

PH2) Properties of Waterborne Polyurethane/Clay Nanocomposites: Effect on Water Vapor Permeability

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1. Introduction

The polymer/clay nanocomposites have attracted much more attention in recent decades because of their unique properties compared to those of the conventional composites. Among those properties are higher strength and modulus, better dimensional and thermal stability, as well as improved barrier property and chemical stability. The polymer/clay nanocomposites can be generally classified into two groups. The intercalated polymer/clay nanocomposites have layered clay dispersed in a polymer matrix with polymer chains inserted into clay layers that retain their lateral order. The exfoliated ones consist of fully delaminated clay platelets dispersed individually in the matrix. Thus, each platelet interacts with the matrix and improves the properties of the nanocomposites more effectively [Wang, 1998]

Waterborne polyurethane (WBPU) is considered as an important alternative material to solvent-based polyurethane for various applications such as coating for wood finishing, glass fiber sizing, automotive topcoats and adhesives due to increasing awareness of health and environmental safety. However, the WBPU is deficient in chemical resistance, thermal resistance, and tensile strength compared to its counterpart solvent-based polyurethane. Many different methods have been employed to overcome these disadvantages of WBPU such as hydrophobic monomers grafted to polyurethane (PU) main chain, the change of the type and content of ionic centers, the adjustment of the ionic neutralization degree, the blending and copolymerization of different polymers, and cross-linking [Lim, Choi and Noh, 2002, Mequanint and Sanderson 2003, Kim and Lee 1996]

The water vapor permeability (WVP) of WBPU coating materials is one of the major challenging issues on many different sectors such as textile, medicine, and biotechnology. With respect to practical applications, the coating materials required high thermal stability, hydrolytic stability, and better mechanical property (tensile

strength and initial modulus). Unfortunately, a few coating materials satisfied the above requirements and also are very scarce due to an unfavorable combinations of price, processibility, and performance. This type of coating materials are often made and used for specialized applications, and are not commonly available commercially.

Recently, the thermal and mechanical properties are improved by making polyurethane clay nanocomposite materials. However, a few reports are found on WBPU/clay nanocomposite in open literature [Kim, Seo and Jeong 2003, Rahman, Yoo, Mi and Kim 2007] In this study, we prepared WBPU/clay nanocomposite coating materials by prepolymer process at various clay contents (0-2 wt%) using organoclay Cloisite 15A. We characterized the surface structure of nanocomposite films by SEM and TEM. The affect of clay content on glass transition temperature and storage modulus was evaluated. We investigated the water resistance, thermal stability and mechanical properties of WBPU/clay nanocomposite films. We also evaluated the WVP of coated nylon fabrics at different temperature (20~80°C) using the prepared WBPU/clay nanocomposite coating materials.

2. Preparation of WBPU/clay nanocomposite dispersions

The WBPU/clay nanocomposite dispersions were prepared by prepolymer mixing process. During preparation, at first PTMG was placed in a four-necked flask equipped with a thermometer, a stirrer, a condenser with a drying tube, an inlet for dry nitrogen, and a heat jacket and was degassed in vacuum at 80°C for 30 min. Clay was mixed with polyol and stirred at 85°C for 3 h. DMPA/NMP (1/1 w/w) was added to the flask, and the mixture was allowed to cool to 40°C under moderate stirring (175~200 rpm). Then, DBTDL (1 drop) and H₁₂MDI were added to the flask, and the reaction continued for 3hours at 85°C. The change of NCO value during reaction was determined with the standard dibutylamine back-titration method (ASTM D 1638). Then, methyl ethyl ketone (MEK, 20 wt%) was added to decrease the viscosity of the reaction mixture. TEA was added to the reaction mixture to neutralize the carboxyl group of the NCO-terminated polyurethane prepolymer. After 30 min of neutralization, distilled water (70 wt%) was added to the reaction mixture with vigorous stirring (1300~1500 rpm). The dispersion was chain-extended by dropping of EDA/H₂O (1/13 w/w) at 40°C for 1 h, and the reaction continued until the NCO peak (2270 cm⁻¹) in the IR spectra had completely disappeared. All of the WBPU/clay nanocomposite dispersions (30 wt% solidcontent) were obtained after evaporation of MEK.

3. Preparation of WBPU/clay nanocomposite films

The WBPU/clay nanocomposite films were prepared by pouring the aqueous dis-

persion on a Teflon disk and dried under the ambient conditions for 48 hours. The films (typically about 0.5 mm thick) were dried in vacuum at 60°C for 1 day and stored in a desiccator at room temperature. The coating materials were formulated from nanocomposite dispersions, thickner (0.5 wt%) and hardener (0.5 wt%). The coating materials were coated onto the nylon fabrics using steel bar and then dried at 100°C for 5 minutes. The thickness of the coated layer was about 0.08 mm.

4. Result and discussion

The sample designation and composition of WBPU/clay nanocomposite is shown in Table 1. The surface structure of a nanocomposite can be observed using TEM images. Figure 1 (A) shows typical images of WBPU/clay nanocomposites. The mixtures of intercalated and exfoliated structures were found with 0.50 wt% and 1.0 wt% clay in WBPU 1 and WBPU 2, respectively. However, the structure with 2 wt% clay (WBPU 3) is different than 0.50 wt% (WBPU 1) and 1.0 wt% (WBPU 2) clay loaded nanocomposites. Some clusters or agglomerated clay particles are observed due to higher clay loaded WBPU/clay nanocomposite.

Table 1. Sample designation and composition of WBPU/clay nanocomposite dispersions.

Sample Designation	Composition (molar ratio)					Clay (Cloisite 15A) (wt%)
	PTMG	DMPA	H ₂ MDI	TEA	EDA	
WBPU 0	2.00	1.10	4.10	1.10	1.00	0.0
WBPU 1	2.00	1.10	4.10	1.10	1.00	0.50
WBPU 2	2.00	1.10	4.10	1.10	1.00	1.00
WBPU 3	2.00	1.10	4.10	1.10	1.00	2.00

TGA is a good method to determine the thermal stability of the WBPU/clay nanocomposite films. The TGA curves (Figure 1B) for all samples indicate that there are two stages of decomposition. The increase of the thermal stability could be attributed to the high thermal stability of the clay and the interaction between the clay particles and the PU-urea matrix. Since the chain motions of polymer molecules in these silicate layers were barred and limited, therefore, thermal stability of the nanocomposites increased. The other probable cause will be the layered silicates make the path longer for escaping of the thermally decomposed volatiles, or in other words clay particles can enhance the thermal stability of the polymer by acting as thermal insulator and mass transport barrier to the volatile products generated during decomposition.

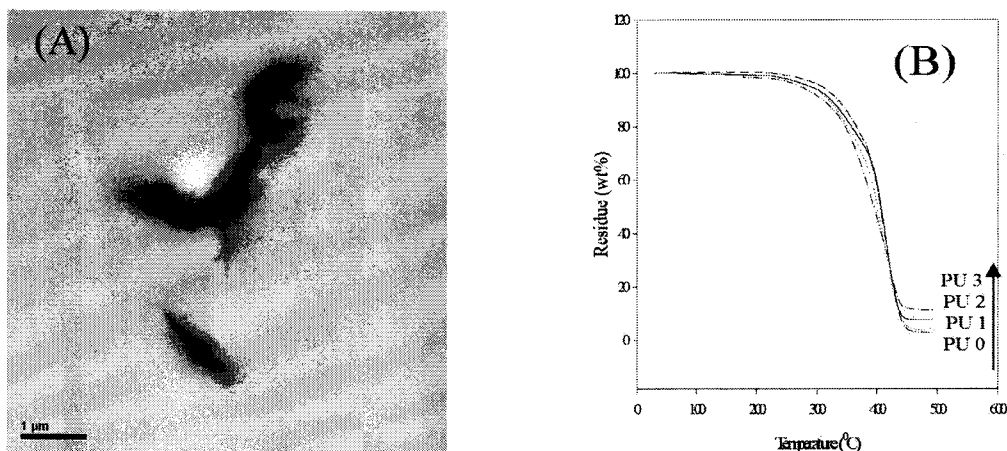


Fig. 1. TEM photographs (A) and TGA (B) of WBPU/clay nanocomposite films.

In Figure 2 the WVP of coated nylon fabrics is shown. The WVP of WBPU/clay nanocomposite coating materials are lower than those for the pristine WBPU coating material. It was found that the WVP of coated nylon fabrics decreased with increasing clay contents. The WVP of this series was decreased in the order: WBPU 0 > WBPU 1 > WBPU 2 > WBPU 3. This result is attributed to the plate-like clays that effectively increase the length of the diffusion pathways and decrease the WVP of coated nylon fabrics. The tight chain packing (confirmed by DMA) of the composite materials also favor to decrease the WVP of coated nylon fabrics. The WVP of coated nylon fabrics was increased with increasing temperature. The polymer chain is changed to loosely bind by increasing temperature leads to the significant increase in diffusion and permeation of small penetrants through the WBPU coating nylon fabrics. However, the low increasing rate of WVP was found with higher clay content.

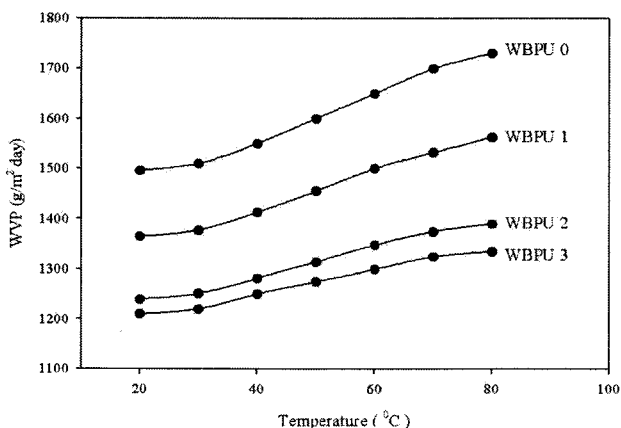


Fig. 2. Water vapor permeability as a function of temperature of cated nylon fabrics using WBPU/clay nanocomposite coating material.

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