

실란유기화제를 이용한 에폭시/클레이 나노복합재료의 기계적 계면 물성 향상

박수진* · 서동일 · 이재락

Improvement of Mechanical Interfacial Properties of Epoxy/Clay Nanocomposites Using Silane Intercalant

Soo-Jin Park*, Dong-Il Seo, and Jae-Rock Lee

KEY WORDS : silane intercalant, mechanical interfacial properties, epoxy resin, clay, nanocomposites

ABSTRACT

In this work, the Na⁺-MMT has organically modified with silane intercalant to prepare the polymer/clay nanocomposites. The pH, X-ray diffraction (XRD), and contact angles were used to analyze the surface properties of clay and the exfoliation phenomenon of clay interlayer. The mechanical interfacial properties of epoxy/clay nanocomposites were investigated by three-point bending test. From the experimental results, the surface modification made by silane intercalant on clay surface leads to an increase of distance of silicate layers, surface acid value, and electron acceptor parameter of organoclay. The treatments are also necessary and useful for epoxy to intercalate into the interlayer by interacting of electron donor-accepter between basic epoxy and clay surface. The mechanical interfacial properties of the nanocomposites was improved by the presence of dispersed clay nanolayer containing low content of organoclay in comparison with the conventional, which increase the interfacial adhesion between dispersed clay and epoxy resins.

1. INTRODUCTION

Hybrid organic-inorganic composites typically exhibit mechanical properties superior to those of their separate components. To optimize the performance of these materials, it is usually desirable to disperse the inorganic components in the organic matrix on a nanometer length scale.^{1,2}

Generally, inorganic materials have neither good interaction with organic polymers to achieve good dispersion nor adequate adhesion. Ion exchange of the Na⁺ or Ca²⁺ gallery cations in the pristine mineral has been commonly used to achieve a better interaction of clay surface to a polymeric matrix. Alkylammonium ions

are chosen to disperse layered silicates that can be broken down into nanoscale building blocks in polymer matrix. Because it leads to a favor of the formation of nanocomposites and to exfoliate the interlayer of clay by several researchers.^{3,4} However, it isn't well known whether the physical bonding between clay interlayer and matrix is increased by surface modification.

In addition, the use of coupling agents improves the interfacial adhesion and hence the resulting mechanical properties of the composites. When silane coupling agents are introduced onto the layered silicates in the composites, two interfaces exist between clay surface and silane coupling agents, and the interface between silane coupling agents and polymer matrix. At the interface between the clay surface and silane coupling agents, the hydroxyl groups of silanes and those of clay surface can react with each other through siloxane bonding or hydrogen bonding. Therefore, the interfacial adhesion can be promoted by this mechanism, which

*Advanced Material Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon 305-600, Korea

shows the adsorption process of the silane coupling agents onto the clay surface.^{5,6}

In this work, the smectitic clay is organically modified with short-length silane intercalant to prepare the polymer/clay nanocomposites. We propose a simple approach for the surface energetics and mechanical interfacial properties of the exfoliated epoxy/clay nanocomposites studied.

2. EXPERIMENTAL

Materials and Sample Preparation

The Na⁺-montmorillonite used in this study was provided by Southern clay Co. (namely MMT). The epoxy resin was used the diglycidyl ether of bisphenol A (YD-128 supplied by Kukdo Chem. Co. of Korea. Epoxide equivalent weight of epoxy resin was 185-190 g.eq-1 and the density was 1.16 g.cm-3 at 25 °C. The 4,4'-diamino diphenyl methane (DDM) was used to a curing agent for epoxy resin. The intercalant was used by synthesizing with amino propyl triethoxy silane (APS), amino ethyl amino propyl triethoxy (AAPS) and hydrochloric acid.

Twenty grams of MMT was dispersed into 500 ml of distilled water at 80 °C. Silane intercalant was prepared by mixing 8.85g of APS and 8.9g of AAPS with 3.55 ml of concentrated hydrochloric acid in 100 ml of distilled water. This solution was poured in the hot MMT/water solution and stirred vigorously for 1 h at 80 °C. A white precipitation formed was separated by centrifuge and washed in distilled water until no chloride was detected in the filtrate by one drop of 0.1 N AgNO₃ solutions. The resulting materials were dried in a convection oven at 80 °C. The dried organic clay was ground with a freezer/mill. The collected powder of organic clay less than 53 μm using a sieve was applied to characterize.

The epoxy resin was mixed with the desired amount of organophilic clay. The modified clay (less than 53 μm) was dispersed uniformly in epoxy monomer at 80 °C for 1 h. Then, curing agent was added into the epoxy/clay hybrid and mixed thoroughly by stirring. The mixtures were then degassed to remove bubbles before they were cast into a mold. The samples were cured with DDM for 3 h at 80 °C.

Characterization and Measurement

The pH of the samples was measured with ASTM D3838. About 0.5g of MK or organoclay was added to 20ml of distilled water, the mixture was shaken for 12 h, and the pH of each sample was measured after filtration. The acid-base values on the surface functional groups of the samples were determined by Boehms titration method. In the case of acid value, about 1.0 g of the samples was added to 100 ml of 0.1N NaOH solution and mixture was shaken for 24 h. The solution was the filtered through a membrane filter and titrated with 0.1N HCl solution. Likewise, the base value was determined

by converse titration.

XRD patterns of these samples obtained with a Rigaku Model D/MAX-III B diffractometer equipped with a rotation anode and CuKα radiation (λ = 0.15418 nm). Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. About 5 μl of wetting liquids is used for each measurement at 20 °C. The testing liquids used were deionized water, diiodomethane, and ethylene glycol.

3. RESULTS AND DISCUSSION

Surface Properties

Table 1 shows the experiment surface properties of pristine MMT and organically modified MMT by APS and AAPS. It can be seen that the treatments largely influence on pH and acid-base values of the clays studied, resulting in increasing the Boehms acid value or decreasing base value. The results of treatment show that an acid value of the modified organoclay is higher than that of as-received MMT due to an increase of cation groups on clay surface or a reaction of OH groups at clay surface.

Table 1. Results of pH and acid-base values of the pristine clay and the modified organoclay.

	pH	Acid value (meq/g)	Base value (meq/g)
Na-MMT	10.20	60	230
APS-MMT	8.75	100	110
AAPS-MMT	8.50	160	60

Synthesis of epoxy/clay nanocomposites

Nanocomposites possess superior properties than the conventional microcomposites due to maximizing the interfacial adhesion because of their nanometer-sized characteristics. Therefore, dispersion of inorganic additives in matrix makes an important role on properties of nanocomposites.

Fig. 1 shows XRD patterns for pristine MMT and organically modified clay to investigate a degree of exfoliation by the surface treatment. The interlamellar spacing of the clay, corresponding to the (001) plane peak, increases from 12.01 Å (2θ = 7.36) for the untreated clay to 18.02 Å (2θ = 4.91) and 18.42 Å (2θ = 4.80) for the organoclay. The results show that the short-length silane intercalant allows for the matrix to intercalate between the layers during the surface treatment process, adopting a lateral monolayer structure or a perpendicular orientation.^{7,8} There are no characteristic peaks for epoxy/organoclay nanocomposites contained with 4 wt% of organoclay. This result indicates that silicate layers have been

completely exfoliated and formed a nanometer-scale exfoliated composite.

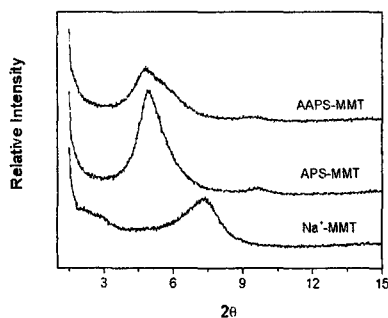


Fig. 1 X-ray diffraction patterns of the pristine clay (MMT), APS-MMT, and AAPS-MMT.

Contact angle measurements

To investigate an effect of surface treatment on intercalation of epoxy resin, changes of the surface free energy of pristine clay and organoclay were determined by contact angle measurements. Fowkes and van Oss suggested that the following equation is obtained:^{9,10}

$$\gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_s^L \cdot \gamma_L^L} + \sqrt{\gamma_s^+ \cdot \gamma_L^-} + \sqrt{\gamma_s^- \cdot \gamma_L^+}\right) \quad (1)$$

where γ_L is surface free energy of liquid and θ is contact angle. γ_s^+ , γ_s^- and γ_s^L are Lewis acid and base parameters of the specific polar component and London dispersive component of surface free energy of solid, respectively.

Values of surface free energy of the pristine clay and organoclay are obtained from Eq. (1) in Fig. 2. The experimental results show that the nonpolar component of organoclay is increased than that of pristine clay. Also, the polar component of organoclay compared with pristine clay is slightly increased. This is resulted that surface treatment by silane intercalant can be attributed to a rising and falling of γ_s^+ and γ_s^- , respectively, resulting in increasing of the interfacial properties between matrix and clay interlayer. Moreover, the results indicate that organically modification is necessary and useful for basic epoxy to intercalate in the clay interlayer by interacting of electron donor-accepter between basic epoxy and clay surface.¹¹

Mechanical interfacial properties

For the epoxy/clay nanocomposites, the mechanical interfacial properties can be measured by a three-point bending test for the critical stress intensity factor (K_{IC}) according to ASTM E 399. For a single edge notched (SEN) beam fracture toughness test, the value of K_{IC} is calculated as follows:^{12,13}

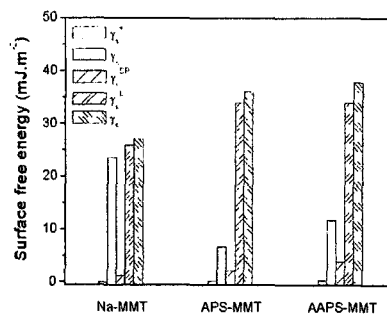


Fig. 2 Surface free energies of pristine clay (MMT) and organoclay using a three-liquid acid-base method.

$$K_{IC} = \frac{PS}{BW^{3/2}} f(a/W) \quad (2)$$

where P (kN) is the rupture force, S (cm) the span between the supports, and W (cm) and B (cm) the specimen width and thickness, respectively.

Fig. 3 shows that values of K_{IC} in epoxy/organoclay nanocomposites dispersed with various organoclay. It is observed that fracture toughness of epoxy/organoclay nanocomposites superior to pure epoxy or conventional composites. The results show that nanoscale organoclay is well dispersed in a matrix on the composites containing lower content of organoclay, resulting in presence of siloxane bonding, hydrogen bonding, and an improving of interfacial interaction between basic matrix and clay surface. However, the mechanical interfacial properties of the epoxy/AAPS-MMT composites decrease slightly due to presence of poorly exfoliated organoclay.

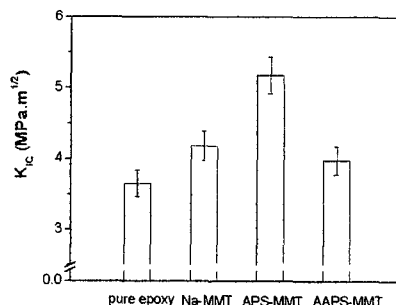


Fig. 3 Evolution of K_{IC} in epoxy/organoclay nanocomposites dispersed with various organoclay.

4. CONCLUSION

The Na^+ -MMT has organically modified with silane intercalant to prepare the polymer/clay nanocomposites.

The surface modification by silane intercalant on clay surface leads to an increase of distance of silicate layers, surface acid value, and electron acceptor parameter of organoclay. The treatments are necessary and useful for epoxy to intercalate into the interlayer by interacting of electric donor-accepter between basic epoxy and clay surface. The mechanical interfacial properties of the nanocomposites is improved by the presence of dispersed clay nanolayer containing low content of organoclay in comparison with the conventional, which increase the interfacial adhesion between dispersed clay and epoxy resins.

REFERENCES

- 1) Vaia, R. A., Jandt, K. D., Kramer, E. J., and Giannelis, E. P., *Chem. Mater.*, Vol. 8, 1996, pp. 2628.
- 2) H. Shi, T., Lan, and T. J., Pinnavaia, *Chem. Mater.* Vol. 8, 1996, pp. 1584.
- 3) Yucai, K., Jiankun, L., Xiaosu, Y., Jian, Z., and Zongneng, Q., *J. Appl. Polym. Sci.*, Vol. 78, 2000, pp. 808.
- 4) Kornmann, X., Lindberg, H., and Berglund, L. A., *Polymer*, Vol. 42, 2001, pp. 1303.
- 5) Ishida, H. and Koenig, J. L., *Polym. Eng. Sci.*, Vol. 18, 1978, pp. 128.
- 6) Park, S. J., Jin, J. S., and Lee, J. R., *J. Adhesion Sci. Technol.*, Vol. 14, 2000, pp. 1677.
- 7) Lan, T., Kaviratna, P. D., and Pinnavaia, T. J., *J. Phys. Chem. Solids*, Vol. 57, 1996, pp. 1005.
- 8) Alexandre, M. and Dubois, P., *Mater. Sci. Eng.*, Vol. 28, 2000, pp. 1.
- 9) Fowkes, F. M., *J. Phys. Chem.*, Vol. 66, 1962, pp. 382.
- 10) van Oss, C. J., Ju, L., Chaudhury, M. K., and Good, R. J., *J. Colloid Interface Sci.*, Vol. 128, 1989, pp. 315.
- 11) Park, S. J., and Donnet, J. B., *J. Colloid. Interface Sci.*, Vol. 206, 1998, pp. 29.
- 12) Chen, M. C., Hourston, D. J., and Sun, W. B., *Eur. Polym. J.*, Vol. 31, 1995, pp. 199.
- 13) Park, S. J., Seo, M. K., and Lee, J. R., *Polym. Sci.: Part A: Polym. Chem.*, Vol. 38, 2000, pp. 2945.