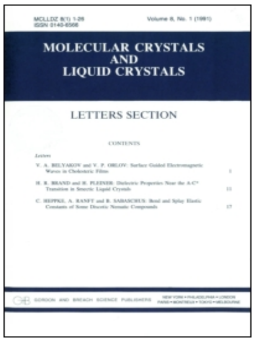

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Syntheses and properties of waterborne polyurethane-epoxy adhesives

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ASBTRACT
In this study, waterborne polyurethanes (WPUs) with an epoxy group and improved hydrolysis resistance and adhesion were synthesized using a polyester polyol, epoxy resin, 4,4-dicyclohexylmethane diisocyanate, and dimethylol propionic acid (DMPA). The properties of the WPU were evaluated by differential scanning calorimetry, tensile strength, elongation, hardness and adhesion strength. The glass transition temperature (Tg) of the synthesized WPU was approximately −50°C. The Tg and tensile strength increased with increasing epoxy resin content while the elongation decreased. The optimum adhesion was achieved with a polyol:epoxy ratio of 99:1.

KEYWORDS
waterborne polyurethane; epoxy; polyester polyol; adhesive

1. Introduction

Polyurethanes (PU) are urethane-containing polymers having an average molecular weight of more than 1000 g/mol. In 1894, Wurtz and Hoffman introduced PU by reacting hydroxyl-containing compounds and isocyanate, and Ottobayer commercialized it in 1937[1]. PU are currently produced by the addition of polyols with active hydroxyl groups and diisocyanate bearing isocyanate (-NCO) functional groups [2, 3].

PU has been traditionally synthesized in solvent-based form because of the high hydrophobicity of the polyols used. However, this method produces hazards related to organic solvent release during production and use, resulting in severe air pollution. To protect the environment and improve working conditions, the use of volatile organic compounds (VOCs) has been restricted, thus limiting the use of organic media. Therefore, organic solvents have been replaced with waterborne PUs (WPUs), environmentally friendly water-based resins that use water as the medium, provided there is no air pollution [4–6].

To enhance the water solubility and dispersion ability, an anionic, cationic, or non-ionic hydrophilic moiety was introduced in the monomer used for WPU production [7, 8]. This hydrophilicity and the hydrophobicity of the main chain of the polymer led to its dispersion in a manner similar to that of surfactants in water. These ionic (or non-ionic) functional groups impart high mechanical strength and elasticity. However, because of their hydrophilicity, the final products can have inferior initial drying rate, as well as water, chemical, and

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hydrolysis resistance compared with solvent-based adhesives, thereby limiting their applications. In this work, to improve the hydrolysis resistance and adhesive properties of WPUs, we employed epoxy resins, which exhibit high tensile strength, elasticity, chemical resistance, electronic properties, and size stability [9, 10]. WPUs with epoxy resins (WPUEs) were synthesized with varying ratios of polyester polyols and epoxy resins. The mechanical properties, hardness, thermal properties, and adhesion strength of the synthesized WPUEs were evaluated by varying the amounts of epoxy resin and isocyanate.

2. Experimental

2.1. Reagents and materials

Polyester polyol(adipic acid/buthandiol, Mw = 2000 g/mol, Daewon Polymer), dimethylol propionic acid (DMPA, Aldrich chemical) was dried at 80°C under 0.1 mmHg until no bubble was observed. Epoxy resin (YD-011, epoxy equivalent weight = 450∼500g/mole–500 g/mol, Kukdo Chemical), 4,4-dicyclohexylmethane diisocyanate(H_{12} MDI, Aldrich chemical) and isophorone diisocyanate (IPDI, Aldrich chemical), ethylene diamine (EDA, Junsei chemical), triethylamine (TEA, Samchun Pure chemical), dibutyltin dilaurate(DBTDL, Aldrich chmical) were used without further purification. Corona-treated polyethylene terephthalate (PET) film, which have been commonly used for electronic devices, was purchased from ESD Korea Co. for the adhesion test.

2.2. Synthesis of WPUE

The WPUE synthesis scheme is depicted in Figure 1, and the reaction conditions are summarized in Table 1. The polyols, epoxy resin, and DMPA were added to a 4-neck flask and dried using a vacuum pump for 1 hr at 80 °C before being mixed homogeneously. After adding DBTDL, the reaction mixture was stirred for 10 min, and diisocyanate was slowly added for 1 hr. Then, the reaction was continued for 3 hr. The reaction between the epoxy resin and isocyanate was performed by connecting the repeating –OH group in the epoxy resin with the –NCO group of the isocyanate. The amount of NCO in the product was confirmed by dibutylamine back-titration, and the reaction was continued until the theoretical NCO content was achieved to prepare the pre-polymer. The neutralization reaction was conducted at 40°C with the addition of a TEA solution in MEK. After the addition of distilled water, the reaction mixture was stirred at 700 rpm for water dispersion, and then, the chain extension reaction was conducted using EDA with 45 wt% of solid contents.

2.3. Characterization of synthesized WPUE

Fourier transform infrared spectrometer (FT-IR, Jasco series 430 Jasco) was used to confirm the completion of the WPUE synthesis (wavelength range: 4000–400 cm^{-1}, 32 scans, resolution: 4 cm^{-1}). Thermal properties were analyzed using differential scanning calorimetry (DSC, TA instrument, DSC Q-100) with a temperature scanning of −90–200°C, with a ramping rate of 10 °C/min. The tensile strength and elongation were determined using a universal testing machine (UTM, DTU-900HMA) with the crosshead speed of 500 mm/min. Samples of 0.5 ± 0.05 mm thickness and 10 ± 0.05 mm width were prepared according to the ASTM

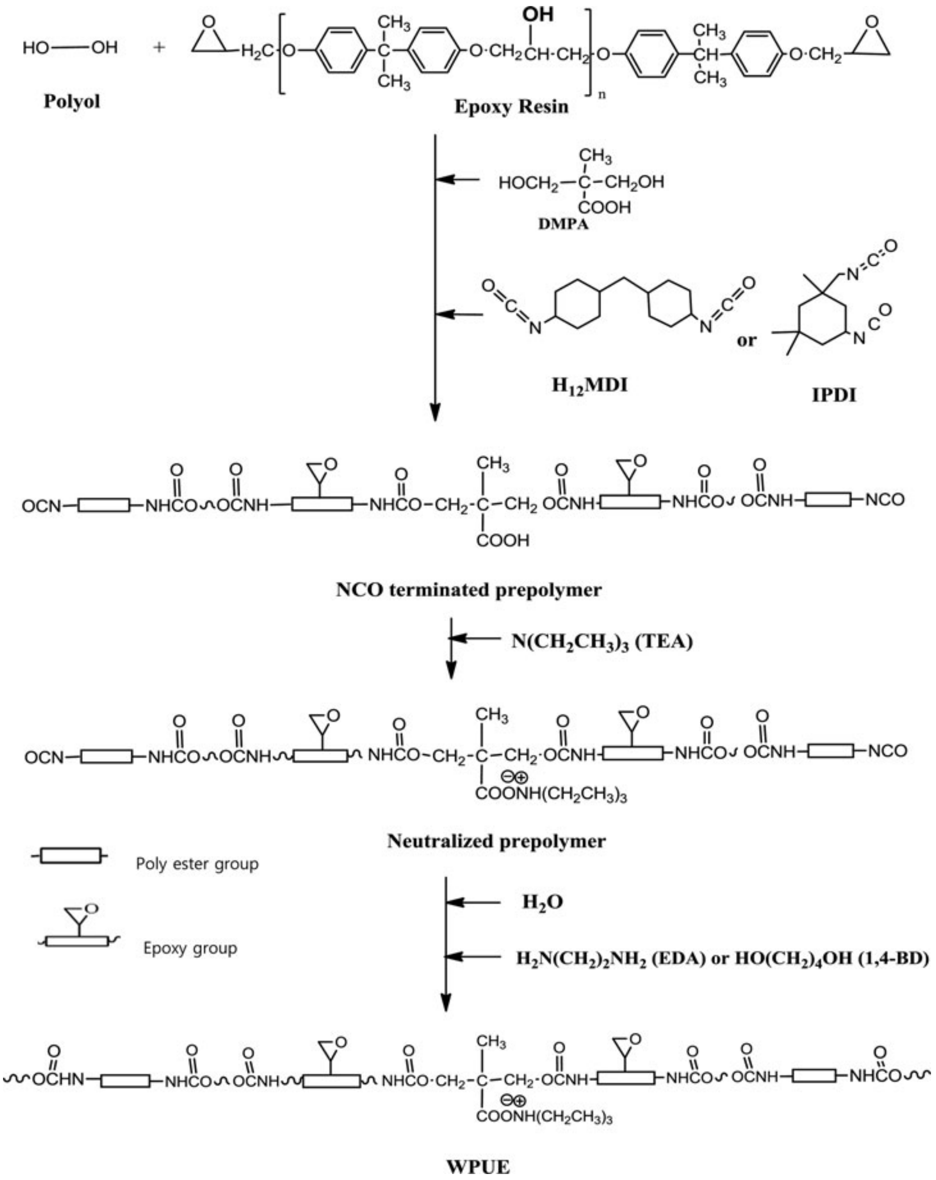


Figure 1. Schemetic diagram of the synthesis of WPUE.

Table 1. Synthesis conditions of WPUE.

	Polyol	Epoxy resin	OH ratio of Polyol: Epoxy resin	H_{12}MDI	IPDI	EDA	DMPA	Pencil Hardness
WPUE-1-0	0.037	0	100:0	0.077		0.018	0.022	7B
WPUE-1-1	0.0366	0.0004	99:1	0.077		0.018	0.022	6B
WPUE-1-5	0.036	0.002	95:5	0.078		0.018	0.022	5B
WPUE-1-9	0.035	0.003	91:9	0.079		0.018	0.022	5B
WPUE-2-0	0.038		100:0		0.078	0.018	0.022	6B
WPUE-2-1	0.0379	0.0004	99:1		0.079	0.018	0.022	6B
WPUE-2-5	0.037	0.002	95:5		0.080	0.018	0.022	5B
WPUE-2-9	0.036	0.004	91:9		0.081	0.019	0.022	5B

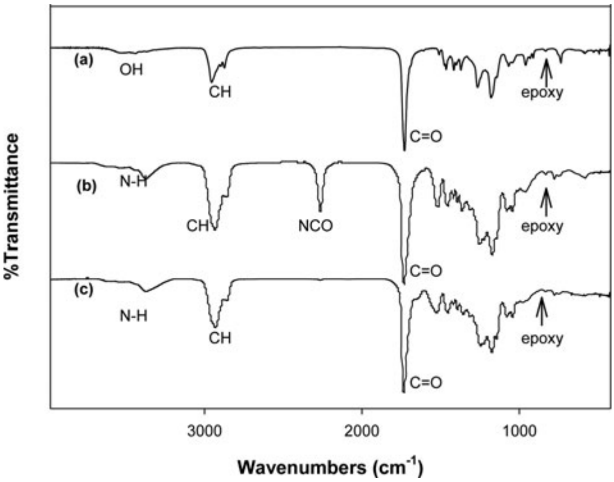


Figure 2. FT-IR spectra of WPUE (a) Polyol + Epoxy + DMPA, (b) NCO terminated prepolymer, (c) WPUE.

D 638. For the adhesion test, the synthesized WPUE was coated on a PET film of 12.5 μm thickness (pre-cut 2 × 15 cm) and then tested together with SUS 304. Five samples were averaged at a test speed of 200 mm/min. The hardness test was analyzed using Pencil Hardness Tester (coretech, CT-PC1) according to the ASTM D3363 at room temperature and five samples were averaged.

3. Results and discussion

3.1. Structure identification of WPUE

The FT-IR spectrum of the synthesized WPUE is presented in Figure 2. Figure 2(a) shows the characteristic peaks of the reaction between the polyol, DMPA, and epoxy resin (polyester C=O stretch at 1730 cm-1, C-H stretching vibration peak at 2880–2990 cm^{-1}, and –OH characteristic peak at 3300–3500 cm^{-1}). The structure of the epoxy resin could be confirmed by the C-O stretching of the oxirane group at 915 cm^{-1}, which overlapped with the polyol peak at 912 cm^{-1}. Aromatic ring C-C stretching at 1509 cm^{-1} and C-O-C stretching of oxirane group at 831 cm^{-1} were also confirmed [11]. Figure 2(b) presents the FT-IR spectrum of the prepolymer. The carbonyl peak of the urethane bond (–COO) is observed at 1700 cm^{-1}, –OH peaks are observed at 3400 cm^{-1}, and N-H stretching vibration peaks are observed at 3200 and 1500 cm^{-1}, confirming the urethane functionality. In addition, a remaining unreacted isocyanate peak was observed at approximately 2270 cm^{-1} [12]. Figure 2(c) presents the FT-IR spectrum after the chain extension reaction with EDA after water dispersion. The isocyanate peak at 2270 cm^{-1} disappeared, and a slight reduction of the –OH characteristic peak was observed at approximately 3300–3500 cm^{-1}. However, because of the overlap between the urethane characteristic peak with the N-H stretching vibration peaks at 3300–3500 cm^{-1}, the intensity of the peak did not change significantly [11,12]. The NMR spectra of the synthesized WPUE are presented in Figure 3. Figure 3(a) presents the NMR spectrum of WPUE-1-0 without epoxy, revealing resonance peaks of C-CH_2-OCO- at 4.1 ppm, C-CH_2-O- at 3.6 ppm, C-CH_2-CO- at 2.3 ppm, and C-CH_2-C at 1.7 ppm, which confirm the complete synthesis of WPUE [13,14]. As observed in Figure 3(b), the existence of an oxirane ring was confirmed

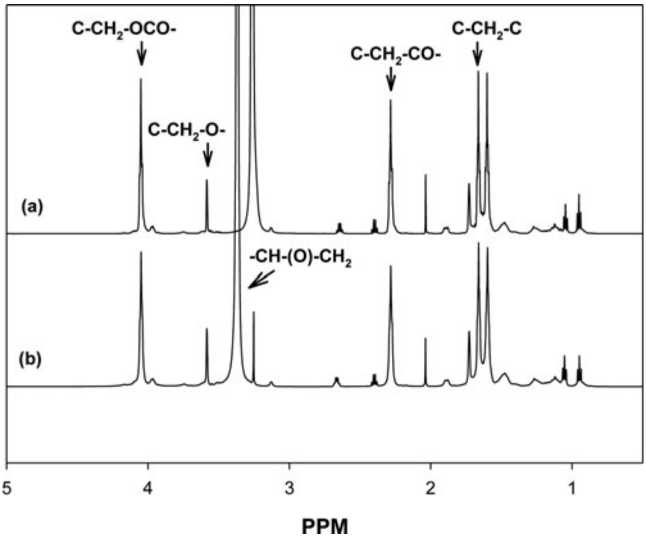


Figure 3. ^{1}H-NMR spectra of (a) WPU and (b) WPUE.

by the presence of a –CH-(O)-CH2 peak at 3. 36 ppm [15], confirming the structure of the synthesized WPUE using epoxy.

3.2. Thermal properties of the synthesized WPUE

DSC thermogrames for WPUEs are presented in Figure 4. As observed in Figure 4(a), Tg increases upon increasing the epoxy resin content. Shorter soft segments can induce a less developed domain of soft segments during the mixing process. As a result, the movement of the soft segments can be limited by neighboring hard segments. The limited movement of the soft segments can induce a higher Tg because of the bond ends both extremities of the soft segments and hard segment [16–18]. Moreover, the higher Tg can be explained by the high Tg of the epoxy resin itself, which can affect the Tg of the final product. In Figures 4(a) and 4(b), when the OH ratio of polyol:epoxy is 100:0 and 99:1, the Tm peak can be observed at approximately 46 °C and it disappears when the epoxy resin content increases. When the content of the epoxy resin, which is the hard segment, is increased, the soft domain content decreases, and the soft segment packs rapidly. Thus, the amorphous polyols in the rapidly cooled soft segments cannot crystallize. We presume that the peak is very broad or not detectable [19].

3.3. Mechanical properties of the synthesized WPUE

Figure 5 shows the mechanical properties of the synthesized WPUE. As observed in Figures 5(a) and 5(b), by increasing the amount of epoxy resin, a highly dense structure was observed, resulting in a high tensile strength and reduced elongation. This behavior is presumed to be due to the increased amount of the hard segment in the PU. In addition, the hydrogen bonding between the oxygen of the carbonyl groups and the hydrogen atoms of WPUE can establish a bridge which can increase the physical strength and affect the molecular flexibility, yielding lower elongation [20–23]. As shown in Table 1, the pencil hardness test was conducted for the synthesized WPUE. The hardness increases

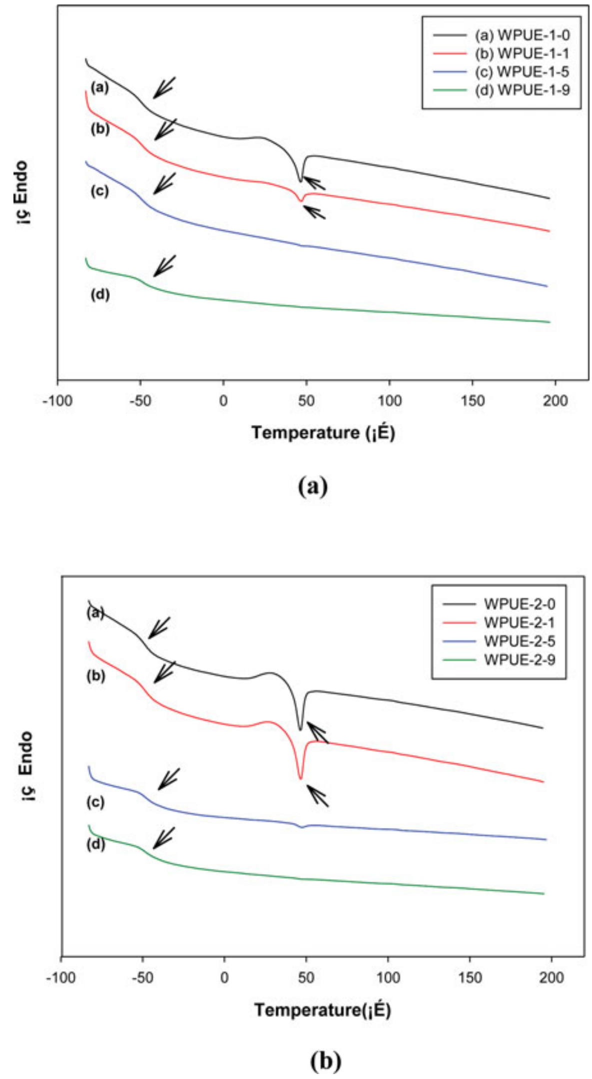
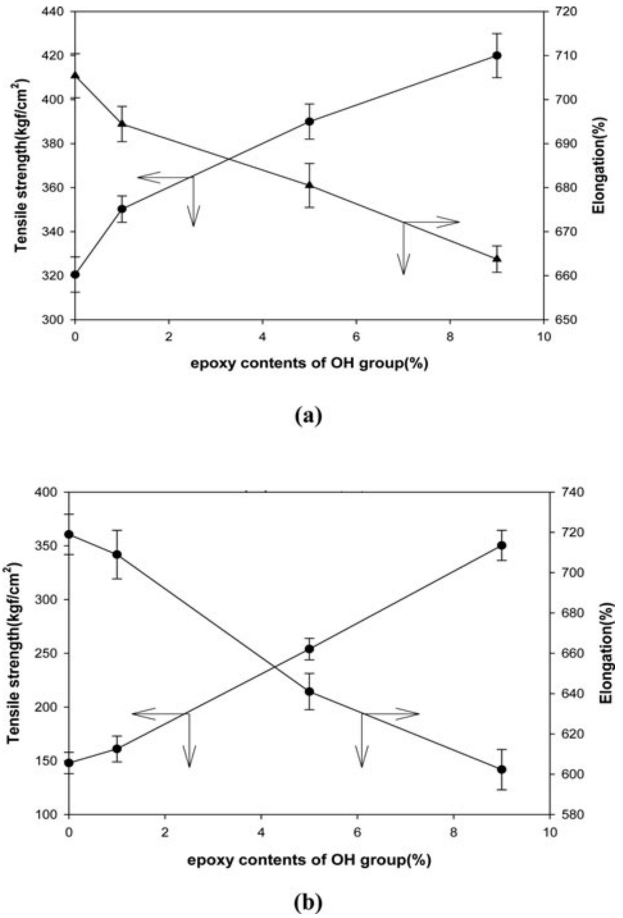


Figure 4. DSC thermograms of WPUE (a)WPUE-1, (b)WPUE-2.

upon increasing the epoxy resin content due to the highly dense structure of the epoxy group.

3.4. Adhesion test of the synthesized WPUE

As shown in Figure 6, an adhesion test was conducted for the synthesized WPUE. By varying the amount of epoxy resin, different adhesion strengths were observed (Figure 6(a)). The highest adhesion strength was obtained for the 99:1 ratio of polyol:epoxy resin. By introducing an epoxy group in the PU chain, higher adhesion was achieved because of the increased amount of hard segments, which might improve the cohesiveness. In addition, the formation of a 3-dimensional network structure of epoxy resin can increase the adhesion strength of the system [24]. However, an excessive increase in the amount of hard segments in the epoxy resin can reduce the adhesive strength because of the hardness of the product and low wettability of epoxy resin.



(a)

(b)

Figure 5. Mechanical properties of WPUE; (a)WPUE-1, (b)WPUE-2.

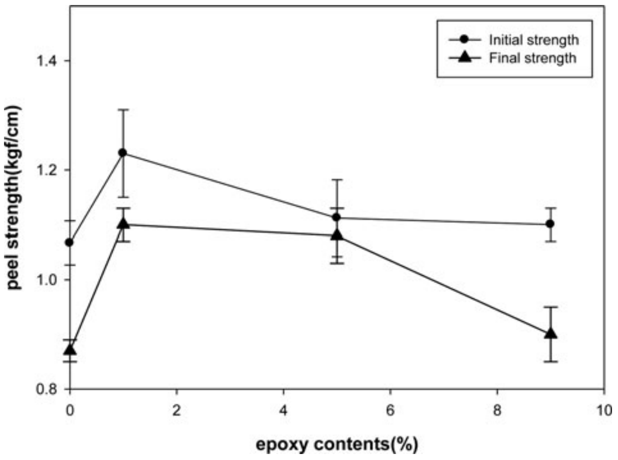


Figure 6. Peel strength of WPUE-1.

4. Conclusions

In this work, we synthesized a WPUE using an epoxy functional group and analyzed its properties. FT-IR and NMR analyses confirmed the synthesis of WPUs. The Tg of the synthesized WPUE was approximately −50°C, and a slight increase of Tg was observed upon increasing the amount of epoxy resin. The Tm peak was not observable or was too broad to be detected. The mechanical properties of the WPUE indicated that increasing the epoxy amount can increase the tensile strength and reduce elongation. The adhesion strength increased upon increasing the OH ratio of polyol:epoxy but then decreased. An excessive increase in the amount of hard segments (epoxy resin), however, can result in a very hard material, which can lead to detrimental effects on the end-use of the WPUE.

Acknowledgments

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References

[1] Woods, G. (1990). *The ICI Polurethane Book*, 2nd ed., John Wiley & Sons: New York.
[2] Vertel, G. (1994). *Polyurethane*, 2nd ed., Hanse Pub.: New York.
[3] Oetel, G. (1994). *Polyurethane Handbook*, Haser: Cincinnati.
[4] Saetung, A., Kaenhin, L., Klinpituksa, P., Rungvichaniwat, A., Munleh, T., Tulyapitak, S., Campistron, I., & Pilard, J. P. (2012). *J. Appl. Polym. Sci.*, *124*, 2742.
[5] Coutinho, F. M. B., Delpech, M. C., & Alves, L. S. (2001). *J. Appl. Polym. Sci.*, *80*, 566.
[6] Lee, J. E., & Kim, H.J. (2005). *Polymer(Korea)*, *29*, 172.
[7] Shin, Y. T., Hong, M. G., Choi, J. J., Lee, W. K., Lee, G. B., Yoo, B. W., Lee, M. G., & Song, K. C. (2010). *J. Korean Ind. Eng. Chem.*, *48*(4), 428.
[8] Shin, Y. T., Hwang, J. H., Hong, M. G., Choi, J. J., Lee, W. K., Lee, G. B., Yoo, B. W., Lee, M. G., & Song, K. C. (2011). *J. Kor. Ind. Eng. Chem.*, *49*(3), 285.
[9] Odinski, J. S., & Manzione, L. T. (1983). In: *Epoxy Resin Cemistry II* Bauer R. S. Ed., ACS symposium series 221, American Chemical Society: Washington, DC.
[10] May, C. A. (1988). *Epoxy Resins: Chemistry and Technology*, 2nd Ed., Marcel Dekker: New York.
[11] Kim, S. M., Kang, Y. U., Kwak, Y. K, Yang, N. S., Cho, J. S., Park, J. W., & Hwang, T. S. (2004). *J. Kor. Ind. Eng. Chem.*, *15*, 537.
[12] Shin, S. H., Jeong, B.Y., Jeong, I. D., Cho, N. J., Cheon, J. M., & Chun, J. H. (2010). *J. Adhes. and Interf.*, *11*(3), 100.
[13] Kim, K. H., Ha, K.J., Wu, J. P., Park, H. S., & Kwon, K.S. (1998). *Kor. J. Oil Fat Chem.*, *1*, 29.
[14] Lee, D. J., & Kim, H. D. (1999). *J. Kor. Fiber Soc.*, *36*, 873.
[15] Sipaut, C. S., Ahmad, N., Adnann, R., Ab. Rahman, I., Bakar, M. A., Ismail, J., Chee, C.K. (2007). *J. Appl. Sci.*, *7*(1), 27.
[16] Kwei, T. K. (1982). *J. Appl. Polym. Sci.*, *27*, 2891.
[17] Seefried, C. G., Koleske, J. V., & Critchfield, F. E. (1975). *J. Appl. Polym. Sci.*, *19*, 2493.
[18] Kim, S. K. (2000). *Elastomer*, *35*(4), 281.
[19] Askari, F., Barikani, M., & Barmar, M. (2013). *J. Appl. Polym. Sci.*, *130*, 1743.
[20] Ahn, J. B., Cho, H. K., Jeong, C. N., & Nho, S. T. (1989). *J. Kor. Ind. Eng. Chem.*, *8*, 230.
[21] McLennaghan, A. W., & Petherick, R. A. (1988). *Eur. Polym. J.*, *24*, 1063.
[22 Lee, J. C., & Kim, B. K. (1995). *Polymer*, *19*, 223.
[23] Xiao, H.X., Frisch, K.C., & MAlwitz, N. (1994). *J. Appl. Polym. Sci.*, *54*, 1643.
[24] Park, S.J., & Jin, F.L. (2004). *Polym. Degrad. Stab.*, *86*, 515.