수분산 폴리우레탄과 그의 블렌드물의 제조 및 물성

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Preparation and Properties of Waterborne Polyurethanes and Their Blend Films

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1. Introduction

Recently, Waterborne polyurethane(WBPU) have been used for a wide range of commercial applications due to the increasing environmental regulation to reduce low-volatile organic compounds in coating and adhesives materials [1-8]. The WBPU was used in coating industry on fiber at first, and its market is increasing these days. Especially, the Waterborne polyurethane film even is widely used in the field of breathable coating fiber or medical science [9-10]. Water vapor permeability(WVP) is the key property for application to breathable coating fiber.

In this study, Two kinds WBPU (soft segment content : 75%, solid content: 40%) were prepared from $H_{12}MDI/DMPA/EDA/triblock$ polyol(caprolactone_{4.5}-PTMG(Mn=2,000)-caprolactone_{4.5}) and PTMG(Mn=3000). Sodium Chloride(NaCl) as a type of salt has a good solubility. As it added to WBPU it will occupy a small space in WBPU, and when we elute it by using water, we can expect a microvoid in the WBPU film. As a result we can expect to get a WBPU which has an excellant WVP. We added NaCl to Waterborne polyurethane(WBPU) by using homogenizer to enhance its water vapor permeability. The effect of NaCl ratio to DSC curve, dynamic thermal properties, and water vapor permeability of WBPU was investigated.

2. Experimental

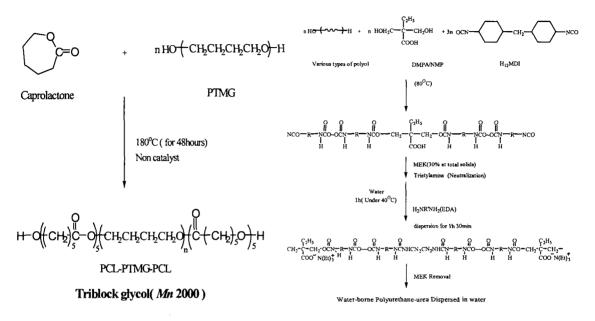
2.1. Materials

Polyoxytetramethylene glycol (PTMG, Mw=2,000, Korea polyol) and ϵ -caprolatone(ϵ -CL, Sigma) were distilled at $95\,^{\circ}\mathrm{C}$ under vacuum(15mmHg) before use. Biscyclohexyl-methane 4,4-diisocynate (H_{12} MDI, Aldrich Chemical), Dimethylol propionic acid (DMPA, Aldrich Chemical), ethylene diamine (EDA, Junsei Chemical), triethylamine (TEA, Junsei Chemical), and N-methyl-2 pyrrolidone(NMP, Junsei Chemical) were used after dehydration with $4\,^{\circ}\mathrm{A}$ molecular sieves for one day. Sodium chloride (NaCl, Junsei Chemical), dibutyl tin dilaurate (DBTDL, Aldrich Chemical), and hardener (Desmodur DA, Bayer) were used without further purification. Distilled water was used as a solvent for polymer blend.

2.2. Synthesis of WBPU

The WBPUs of triblock polyol type and PTMG type were prepared as the preceding way in our laboratory [11]. WBPU was added in various ratio of NaCl (0, 0.01, 0.03, 0.05, 0.1, and 0.3 wt% of WBPU). And it was stirred about 11,000 rpm by homogenizer for 5min at $36\,^{\circ}$ C.

Films were prepared by pouring the aqueous dispersion into a Teflon disk at ambient conditions. The films (typically about 0.5mm thickness) were dried in vacuum at 50°C for 2 days.



Scheme 1. Reaction of ε-Caprolactone and PTMG.

Scheme 2. The preparation process for PU dispersion.

2.3. WBPU/NaCl blend-coated Nylon Fabric

WBPU(containing NaCl)-coated high density Nylon fabrics were formulated from WBPU/NaCl blend, thicker(L75N) and hardener(Desmour, DA). The coating materials were coated to the high density Nylon fabrics using steel bar, and cured 80°C for 3.0 min. The thickness of coated PU layer was about 0.04mm.

2.3. Measurements

FTIR (Nicolet Impact 400D) spectrophotometer was used to identify the structure of polymer blends. For each 32 scans at cm⁻¹ resolution were collected in the transmittance mode. The thermal behavior of polymer blend was examined by using a DSC 220C(Seiko) at a heating rate of 10°C/min under a nitrogen atmosphere. The dynamic mechanical properties of film samples were measured at 5Hz using DMTA MK III(Rheometric scientific) with heating rate of 3°C/min in the temperature range of -80~250°C. The dimension of film was a 8×5×0.5(mm/mm/mm) for DMTA measurement. The water vapor permeability (WVP) was examined by using an evaporation method described in ASTM E 9663-T. The structure and morphology of blend films were observed by Scanning Electron Microscope(SEM) (HITACH S-4200). The measurement of thermal stabilities were performed on Perkin Elimer LTD(U.S.A.)TGA7 in the temperature rage of 25 -700°C at a heating rate of 10°C/min in the presence of nitrogen atmospheres.

3. Result and discussion

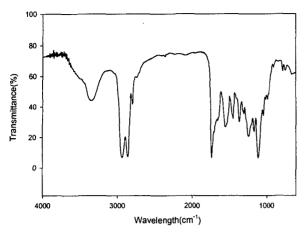


Figure 1. IR-Spectra of WBPU

Figure 1 shows IR spectra of WBPU prepared from triblock polyol. The N=C=O stretching band near 2270cm⁻¹ completely disappeared, indicating the completion of reaction.

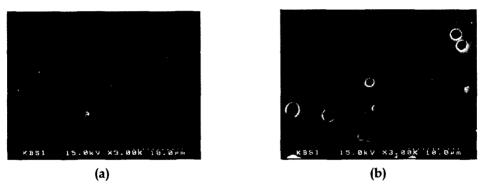


Figure 2. SEM micrographs for WBPU(a) and WBPU/NaCl (b)

Figure 2 shows SEM micrographs for WBPU(a) and WBPU/NaCl(b, 0.01 wt% NaCl). It is indicating the microvoids on the film surface after the elution of NaCl by using water. It may be very helpful to improve water vapor permeability.

4. References

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