EFFECT OF CLAY CONTENT ON THE OXYGEN BARRIER AND MECHANICAL PROPERTIES OF URETHANE ACRYLATE/CLAY COMPOSITES FILM

Eun kyoung Kim, Jae Young Kim, Hyun Jin Yoon, Seung Yong Jeong, Sangkug Lee, Gyo jic Shin, Kyung Ho Choi

Center for Green Materials Technology, Korea Institute of Industrial Technology, 35-3, Hongcheon-ri, Ipjang-myeon, Seobukgu, Cheonan-si, Chungnam-do 330-825, Republic of Korea

imkek@kitech.re.kr, soo@kitech.re.kr, hj_yoon@kitech.re.kr, jsy2837@kitech.re.kr, skdlee@kitech.re.kr, gyshin@kitech.re.kr, khchoi@kitech.re.kr

Abstract

Urethane acrylate (UA)/clay nanocomposites prepared by solution synthesis with various organically modified clays (C10A, C30B, C8, C18). We investigated that dispersion states affected thermal conductivity of UA/clay nanocomposites and confirmed their mechanical properties and thermal stability. UA/C10A, UA/30B nanocomposites assumed intercalated or exfoliated structure depending on the clay content. UA/C8, UA/C18 nanocomposites were showed exfoliated structure throughout d-spacing change regardless of clay contents. We observed the enhancement of thermal stability and mechanical property by adding clay, also found the decreased oxygen permeability due to oxygen barrier effects induced exfoliated structure. These results indicated that the d-space of all samples increased with increasing contents of clay and the oxygen permeability and mechanical properties sensitively depend on the clay contents. These nanocomposites are promising for application in transparent gas barrier coatings.

Keywords: Nanoclay, Exfoliation, Thermal stability, Mechanical property, oxygen permeability

1. INTRODUCTION

In recent years, nanocomposites have been attracted to be the most potential hybrid-organic materials because of theirs have several advantages. They usually were exhibited superior properties by the loading small amounts of inorganic nanoparticles. Particularly, organoclay can improve miscibility with polymer or monomer and can strongly influence the resulting morphologies and properties of nanocomposites induced from the strong interfacial contact between the polymer and clay layers [1-3]. Nanoclay also is widely known that has larger surface area and aspect ratios and well-dispersed particles within the polymer. Moreover, this kind of nanocomposite usually exhibits decreased gas permeability [4-6]. The improvement in barrier performance has been presented for many polymer systems due to the high-aspect ratio characteristics of clay monolayers.

In this study, we prepared a series of UA/clay nanocomposites with intercalated or exfoliated structure and investigated their properties with respect to their structures and morphologies with various organoclays. Through these works, we confirmed the enhancement of thermal and mechanical properties of UA/clay nanocomposites and observed the effects of nanoclay dispersion in polymer matrix on oxygen barrier performance of UA/clay nanocomposites. Furthermore, we examined the possibility as transparent barrier material to gas.
2. EXPERIMENTALS

2.1. Materials
Sodium montmorillonite nanoclay named Cloisite® Na⁺, with cation exchange capacity (CEC) was 92.6 meq/100 g was from Southern Clay Products, Inc., USA. Octylamine, octadecylamine (Aldrich Chemical Co. Inc.), were used as organic modifiers. N, N-Dimethylformamide (DMF) was used as a primary dispersion solvent (Aldrich Chemical Co. Inc.). Urethane acrylic UV binder was from Omnichem Co. Ltd., Korea.

2.2. Preparation of organoclay
Organoclay was prepared by cation exchange reactions between pristine montmorillonite (Cloisite® Na⁺) and excess organic modifier. 6g pristine montmorillonite was dispersed in 300 ml distilled water and stirred for 12 h at 80 °C. Octylamine (5.4 mmol; 1.05 g), octadecylamine (5.4 mmol; 2.19 g) were dissolved into 150 ml of distilled water at 80 °C for 12 hr. And HCl (1.2 ml) dropped into the organic modifier solution to quaternize the amine group at 80 °C for 2 hr. Then, it was poured into the pristine montmorillonite suspension and stirred for 24 h at 80 °C. The cation exchanged clay was washed several times with hot distilled water and checked with AgNO₃ for residue Cl⁻. It was completely dried using a freeze drying for 24 hr to yield the final organoclays. These are labeled C8 and C18 according to the organic modifier.

2.3. Preparation of UA/clay nanocomposites
Organoclays were pre-dried in vacuum oven at 80 °C for 24 hr. A series of clay (C8 and C18) were dispersed in DMF and applied for sonication for 30 min. The suspension was poured into urethane acrylic UV binder with clay contents 1, 2, 3, and 5 wt%. Then, the UA/clay nanocomposites were dispersed using sonication for 60 min. and coated onto the PET film using a micrometer applicator (KEEPAE CO. Ltd comate™ 3000VM) and baked at 80 °C for 1 min and exposed to UV light for 2 min to result in the UA/ clay nanocomposites.

2.4. Characterization
Change of the d-spacing were determined from X-ray diffraction (XRD), using a D8 Discover with Bruker AXS GADDS equipped with CuKa generator (λ= 0.154178 nm). Each sample was scanned from 2° to 8° at 2°/min. Transmission electron microscope (TEM, CARL ZEISS Libra 200FE, acceleration voltage 200 kV) was used to observe the morphologies of the clay layers: specimens were prepared by using a CARL ZEISS 1540 EsB. Thermo gravimetric analysis (TGA) has been usually used to evaluate the thermal stability of polymer and polymer/clay nanocomposites. Thermal gravimetric analyses were conducted on NETZSCH TG209F3 heating from room temperature to 600 °C at 20 °C/min under the air atmosphere. Mechanical testing was performed according to the ASTM D412. All the results were measured by a Zwick Z005TN testing machine with the average of three measurements. OTR testing was performed by MOCON (Minneapolis, MN) in accordance with ASTM D-3985 using an Oxtran 2/21 ML instrument at 23 °C and 0 % or 100 % RH.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction patterns
The WXRD patterns of UA/clay nanocomposites are shown in Figure 1. In case of UA/C10A, diffraction peak is low angle shifted from 4.54° (d= 1.95 nm) to 2.38° (d= 3.70 nm) for UA/C10A 1 wt%. Similarly, the peak of UA/C10A 2 wt% appeared at 2.34° (d= 3.77 nm), 4.98 ° (d= 1.77 nm) weakly. The XRD patterns of the UA/C10A 3, 5 wt% showed a strong diffraction peak with high intensity at 2.37° (d= 3.73 nm), 2.45° (d= 3.61 nm), and a broad peak with low intensity at 4.92° (d= 1.80 nm), 4.95° (d= 1.78 nm). It is implying that some of the clay layers dispersed not enough and have the intercalated structure. UA/30B nanocomposites did not
show a diffraction patterns up to 2 wt% of clay contents. But the weak intensity peak of UA/C30B 3 wt% appeared at 4.88° ($d = 1.81$ nm). In case of UA/C30B 5 wt%, the diffraction peak showed at $2\theta = 2.27°$ ($d = 3.89$ nm) strongly and at 4.83° ($d = 1.83$ nm) weakly. Similarly UA/C10A, clay layers agglomerated together and only intercalated in polymer matrix over clay content 3wt%.

In case of UA/C8 and UA/C18 nanocomposites, regardless of clay content increasing, there are no obvious diffraction peaks, indicating that the clay layers were disordered and fully exfoliated in polymer matrix. These results indicate that the organically modified clay nanocomposites (C8, C18) are fully exfoliated structure than commercial clay nanocomposites (C10A, C30B) depending on the clay contents.

| Fig.1. XRD patterns of UA/ clay nanocomposites (a)UA/C10A, (b)UA/C30B, (c)UA/C8, (d)UA/C18 nanocomposites |

3-2. Transmission electron microscope

TEM micrographs of UA/clay nanocomposites (3 wt%) were recorded at both higher and lower magnification (Fig. 2). The low magnification gets to study the dispersion state of clay in polymer and higher magnification gets to observe the structure of clay layers.

UA/C10A nanocomposites had intercalated structure of agglomerated ~20 nm thick clay layers. Similarly, UA/C30B nanocomposites show slightly more dispersed ~20nm thick sheets of clay (Fig. 2 (a), (b)). On the other hands, the image of UA/C8, UA/C18 nanocomposites is shown in Fig. 2 (c), (d). The sheets of the clay are completely disordered about 5 nm thickness and well dispersed in polymer matrix. This result clearly confirms that the structure of UA/C10A, UA/C30B nanocomposites is intercalated structure, but that of UA/C8, UA/C18 nanocomposites is completely exfoliated structure corresponding with the XRD results [7, 15].
3-3. Thermal stability

The TGA curves of the various UA/clay nanocomposites are shown in Figure 3. The onset decomposition temperature of UA/clay nanocomposites is higher about 30 °C than the pure UA binder, indicating that the enhancement of thermal stability of UA by adding clay. The onset decomposition temperature of various UA/clay nanocomposites was ranked: UA binder < UA/C10A < UA/C8 < UA/C30B < UA/C18. This decomposition mechanism relates to some interaction between the clay layers and the UA binder. The clay layers act as superior insulation and mass transport barrier to the volatile products generated during decomposition, which enhances the overall thermal stability of the system, as well as assist in the formation of char after thermal decomposition. The strong interfacial interaction restricted mobility of polymer chain and hindered their scission [7-10].

3-4. Mechanical property

Figure 4 represented tensile strength UA/clay nanocomposites with various types of clay. All the UA/clay nanocomposites showed steadily increased tensile strength with increasing the clay loading. Especially, for UA/C8, tensile strength increased from 1016 to 1177 Mpa with clay loading and showed the best reinforcement of all of case, consistent with XRD, TEM results that showed good dispersion state of UA/C8 nanocomposites. The large interfacial interaction between clay platelet and urethane acrylate matrix leads to
significant improvement in tensile strength, implying that the increase of tensile strength is depended mainly on the good dispersion state [2, 11-13]. Furthermore, some researchers reported about percolation threshold, critical clay contents above certain contents. As already discussed clay layers begin to agglomerate together and dispersed larger scale in polymer matrix above percolation threshold. This result is generally known that poor dispersion state leads to deteriorate mechanical properties due to decreased interfacial interaction [10, 14, 15].

3.5. Oxygen permeability

The plot of oxygen permeability versus clay content in UA/C8 nanocomposites is shown in Figure 10. We observed that oxygen permeability decrease with increase of clay content from 416 cc / m² day for pure UA binder to 170 cc / m² day for UA/C8 5wt% almost 59%. Especially, UA/C8 1wt% showed significant decrease of oxygen permeability. And this indicates that have sufficient tortuous path and barrier effect just small amount of clay loading. The oxygen permeability observed similar level with UA/C8 1wt% and 5wt% and saturated over 5wt%, probably. We assumed that oxygen permeability depended on aspect ratio of clay layers. Highest aspect ratio of individual clay layers induced their exfoliated structure have more tortuous path to limit the migration of oxygen molecule, thus, improved barrier effect on gas, moisture. Above mentioned, highest aspect ratio is strong interfacial interaction between individual clay layers and polymer, thus leads to reduction of oxygen permeability.

![Bar graph showing oxygen permeability vs clay concentration](image)

**Fig. 5** Oxygen permeability as a function of clay concentration for the nanocomposite films.

4. CONCLUSION

Various UA/clay nanocomposites were prepared and the effects of clay dispersion on oxygen barrier were measured. Organoclays were synthesized to increase miscibility between the clay layers and the polymer through ion-exchange reactions (C8 and C18). XRD and TEM demonstrated that nanocomposites UA/C10A and UA/C30B could show intercalated or exfoliated structures and that UA/C8 and UA/C18 nanocomposites showed fully exfoliated structures, implying that C8 and C18 were better dispersed in the urethane acrylate matrix than C10A or C30B. All the nanocomposites decomposed at ca. 30 °C above pristine UA, indicating that the added clay improved thermal stability. The composites' tensile strengths improved with increasing clay content because of strong interfacial interactions between the clay layers and the polymer. The oxygen permeability reduced with increasing clay content because the exfoliated clay layers acted as barrier materials and provided a oxygen barrier effect. The oxygen permeability of composites UA/C8 and UA/C18 showed much greater decreases than those of UA/C10A or UA/C30B due to the exfoliated clay structures. UA clay nanocomposites were shown to have enhanced thermal and mechanical properties, good optical properties and reduced oxygen permeability, making them suitable for use as transparent barrier material due to the oxygen barrier effects of the clay layers.
REFERENCE