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Novel light reinforced materials using surface modified alumina using silane coupling agents

Yong-Joo Jeong[a] and Cheol-Woo Yi[b,*]
[a]*Department of Chemistry, Korea University, Seoul 136-701, South Korea*
[b]*Department of Chemistry and Institute of Basic Science, Sungshin Women's University, Seoul 136-742, South Korea*

Novel light reinforced material is prepared by surface modified alumina and poly (methyl methacrylate) (PMMA). The composite has a stacking structure with inorganic and organic materials each other like brick and mortar model. Moreover, the surface modified alumina has a strong interaction with organic material due to an increase in matrix wetting and matrix adhesion. The surface modification of alumina is prepared by various silane coupling agents (SCAs) in order to provide stable chemical interactions between organic and inorganic materials. The alkoxy silane on the other side of SCA reacts with inorganic material. In addition, SCAs with different terminal functional groups are employed in the surface modification of alumina, and the functional group reacts with an organic material. Through the pretreatment process generate more hydroxyl group on the surface of Al_2O_3 and it can make easily forming silanol with epoxy silane coupling agent. The silane coupling agent on the Al_2O_3 platelets were good interact with organic filler material (PMMA) and it effect to increasing mechanical strength.

Key words: Al_2O_3, PMMA, Bio-inspired technology, Silane coupling agent.

Introduction

Metals and/or metal alloys, which are aluminum, carbon steel, stainless steel, etc., have long been employed in reinforced structural materials because these materials have several advantages such as high strength and flaw tolerance [1-12]. However, due to the increase in oil price, the shortage of energy source and the quest for more efficient energy related technology, the development of a material with lightweight and high mechanical strength is requested. Even though many researchers have spared no effort in finding these materials, a new structural material having high mechanical strength and light weight is not easy because these two properties (high mechanical strength and light weight) are mutually exclusive. For this reason, the structure in nature has been paid attention to preparing a new structural material, and it called bio-inspired technology [1-12]. Bio-inspired technology is not only mimicking the structure in a biological system which has remarkable mechanical strength and toughness but also application of advanced stage and synthetic a new material. In nature, there are lots of materials having light weight and high mechanical strength such as human bone and dentine and these materials have a composite structure of inorganic material (e.g. $CaCO_3$) and polymers (e.g. protein). Especially, many scientists are studied about growth process and structure of sea shell [5-11]. Sea shell is composite of > 95 wt.% $CaCO_3$ platelet and < 5 wt.% protein, protein is homogeneously dispersed between calcium carbonate platelets and calcium carbonate platelet has < 1 μm thickness and 5 ~ 10 μm length. Calcium carbonate platelet alone is very brittle but mechanical strength of sea shell has ~ 3,000 times greater than calcium carbonate platelet[7] due to the role of protein in the abalone shell. The structure of sea shell is a brick and mortar, which is calcium carbonate as a brick and protein as a mortar, and adhesive protein sandwiched between laminated calcium carbonate platelet [6]. Moreover, elastic polymer layer between the mineral platelet can efficiently disperse the external stress maintain the original structure. Therefore, recently, the composite materials with inorganic compound and polymer composite material for improving mechanical strength have been studied using various inorganic materials (e.g. $Mg(OH)_2$, $CaCO_3$, carbon nano tubes/fibers) and polymer matrix [1-13]. In spite of the tremendous efforts, the contact and/or adhesive properties between inorganic and organic materials in composites are still challenging points to improve the mechanical properties and disperse the external stress [1-13].

In this study, the composite material of alumina and poly(methyl methacrylate) (PMMA) are prepared and the surface of alumina is modified with silane coupling agent (SCA) in order to improve the contact property between inorganic material and polymer. The resulting composite material shows a good mechanical strength compared to the composites of pristine alumina and PMMA. This type of material and the procedure can be applied to the part of structural materials and light weight reinforced materials

*Corresponding author:
Tel : +82 2 920 7666
Fax: +82 2 920 2047
E-mail: cheolwoo@sungshin.ac.kr

Experimental

Al_2O_3 platelet is ~ 1 μm thick and 5 ~ 10 μm width (RonaFlair® White Sapphire, Germany) and 2-(3,4 epoxycyclohexyl) ethyl trimethoxysilane (Shinetsu, Japan), 99.5% toluene (Daejung, R.O.K.), 30% hydrogen peroxide (Daejung, R.O.K.), 99% methyl metacrylate (Aldrich, USA) and Luperox® A70S, benzoyl peroxide (Aldrich, USA) are used in the preparation of alumina/PMMA composite materials. Prior to the surface modification of alumina, the alumina platelets are pre-treated with hydrogen peroxide to generate hydroxyl group on the surface because these hydroxyl group reacts with SCA to produce the chemical bond. Aluminum oxide powders (10 g) were refluxed with 200 mL 30% hydrogen peroxide stirring 2 hours at 60 °C, and then they are filtered and dried at 80 °C for 3 hours. Then, this pre-treated alumina is reacted with a silane coupling agent, 2-(3,4-epoxycyclohexyl) ethyl trimethoxysilane (epoxy-SCA). In this process, 10 g of pre-treated alumina platelets were refluxed in 200 mL of toluene and epoxy-SCA solution at 115 °C 12 hours. After refluxing, the resulting materials were filtered and washed with toluene and then dried at 120 °C for overnight.

Bar type of composite material (5 × 50 mm) was prepared. The surface modified alumina by epoxy-SCA (10 g) was mixed with 0.5 g of a phenolic resin (Chosun Refractories Co., Ltd) as a binder to make a green body, and then, 1.5 g of mixed sample was pressed. It was heated at 120 °C for 3 hours to cure it. After curing, it was transferred to the methyl methacrylate (MMA) and benzoyl peroxide (BPO) solution at 80 °C, 30 minutes for infiltration of PMMA into the green body. Followed by infiltration process, PMMA infiltrated composite bar is transferred to the mold and warm-pressed [12] at 100 °C, and the temperature is raised to 200 °C at the heating rate of 10 °C/min and then cooled down.

The surface area of alumina platelets are determined by BET measurement (Autopore IV, micrometrics). The structure, cross-section, and elemental analysis of surface modified alumina/PMMA composite are investigated by field emission-scanning electron microscopy (FE-SEM, JSM-7500F, JEOL) and energy-dispersive x-ray spectroscopy (EDS, INCA PentaFETx3, Oxford instruments). Fourier transform-infrared spectroscopy (FT-IR, Nicolet380 and Nicolet 6700, Thermo) is employed in figuring out the reaction of epoxy-SCA and pretreated alumina platelets. The structural changes of alumina platelets for whole process are investigated by x-ray diffraction (XRD, D8 focus, Bruker). To measure the mechanical properties of composite material, 3-poing bending test (Instron 5848 tester) is performed.

Results and Discussion

In order to prepare the surface modified alumina, alumina platelet was pre-treated by hydrogen peroxide. Even if alumina, which is kept in air, has a surface hydroxyl group, the pre-treatment forms enough hydroxyl groups on the surface as well as removes residual impurities. Thus-formed surface hydroxyl group can react with the silanol in various SCAs. Figure 1 shows FT-IR spectra of alumina before/after pre-treatment. The vibrational features below 1000 cm^{-1} are originating from alumina, and the broad band between 3200 and 3600 cm^{-1} is for the stretching of hydroxyl group. After the pre-treatment, the increase in the concentration of surface hydroxyl group is obviously observed. Silane coupling agents has different terminal groups. One end has three silanol groups and the other end has various functional groups (epoxy, mercapto, amino, etc). Through the modification process, surface modified alumina is obtained from the reaction of thus-formed surface hydroxyl group with silanol group in SCAs. Figure 2 shows the morphology and Si distribution of the surface modified alumina. The morphology was investigated by SEM as shown in Figure 2(a). There is no change in the morphology of alumina before/after the modification reaction. In addition, the structure of surface modified alumina was investigated by XRD and there is absolutely no evidence in structural change. However, Si is observed on the alumina platelet after the surface modification and the distribution is homogeneous as shown Figure 2(b). Because appropriate amount of SCA that covering about 1 monolayer of alumina platelet was added in the surface modification, the silicon EDS

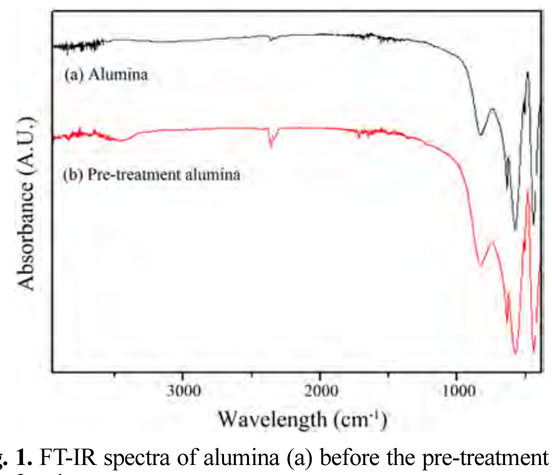

Fig. 1. FT-IR spectra of alumina (a) before the pre-treatment and (b) after the pre-treatment.

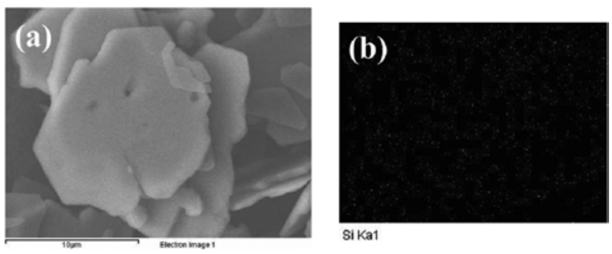

Fig. 2. (a) The morphology and (b) the Si distribution of the surface modified alumina.

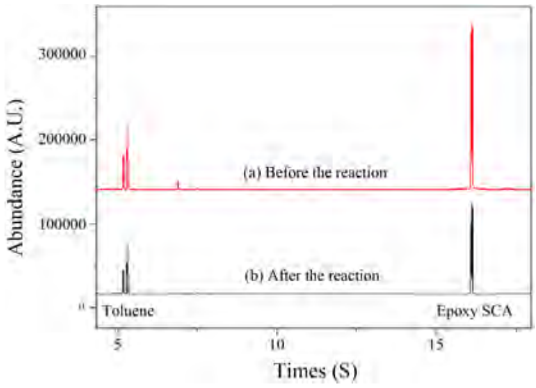

Fig. 3. GC-MS data for the refluxing solution (a) before the reaction and (b) after the reaction.

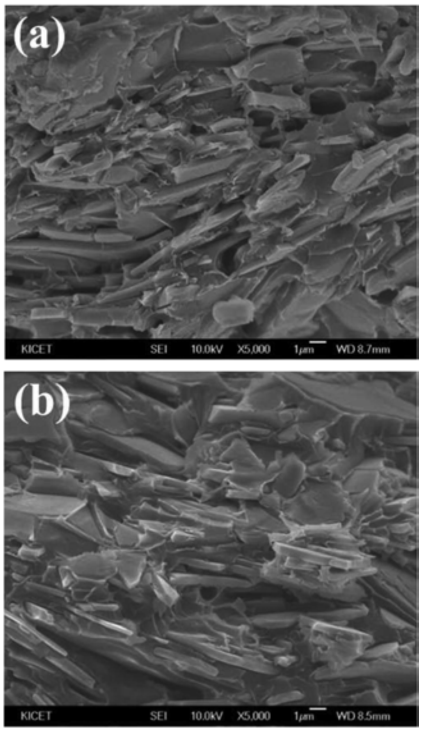

Fig. 4. SEM images for the cross-section of composite material consisting of (a) pristine alumina and PMMA and (b) surface modified alumina and PMMA.

signal is weak. Moreover, the change of the concentration of epoxy terminated SCA in the refluxing solution before and after the surface modification was investigated by GC-MS spectroscopy, as shown in Figure 3, to confirm if the added SCA attaches on the alumina surface or not. The concentration of epoxy terminated SCA is estimated by the internal standard, toluene peak at the retention time of 5 min. After the modification reaction, the concentration of epoxy terminated SCA in the refluxing solution is reduced and the amount of loss through the modification is exactly the same as the amount to from 1 ML of SCA on the alumina surface. Furthermore, the surface modified alumina was investigated with FT-IR spectroscopy using MCT detector and Zn/Se ATR

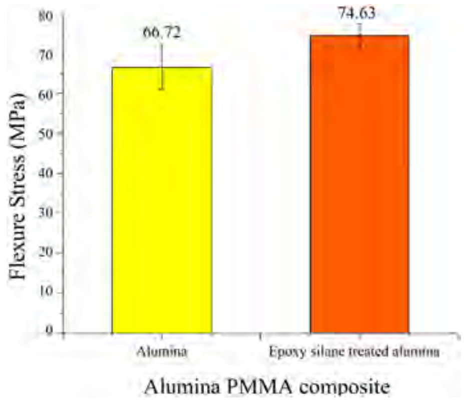

Fig. 5. 3-point bending test data for composite material consisting of alumina and PMMA.

crystal in N_2 atmosphere. FT-IR spectrum of surface modified alumina shows the combined feature of untreated alumina and SCA. Therefore, it is evident that the SCA reacts with pre-treated alumina and SCA layer exists on the alumina surface.

The composite material is prepared by the infiltration of PMMA. At first, the surface modified alumina is mixed with phenolic resin, which acts as a binder, and it was pressed. Then, the alumina green body is put into methyl metacrylate and benzoyl peroxide solution wetting well. At the curing temperature, MMA/BPO is polymerized inside the green body. Polymer layer is located among the alumina platelets. The interaction between SCA attached on the alumina surface and PMMA is stronger than the interaction between alumina and PMMA. Therefore, the contact properties between organic and inorganic material should be enhanced for the surface modified alumina and PMMA composite. Figure 4 shows the SEM images for the cross section of the alumina and PMMA composites. As expected, the composite consisting of pristine alumina and PMMA shows poor intrusion of PMMA into alumina green bar. However, for the composite of the surface modified alumina and PMMA, PMMA is homogeneously distributed on the whole sample, and the contact between the alumina is much more improved than the composite with pristine alumina. Fracture toughness is measured to confirm that the composite with surface modified alumina has better stress transfer because the composite that filler (alumina) has a chemical connection with organic matrix (PMMA) shows good stress transfer. Figure 5 shows the fracture toughness data of alumina/PMMA composite. Flexure toughness of surface modified alumina/PMMA ceramic bar increases by $>16\%$ with respect to the pristine alumina /PMMA ceramic bar.

Conclusion

The surface of alumina platelets is modified using epoxy terminated SCA to increase the interaction between inorganic and organic material in the composites. The epoxy terminated SCA is successfully modified alumina surface. It is confirmed that the distribution of SCA on the alumina surface is homogeneous and the structure and morphology of alumina platelet are not changed after the surface modification with various spectroscopic techniques. Thus-obtained surface modified alumina shows much better contact properties with polymer matrix (PMMA). The enhanced contact properties between alumina and PMMA composite improve mechanical properties.

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