투습방수용 수분산 폴리우레탄의 합성 및 특성에 관한 연구 - PEG와 DMPA 함량의 영향 -

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A Study on the Synthesis and Characterization of Waterborne Polyurethanes for Water Vapor Permeable / Waterproof - Effect of PEG and DMPA Content

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1. Introduction

Polyurethane(PU) products are generally used in the automobile, paint, furniture, adhesive, the medical and textile industries. Recently, the increasing acceptance of waterborne polyurethane (WBPU) is motivated by more stringent environmental requirements, such as the reduction of solvent emissions into the atmosphere[1]. The application for textiles includes suede processing, soft-hand processing, wrinkle-free processing, antistatic processing, sizing and adhesives.

The variation in the compositions of the soft and hard segments give PU film a wide range of physical properties. In general, the ester-type polydiol-based PU displays better mechanical properties, whereas the ether type PU displays better hydrolysis resistance, softness, and water-vapor permeability(WVP)[2-6]. To improve the physical properties, a mixed or special type of polyol soft-segment PU was used for imparting PU with specific properties[7-11].

This article was focused on the effects of the PEG and DMPA compositions on the structure and physical properties of synthesized WBPU by using the PCL-PTMG-PCL triblock glycol as the soft-segment. In the synthesis of the PCL-PTMG-PCL triblock glycol from fixed molecular weights of PTMG by end-capped ε-caprolatone(ε-CL), the molecular weight was about 3000[12].

2. Experimental

2-1. Materials

Poly (tetramethylen oxide) glycol(PTMG, Mw= 2,000, Korea Polyol) and ε -caprolatone (ε-CL, Sigma) were distilled at 95℃ under vacuum before use. Biscyclohexylmethane4,4-diisocynate(H_{12}MDI, Aldreich Chemicals), Poly(ethylene glycol(PEG, Mw=400, Korea Polyol), 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 4Å molecular sieves for one week. Dibutyl tin dilaurate(DBTDL, Aldrich Chemical), thickener(L75N, Bayer), and hardener(Desmodur DA, Bayer) were used without further purification.

2-2. Synthesis of Triblock Glycol and Waterborne Polyurethanes

Synthesis of triblock glycol (TBG, (CL)4.5-PTMG(Mw=2000-(CL)4.5, theoretical Mw=3000, measurement Mw=2998) : TBG was synthesized by the reation of the stoichiometric amount of PTMG(Mw=2000, 100g, 0.05mole) and ε-caprolatone(CL, 51g 0.45 mole) under mild stirring (150 rpm) with nitrogen gas atmosphere for 48hrs at 180℃ . Then the reaction mixture was distilled to remove the unreacted component CL in vacuum condition for 2hrs at 150℃. The CL/PTMG mol ratio was about 9. TBG obtained with the yield about 95% was dried in vacuum oven at 100℃for one week. The average molecular weight(Mw=2998) of TBG was determined by titration and its molecular weight(Mw=2998) was almost same as theoretical molecular weight(Mw=3000)

Synthesis of waterborne polyurethane : A 500ml round-bottom,4-necked separable flask with a mechanical stirrer thermometer, condenser with drying tube, and a pipette outlet was used as reactor. Reaction was carried out in a constant temperature oil bath, with ±1℃ precision. TBG, PEG, DMPA, NMP, and DBTDL were charged into the dried flask while stirring the mixture was heated to 80℃for about 30 min., Homogenized mixture were cooled to 45℃, then H_{12}MDI was added. The mixture was heated to 85℃ for about 3hrs to obtain NCO terminated prepolymers. The change of NCO value during the reaction was determined using standard dibuthylamine back titration upon obtaining the theoretical NCO value, the prepolymers were cooled to 50℃, and TEA neutralizing solution was added and stirred 30min while the temperature was maintained at 40℃ while stirring rapidly, demineralized water was added to the solution to foam dispersion EDA solution dissolve in water were then fed to the emulsion for a period of 30 min, and chain extension was carried out for the 2hrs. Waterborne polyurethane was adjusted to solid content about 39-40%.

2-3. Preparation of films and WBPUs coated Nylon fabrics

Preparation of films : Films were prepared by pouring the aqueous dispersion into a Teflon disk at ambient conditions. The films(typically about 0.1mm thick) were dried in vacuum at 50℃ for 3 days and stored in a desicator at room temperature.

Preparation of WBPU coated Nylon fabrics : Coating materials were formulated from WBPU, thickener (L75N, 0.5%) and hardener (Desmodur DA, 5%). The coating materials was coated to Nylon fabrics using steel bar filler, and then cured at 85℃for 3min. The thickness of coated PU layer was about 0.04mm.

2-4. Characterization

Particle size analysis was done using lazer-scattering equipment (Autosizer, Melvern IIC). A few drops of the dispersion were diluted in non-ionized water before the measurement. The viscosity of waterborne polyurethane dispersion was measured at 25℃ using a Brookfield digital viscometer(Model LVDV-II+). FTIR (Nicolet Impact 400D) spectrometer was used to identified the structure of TBG. For each IR spectrometer sample, 32 scans at $4cm^{-1}$ resolution were collected in the trasmittance model. The thermal behavior of TBG was examined by using a DSC 220C (Seiko) at a heating rate of 10℃/min under a nitrogen atmosphere. The water vapor permeability was examined by using an evaporation method described in ASTM E 9663-T

3. Results and Discussion

The sample designation, composition of waterborne polyurethanes prepared in this study are shown in Table 1. The particle size and viscosity of waterborne polyurethane dispersion and the water vapor permeability(WVP) of waterborne polyurethane coated fabrics are shown in Table 2. The particle size of WBPU dispersion increased with increasing PEG content. However, the viscosities of WBPU dispersion decreased a little with increasing DMPA content. Water vapor permeability was increased with increasing PEG content. As the PEG content increased, the water vapor permeability of WBPU-coated Nylon fabrics increased with increased with increasing PEG content (see Table 2). The higher water vapor permeability of the coated fabric containing higher PEG content material might be due to the higher flexibility of soft segment and to the large interface region between various domains.

4. Reference

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Table1. Sample designation and composition(mole ratio) of waterborne polyurethane

Sample designation	$H_{12}MDI$	TBG	DMPA	PEG	EDA	TEA
DE-1	3	0.8	1	0	1.2	1
DE-2	3	0.8	0.7	0.3	1.2	1
DE-3	3	0.8	0.4	0.6	1.2	1
DE-4	3	0.8	0.1	0.9	1.2	1

Table2. Particle size and viscosity of dispersion and watervapor permeability of WBPU-coated fabric.

Sample designation	Particle size (nm)	Viscosity (cps/25℃)	WVP (g/m^2 day)[1]	% [2]
DE-1	95	15	2984	61
DE-2	120	19	3218	65
DE-3	153	27	3532	72
DE-4	190	35	3736	76

1) WVP of Non-coated fabric : 4924
2) % = WVP of coating fabric / WVP of non-coating fabric × 100