

Preparation and Properties Measurement of 2-hydroxyethyl methacrylate / Water-dispersed polyurethane composites

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Abstract : In this study, 2-hydroxyethyl methacrylate (2-HEMA) was graft synthesized on water-dispersed polyurethane using polytetramethylene ether glycoll (PTMG), and then the film of resin was prepared and the physical properties of polyurethane resin were measured. The mechanical properties of the synthesized polyurethane resin were measured by using FT-IR, UTM, adhesion performance measuring instrument. As a result of tensile strength measurement, the tensile strength of HPUD4 with high 2-HEMA content was increased to 5.05 kgf / mm², the elongation was measured as 285% of the HPUD1 sample not containing 2-HEMA and adhesive strength of HPUD4 sample was measured at 9.1 sec to 635 psi.

Keywords : polyurethane, dispersion, 2-HEMA, graft, PTMG

1. Introduction

Waterborne coatings using natural hardening techniques are gaining interest throughout the industry because they reduce air pollution, reduce the risk of fire, improve industrial health and safety aspects, lower energy consumption and simplify the conditions required for hardening. These features offer advantages such as immediate drying, extensive formulation, economic and energy savings [1-5].

Solvent-based one-part curing resins contain structures that require adjustments in viscosity, rheological behavior and cure rate due to their high viscosity. So it is necessary to use diluted solution.

Most of the diluents used at this time are toxic to the human body and the environment. This problem can be solved by using environmentally friendly water-curable coatings containing a small amount of diluent [6-9].

However, it has been proven that water-based resins are more environmentally friendly than conventional solvent-based coatings, but have defects such as lower curing speed and lower efficiency than solvent-based resins. The water-base coating is known as a problem to be solved that the resistance to water and solvent weaker than the solvent-based coating.

In order to improve the physical properties of this water dispersion system, we have tried to copolymerize 2-hydroxyethyl methacrylate (2-HEMA) with good cross-linking property.

2-HEMA, which is added and reacted in water-dispersed polyurethane synthesis, is a monomer used to prepare polymer

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polyhydroxyethyl methacrylate [10,11]. Usually polymers are hydrophobic but have the property of swelling due to the hydrophilic pendant group of molecules when the polymer is exposed to water so that it is possible to use water based on the physical and chemical structure of the polymer, Absorbing property capable of absorbing moisture[12-15], Because of this property, 2-HEMA is used in the manufacture of soft contact lenses.

Therefore, in this experiment, we used 2-HEMA to compensate the physical properties of the water-dispersed polyurethane, and studied how the physical properties are changed of the resin synthesized by the crosslinking system.

In this study, prepolymer was synthesized by using poly (tetramethylene ether, PTMG) and isophorone diisocyanate (IPDI). Dimethylol propionic acid (DMPA) was used to impart ionic properties to the end of the synthesized prepolymer,

In this study, a prepolymer was synthesized by using poly (tetramethylene ether, PTMG) and isophorone diisocyanate (IPDI), and dimethylol propionic acid(DMPA) was used to impart ionic properties to the prepolymer terminal. 2-Hydroxyethyl methacrylate (2-HEMA) was added to the prepared prepolymer to conduct a graft reaction, followed by neutralization with a tertiary amine to prepare a water-dispersed polyurethane[13-15].

After that, HPUD was analyzed by FT-IR, UTM and adhesion tester to confirm the synthetic reaction structure and physical properties such as tensile strength, elongation and adhesion performance of the film were analyzed.

2. Experiment

2.1.

The polyol used in this study was polytetramethylene ether glycol (PTMG,

molecular weight 2000, Junsei chem.Co.) And aliphatic isoporon diisocyanate (IPDI, Bayer). Dimethylolpropionic acid (DMPA, GEO) was used to impart hydrophilic groups using carboxyl groups, and acetone (BASF) was used to dilute the viscosity of the prepolymer. 2-HEMA(Junsei Chem. Co) was used for the graft reaction, and dibutyltin dilaurate (DBTDL, Aldrich) was used as the catalyst. Triethylamine (TEA, Fluka) was used for neutralization and ethylene diamine (EDA, Fluka) was used for chain extension. Fourier transform infrared spectrophotometer (FT-IR 430, Jascow, U.S.A) was used to analyze the synthesis of the synthesized water-dispersed urethane. Tensile Strength and Elongation Properties UTM (Universal testing machine, Instron Co., U.S.A.) was used for the measurement of physical properties. PosiTest AT-A (DeFelsko, USA) was used to measure the surface adhesion strength of the resin.

2.2. Synthesis method

In this experiment, polyether-based polyol was used as a polyol in the copolymerization reaction with 2-HEMA after synthesizing prepolymer prepared by polyol and isocyanate, as the isocyanate, polymerization was carried out using IPDI. In the synthesis of prepolymer, various physical properties vary greatly depending on the conditions of the reactants. Particularly, the 2-HEMA used in this experiment determines the physical properties such as adhesion strength and flexibility by forming a soft segment of the polyurethane adhesive.

After the synthesis of the prepolymer, the mixture was cooled to 40 °C or lower, neutralized with TEA (triethyl amine), dispersed in water, and EDA was added to extend the chain to complete the synthesis. Table 1 shows the composition of the samples used for the synthesis. The film samples used in the experiment were weighed in an amount of 20 g on a 120 mm glass shaker, air-dried for 12 hours, and thermally dried at 120 °C

Table 1. Polymerization condition of polyurethane dispersion with different 2-HEMA Content

Sample	PTMG(mol)	DMPA(mol)	IPDI(mol)	TEA(mol)	EDA(mol)	2-HMA(mol)
PUD	4.00	0.02	4.00	0.02	0.015	0
HPUD1	3.90	0.02	4.00	0.02	0.015	0.1
HPUD2	3.70	0.02	4.00	0.02	0.015	0.3
HPUD3	3.50	0.02	4.00	0.02	0.015	0.5

for 1 hour to form a film having a width of 50 mm and a length of 100 mm.

3. Results and Discussion

3.1. FT-IR analysis

The reaction structure of the synthesized water-dispersed polyurethane can be confirmed by FT-IR spectrum. Asymmetric C-H stretching peaks were observed at around 2780 cm^{-1} and at $3340\text{ to }3350\text{ cm}^{-1}$, stretching vibration absorption of the urethane group N-H bond is confirmed. The expansion and contraction of the C-O functional group could be confirmed at around 1730 cm^{-1} . It is not possible to confirm an N = C = O absorption peak near 2500 cm^{-1} , so that it can be confirmed that the -NCO- group of the isocyanate participates in all the urethane reaction.

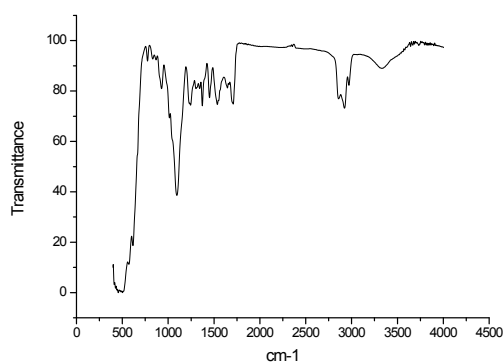


Fig. 1. FT-IR spectra of water dispersion polyurethane.

3.2. Analysis of mechanical properties of samples (tensile strength, elongation, adhesive strength)

Samples prepared for measuring the tensile strength were measured by setting the tensile speed to $100 \pm 20\text{ mm/min}$ by UTM, The elongation of the film was measured by using a measuring machine (UTM) identical to the tensile strength. The measurement method was calculated by dividing the final length change when cut compared to the initial length of the film into the initial length and calculating it as a percentage.

Figure 2 shows the tensile strength of HPUD's with 2-HEMA grafted at different molar ratios.

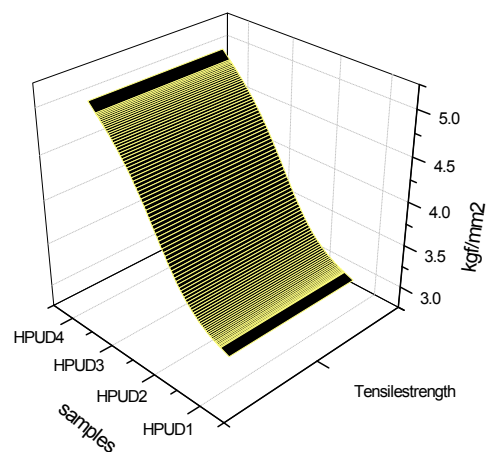


Fig. 2. Tensile strength measurement graph of polyurethane dispersion samples containing 2-HEMA.

The tensile strength of 2-HEMA-free HPUD1 ($3.11\text{ kg}_f/\text{mm}^2$) showed lower tensile

strength than HPUD3(5.05 kg/mm²) with the highest content of grafted 2-HEMA.

Fig. 4 is the result of measuring elongation of HPUD's urethane film. 2-HEMA-free HPUD1 exhibited an elongation of 285% and HPUD3 synthesized with 0.5 mol of 2-HEMA had a 220% elongation reduction.

As a result, as the content of 2-HEMA was increased, the active terminals of the polyurethane polymer chain were reacted with 2-HEMA, resulting in coupling of the polymer chain, and the tensile strength was increased and the elongation was lowered .

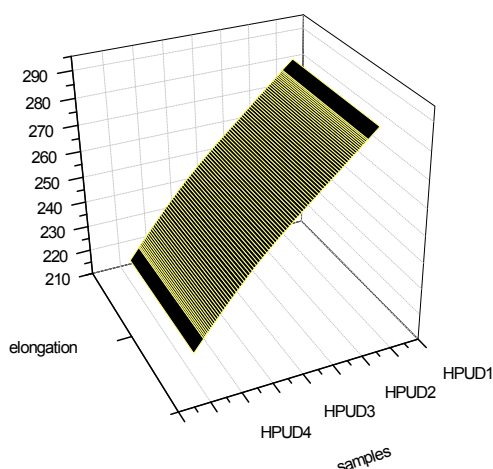


Fig. 3. Elongation measurement graph of 2-HEMA grafted polyurethane dispersion samples.

To measure the adhesive strength of the synthesized polyurethane resin, the PoisiTest machine from Defelsko was used. The Dolly size used was 20 mm. The tensile rate useIn order to measure the adhesive strength, the stainless steel surface was treated with hydrochloric acid, and then the resin synthesized on the metal surface was coated and dried. Then, epoxy adhesive (EP11 HT, Resinlab) was applied to the dolly, and then adhered to the coated surface. After 24 hours, adhesion performance was measured. The measured results are presented in Fig. 4 and Fig. 5. Fig. 5 showed that HPUD3 grafted

with 0.5 mol of 2-HEMA was measured at 9.1 sec 635 psi and peeled at higher pressure than HPUD (7.3 sec 558 psi) without 2-HEMA as shown in Fig. 4.

The above results indicate that the polymer chain bond reacted with 2-HEMA affects the adhesive strength of the resin.

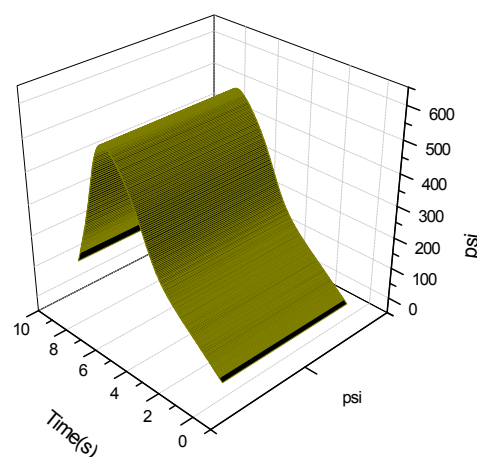


Fig. 4. Results of measurement of adhesive strength of water-dispersed polyurethane without 2-HEMA.

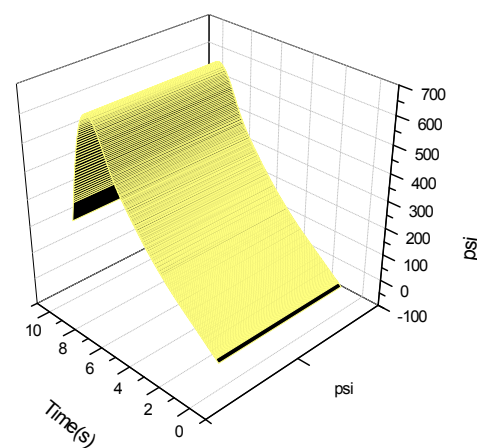


Fig. 5. Results of measurement of adhesive strength of water-dispersed polyurethane containing 0.5 mol of 2-HEMA.

4. Conclusion

For the present study, polytetramethylene ether glycol (PTMG), isophrone diisocyanate (IPDI) and dimethylol propionic acid (DMPA) were reacted as starting materials for synthesis. 2-HEMA was copolymerized with the prepared prepolymer, neutralized with TEA, and dispersed in water to complete HPUD synthesis.

The results were as follows. The tensile strength, elongation, and adhesive strength were measured by preparing HPUD's which were synthesized by varying the content of 2-HEMA.

Tensile Strength Test The tensile strength of HPUD1 without 2-HEMA was the lowest at 3.11 kg_f/mm². As the 2-HEMA graft increased, the tensile strength gradually increased and the tensile strength of HPUD4 which had the highest amount of 2-HEMA, increased to 5.05 kg_f/mm².

Conversely, in the case of elongation, the elongation rate of HPUD1 without 2-HEMA graft was measured to be 285%, and the elongation was decreased to 220% of HPUD4 having the highest content of 2-HEMA.

In the adhesion measurement of the urethane surface hardening degree, HPUD1 was peeled at a pressure of 558 psi at 7.3 seconds and measurement results of HPUD4 containing 2-HEMA were confirmed to be 635 psi at 9.1 sec. It was confirmed that the bonding strength increases with the addition of 2-HEMA. Based on the above results, the conclusions can be drawn as follows.

As the content of 2-HEMA increases, active terminals of the polyurethane polymer chains react with 2-HEMA to cause polymer coupling phenomenon. It is judged that the tensile strength of the naturally cured resin becomes strong, the elongation becomes low, and the peeling pressure of the adhesive increases.

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