

## Interfacial Characteristics of Epoxy Composites Filled with $\gamma$ -APS Treated Natural Zeolite

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### $\gamma$ -APS로 표면처리된 천연 제올라이트/에폭시 복합재료의 계면특성

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#### 요약

$\gamma$ -APS ( $\gamma$ -aminopropyltriethoxysilane)로 표면처리된 천연제올라이트와 에폭시 수지 복합재료의 표면 자유 에너지, 인장강도 및 계면 모폴로지에 대해 연구하였다. 표면처리하지 않은 천연제올라이트의 표면 자유에너지 성분 중에서 무극성 성분인 Lifshitz-van der Waals 성분,  $\gamma_{SV}^{LW}$ 는 19.22 mJ/m<sup>2</sup>이었고, 극성 성분인 Lewis acid-base 성분,  $\gamma_{SV}^{AB}$ 는 15.27 mJ/m<sup>2</sup>이었다.  $\gamma$ -APS의 처리농도가 증가함에 따라  $\gamma_{SV}^{LW}$  값은 증가하였지만  $\gamma_{SV}^{AB}$ 는 감소하였으며, 이는  $\gamma$ -APS의 소수성 성분인 알킬기의 영향이 친수성 기인 아민이나 수산기의 영향보다 커지기 때문이다. 인장강도와 Young율은  $\gamma$ -APS 처리에 의해 개선되었으며, SEM 분석에 의해 계면특성이 향상되었음을 확인하였다.

#### ABSTRACT

Epoxy composites filled with natural zeolite was prepared to investigate the effects of silane coupling agent,  $\gamma$ -APS ( $\gamma$ -aminopropyltriethoxysilane) on the surface free energy, tensile properties and interfacial morphology. The value of Lifshitz-van der Waals component,  $\gamma_{SV}^{LW}$  for apolar was 19.22 mJ/m<sup>2</sup> and increased, while that of Lewis acid-base component,  $\gamma_{SV}^{AB}$  for polar was 15.27 mJ/m<sup>2</sup> and decreased with the increasing content of  $\gamma$ -APS treatment. It is due that the surface of the zeolite is more coated by hydrophobic alkyl group than hydrophilic amine or hydroxyl groups. The tensile strength and Young's modulus of epoxy system were improved by the treatment with  $\gamma$ -APS due to the strong interfacial bonding, which was confirmed by SEM.

**KEYWORDS : SURFACE FREE ENERGY, EPOXY, NATURAL ZEOLITE, SILANE COUPLING AGENT, INTERFACE**

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## INTRODUCTION

Many polymer composites filled with inorganic materials have been studied to improve their properties in various applications, such as polymer composites, paints, cosmetics, etc.,<sup>(1-5)</sup> The properties of them are dependent not only upon the each characteristics of the polymer and the filler but also upon the characteristics of the interface. However, those of them are so dissimilar that repulsion acts on the interface between the organic polymer and the inorganic filler. Therefore, when external force is given to the polymer composite, the stress concentrate on the most weak point, that is the interface between organic and inorganic materials, from which crack initiates to break up the bulk composites. So, the interface characteristics are much more important especially, and many researchers have investigated to characterize the dissimilar materials and they find that the surface of them are classified into two categories: one is hydrophilic whose surface free energy is high and the other is hydrophobic whose surface free energy is low.<sup>(6-8)</sup> To facilitate the adhesion of two different materials, the apolar surface should be modified into a high-energy polar surface or the polar surface should be changed to apolar surface by a number of modifying methods. Generally, the hydrophilic surface of inorganic fillers such as clay minerals, zeolites, alumina, silica, etc. are treated with coupling agents in order to decrease the surface energy of them.

In this system, natural zeolite as an inorganic filler is treated with silane coupling agent with amine end-group in order to give them similarity of surface characteristics, and the surface energy, tensile properties and morphology of the

interface were investigated.

To get surface free energy, the contact angle method as shown in Figure 1 is used with the equilibrium among the interfacial tensions of solid/liquid  $\gamma_{SL}$ , solid/vapor  $\gamma_{SV}$  and liquid/vapor  $\gamma_{LV}$  expressed by the following Young's equation<sup>(9-12)</sup>:

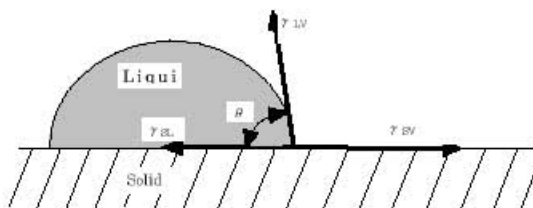
$$\gamma_{LV} \cos \theta = \gamma_{SL} - \gamma_{SV} \quad (1)$$

Where,  $\theta$  is contact angle. However, the contact angle for a particle can't be measured, so column wicking method is used by determining the rate of penetration of probe liquids(usually methylene iodide, water and formamide) through the packed beds of the powder, using the following Washburn's equation,<sup>(10,11)</sup>

$$h^2 = \frac{t R \gamma_{LV} \cos \theta}{2 \eta} \quad (2)$$

where,  $h$  (cm) is the penetrated distance of the probe liquid in a selected time  $t$  (sec),  $R$  (cm) is the effective interstitial pore radius between the packed particles in column and  $\eta$  (cP) is the viscosity of the probe liquid.

It has been well-known that the surface free energy of a solid,  $\gamma_{SV}$  is consisted of Lifshitz-van der Waals component,  $\gamma_{SV}^{LW}$  for apolar and the Lewis acid-base component,  $\gamma_{SV}^{AB}$  for polar. The Lewis acid component,  $\gamma_{SV}^{\oplus}$  is acted as an electron acceptor site and the Lewis base compo-



**Figure 1.** Contact angles between liquid and solid surface.

nent,  $\gamma_{SV}^{\ominus}$  is electron donor site.<sup>(9,12)</sup> To get the values of these components, the values of the probe liquids in Table 2 were applied to Eq.3.<sup>(9)</sup> Methylene iodide was used as a probe liquid to determine the  $\gamma_{SV}^{LW}$  component of the zeolite surface free energy and water and formamide were for  $\gamma_{SV}^{\oplus}$  and  $\gamma_{SV}^{\ominus}$  components.

$$\gamma_{LV}(1 + \cos \theta) = 2(\sqrt{\gamma_{SV}^{LW} \cdot \gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{\oplus} \cdot \gamma_{LV}^{\oplus}} + \sqrt{\gamma_{SV}^{\ominus} \cdot \gamma_{LV}^{\ominus}}) \quad (3)$$

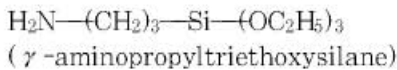
The polar component,  $\gamma_{SV}^{AB}$  and the total surface free energy,  $\gamma_{SV}$  were calculated from Eq.4 and 5.

$$\gamma_{SV}^{AB} = 2 \sqrt{\gamma_{SV}^{\oplus} \gamma_{SV}^{\ominus}} \quad (4)$$

$$\gamma_{SV} = \gamma_{SV}^{LW} + \gamma_{SV}^{AB} \quad (5)$$

## EXPERIMENTAL

The materials for epoxy matrix were diglycidyl ether of bisphenol A (DGEBA), 4,4'-methylene dianiline (MDA, curing agent) and malononitrile (MN, reactive additive).<sup>(13)</sup> The inorganic filler was clinoptilolite type natural zeolite from Kampo area in Korea whose average particle size was  $9.9 \mu\text{m}$ <sup>(11)</sup> and the coupling agent whose trade name is A-1100 was  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) supplied by Union Carbide and the formulation is



The silane treatment of the natural zeolite was as follows. 0, 0.5, 1.0, 1.5 and 2.0 wt% silane coupling agent was hydrolyzed in the mixture of ethanol/water = 95/5(vol%) for 15 mins at room temperature, and then the natural zeolite

was treated with the hydrolyzed solutions for 30 mins at  $50^\circ\text{C}$  and dried for 24 hrs at  $120^\circ\text{C}$ . The dried zeolite was grinded and sieved into 325 mesh under. They were stored at desiccator to prevent water molecules from being adsorbed.

Column wicking experiment was carried out in the following manner. Glass tube with 100 mm long and 9 mm diameter was plugged at the bottom with a small wad of cotton wool and the tube was packed with 3g of zeolite powder at the height of 7 cm. Wicking was done with n-alkanes(hexane, heptane, octane and decane), methylene iodide, water and formamide at  $20^\circ\text{C}$ , and the penetration rates of the liquids were measured.

The procedure of the preparing the specimen for tensile test was as follows: To disperse the zeolite filler effectively, DGEBA and zeolite (0~40 phr) were poured into the agitator connected with vacuum pump and agitated for 2 hrs at  $80^\circ\text{C}$  under the vacuum condition. The melted MDA (30 phr) and MN (10 phr) were well mixed with the DGEBA/zeolite mixtures and vacuumed for 20 min in the agitator. The zeolite/epoxy mixture was poured in mold. The viscosity of the mixture was so proper that it can flow into the mold easily, however, the zeolite filler didn't settle down. The optimum curing condition was first curing at  $80^\circ\text{C}$  for 70 min and second curing at  $150^\circ\text{C}$  for 60 min.

The morphology of the interface was observed by SEM (JSM 840A, England).

## RESULTS AND DISCUSSION

### Surface Free Energy

Eq.2 has a fundamental difficulty that there are two unknowns ( $R$  and  $\cos \theta$ ). So,  $R$  should be ascertained indepen-

dently before determining the  $\cos\theta$  and this difficulty can be easily solved by using the spreading liquids which can completely wet the solid surface, so that the contact angle  $\theta=0$ , that is  $\cos\theta=1$ . Generally, n-alkanes are used as spreading liquids and Eq.2 can be changed as follows<sup>[14]</sup>.

$$R = \frac{2\eta h^2/t}{\gamma_{LV}} \quad (6)$$

After ascertaining the value of  $R$ , the contact angle for each probe liquid with the solid powder is calculated via Eq.2 and the surface free energy can be determined.

Figure 2 shows the penetrated distances squared,  $h^2$  as a function of time,  $t$  obtained by wicking of a series of n-alkanes on 0.5 wt%  $\gamma$ -APS treated natural zeolite. The slopes for all n-alkanes are wholly decreased comparing with those of untreated natural zeolite and the trend of slope is similar. The values of Table 1 are joined to Eq.6 to determine the value of  $R$  and the relationships between  $2\eta h^2/t$  and  $\gamma_{LV}$  are displayed in Figure 3. The value of  $R$  calculated from the slope is  $3.72 \times 10^{-5}$  cm.

To get the contact angles between the 0.5 wt%  $\gamma$ -APS treated natural zeolite and the probe liquids by using Eq.2, each slope of the straight line in Figure 4 are joined to  $R$  value and the data of Table 2. The contact angles for methylene iodide,

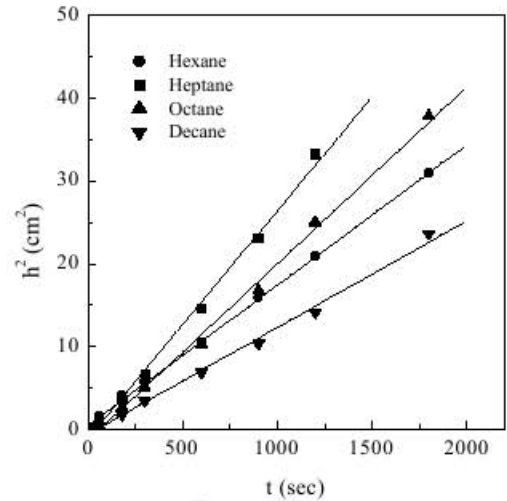


Figure 2. Plots of  $h^2$  vs.  $t$  obtained by wicking with n-alkanes on the natural zeolite treated with 0.5 wt%  $\gamma$ -APS.

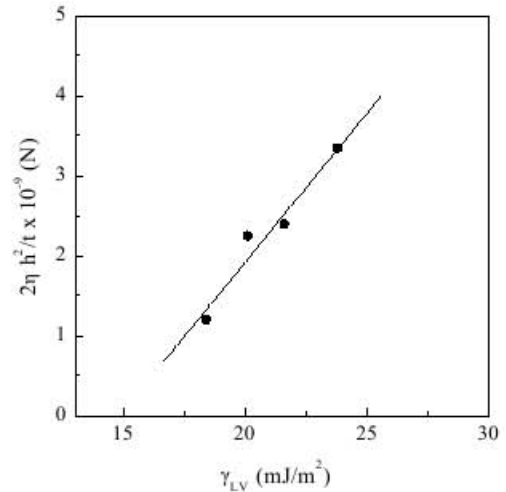


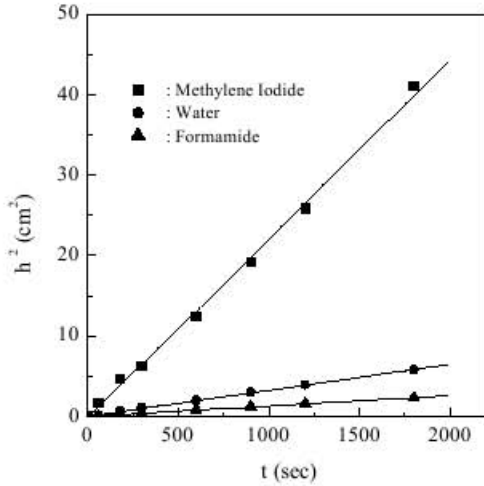
Figure 3.  $2\eta h^2/t$  vs.  $\gamma_{LV}$  for wicking with n-alkanes on natural zeolite treated with 0.5 wt%  $\gamma$ -APS.

Table 1. Viscosity,  $\gamma_{LV}$ ,  $\gamma_{LV}^{LW}$ ,  $\gamma_{LV}^{\oplus}$  and  $\gamma_{LV}^{\ominus}$  of n-Alkanes at 20°C.

n-Alkanes	$\eta$ (cP)	$\gamma_{LV}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{LW}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{AB}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{\oplus}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{\ominus}$ (mJ/m <sup>2</sup> )
n-Hexane	0.326	18.4	18.4	0	0	0
n-Heptane	0.409	20.1	20.1	0	0	0
n-Octane	0.542	21.6	21.6	0	0	0
n-Decane	0.907	23.8	23.8	0	0	0

**Table 2. Viscosity,  $\gamma_{LV}$ ,  $\gamma_{LV}^{LW}$ ,  $\gamma_{LV}^{\oplus}$  and  $\gamma_{LV}^{\ominus}$  of Probe Liquids at 20 °C.**

Probe Liquids	$\eta$ (cP)	$\gamma_{LV}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{LW}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{AB}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{\oplus}$ (mJ/m <sup>2</sup> )	$\gamma_{LV}^{\ominus}$ (mJ/m <sup>2</sup> )
Methylene iodide	2.80	50.8	50.8	0	0	0
Water	1.00	72.8	21.8	51.0	25.5	25.5
Formamide	4.55	58.0	39.0	19.0	2.28	39.6


**Figure 4. Plots of  $h^2$  vs.  $t$  obtained by wicking with probe liquids on natural zeolite treated with 0.5 wt%  $\gamma$ -APS.**

water and formamide are  $\theta = 62.6^\circ$ ,  $68.4^\circ$  and  $64.2^\circ$ , respectively.

By introducing the  $\theta = 62.6^\circ$ ,  $\gamma_{LV}^{LW}$ ,  $\gamma_{LV}^{\oplus}$  and  $\gamma_{LV}^{\ominus}$  for methylene iodide of Table 2 to Eq.3, the apolar component,  $\gamma_{SV}^{LW} = 27.08$  mJ/m<sup>2</sup> was obtained and the polar components,  $\gamma_{SV}^{\oplus} = 4.12$  mJ/m<sup>2</sup> and  $\gamma_{SV}^{\ominus} = 9.09$  mJ/m<sup>2</sup> were also obtained from Table 2 and Eq.3. By substituting the value of  $\gamma_{SV}^{\oplus}$  and  $\gamma_{SV}^{\ominus}$  into Eq.4,  $\gamma_{SV}^{AB} = 12.23$  mJ/m<sup>2</sup> was obtained and the total surface free energy,  $\gamma_{SV} = 39.31$  mJ/m<sup>2</sup> is calculated from Eq.5.

The surface energy components for the natural zeolite treated and untreated are put together on Table 3. The value of  $\gamma_{SV}^{LW}$  component increase, while that of  $\gamma_{SV}^{AB}$

component decrease with the increasing content of  $\gamma$ -APS treatment. It is due that the surface of the zeolite is more affected by alkyl group (hydrophobic) than amine or hydroxyl groups (hydrophilic).

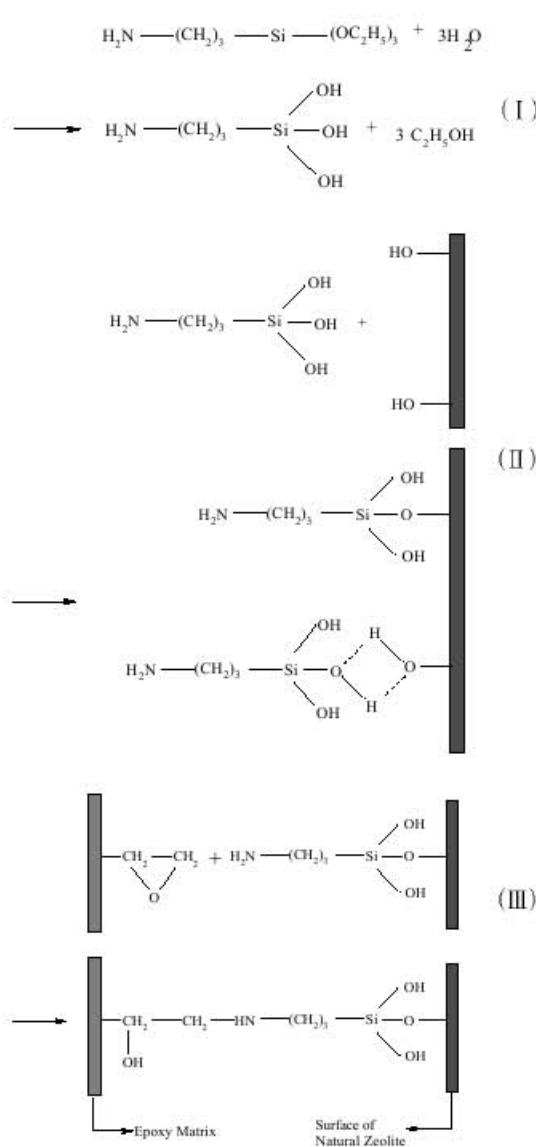
### 3.2. Tensile Properties

When silane coupling agent is hydrolyzed at pH=3.5, three silanols are produced (mechanism I), and the silanols react with the hydroxyl groups on the surface of natural zeolite forming siloxane linkage splitting out water molecules or hydrogen bonding (mechanism II). And, the amine group will react with epoxide group of the epoxy matrix as shown in the mechanism III. By these reactions, the interfacial strength is improved and the mechanical properties of the epoxy composites is affected.

Figure 5 shows the tensile strength for epoxy/natural zeolite composite. The tensile strength of epoxy system is improved by the treatment with  $\gamma$ -APS due to the strong interfacial bonding, which makes the rate of crack initiation slow. Figure 5 also shows the decrement of tensile strength with the increasing content of natural zeolite regardless of the silane-treated concentration. When natural zeolite is added to the epoxy matrix, a new crack initiation region is formed because of the difference of linear expansion coefficient between epoxy matrix and zeolite filler on the interface and the secondary

**Table 3. Surface Energy Components for the Natural Zeolite at 20°C.**

Contents of $\gamma$ -APS treatment (wt%)	$\gamma_{SV}$ (mJ/m <sup>2</sup> )	$\gamma_{SV}^{LW}$ (mJ/m <sup>2</sup> )	$\gamma_{SV}^{AB}$ (mJ/m <sup>2</sup> )	$\gamma_{SV}^{\ominus}$ (mJ/m <sup>2</sup> )	$\gamma_{SV}^{\oplus}$ (mJ/m <sup>2</sup> )
0	34.49	19.22	15.27	4.28	13.63
0.5	39.31	27.08	12.23	4.12	9.09
1.0	41.24	29.45	11.79	4.08	8.52
1.5	42.54	31.26	11.28	3.92	8.12
2.0	42.95	32.81	10.14	3.45	7.45



crack initiates ahead of the primary crack fronts, so tensile strength decreases with

the increasing zeolite content.<sup>[15]</sup>

The effect of  $\gamma$ -APS on the Young's modulus for epoxy/natural zeolite composite are shown in Figure 6. With the treatment of  $\gamma$ -APS, Young's modulus is modified due to the local plastic deformation on the zeolite surface. The friction between epoxy resin and untreated natural zeolite disturbed the flow of polymer chain and the strong interfacial strength obtained by the chemical bonding of coupling agent more effectively disturbed. It also shows the increment of Young's modulus with the increment of zeolite content as explained by the following rule of mixture.<sup>[15]</sup>

$$E_c = V_z \cdot E_z + V_e \cdot E_e \quad (7)$$

where, E is the Young's modulus, V is the volume fraction and subscripts c, z and e are composite, natural zeolite particle and epoxy matrix, respectively. The volume fraction of the natural zeolite,  $V_z$  increase with the increasing zeolite content, so the total modulus of the composite increase.

Figure 7 shows the morphology of the interface and the surface of zeolite particle untreated (A) and 1.0 wt%  $\gamma$ -APS treated. There is no epoxy trace on the surface of the untreated zeolite which results in the no adhesion at the interface as shown in Figure 7(A). However, the surface of the treated zeolite is coated with the polymer and the interface adhesion is modified as



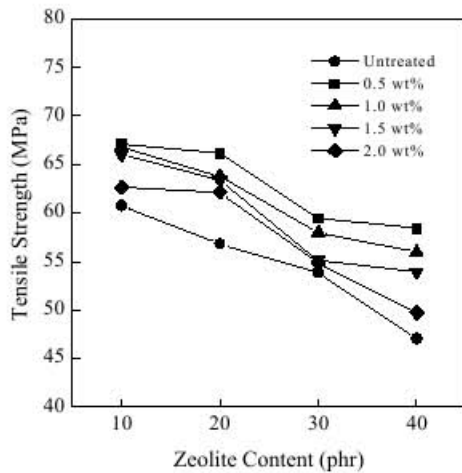


Figure 5. Tensile strength for epoxy with various contents of  $\gamma$ -APS treated zeolite.

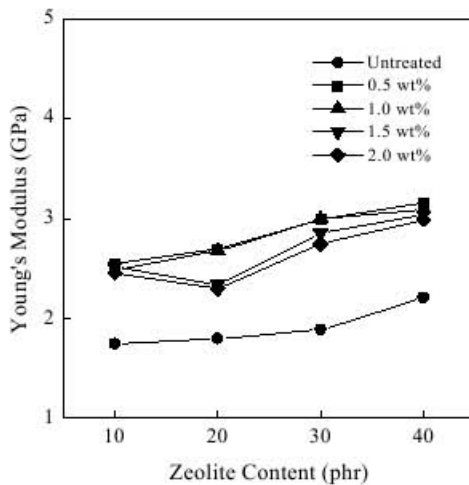
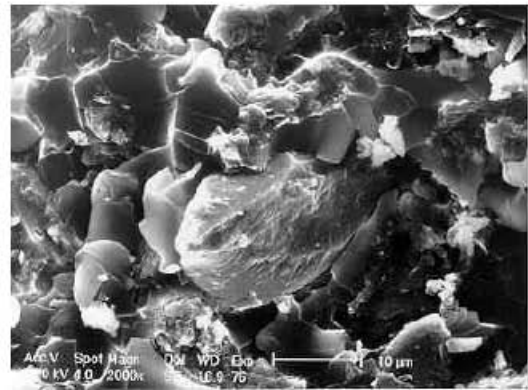


Figure 6. Young's modulus for epoxy with various contents of  $\gamma$ -APS treated zeolite.

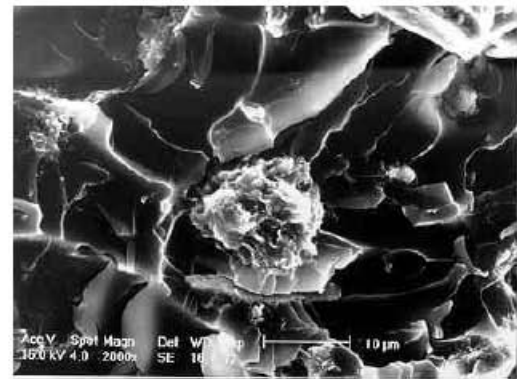
shown in Figure 7(B). So, it is the natural result that the tensile strength increase as the surface of zeolite is treated with coupling agent.

## CONCLUSION

The effects of  $\gamma$ -APS on the surface free energy, tensile properties and interfacial morphology of epoxy/natural zeolite



(A)



(B)

Figure 7. The interface morphology between epoxy and natural zeolite. (A) untreated and (B) treated with 1.0 wt%  $\gamma$ -APS.

composites are investigated. The value of Lifshitz-van der Waals component,  $\gamma_{SV}^{LW}$  for apolar increased, while that of Lewis acid-base component,  $\gamma_{SV}^{AB}$  for polar decreased with the increasing content of  $\gamma$ -APS treatment. It is due that the surface of the zeolite is more affected by alkyl group (hydrophobic) than amine or hydroxyl groups (hydrophilic). The tensile strength and Young's modulus of epoxy system were improved by the treatment with  $\gamma$ -APS due to the strong interfacial bonding, which made the rate of crack initiation slow. The increasing interfacial adhesion was observed by SEM.

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## REFERENCES

1. F. Lin, G. S. Bhatia and J. D. Ford, *J. Appl. Polym. Sci.*, **49**, 1901 (1993).
2. Y. Zhang and J. Cameron, *J. Composite Materials*, **27**, 1114 (1993).
3. D. He and B. Jiang, *J. Appl. Polym. Sci.*, **49**, 617 (1993).
4. P. Yeoung and L. J. Broutman, *Polym. Eng. Sci.*, **18**, 62 (1978).
5. M. Goldman, D. Fraenkel and G. Levin, *J. Appl. Polym. Sci.*, **37**, 791 (1989).
6. E. Chibowski, *J. Adhesion Sci. Tech.*, **6**, 1069 (1992).
7. C. J. Wu, C. Y. Chen, E. Woo and J. F. Kuo, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 3405 (1993).
8. J. S. Shukla, S. C. Tewari and G. K. Sharma, *J. Appl. Polym. Sci.*, **34**, 191 (1987).
9. R. J. Good, "Contact Angle, Wettability and Adhesion", ed. K. L. Mittal, VSP, p.3 (1993).
10. M. Salou, S. Yamazaki, N. Nishimiya and K. Tsutsumi, *Colloids Surfaces, A:Physico-chemical Eng. Aspects*, **139**, 299 (1998).
11. J. Y. Lee, S. H. Lee and S. W. Kim, *Mater. Chem. Phys.*, **63**, 251 (2000).
12. E. Chibowski, "Contact Angle, Wettability and Adhesion", ed. K. L. Mittal, VSP, p. 641 (1993).
13. J. Y. Lee, M. J. Shim and S. W. Kim, *J. Ind. & Eng. Chem.*, **4**, 1 (1998).
14. A. Ontiveros-Ortega, M. Espinosa-Jiménez, E. Chibowski and F. González-Caballero, *J. Colloid Interface Sci.*, **202**, 189 (1998).
15. J. Y. Lee, M. J. Shim and S. W. Kim, *Polym. Eng. Sci.*, **39**, 1993 (1999).