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실란 결합제 처리된 에폭시 수지 복합재료의 계면 특성

이재영 · 이홍기* · 심미자** · 김상욱†
서울시립대학교 공과대학 화학공학과
*우석대학교 화학공학과
**서울시립대학교 문리과대학 생명과학과

Interface Characteristics of Epoxy Composite Treated with Silane Coupling Agent

J. Y. Lee, H. K. Lee*, M. J. Shim** and S. W. Kim†
Department of Chemical Engineering, The University of Seoul, Seoul 130-743
**Department of Chemical Engineering, Woosuk University, Jeonbuk 565-800*
***Department of Life Science, The University of Seoul, Seoul 130-743*

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Abstract The effects of coupling agent on the interface characteristics between epoxy resin and natural zeolite were studied by SEM, optical microscope and universal testing machine (UTM). Epoxy resin as a matrix was diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA)/malononitrile (MN) system and natural zeolite as an inorganic filler was produced in Korea. With the increment of zeolite content, tensile strength decreased and it was due to the different elastic moduli of two materials. When external stress was loaded on the composites, the stress concentrated on the weakly bonded interface and crack grew easily. To improve the interface characteristics, the surface of the natural zeolite was treated with the silane coupling agent and it was found that the tensile strength was increased. The morphology of the interface showed that the bonding characteristics were modified by coupling agent.

Key words: Epoxy composite, silane coupling, interface, mechanical strength

1. Introduction

With the increasing demands of new polymer composites for many applications, researchers have investigated the characteristics between polymer matrix and inorganic filler. Many species of inorganic fillers, such as silica, calcium carbonate, mica, talc, carbon black, kaolin and metal powder have been used to improve the mechanical, thermal, electrical, rheological and optical properties of polymers.[1~8] The properties of the polymer composites are affected not only by the characteristics of the matrix and filler but also by the characteristics of the interface.[1~3] In general, two dissimilar components of the composites have little affinity, for the surface of the inorganic filler is hydrophilic and that of the matrix is hydrophobic. So, the micro crack and craze are initiated from the interface and the mechanical fracture takes place, finally. It is the reason why the characteristics of the interface is the most important factor to determine the properties of the polymer composites. Many techniques are studied and developed to improve the affinity between matrix and inorganic filler at the interface and one of the most well-known methods is to connect the dissimilar components by coupling agent.[4~6]

In this study, the effects of silane coupling agent on the interface characteristics of epoxy resin and natural zeolite were studied. Zeolites are crystalline aluminosilicate minerals having high specific surface area due to the channels and pores and the natural zeolite used in this study was clinoptilolite type.[9~11]

2. Experiment

Epoxy resin was diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA)/malononitrile (MN) system and inorganic filler was clinoptilolite type natural zeolite (under 325 mesh) which was plentifully produced in Korea. The silane coupling agent was γ-glycidoxypropyltrimethoxysilane (A-187, Union Carbide Co.).

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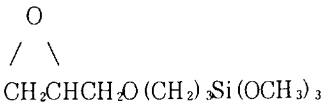
† E-mail: swkim@uos.ac.kr



$$\overset{O}{\overbrace{CH_2CH}}CH_2O(CH_2)_3Si(OCH_3)_3$$

The surface of the natural zeolite was treated with coupling agent by the following procedure. Methanol : water = 9 : 1 at the weight ratio was mixed with 1.0 and 2.0 wt% of A-187 and the pH of the mixtures was adjusted to 3.5 by the addition of acetic acid. Natural zeolite was added to the mixtures and treated for 12 hrs at 25℃. The silane treated natural zeolite was dried for 12 hrs at 110℃ and ground into the powder 325 mesh under. They were stored at desiccator to prevent water molecules in the air from being adsorbed.

The procedure for the preparation of the test specimens was as follows. To disperse the natural zeolite and to remove the bubble, DGEBA and natural zeolite (10, 20, 30 and 40 phr) were mixed and vacuumed for 2 hrs at 80℃ of reactor connected with vacuum pump and agitator. 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, and the zeolite/epoxy mixture was poured into the mold. The epoxy compound was cured at 80℃ for 70 min and post-cured at 150 for 60 min.

Tensile test was carried out by universal testing machine (AGS-D, Shimadzu, Japan) according to ASTM D638 at the cross-head speed of 5 mm/min and the morphology of the fracture surface was observed by SEM and optical microscope. Particle size distribution of the natural zeolite was measured by Mastersizer X (Malvern Instruments Ltd., U.K).

3. Results and Discussion

Fig. 1 shows the particle size distribution of the zeolite sample. The range of the particle size was from 0.50 ㎛ to 56.09 ㎛ and the average value was 17.30 ㎛. The portion of the particle size under 10 ㎛ was about 50% and that of 17~25 ㎛ was about 41%. The rest was for the particle size over 25 ㎛. The surface area of the zeolite was 129.96 m^2/g and the hydroxyl group density was 3.22×10^{-3} mol/g measured by chemical titration.

Fig. 2 shows the tensile strength and Young's modulus for the epoxy system filled with various contents of the untreated natural zeolite. With the increment of zeolite content, tensile strength decreased, while Young's modulus increased and it's the general results shown in the brittle-brittle composites. The difference of the thermal expansion coefficients between epoxy matrix and

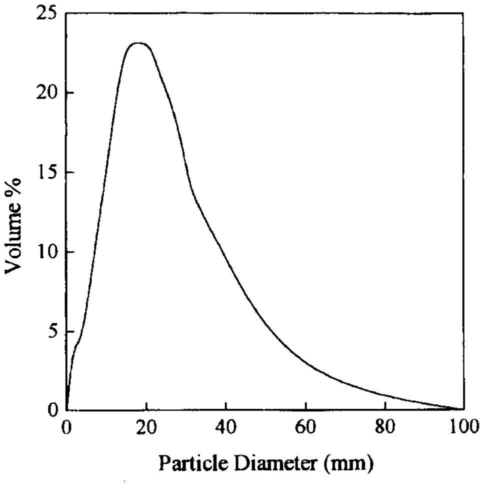


Fig. 1. Particle size distribution of the natural zeolite.

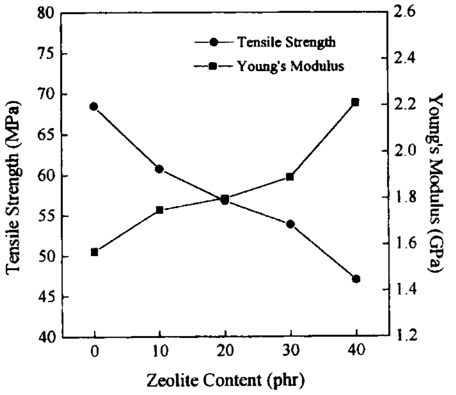


Fig. 2. Tensile strength and Young's modulus for DGEBA/MDA/MN system with the various contents of the untreated natural zeolite.

natural zeolite filler was the cause of the internal stress at the interface, when the composite was cured and cooled. The difference of the elastic moduli of two materials was another cause of the concentration of internal stress at the interface, when the composite was pressed by external force. The concentrated internal stress made the crack start easily from the interface, and the interface area increased with the increment of zeolite content, so the tensile strength decreased with the increment of zeolite content. However, the local flow of the matrix chains at the interface was disturbed by the natural zeolite particles due to the friction. So, Young's modulus increased with the increment of zeolite content.

Fig. 3 shows the tensile strength for epoxy/natural zeolite composite. When the treatment concentration of A-187 increased, tensile strength increased due to the improved interfacial condition of the matrix and filler. A-187 coupling agent linked the hydrophilic zeolite to

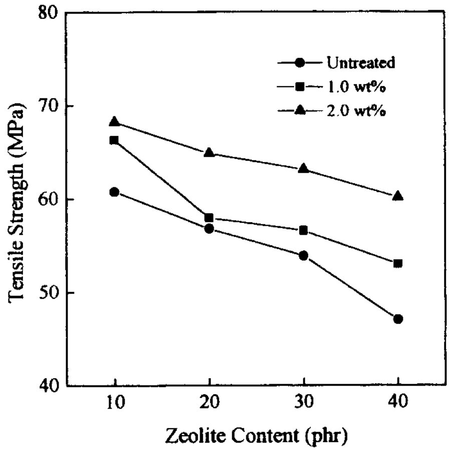


Fig. 3. Tensile strength for DGEBA/MDA/MN system with the various contents of the silane-treated natural zeolite.

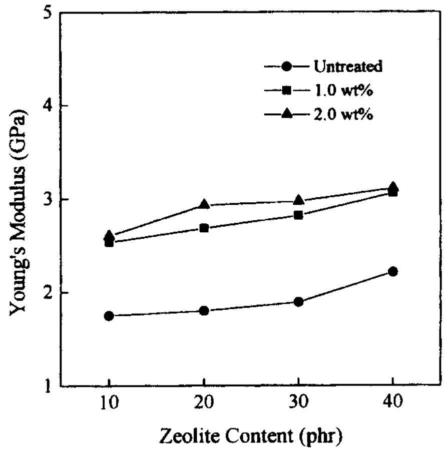
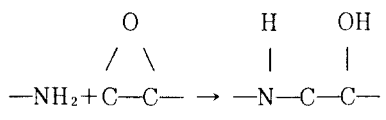


Fig. 4. Young's modulus for DGEBA/MDA/MN system with the various contents of the silane-treated natural zeolite.

the hydrophobic epoxy resin by the chemical bonds and the strong interfacial bonding strength made the rate of crack initiation slow, so it resulted in the increment of tensile strength. The chemical reaction between coupling agent and natural zeolite was as follows. The silanol (Si-OH) of A-187 reacted with the hydroxyl group (-OH) on the surface of natural zeolite and formed siloxane linkage (Si-O-Si) splitting out one water molecule. In the Si-O-Si, one Si was from the coupling agent and the other was from the structure of natural zeolite. On the other hand, the reaction between epoxide group on the other side of the coupling agent and amine group of epoxy matrix was as follows:



$$-NH_2 + \overset{O}{\overset{/\ \backslash}{C-C}}- \rightarrow -\overset{H}{\overset{|}{N}}-C-\overset{OH}{\overset{|}{C}}-$$

An active hydrogen atom of amine group was donated to epoxide group with forming -N-C- covalent bonding through the cleavage of epoxide ring. These two reactions have been well known.[12,13]

Fig. 3 also shows the decrement of tensile strength with the increasing content of natural zeolite regardless of the silane-treated concentration. However, the slope of the untreated composite was steeper than that of the 2.0 wt% treated composite.

The effects of A-187 coupling agent on the Young's modulus for epoxy/natural zeolite composite were shown in Fig. 4. With the increment of A-187 treating concentration, Young's modulus increased 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.

Fig. 4 also shows the increment of Young's modulus with the increment of zeolite content and it can be explained by the following rule of mixture:

$$E_c = V_f \cdot E_f + V_m \cdot E_m$$

where, E is Young's modulus, V is volume fraction and subscripts c, f and m are composite, zeolite filler and epoxy matrix, respectively. The modulus of the natural zeolite was higher than that of the epoxy matrix. So, the total modulus of the composites increased with the increasing volume fraction of natural zeolite.

Fig. 5 shows the morphology of the fracture surface in epoxy system without natural zeolite that failed in tension and it can be divided into three characteristics regions. The crack is initiated from the center of the mirror-like circular periphery of Fig. 5(A) which is surrounded by smooth river markings. The smooth river markings in Fig. 5(B) are located between the mirror-like region and the rough parabolas in Fig. 5 (C). The mirror-like and smooth river marking region are associated with the slow velocity of crack growth and the rough parabola region is the result of complex, unstable and brittle failure. The surface roughness is primarily caused by the generation of secondary crack fronts ahead of the primary crack fronts and the interconnection of these crack fronts from different planes. The fracture energy involved in the slow crack growth is far higher than that of the fast work.[14]

When natural zeolite was added, however the morphology of the surface was more complex and there was no characteristics regions regardless of the silane

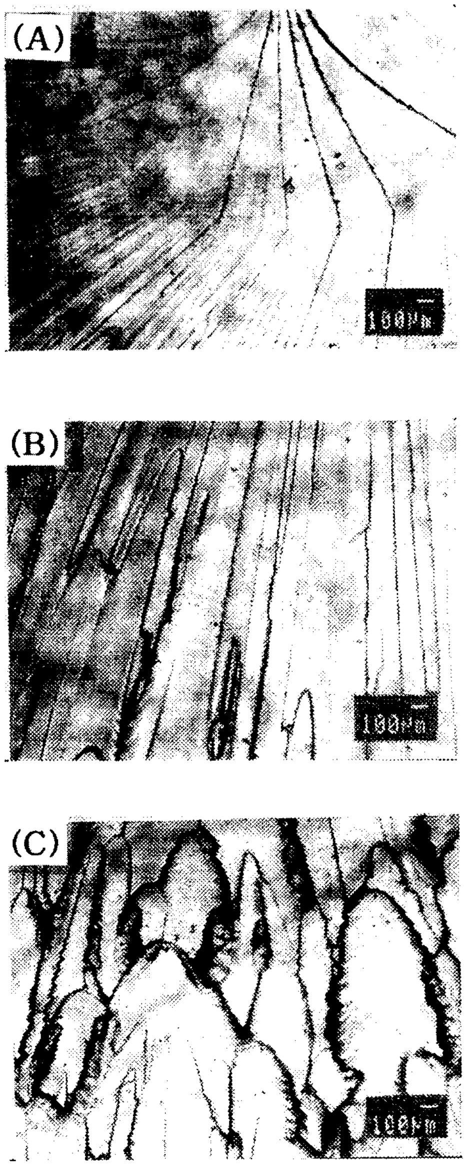


Fig. 5. The morphology of the fracture surface in DGEBA/MDA/MN system without natural zeolite. (A) a crack initiation region, (B) a slow crack-growth region and (C) a fast crack-growth region

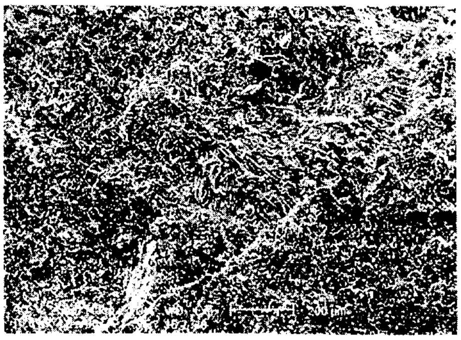


Fig. 6. The morphology of the fracture surface in DGEBA/MDA/MN system with the 20 phr of the 1.0 wt% silane-treated natural zeolite.

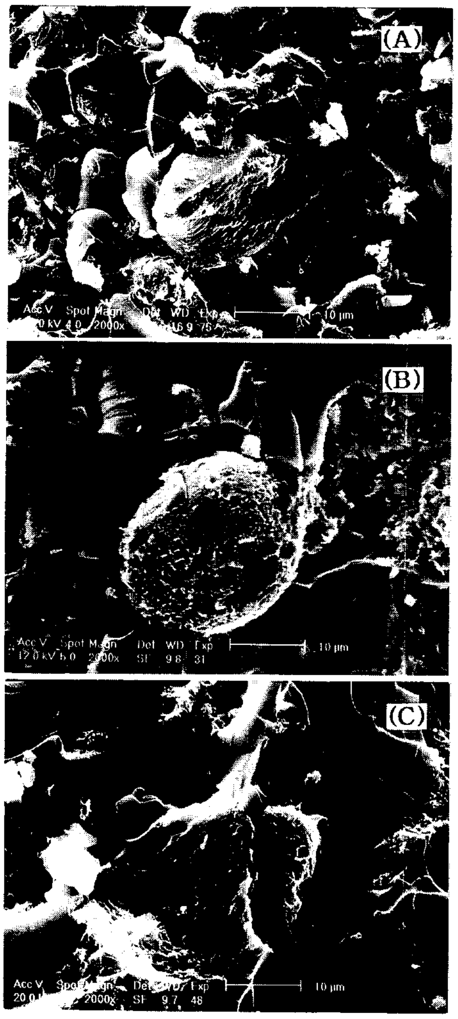


Fig. 7. The interface morphology between epoxy matrix and natural zeolite treated with (A) 0 wt%, (B) 1.0 wt% and (C) 2.0 wt% silane coupling agent.

treatment as shown in Fig. 6. The interface between zeolite and matrix is a new crack initiation region because of the difference of linear expansion coefficient between epoxy matrix and zeolite filler and the morphology becomes more complex. So, tensile strength decreased with the increment of zeolite content.

Fig. 7 shows the morphology of the interface and the surface of the zeolite particle treated with different concentration of silane coupling agent. There is no polymer traces on the surface of the untreated zeolite and there is no adhesion at the interface. However, the surface of the zeolite is coated with the polymer and the interface adhesion is modified, when the natural zeolite treated with 1.0 wt% concentration is used. The morphology of the interface treated with 2.0 wt% is well adhered, so there is no boundary at the interface and it made the stress disperse to the matrix around the zeolite. So, the tensile strength increased with the increasing concentration of silane coupling agent.

4. Conclusion

The effects of coupling agent on the interface characteristics between epoxy resin and natural zeolite were studied. Tensile strength decreased with the increment of zeolite content and the decrement of the silane treated concentration, while Young's modulus increased with the increment of zeolite content and the silane treated concentration. The surface morphology of the epoxy system without natural zeolite was divided into three characteristics regions : one was initiation region, another was smooth region of slow crack-growth, and the other was rough region of fast crack-growth. When natural zeolite was added, however the morphology of the surface was more complex and there was no characteristics regions regardless of the silane treatment. The adhesion of the interface between epoxy resin and zeolite particle was more improved by the increasing concentration of silane coupling agent. So, the tensile strength increased with the increasing concentration of silane coupling agent.

Acknowledgement

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