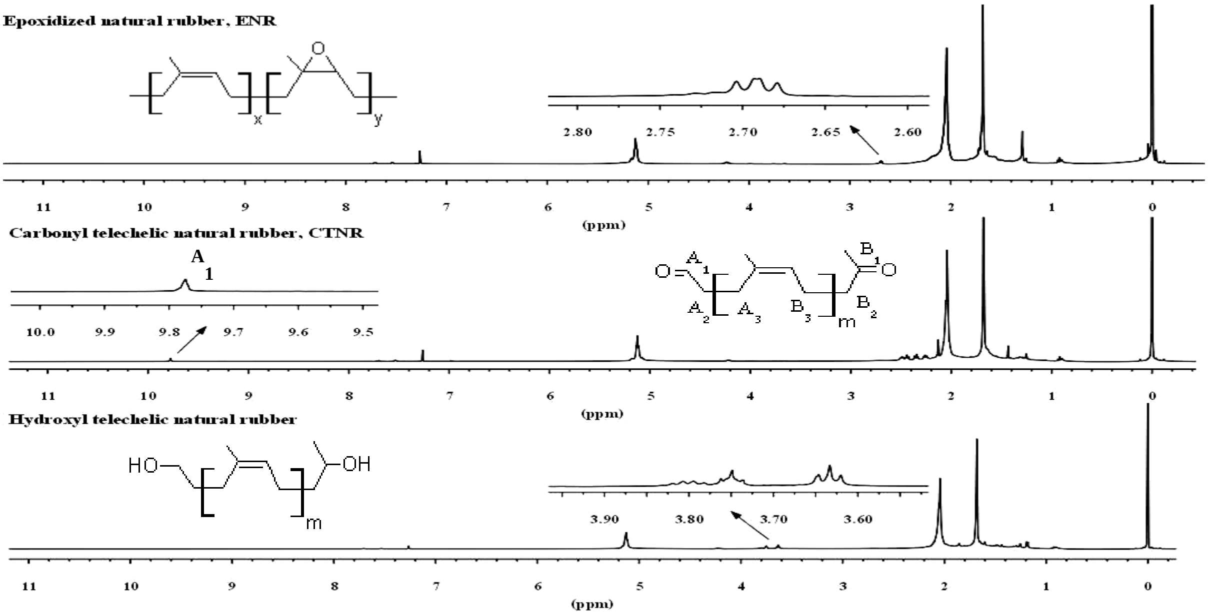


Figure 1. ^{1}H-NMR spectra of ENR, CTNR and HTNR

Table 3. WPUs and WPUs/MMA properties

Sample	Properties		
	Stability	Appearance	Particle size (nm)
PMMA	Stable	Transparent	68
WPU1000	Stable	Milky blue	80
WPU3000	Stable	Milky blue	79
WPU1000/MMA10	Stable	Light brown	90
WPU3000/MMA10	Stable	Opaque brown	93

For these samples, the NCO/OH equivalent mole ratio as 1:1 and DMPA content at 5.6 wt% were kept constant in formulations based on HTNR (1,000 and 3,000 g mol^{-1}) were synthesized by prepolymer technique in MEK medium following in Scheme 2. The influence of molecular weight on the particle size and particle size distribution of the WPU1000 and WPU3000 is shown in Table 3 and Figure 2, respectively. The particle size of WPUs (WPU1000 and WPU3000) was varied from 79 to 80 nm. The resulting of WPUs grafted MMA in ratio 90:10 (WPUs:MMA) presence particle size increases with molecular weight of HTNR. The particle size of WPUs grafted MMA increases from 79 to 93 nm (WPU3000 and WPU3000/MMA10) and from 80 to 93 nm (WPU1000 and WPU1000/MMA10) by comparison with WPUs at the same molecular weight of HTNR.

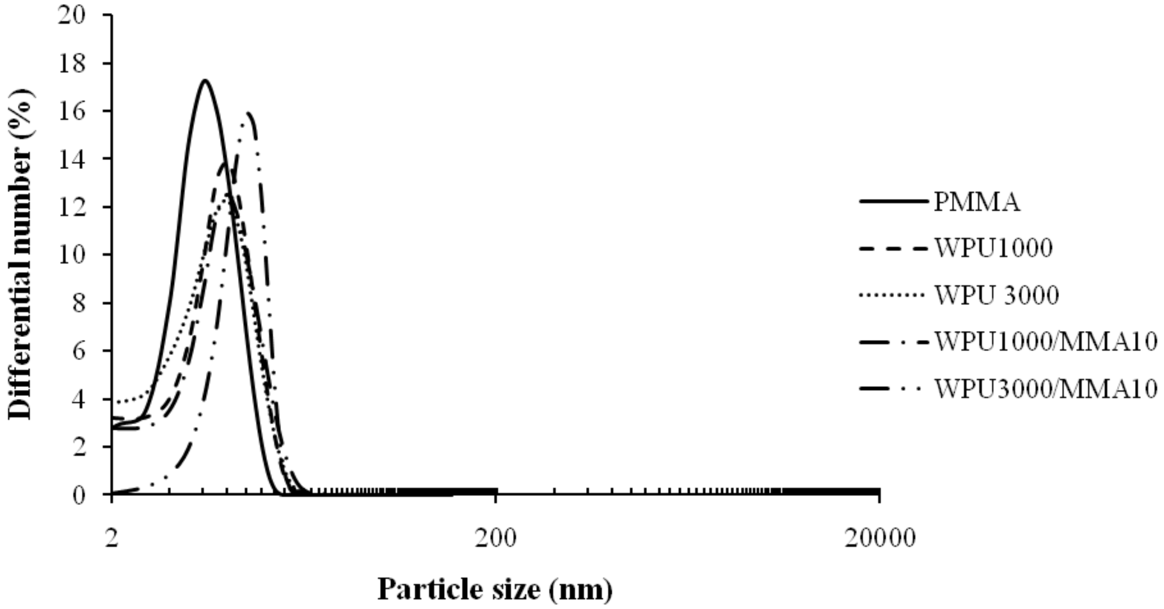


Figure 2. Particle size distribution of WPU samples

The conversion-time profiles for the emulsion polymerization at 80◦C are shown in Figure 3. The emulsion polymerization of the pure methyl methacrylate was complete within about 30 min. and essentially all of the monomers were polymerizated. However, when compared with the pure methyl methacrylate emulsion, the hybrid emulsion WPUs exhibited a decrease rate of polymerization with increasing PU content. The reason may be that some impurities in the resin inhibit polymerization or the resin itself reduces the polymerization rate by diluting the monomer concentration and by transfer that produces less active radicals. Although a slightly lower rate of polymerization is observed for the hybrid emulsion, greater than about 90% of monomers have been polymerized after 2 h.

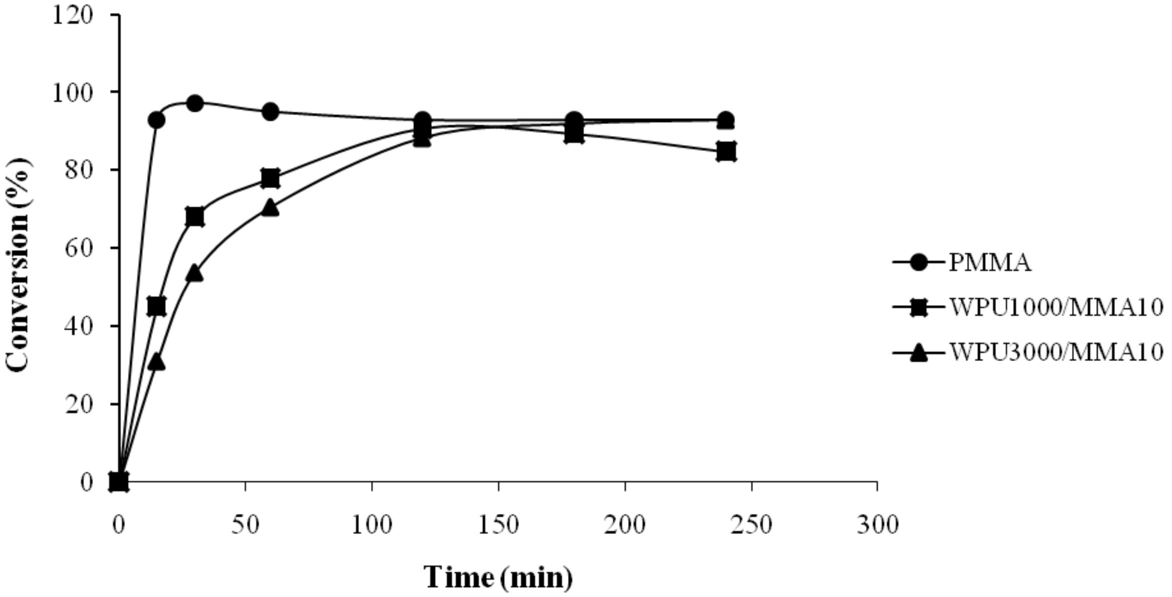


Figure 3. Total monomer conversion of the emulsion polymerization as a function of time for the lattices

Hybrid polyurethane films show the great excellent swelling properties than that from WPU1000 and WPU3000 films as shown in Figure 4. It indicated that graft copolymerization or crosslinking reactions had occurred in the latex systems.[3] In addition, the hybrid polyurethane films based on the different molecular weight of HTNR were also observed. It was found that the good solvent resistance of hybrid polyurethane films obtained from a lower molecular weight of HTNR.

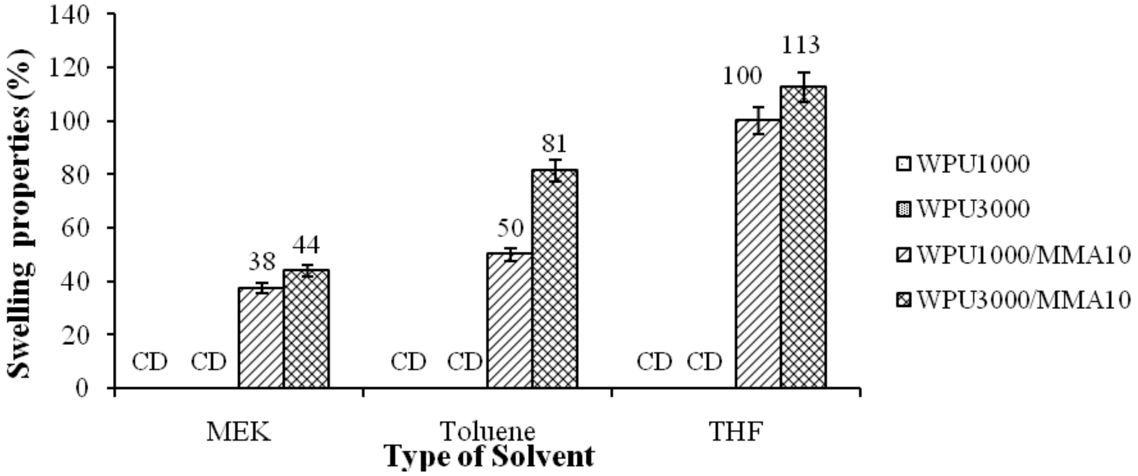


Figure 4. Percent swelling of films (CD: Completely dissolved)

Table 5. Thermal properties of WPU and WPU/MMA

Sample	Thermal degradation							
	1st step		2nd step		3rd step		4th step	
	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)
WPU1000	7.75	267	32.96	327	59.88	373	-	-
WPU3000	4.51	270	16.94	315	77.57	375	-	-
WPU1000/MMA10	2.11	197	32.78	309	25.31	327	39.52	412
WPU3000/MMA10	6.68	193	26.97	295	28.79	318	38.32	406
PMMA	3.00	166	13.09	214	16.50	355	68.12	426

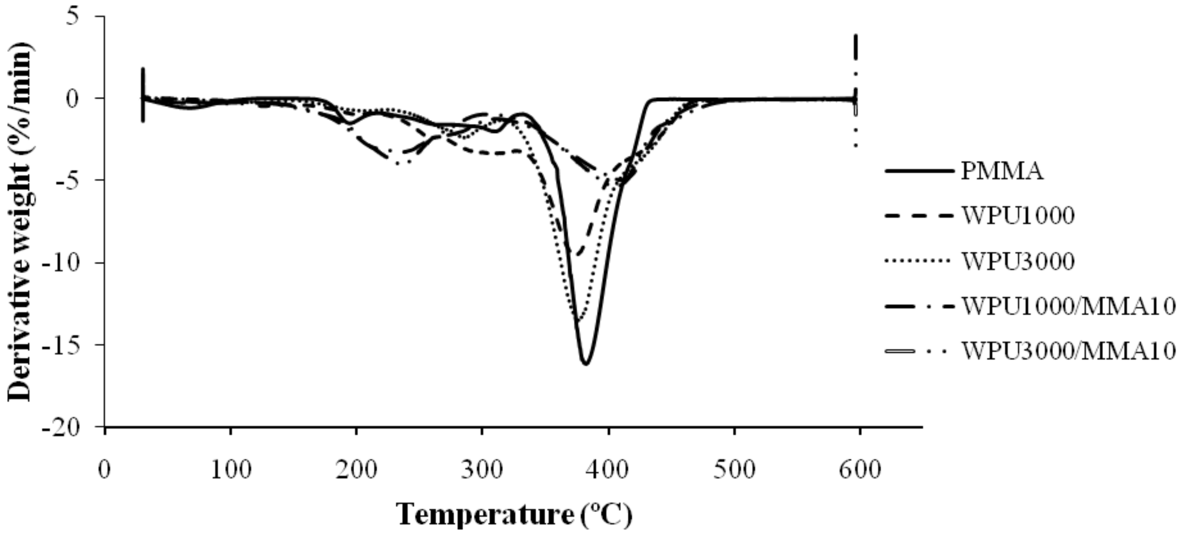


Figure 5. DTGA thermogram of sample films

TGA data for the WPUs films from HTNR with different molecular weight and the WPUs grafted MMA films in ratio 90:10 (WPUs/MMA) are shown in Table 5 and Figure 5. Weight loss and characteristic temperatures were determined from the derived curve (T_{max}). A three-stage loss thermal degradation was observed for all WPU films. The first stage degradation at 267-270°C corresponds to the approximate content of weight loss the ammonium salt of carboxylic parts formed with TEA and DMPA. The second stage at 315-327°C can be attributed to urethane bond breaks that occur through the dissociation to HTNR and isocyanates, the formulation of primary amines and olefins, or the formulation of secondary amines, which results in the loss of carbon dioxide from the urethane bond.[2] Finally, stage at 368-383°C related to the decomposition of structure of oligoisoprene. For the WPU films based on HTNR 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. The temperature of decomposition of methyl methacrylate (MMA) in fourth-stage at 412-426°C[3] was investigated.

Conclusion: A novel bio-based hybrid waterborne polyurethanes-grafted methyl methacrylate (MMA) has been successfully synthesized in two-step, the first reaction was watweborne polyurethanes based HTNR (1,000 and 3,000 g mol^{-1}) and the other reaction was graft emulsion polymerization with methyl methacrylate (MMA) monomers in ratio at 90:10 (WPUs:MMA). The molecular weight of HTNR also affected the particle size of WPUs. The resulting WPUs grafted MMA exhibit enhanced thermal stability and solvent resistance because of the occurrence of graft copolymerization between WPUs and MMA. This work provides promising new environmentally-friendly latices for coating applications, which are prepared from bio-renewable resource.

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Acknowledgment

We would like to thank Thai research fund, Office of the higher education of commission and Prince of songkla university for financial support (Contract no. MRG 5580108)

Keywords: Hybrid waterborne polyurethanes, Natural rubber polyols

Preparation and properties of waterborne polyurethane based on natural rubber: Effect of chain extender contents and the ratios of NCO and OH

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Keyword: Polyurethane, Waterborne polyurethane, Chain extender, Natural rubber, NCO/OH

Abstract

In this work, the effect of chain extender content (0-2 mole) and the ratio of NCO/OH (1/1, 1.5/1 and 2/1) on the properties of waterborne polyurethane based on natural rubber were investigated, for instant, the waterborne polyurethane properties, morphological properties, water uptake, swelling in solvent, mechanical and thermal properties as well as chemical structure by FT-IR. It was found that the particle size of WPU dramatically increases when an amount of the NCO/OH ratio was increased in the presence of chain extender. However, the increasing of EDA content had no affect on particle size of WPUs. The water uptake of WPU-based films and increased with an increase of EDA content. But the swelling of WPU films was decreased. The decomposition in second stage of WPU films was increased with an increase of EDA content and the NCO/OH ratio. The increasing of EDA content and the NCO/OH ratio in WPU films had an effect to improve mechanical properties. The stress-strain curve of WPU films clearly show in changing behavior from soft elastomeric materials to ductile and hard plastics.

Introduction

Polyurethanes play a vital role in many industries from footwear to shipbuilding or from automobile to construction. They appear in very surprising various forms that is continuously increasing [1]. Waterborne polyurethane is a binary colloid systems in those polyurethane particles containing ionic or non-ionic groups are dispersed in continuous aqueous medium[2-4]. Since the late 1960s, they have been commercially important and have been increasingly in a market to replace solvent based polyurethane [3]. There are more important advantages than solvent based polyurethane. The first advantage is less or no environmental concerns regarding volatile organic compound (VOCs) that caused the pollution and health problems. The second advantage is nonflammable and economical issue. The finally advantage is the most interesting that it is comparable to or better than the solvent based polyurethane for many application [2-3, 5-8]. Waterborne polyurethanes are applied in many areas to coat a wide range of substrates such as wood, leather, plastic, automotive and printing ink [6, 9].

Normally, the mostly polyurethane were synthesized from the different isocyanate with petroleum based polyols *i.e.,* polyether or polyester including polydienes diols acted as soft segments in polyurethane structure [10]. 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 [11]. For these problems, many researchers are increasingly dedicating their attention and effort to the possibility using of renewable sources as potential raw materials for the manufacture of polymers. Natural polyol is an important candidate due to abundant, renewable sources, cheap and environmental friendly. The castor oil [12-14] and modified vegetable oils [7, 15-17] have been used to prepare a various polyurethane materials for examples, waterborne, foam, film and adhesive. Lu and Larock [18] prepared a novel polyurethane dispersions based on modified soybean oil (MSOLs) with OH functionalities ranging from 2.4 to as high as 4.0. The particle size of the dispersions and the structure and the thermo-physical and mechanical properties of the resulting Polyurethane films containing 50−60 wt % of bio-renewable MSOL depend strongly on the polyol functionality and the hard segment content. The results showed that an increasing the OH functionality of the MSOLs can significantly increase the cross-link density of the polyurethanes, whereas an increasing the hard segment content of the polyurethanes can effectively improve the interactions caused by hydrogen bonds, resulting in vegetable-oil-based materials ranging from elastomeric polymers to ductile plastics and rigid plastics.

In addition, natural rubber is the greatest alternative in all natural polymers. It is the important economic plants in the South East Asia, especially; Thailand is the largest export in the world around 20 metric tons in 2013 [19]. With an abundant renewable natural polymers and a unique in strength and elastic properties, it has exploited in many applications since Goodyear had revealed the vulcanization reaction i.e. tires, medical products, footwear, etc. Moreover, its chemical structure is *cis* 1,4-polyisoprene. The rich double bonds on backbone structure are great opportunities to easy chemical modify to be polyols. During decade years ago, our laboratory have successfully modified natural rubber with control their molecular weights and functionalities to be polyol called “hydroxytelechelic natural rubber” (HTNR) and its modification such as epoxidation, hydrogenation [20], amination [21-22] etc. These HTNRs have continuously been used as starting materials for the different type of polyurethanes, for examples, antibacterial film [11], foam [20, 23], waterborne [24], adhesive, elastomers [10], biodegrable polymer [25]. Previously work, we synthesized also the new waterborne polyurethane based natural rubber by prepolymer technique. The effects of interior emulsifier content, molecular weight and of HTNR and its modified structure on the physical and thermal properties were investigated.

Chain extender is an important additive on the polyurethane formulations. Its structure (linear or aromatic), functionalities and reactive groups (amine or hydroxyl groups) have an effect to the properties of polyurethane. Kebir *et al.* [10] reported the influence of type and chain extender contents on the properties of a new hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) based polyurethane films. It was summarized that the material behaviors of polyurethane films depend on the nature or content of chain extender and isocyanates. Thermosetting materials were obtained with isocyanates or with chain extender possessing functionality higher than 2. The thermoplastic materials were obtained at the mole ratio of chain extender and HTPI equal to 2. However, the elastomeric behaviors were obtained from without chain extender.

Ligadas and coworkers [26] studied the effect of 1,3-propandiol contents on the properties of poly(ether urethane) networks from epoxidizd methyl-oleate-based polyether polyol and L-lysine diisocyanates. It was observed that the chain extender (increasing of hard segments) played a role to control the physical, mechanical, and degradation properties of these polymers. However, there have been never reported the effect of chain extender content and the ratio of NCO/OH on waterborne polyurethane based on natural rubber. Therefore, we would like to investigate the influence of chain extender contents and the ratios of NCO/OH on physical properties of waterborne polyurethanes. Their films were also analyzed the mechanical, thermal, water absorption and swelling properties.

Experimental

Materials

Toluene diisocyanates (TDI), Dimethylol propionic acid (DMPA), 2-Butanone or Methyl ethyl ketone (MEK), Dibutyltin dilaurate (DBTL), Triethylamine (TEA) were purchased from Sigma-Aldrich. Toluene and tetrahydrofuran (THF) were obtained from LabScan. All chemicals were used without further.

Syntheses

Hydroxyl telechelic natural rubber (HTNR) was prepared from carbonyl telechelic natural rubber (CTNR) according to a methodology previously described. Their chemical structures were shown in scheme 1.

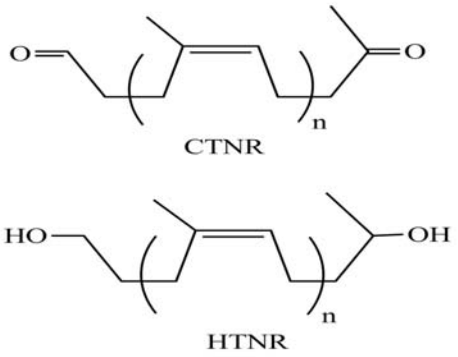


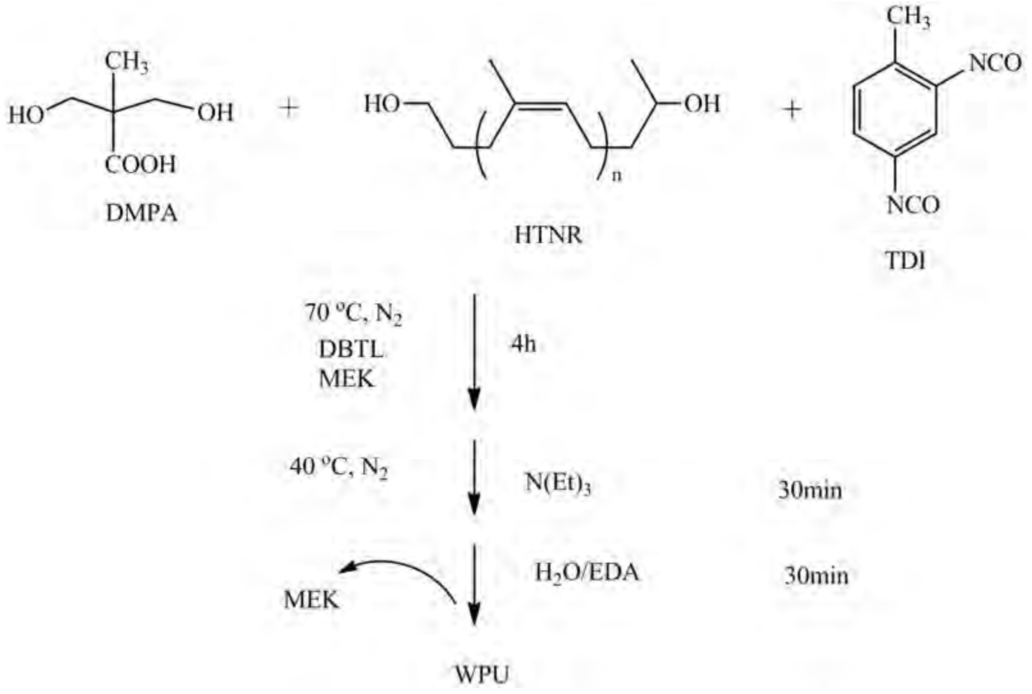
Figure 1 Chemical structure of telechelic natural rubbers

Table 1 General properties of hydroxytelechelic natural rubber

Precursors	Tg (^{o}C)	$\overline{Mn}_{\mathrm{NMR}}{}^{a)}$ (g mol^{-1})	$\overline{Mn}_{\mathrm{SEC}}{}^{b)}$ (g mol^{-1})	PDI	$\overline{fn}_{\mathrm{(OH)}}$	Appearance
HTNR3500	-62	3500	3800	2.04	2	Yellowish, Viscous liquid

Synthesis of waterborne polyurethane

All samples were synthesized by prepolymer mixing technique as shown in scheme 2 according to a methodology previously described [24] and their formulations synthesis are showed in Table 2. Briefly, all samples were added the amount of DBTL equal to 0.5 wt. % of the total solid content. The amount of TEA equal to 5% excess of DPMA content was added. The waterborne polyurethanes were synthesized in a 100 mL round-bottomed, four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser and thermometer. A reaction temperature was controlled using constant temperature oil bath. The HTNR, DMPA and DBTL were weighed and transfered into the reactor. The concentration of mixtures was controlled at 40 wt. % by adding MEK. The mixtures were heated to 70 ^{o}C under nitrogen atmosphere for 20 min. After that the TDI was added dropwise into the flask and reacted continuously at 70 ^{o}C under nitrogen atmosphere for 4 h. The prepolymer temperature was allowed to drop to 40 ^{o}C. The carboxylic acid groups in DMPA were then neutralized by the addition of TEA. The mixture was stirred for further 30 min to ensure that neutralization was completely occurred. The next step is dispersion step. The prepolymer ionomers was dispersed by adding of desired deionized water and ethylene diamine (EDA) together with vigorously stirring and carried out for 30 min. After that the solvent was evaporated to obtain the waterborne polyurethane. All samples were controlled a solid concentration of around 20%.



Scheme 2. Synthesis of waterborne polyurethane

Table 2. 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%

Film preparation

Films from all samples were prepared by casting the dispersions onto polypropylene mold without a releasing agent. The films were allowed to dry at room temperature for 2 days and kept under 50 °C for 7 days before testing.

Analysis

FT-IR

FT-IR spectra were recorded on a Nicolet Avatar 370 DTGS FT-IR spectrometer in a range of 4000-500 cm^{-1} on with a diamond attenuated total reflection (ATR) device and controlled by OMNIC software

Particle size

Particle sizes and particle size distributions of the WPUs for 3 months were measured with laser particle size analyzer model Beckman coulter LS 230 was produced by Coulter LTD. The samples were diluted with deionized water to the concentration of 10% before testing without filtering and ultrasonic treating.

Dispersion morphology

The morphology of the WPU was observed on a transmission electron microscopy (TEM) model JEOL JEM-2010. The samples were 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 tertraoxide. After drying, the samples were characterized.

Tensile properties

The sample films were preformed following an ISO 37 with type 2 die. Tensile properties of all waterborne polyurethane films were tested using a Housfield moldel H 10KS from Hounsfield test equipment LTD. It was equipped with 100 N load cell and grips including with a laser detector for detecting a elongation. The crosshead speed was controlled at 100 mm min^{-1}.

Water absorption

The water-swelling measurements were carried out by immersing the cast PU films 10 mm × 10 mm × 1 mm) in distilled water at 20 ^{o}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 shown as:

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

Where W_s is the weight of the swollen film and W_0 is the weight of the original dry film.

Swelling properties

Swelling property was performed in a solvent (THF, MEK and Toluene) with a diameter 16 mm of circle dry latex film. The samples were immersed in solvent for 24 h. The diameter of swell specimens was determined and used to calculate the swelling property of the WPU films.

Thermal properties

TGA analysis was performed on a PerkinElmer (moldel STA 6000) with Pyrist software. heating rate of 10 ^{o}C min^{-1} from room temperature to 600 ^{o}C under nitrogen atmosphere at a flow rate 90 mL min^{-1} were controlled. The sample weight was about 10 mg.

Results and discussions

1. Effect of chain extender content at constant the NCO/OH ratio at 1/1

Table 4. Results of EDA content on TSC, pH and particle size of WPU3000

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	Non-stable

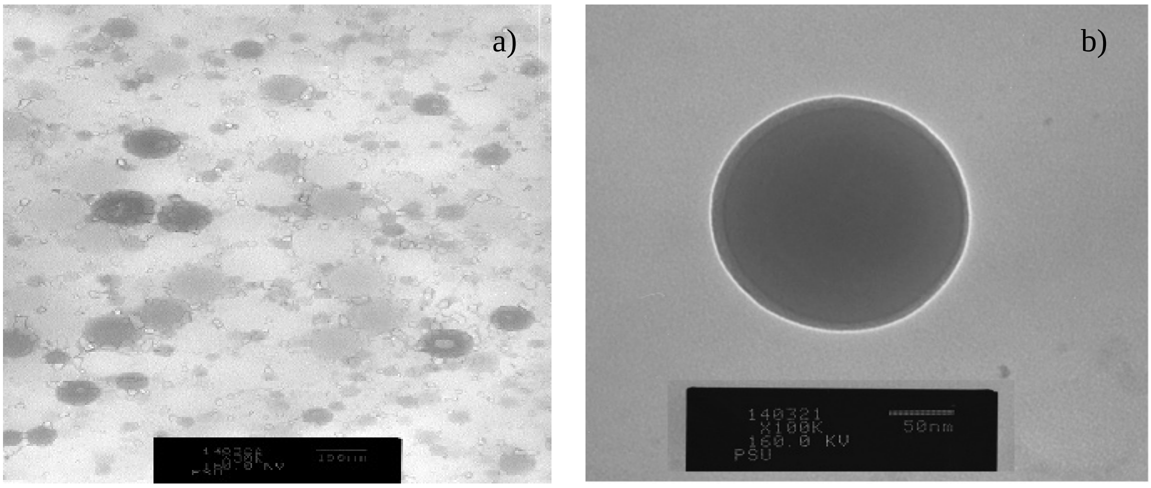


Figure 1. TEM image of particle size of WPU3 a) 50K and b) 100K

Table 4 represents the particle size for WPU with different EDA contents from light scattering technique. For these experiments, the each formula of WPU were controlled the amount of internal emulsifier, DMPA, at 5.6% wt (Table 2), resulted the average particle size of WPUs varied from 75 to 88 nm as shown in Table 4. It was not significantly an influence of EDA content to particle size of WPUs. Normally, there are several factors in influencing the particle size of WPU, for instants the hydrophilicity, prepolymer viscosity, ionic group position, chain rigidity, and chemical structure of soft segment of soft segments[18, 27]. In Figure 1 shows sample of TEM images of WPU3 at the magnification 100K and 50K, respectively. It was clearly seen that the sharp of particle size of WPU3 is round and well distributed in the dispersion. The appearance of WPUs was also observed. It was found that the WPU was higher viscous and dark color when increase the EDA content from o to 2 mole (Table 4) and their films were also showed in Figure 2. It was observed that they are yellowish, soft and flexible.

For the ratio of NCO/OH series, they had a clearly effect on average particle size, especially, in the case of increasing of NCO/OH with fixing EDA content at 1 mole (WPU7, WPU32 and WPU33). The average particle size increase from 88 to 143 nm and partially precipitate for the ratio of NCO/OH equal to 1, 1.5 and 2, respectively at fixing EDA at 1 mole. It was explained that with the same content of DMPA, the increase in particle size for the resulting WPU with different NCO/OH ratio in this study is mainly due to occurrence of higher crosslink in the WPU.

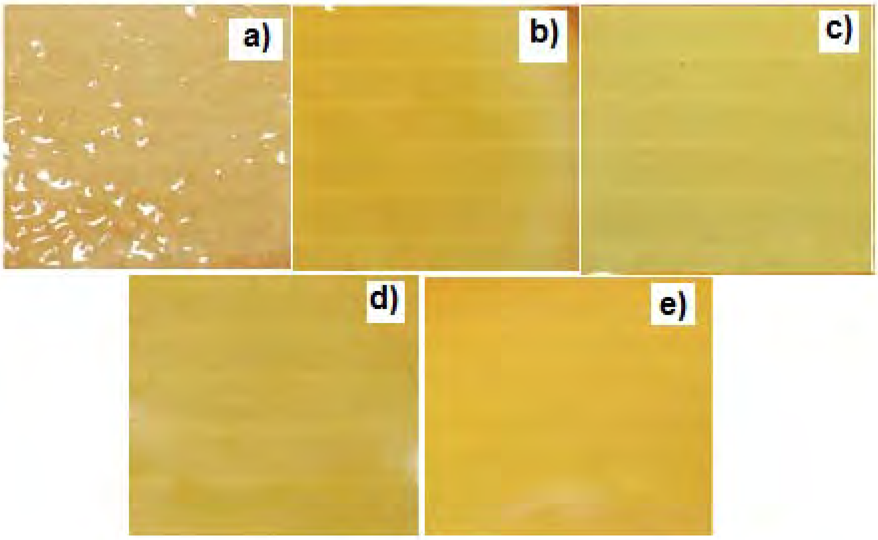


Figure 2. Film appearance of WPUs: a)WPU3, b)WPU5, c)WPU7, d)WPU9 and e)WPU11

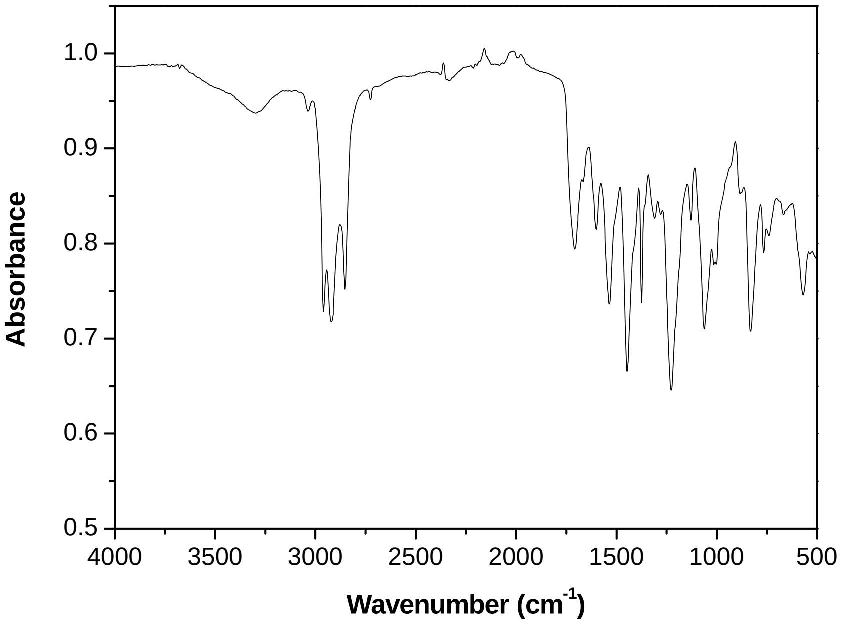
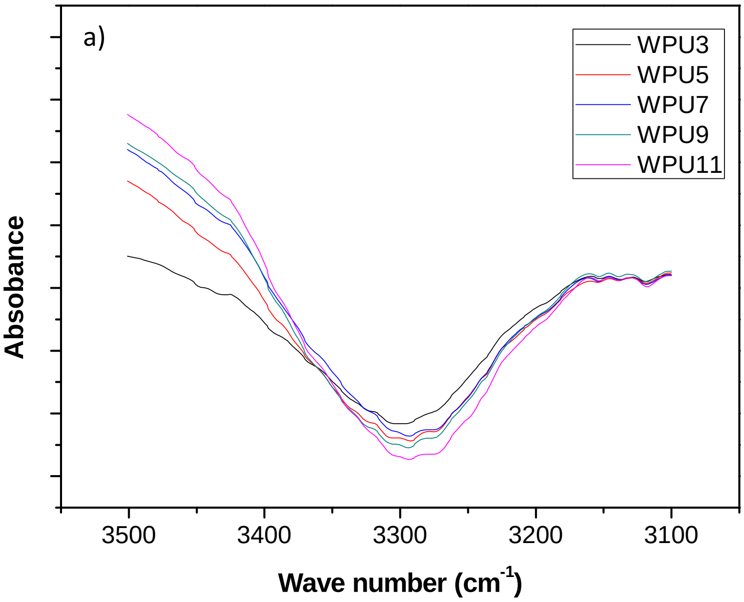


Figure 3. FT-IR spectrum sample of waterborne polyurethane (WPU3)



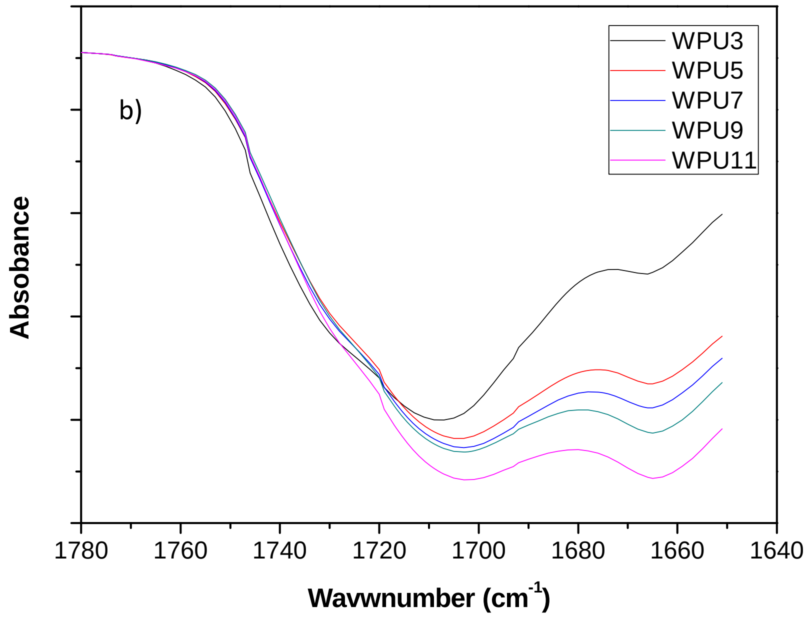
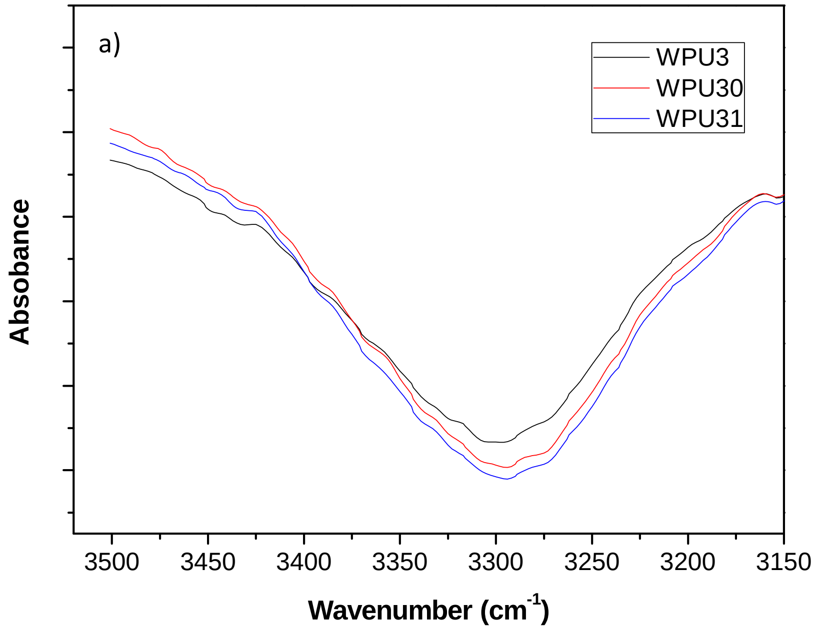


Figure 4. FT-IR spectra absorbance of waterborne polyurethane with various ethylene diamine (0-2 mole) a) at 3300 cm-^{1} b) and at 1700 cm-^{1}



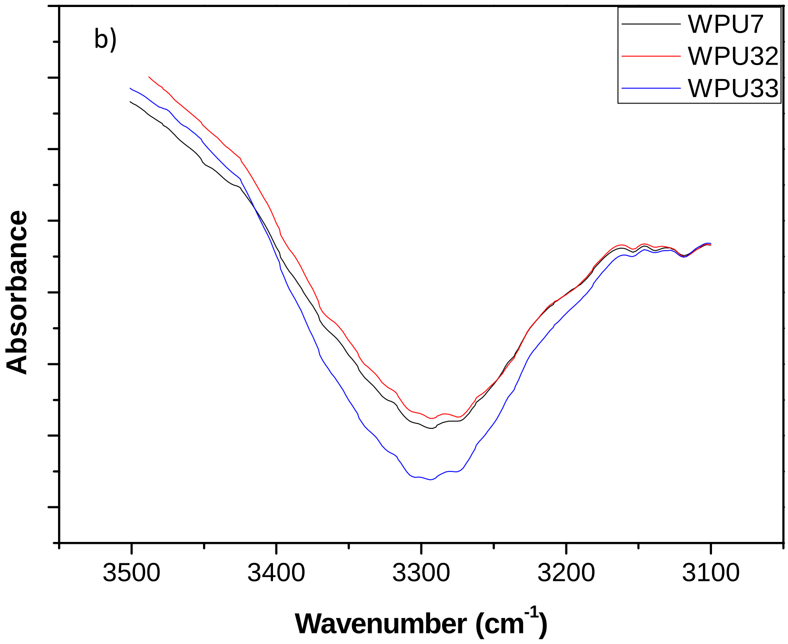


Figure 5. FT-IR spectra absorbance at 3300 cm-^{1} of waterborne polyurethane with various the NCO/OH ratio: a) without ethylene diamine; b) with ethylene diamine 1 mole

Figure 3, shows that the chemical structures of WPU films were characterized by FTIR (ATR technique). The FTIR revealed that the chemical structure of polyurethane is represented in the absorption bands at around 3330, 1700, and 1530 cm^{-1}, which correspond 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 absorption peak at 2270 cm^{-1} confirms that there was no residual-free NCO in WPU films. It was summarized that the synthesis of waterborne polyurethane based on natural rubber was well-achieve.

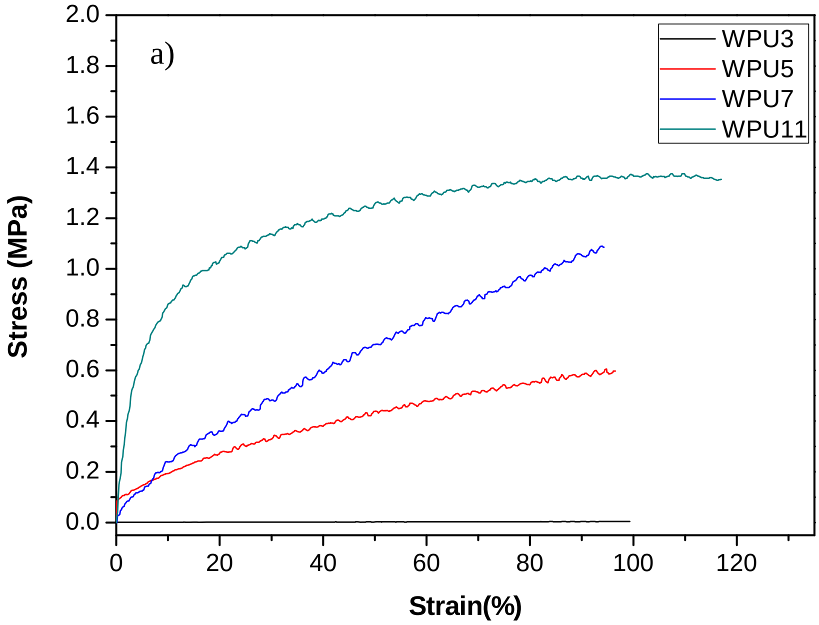
A physical bonding (hydrogen bonding) is an important role in polyurethanes and has an influence on their properties. The hydrogen bonds occurred between the N-H absorbance of amide group (i.e., urethane or urea) as donor and carbonyl group in amide groups as the acceptors. Therefore the FT-IR analysis is a good technique to use for approving the effects in WPU film. The FT-IR spectra of the WPU series on chain extender content, ethylene diamine (EDA) was shown in Figure 4. Their FT-IR spectra have pointed on two important vibration regions. The first one is the NH-stretching vibration around 3200-3500 cm^{-1} and another is the carbonyl (C=O) stretching vibration amide region (1700-1730 cm^{-1}). It was found that the intensity of the N-H vibration region around at 3300 cm^{-1} and 1700 cm^{-1} an increase with an increase in the hard segment content from 21.2 to 29.9 %. It was explained that the urethane or urea groups in WPU11 were more degree than that in WPU3. In addition, it was clearly observed that the bond N-H stretching shift to a lower wave number for

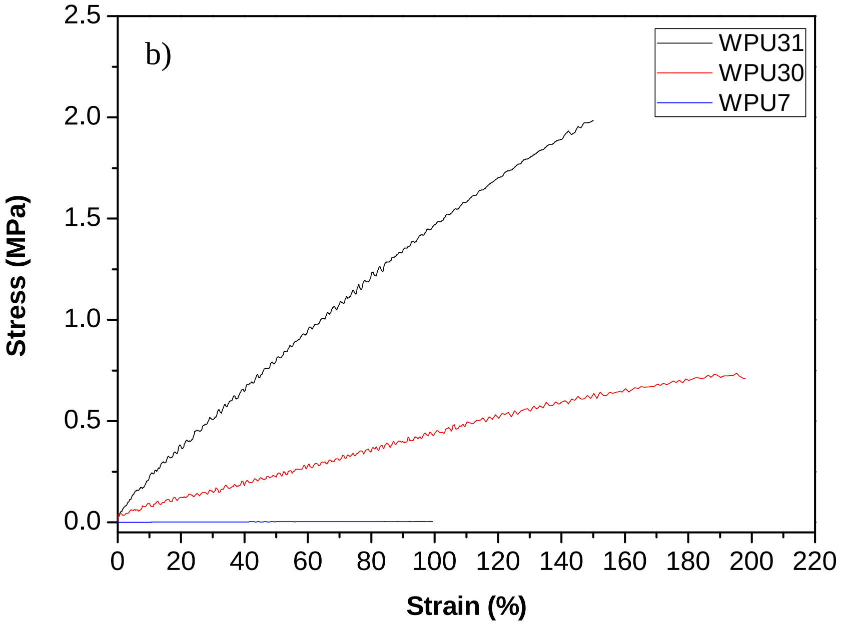
WPU11 when compared with that for WPU3 due to an increase in the degree of association in WPU films with higher hard segment content [18]. In agree with a shift of peaks from 1710–1720 cm^{-1} to approximately 1700 cm^{-1} with the increase of hard segment content for EDA extended one suggests that stretching vibration mode of carbonyl group becomes easier because the hard segment interrupts dipole–dipole interaction among carbonyl groups, thus freeing each carbonyl group from interaction with the neighboring groups. In addition, the intensity of carbonyl of urea region around at 1660 cm^{-1} is higher for WPU films with an increase of EDA content [26, 28].

In addition, the FT-IR spectra of the WPU series on the ratio of NCO/OH of WPU films with EDA and without EDA at wave number 3300 cm^{-1} were also shown in Figure 5. It was found that the intensity of N-H vibration region around at 3300 cm^{-1} increase with an increase in the ratio of NCO/OH in both conditions due to increasing of isocyanate level in a formula to more form amide structures. In addition, it was showed that the bond N-H stretching slightly move to a lower wave number for WPU film with or without EDA at a higher NCO/OH ratio when compared with that for WPU at a lower NCO/OH ratio due to an increase in the degree of association in WPU films with higher hard segment content.

Table 5. Mechanical properties of the WPU films

Samples	Hard segment (%)	Young 's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WPU3	21.2	1.47±0.7	0.09±0.0	100±11.0
WPU5	23.4	10.72±5.5	0.60±0.0	97±0.2
WPU7	25.7	11.14±2.2	1.09±0.2	94±29.8
WPU11	29.9	64.44±0.0	1.35±0.0	117±42.8
WPU30	22.7	5.91±0.1	0.75±0.0	200±4.2
WPU31	24.2	15.95±11.5	2.0±0.1	150±31.2
WPU32	27.4	143.14±15.8	2.35±0.1	54±7.5
WPU33	28.4	229.33±0.0	3.19±0.0	38±0.0


a)
Stress (MPa)
Strain(%)
WPU3
WPU5
WPU7
WPU11
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
20
40
60
80
100
120


b)
Stress (MPa)
Strain (%)
WPU31
WPU30
WPU7
0.0
0.5
1.0
1.5
2.0
2.5
0
20
40
60
80
100
120
140
160
180
200
220

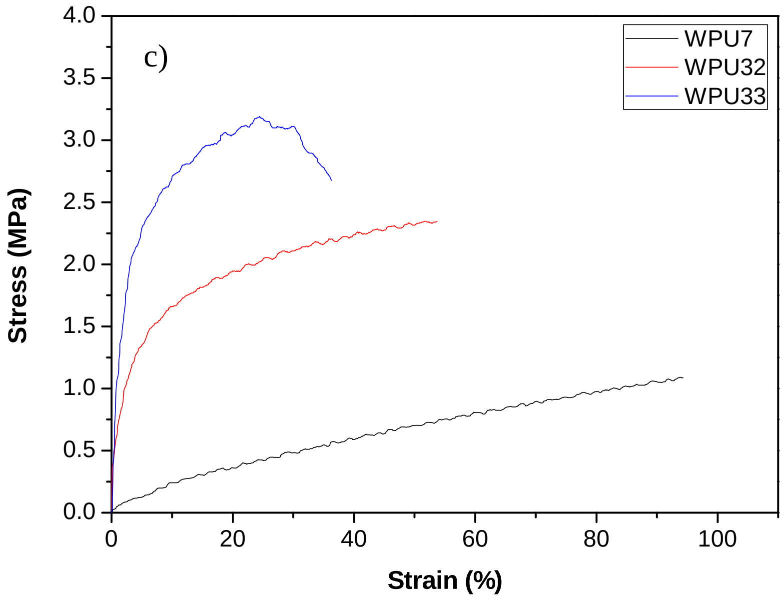


Figure 6. Stress and strain curve of WPU a) EDA content, b) NCO/OH without EDA and c) NCO/OH with EDA 1 mole

Table 5 summarized tensile strength, elongation at break and young's modulus of WPU films from HTNR3500 with various EDA contents, the ratio of NCO/OH with and without EDA 1 mole, and tensile stress-strain curve are shown in Figure 6. The WPU3 film shows a very soft rubbery modulus of 1.47 MPa, tensile strength of 0.09 MPa, and elongation at break of 100 % (Table 5). When the EDA content in WPU formula is further increased, the modulus and ultimate stress of the resulting WPU11 (EDA 2 mole) clearly increase but they had been no significantly effected on elongation at break.

We found that among WPU films (WPU3-7) exhibit a strain of around 100% due to their relatively low crosslink density. This behavior is similar to the tensile test behavior of an soft elastomeric polymer [18]. However, the WPU11 film shows behavior that is typical of a ductile plastic with a clear yield point and shows a modulus and a tensile strength that are approximately 43 and 135 time higher, respectively than those of WPU3 film. In addition, the NCO/OH ratio without EDA series in WPU films show behavior of elastomeric polymer. Their modulus and tensile strength increase with an increase of the NCO/OH ratio, for instant, the WPU31 film (NCO/OH =2/1) gave a tensile properties higher than that of WPU3 film (NCO/OH = 1/1) around over 200%. Moreover, the NCO/OH at 2/1 in presence of EDA 1 mole (WPU 33) shows the highest modulus and tensile strength with relatively smaller elongation at break (38% ± 0) in all WPU films. It results in a relatively hard plastic, which shows yielding behavior, followed by strain softening. It was described that these changes in the mechanical behavior are a result of the increase in the hard segments content led to increase the interaction by hydrogen bonding from the part of hard segment in the resulting WPU films from the HTNR.

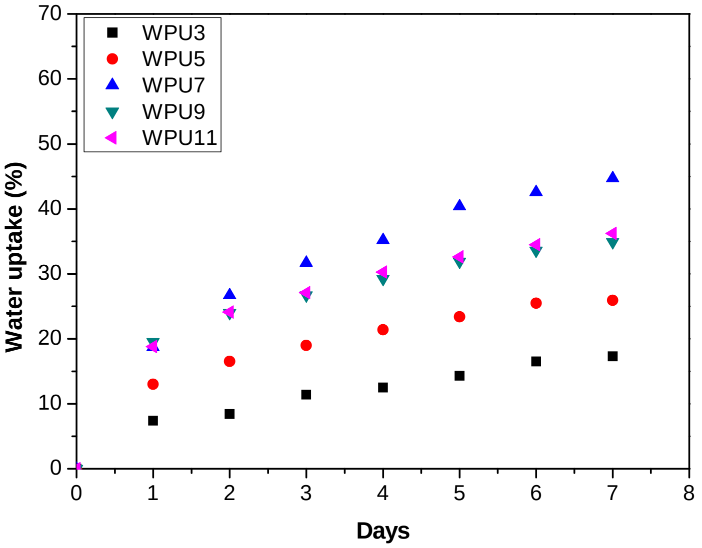


Figure 7. Water uptake of WPU films with different EDA content

The films formed after drying of WPUs at 60°C are non-tacky, flexible, and yellowish as shown in Figure 2. The water uptake of WPU films for the various EDA content with constant of DMPA content at 5.6% is represented in Figure 7. It was clearly observed that the water uptake of WPU films increased with immerse time. In addition, the result revealed that the higher EDA content in WPU films were added, the higher water uptake of their films were obtained because of the enhancement of hydrophilic block from hard segment of urea and urethane groups. For example, the series of WPU3, without EDA, was the minimum water uptake (17%) while that of WPU7 was the maximum (45%) during 7 days.

Table 6. Swelling and thermal properties of WPU films

Code	Swelling (%)			Thermal degradation					
	THF	Toluene	MEK	First step		Second step		Third step	
				*T*max (°C)	Weight loss (%)	*T*max (°C)	Weight loss (%)	*T*max (°C)	Weight loss (%)
WPU3	*Sol.*	*Sol.*	*Sol.*	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	*Sol.*	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

The swelling properties of WPU films in some solvents such as tertrahydrofuran (THF), toluene, and methyl ethyl ketone (MEK) was shown in Figure 8 and Table 6. It was observed that the WPU3 film was completely dissolved in each solvent due to low crosslink, non polar and linear structure. In addition, the toluene was a good solvent to swell of these polyurethane film based HTNR in all conditions. However, the swelling of WPU films was decreased with increasing the EDA content and the NCO/OH ratio, for instant the WPU films with increase in the EDA content from EDA 0.5 mole (WPU5) to EDA 2 mole (WPU11) indicating that the percentage of swelling decrease to 100%. As it was expect that the content of EDA and NOC/OH ratio are increased, the obtained polyurethane with higher hard segment has a greater opportunity to form hydrogen bonding or physical networks because it has more active proton positions than a lower hard segment. The highest hard segment, WPU33, exhibits a lowest swell of 23.8% in toluene and 5.4 % in MEK.

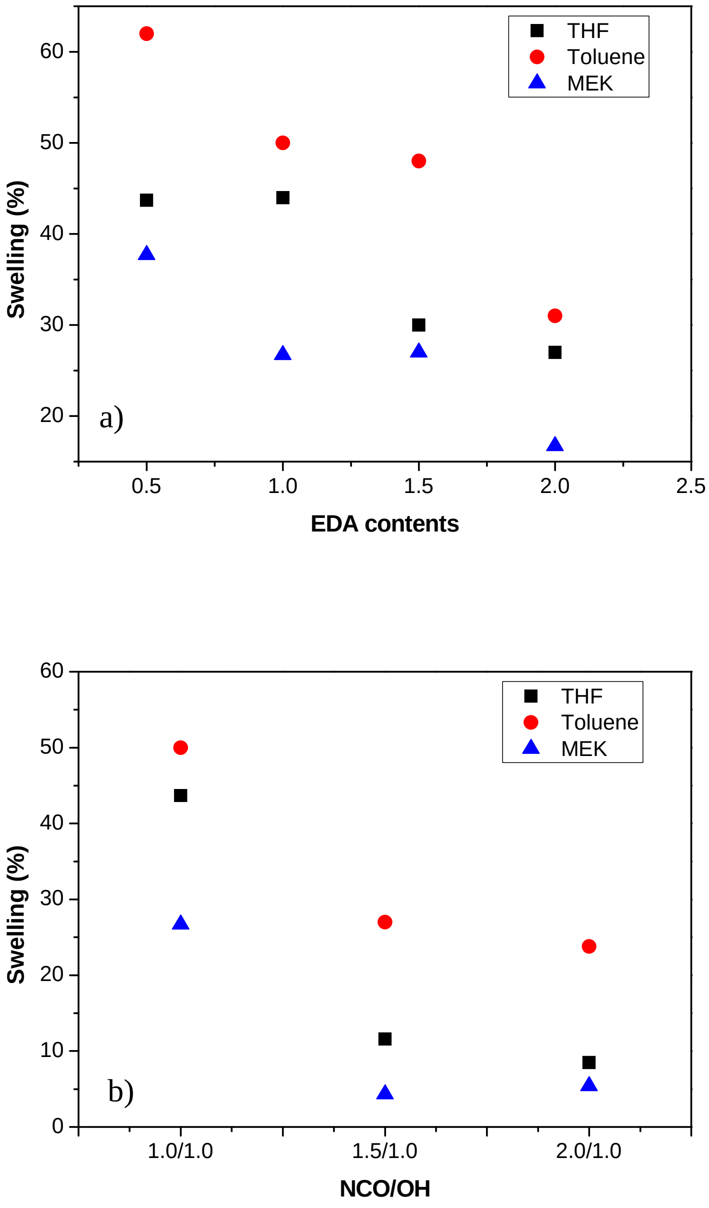


Figure 8. Swelling of WPU films a) EDA content and b) NCO/OH ratio with EDA 1 mole

A three-stage loss thermal degradation was observed for all WPU films. The first stage degradation at 162°C–197 °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 250°C–270 °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.

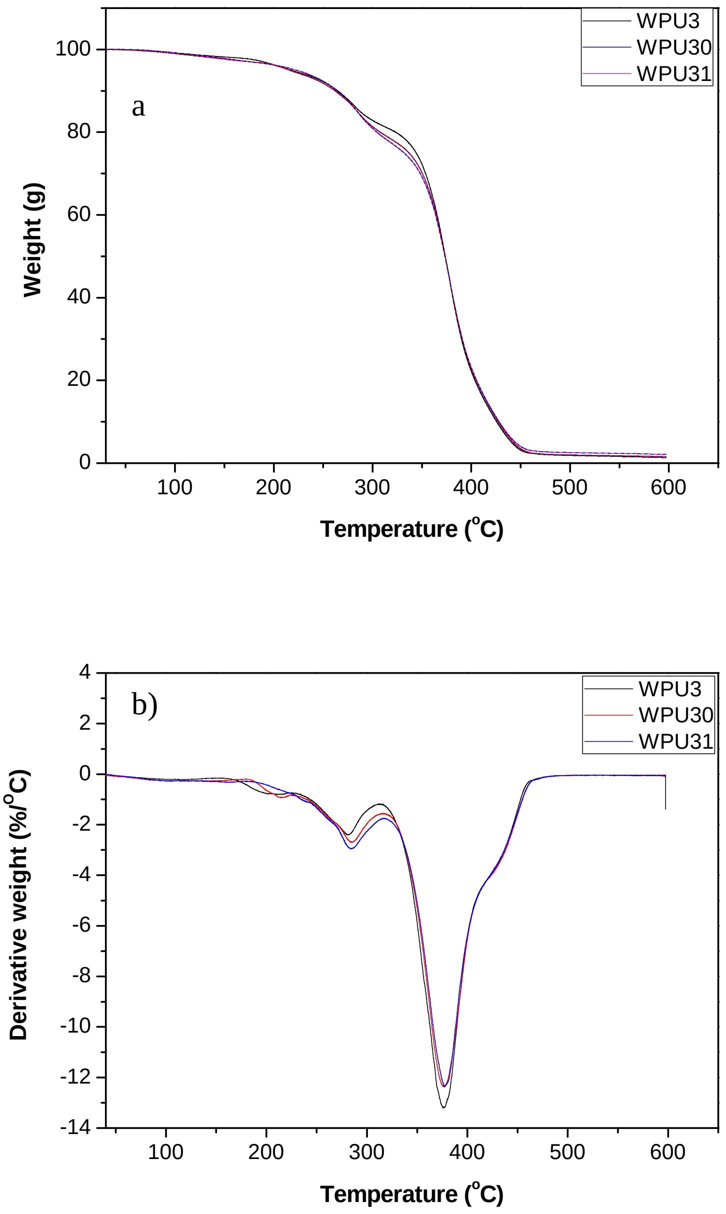


Figure 9. TGA curve of WPU films from HTNR with different the ratio of NCO/OH without EDA

Finally, stage at 375 °C–377 °C relates to the decomposition of structure of oligoisoprene [24]. We observed that the increased EDA contents in sample for WPU3–WPU11 led to an increased second step of weight loss from 8.8 to 22.0 percent of weight loss, respectively. The results of the increased ratio of NCO/OH in WPU films with NCO/OH from 1/1 to 2/1 (WPU3, WPU30, WPU31) also show an increasing of the second step degradation from 8.8 to 19.8 percent of weight loss. Their degradations were assumed that the cleavage of urethane or urea groups of EDA or polyol and diisocyanates were occurred (Figure 9). The results agreed with the previous work, which studied on hydroxyl telechelic polybutadiene (HTPI) in which the thermal decompositions in second step of film polyurethane dispersion were increased with an increase of NCO/OH ratio [28]. However, the first step of weight loss of all WPU films was slightly changed from 2.0 to 4.6 percent of weight loss due to fixing the amount of DMPA at 5.6%wt.

Conclusions

For this study, WPUs based on HTNR were successfully prepared by prepolymer process with various amounts of chain extender content (EDA), the NCO/OH ratio in presence of chain extender or without chain extender. It was found that the particle size of WPUs were not change with increasing of EDA content but it dramatically increases when an amount of the NCO/OH ratio was increased in the presence of chain extender. The FT-IR technique is a good candidate to use for examination of the chemical structure of WPU films and analysis in occurrence of hydrogen bonding. In addition, the highest hard segment, WPU33, exhibits a lowest swell of 23.8% in toluene and 5.4 % in MEK whereas the lowest hard segment, WPU3 was completely dissolved in all solvents. For mechanical properties, the WPU3 film shows a very soft rubbery modulus of 1.47±0.7 MPa, tensile strength of 0.09 ±0.0 MPa, and elongation at break of 100 % whereas the NCO/OH ratio at 2/1 in presence of EDA 1 mole shows the highest modulus (233.3±0.0 MPa) and tensile strength (3.19±0.0 MPa) with relatively smaller elongation at break (38% ± 0) in all WPU films as well as like a ductile material. Moreover, the decomposition in second stage of WPU films was increased with an increase of EDA content and the NCO/OH ratio. Therefore, NR-based polyols has a potential to develop a synthesis of new WPUs based on renewable source and improve their mechanical properties by changing some chemicals. It has been motivated by environmental considerations, *i.e.,* replacement of petroleum-based products, and use of solvent-free products.

Acknowledgments

We would like to thank Thai Research Fund and Office of the Higher Education Commission as well as Faculty of Science and Technology, Prince of Songkla University for financial support under contract grant on: MRG 5580108.

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