Synthesis of Waterborne Polyurethane with Mixed Polyols and Its applications as an Impregnation Finishing Agent

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1. INTRODUCTION

Polyurethane (PU) is a polymer of a serial urethane group in a row. It is a segmented block copolymer composed of soft segment (SS) and hard segment (HS) which are formed through a reaction with active hydrogen compounds such as isocyanate and polyol. It will have a phase-separated structure due to the incompatibility of the two segments. Accordingly, the specific characteristic of PU depends upon the structure of hard segment and soft segment which show a phase separation. In other words, elasticity is generated from the structure composed of two domains with different characteristics. PU can have various structures and mechanical properties according to polyol types and synthetic methods. Due to its features, it can be used for many industrial sectors as coating agent, adhesive, paint, waterproof agent, etc.

Traditionally, PU has been manufactured by using organic solvents due to strong hydrophobicity of a polyol. However, concerns on environmental problems have emerged globally, and regulations have been enforced against the use of organic solvents such as DMF and DMAc (which were used for PU), for they cause environmental contamination and inflict critical hazards to human body. Hence, PU is being replaced with waterborne polyurethane (WPU) which uses water as solvent within the extent of not causing pollution. In synthesis of WPU, the method to compel dispersion with an emulsifier was used in the past, which however resulted in lowering chemical and physical properties due to the emulsifier. For that reason, recently, the mainly used method is to obtain WPU dispersible in water by adopting a hydrophilic group inside a PU main chain.

In this study, Waterborne polyurethanes, (WPUs) based on isophorone diisocyanate (IPDI), and mixed polyols of poly(tetramethylene glycol) (PTMG)/ polycarbonate diol (PCD) were synthesized. Generally in making WPU, PTMG (as a polyester polyol) would be used alone. However, PTMG has weak durability in hydrolysis and oxidation with low heat resistance. To advance such weakness of WPU, polycarbonate polyol that had excellent mechanical properties was used. PCD retains excellent mechanical strength and abrasion resistance, so it is expected to have better properties than those of WPU produced with PTMG only. Also, the synthesized WPU solutions were used as impregnating resins for the production of PET artificial leathers.

2. EXPERIMENTAL

2.1. Materials

Soft segments are polycarbonate diol (PCD) (molecular weight of 2,000 g/mol) and polytetramethylene glycol (PTMG) (molecular weight of 2,000 g/mol), supplied by Asahi Kasei Co. and Dupont respectively. Isophorone diisocyanate (IPDI, Bayer) was used as a hard segment. DMPA, TEA and EDA were also used for syntheses of WPU.

2.2. Synthesis of WPU

PCD, PTMG and DMBA were weighed and placed in a four-necked flask reactor, which was heated up to 120°C with stirring. When DMBA was completely dissolved, the reactor was cooled down to 70°C, and IPDI was input into the reactor. When the reaction reached theoretical -NCO content, the reactor was cooled down to 60°C and TEA was added to the reactor as a neutralizer for 40 minutes. Distilled water was added into prepolymers, and the dispersion process continued for one hour. After EDA was input into the reactor, the chain extend reaction was proceeded, and WPU was completely synthesized.

2.3. Characterizations and Dyeing Fastness

FT-IR (FT/IR-6300 spectrophotometer, Jasco Co.) spectra were collected to confirm the formation of silica by using the Attenuated Total Reflectance (ATR) method at a resolution of 4 cm-1. 512 scans were signal-averaged at room temperature.

A universal testing machine (Hounsfield H10K-S, England) was used to obtain stress–strain curves with a gage length of 10 mm and a cross-head speed of 500

mm/min. Each sample was measured 10 times to get the average of breaking stress and elongation.

3. RESULT and DISCUSSION

A peak of PCD, originated from a carbonyl group, was observed at around 1780 cm^{-1} and peak, originated from C—O—C stretching, was observed around 1260 cm^{-1} while a broad peak, originated from —OH, appeared at 3300-3500cm^{-1}. The broad peak at 3300-3500 cm^{-1} from PTMG was also observed. After the reaction in nitrogen atmosphere at 70°C for 20 minutes, the peak at 2257 cm^{-1} originated from isocyanate's —NCO was shown. The peak at 2257 cm^{-1}, originated from —NCO and at 3300-3500 cm^{-1} from —OH of PCD and PTMG, had disappeared and declined from prepolymers after the synthesis, whereas 1703 cm^{-1} peak (that is the carbonyl group of urethane) and 1640 cm^{-1} peak (that is the carbonyl group of urea) were observed. Through the result, the synthesis of WPU had been confirmed.

Waterborne Polyurethanes were prepared by using a two-step bulk polymerization procedure. The prepolymer (attached with —NCO at both ends) was prepared from IPDI, PCD and PTMG until it reached theoretical —NCO content. At synthesizing stage of the prepolymer, the molecular weight increased as the reaction proceeded, and the coefficient of viscosity also increased proportionally. Figure 1 shows the relation of viscosity variation and —NCO content of prepolymer. In this case, the time of reaching theoretical —NCO content can be ascertained through the DBA back titration. From this result, appropriate synthetic time with the viscosity of prepolymer was carried out.

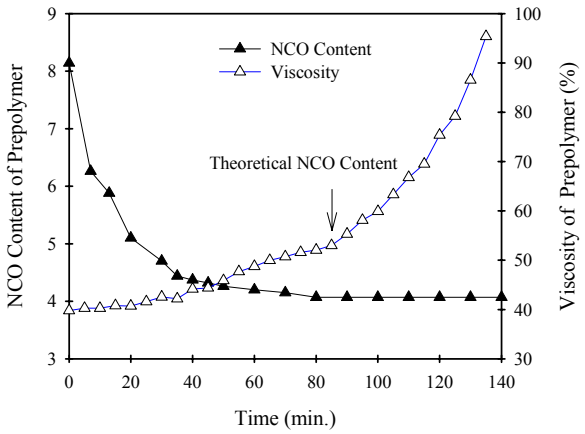

Figure 1. Relation of NCO content and viscosity variation in prepolymerization at 70 °C

To confirm the mechanical properties of WPU resins, WPUs with various ratios of PCD/PTMG contents were synthesized and WPU films were prepared. Tensile strength and elongation of WPU films with various contents of PCD/PTMG were shown in Figure 2. When PTMG was used for soft segment only, the film with excellent elasticity (that raised elongation at break up to maximum 1400%) was produced. When PCD was used alone instead of PTMG, tensile strength of the film was enhanced but elongation at break fell down to 670%. As PCD content increased, tensile strength was enhanced but elongation at break showed a tendency of gradual decrease.

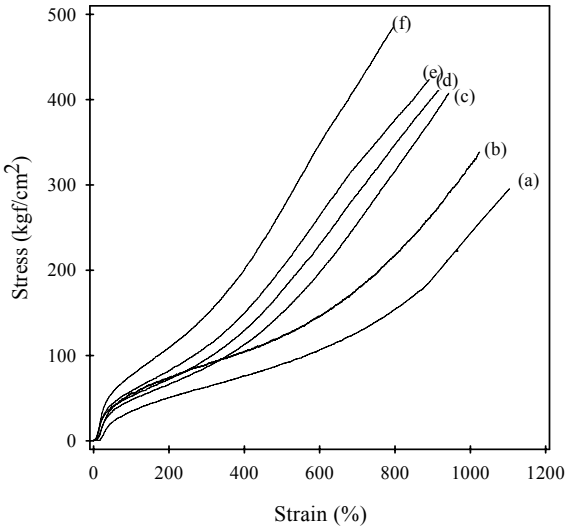

Figure 2. Stress-strain curves of WPU films; PCD/PTMG; (a) 0:100, (b) 20:80, (c) 40:60, (d) 60:40 (e) 80:20, and (f) 100:0.

In this study, PET artificial leathers were impregnated by using WPU that had been synthesized with various ratios of PCD/PTMG content and dyed with a black disperse dye. From the result, it can be confirmed that as PCD content increases, the color fastness becomes enhanced.

4. CONCLUSION

Waterborne polyurethanes (WPUs) based on isophorone diisocyanate (IPDI) and mixed polyols of poly(tetramethylene glycol) (PTMG)/polycarbonate diol (PCD) were synthesized. The changes in mechanical and dyeing properties and alkali resistance of the WPU films according to the polycarbonate (PC) content were analyzed. The tensile strength of the films increased and the elongation at break decreased with increasing PC content in the WPU film.

5. REFERENCES

[1] Y. N. Osin, L. Y. Makhotkina, L. N. Abutalipova, and I. S. Abdullin Agarwal; *Vacuum*, 51, 221-243(1998).