가교된 수분산폴리우레탄/폴리비닐알콜 블렌드 필름의 제조 및 특성

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Preparation and Properties of Crosslinked Waterborne Polyurethane/Poly(vinyl alcohol) Blend Films

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1. Introduction

Polymer blending constitutes a most useful method for the improvement or modification of the physicochemical properties of polymeric materials. So polymer blends have gained an increasing interest in both industrial and scientific fields. Some of the polymer blends exhibit unusual properties, unexpected from homopolymers. An important property of a polymer blend is the miscibility of its component, because it affects the mechanical properties, the morphology, its permeability and degradation[1,2]. Numerous investigations regarding the miscibility in multi-component polymer systems have been carried out.

Polyvinyl alcohol, PVA is a crystalline polymer which has biodegradable and water-soluble and it has good film formation ability. And its flexibility and toughness are good, so it is a typical synthetic polymer that used in improving the physical properties by mixing with other materials which has poor physical properties[3-5].

In this study, the WBPU (soft segment content : 75%, solid content : 40%) was prepared from H_{12}MDI/DMPA/EDA/triblock polyol(caprolactone$_{4.5}$-PTMG(Mn=1,000)-caprolactone$_{4.5}$). The WBPU/PVA blends with blend ratios (100/0, 90/10, 75/25, and 50/50) were prepared by solution blending. In the WBPU/PVA blend system, PVA with molecular weights 13,000-23,000 were used. The blend films were crosslinked with glutaraldehyde. The effect of crosslinking on water resistivity, thermal and mechanical properties, morphology, and the water-vapor permeability was investigated.

2. Experimental

2.1. Materials

Polyoxytetramethylene glycol (PTMG, Mw= 2,000, Korea polyol), ε-caprolatone(ε-CL, Sigma), 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), N-methyl-2 pyrrolidone(NMP, Junsei Chemical), polyvinyl alcohol(PVA, Aldrich Chemical, Mw=13,000-23,000), dibutyl tin dilaurate (DBTDL, Aldrich Chemical), hardener (Desmodur DA, Bayer), glutaraldehyde(Junsei Chemical), sulfuric acid, and distilled water were used.

2.2. Preparation and characterization

PVA (Mw=13.000) was dissolved in water: the solid content was 40wt%. Dissolved PVA was blended with WBPU which was solid content 40wt% at room temperature with stirring. Films were prepared by pouring the aqueous dispersion into a Teflon disk at ambient conditions. The films were dried in vacuum at 50℃ for 2 days and stored in a desiccator at room temperature. The blend film was placed in 5% aqueous solution containing glutaraldehyde and 1% sulfuric acid as catalyst. The crosslinking reaction was allowed to proceed at 25-50℃ for various times(0, 5, 10, 30 and 60 min).

FTIR (Nicolet Impact 400D) spectrometer was used to identify the structure of polymer blend. 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℃ /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℃/min in the temperature range of -80~250℃. The dimension of film was a $8\times5\times0.5$(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℃ at a heating rate of 10℃/min in the presence of a nitrogen atmosphere.

3. Result and discussion

The water vapor permeability(WVP) of WBPU/PVA blend coated Nylon fabrics were higher values compared with that of pure WBPU coated Nylon fabric. It was found that WBPU/PVA (blend ratio 75/25) coated fabric has the highest WVP value(3701 g/m^2day). But as increasing PVA contents, the strength and the strain of films were decreased, PVA of blend films was come off. So we prepared PVA of blend films by crosslinking to improve the mechanical properties. And the effect of crosslinking on water resistivity, thermal and mechanical properties, morphology, and the water-vapor permeability was investigated.

4. References

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