

# Synthesis and Characterization of Alumina Flakes/Polymer Composites

Nasima S. Afsharimani,<sup>1</sup> Azam Iraj Zad,<sup>1,2</sup> Majid Jafar Tafreshi,<sup>3</sup> Saeed Salartayefeh<sup>3</sup>

<sup>1</sup>Department of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, Iran

<sup>2</sup>Institute for Nanoscience and Nanotechnology (INST), Sharif University of Technology, P.O. Box 14588-89694, Tehran, Iran

<sup>3</sup>Department of Physics, Semnan University, P.O. Box 35351, Semnan, Iran

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**ABSTRACT:** Alumina flakes were prepared by solution combustion method and milled to provide powder. XRD and SEM data exhibited microsized flakes with 100 nm thickness and nanosized grains. Then the powders were dispersed in polystyrene (PS) and poly methyl methacrylate (PMMA) matrixes and thin sheets of composites were produced by solution method. Mechanical properties of the composites were characterized using tensile test and their fracture surfaces, elemental composition and hydrophobic property were tested by

SEM, EDX and contact angle techniques, respectively. The results exhibited better mechanical properties compared to pure polymer samples i.e. the elastic modulus in PMMA and PS composites, were increased about 107 and 109%, respectively. In addition the composite surfaces became more hydrophobic than pure polymer systems. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3716–3720, 2010

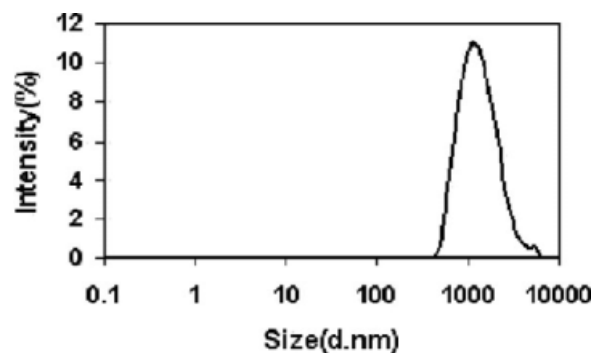
**Key words:** alumina; films; nanocomposite

## INTRODUCTION

Inorganic fillers combined with polymeric materials that lead to a composite system, have been a common practice in plastic industries to improve the mechanical properties of thermoplastics such as heat distortion temperature, hardness, toughness, stiffness, mold shrinkage and so on. The typical filler contents needed for such an enhancement of properties are as high as 20% by volume.<sup>1,2</sup> As a result of this high particle loading, the process ability and transparency of the compounds are inevitably deteriorated and the weight of the end-products becomes much higher than that of the neat polymers. On the other hand, in some cases nanocomposites, composites filled with particles that are nanometric at least in one dimension, show better mechanical, thermal, and optical properties with even a small amount of nanoparticles. Hence they are much lighter in weight and can be transparent compared with conventional composites.<sup>3</sup> To achieve such a composite, several types of nanoparticles and preparation methods have been investigated. In this way, preparation and properties of numerous nanocomposites filled with nanoparticles such as carbon nanotubes,<sup>4,5</sup> silica,<sup>6</sup> calcium carbonate,<sup>3</sup> clay,<sup>2,7</sup> alumina,<sup>8–10</sup> and nanofibers like polyaniline fibers<sup>11</sup> using melt mixing,<sup>2,3</sup> *in situ* po-

lymerization<sup>1</sup> and solution<sup>8</sup> methods have been studied. Among these widespread types of polymer nanocomposites, alumina/PMMA and PS nanocomposites with different preparation methods have also been considered.<sup>8,10,12</sup> They were chosen on the basis of their different reactivity with metal oxides. Ciprari et al. prepared Al<sub>2</sub>O<sub>3</sub>/PMMA and PS nanocomposites filled with spherical alumina nanoparticles by solution method.<sup>8</sup> Their results didn't show improvement in mechanical properties over pure PMMA and PS systems and interface characterization showed limited interaction between the Al<sub>2</sub>O<sub>3</sub> nanoparticles with either of the polymer matrices. In another study, coated spherical alumina nanoparticles (36 nm in diameter) with (3-acryloxypropyl) dimethylmethoxysilane embedded in PMMA matrix using *in situ* polymerization method was studied. The most significant result was the dramatic increase in strain to failure, in the 5 wt % filled samples. This represented an increase of 400% over that for neat PMMA tested at 25°C but, the elastic modulus for all nanocomposite concentrations were lower than for pure PMMA.<sup>10</sup> Furthermore *in situ* polymerization method was performed to prepare alumina/PMMA nanocomposite by Ash and coworkers. The used alumina nanoparticles were synthesized using forced gas condensation method. At an optimum weight percent, the resulting nanocomposites showed, on an average, a 600% increase in the strain-to-failure and the appearance of a well-defined yield point when tested by uniaxial tension. However a decrement in modulus of the samples was observed.<sup>12</sup>

Correspondence to: A. Iraj Zad (irajizad@sharif.edu).



**Figure 1** Size distribution of Al<sub>2</sub>O<sub>3</sub> particles after milling.

One of the characteristics which determine the properties that filler will impart to a composite is particle shape. The shape of most mineral filler particles can be approximated as a sphere, cube, flake, plate, needle or fiber. Some fillers contain a mixture of shapes. Mineral particles resembling plates, flakes, needles and fibers are further characterized by their aspect ratio.

In composites, applied stress is transferred from the polymer matrix to the strong and stiff mineral. Therefore, it seems reasonable that this stress transfer will be better affected if the mineral particles are smaller, because greater surface is thereby exposed for a given mineral concentration. Moreover, if these particles have a high aspect ratio (needle-like, fibrous or platy in shape), they will better intercept the stress propagation through the matrix.

In this study we have produced alumina nanostructured flakes by solution combustion method. Then the flakes were embedded as filler in PMMA and PS matrices using solution method. It is a simple, low cost, safe and rapid fabrication process which results to synthesizing a homogenous, high purity oxide ceramic powders including ultra fine alumina flakes.

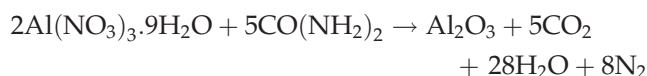
After structural investigation of the sheets, mechanical property of the samples were tested and compared with samples without fillers.

## EXPERIMENTAL

### Preparation of alumina nanostructured flakes

$\alpha$ -phase nanostructured alumina flakes were prepared by rapidly heating an aqueous redox mixture containing stoichiometric amounts of aluminum nitrate, urea (U) and ammonium acetate (AA). After introducing a beaker containing the solution to a preheated furnace ( $\sim 400^\circ\text{C}$ ), the content boiled, foamed, caught fire and burnt with an incandescent flame of gases such as N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O from reaction medium. Depending on the solution in the beaker, the burning took place 3–5 min. After evolution of gases from beaker the only remaining material was very low density spongy material.

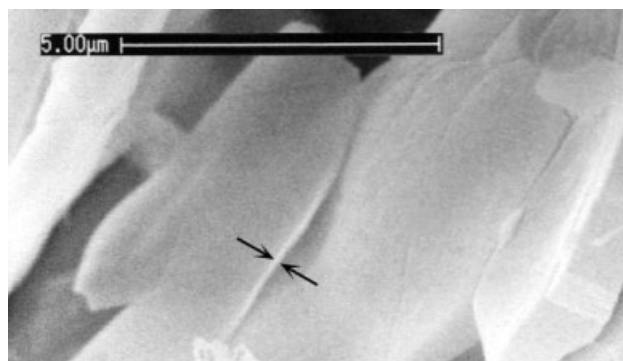
The theoretical stoichiometric reactions for the formation of Al<sub>2</sub>O<sub>3</sub> in the present work are as follow:



The produced alumina flakes were milled to provide powder using an attritor ball mill (Union Process, OH) with 5 mm in diameter zirconium balls in distilled water for 2 h. Ball to powder weight ratio was equal to (80 : 1). After the milling process, the powdered alumina was precipitated using centrifuge technique (Hettich, Rotofix 32) at 4000 rpm three times for 20 min. After centrifuge process, particle size analyzer (Zetasizer, MALVERN Instruments-Nano series) was used to study size distribution of particles. The structure of the flakes was determined by X-ray diffraction method using D4 BRUKER X-ray diffractometer.

### Preparation of the composite sheets

To prepare PMMA solution, 5.23 g of PMMA powder (Merklik, Batch, and No. ph82011) was added into 60 mL acetone (Merck) and mixed for 1 h. Pure PS solution was prepared similar to the PMMA solution i.e. 3.326 g of PS (Merck) added into 40 mL CCl<sub>4</sub> and mixed for 1 h. Composites were prepared as follows: 0.391 g of alumina powder was introduced into the PMMA and PS solutions and sonicated for 24 h. To make thin sheets of pure polymers and composites, the solutions were poured into Petri dishes and left to dry at room temperature for 72 h till constant weight obtained. Finally thin sheets of pure polymer and composite samples with 1 wt % of alumina and thickness about 0.1 mm were obtained.



**Figure 2** SEM micrograph of alumina flakes.

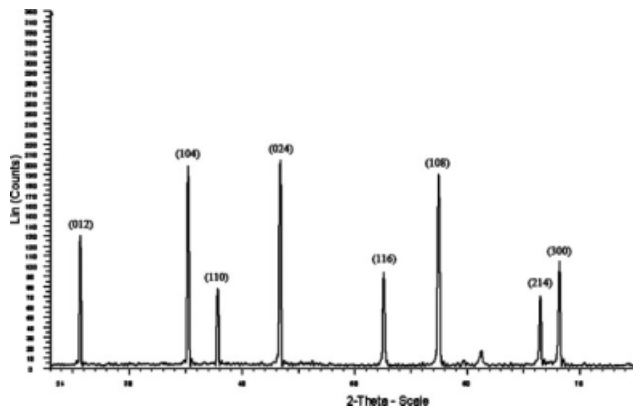


Figure 3 XRD pattern of the  $\text{Al}_2\text{O}_3$  flakes.

### Characterization of the samples

Surface morphology and particles' dispersion in the polymer matrixes were studied using scanning electron microscopy (SEM) (Philips XL30) at 20 kV energy. To observe dispersion in the sheets they were submerged in liquid nitrogen and fractured. Contact angle system SCA20 was used to study hydrophobic properties of the samples by measuring their contact angles. To increase the accuracy, we tested different points on the surface of each sample.

Tensile testing was performed to characterize mechanical properties, using Hounsfield H10KS tensile testing equipment with a loading rate corresponding to a 0.000041 m/sec displacement rate. Samples were prepared according to ASTM D882-00 standard. The elastic modulus of the samples was defined as the slope of the linear portion of the stress-strain curves. At least five specimens of each sample were tested and the mean values were calculated.

## RESULTS AND DISCUSSION

We prepared many solutions containing ratios of urea and AA to obtain flakes with different crystalline structures and flakes' thicknesses.

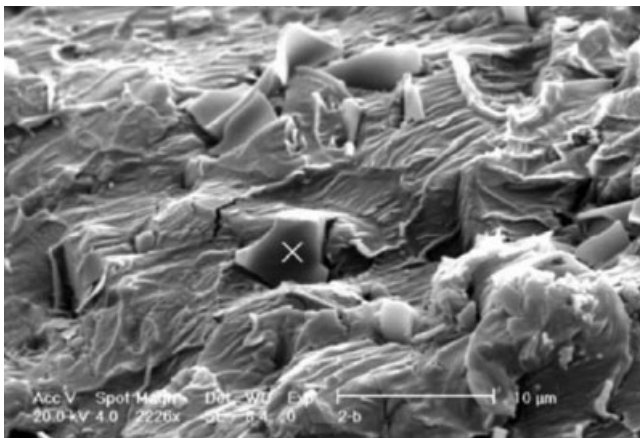


Figure 4 SEM micrograph of PMMA- $\text{Al}_2\text{O}_3$  fracture surface.

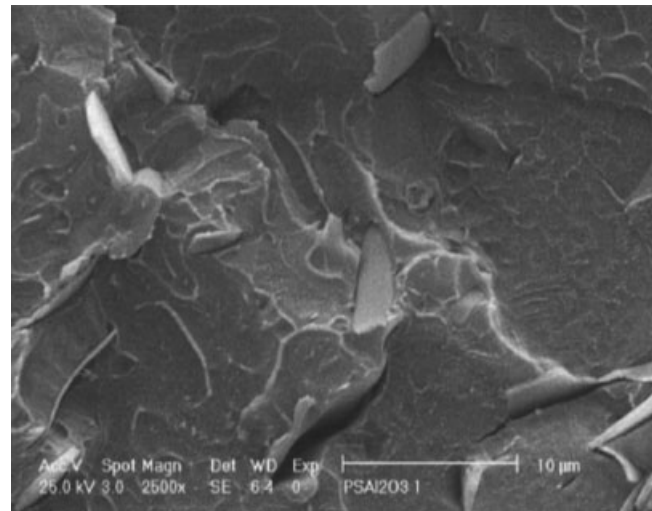


Figure 5 SEM micrograph of PS- $\text{Al}_2\text{O}_3$  fracture surface.

When pure urea was used as fuel, the combustion reaction was highly exothermic. By adding AA as fire extinguisher to the urea the reaction started changing from flame type to smoldering type. When contribution of urea in fuel composition comes less than 60%, the flame temperature is not enough for crystallization and results to synthesizing amorphous particles. So we selected 0.75 U + 0.25 AA fuel compositions for the present study.

As we mentioned above the alumina flakes were milled to provide fine powder. Particle size analyzer's result from dispersed minced flakes in water showed mainly a wide peak around  $1.4 \mu$  as is shown in Figure 1. Further ball milling could not reduce the average size of the alumina flakes much. Figure 2 shows the typical SEM image of the micro-sized flakes with small thickness about one hundred

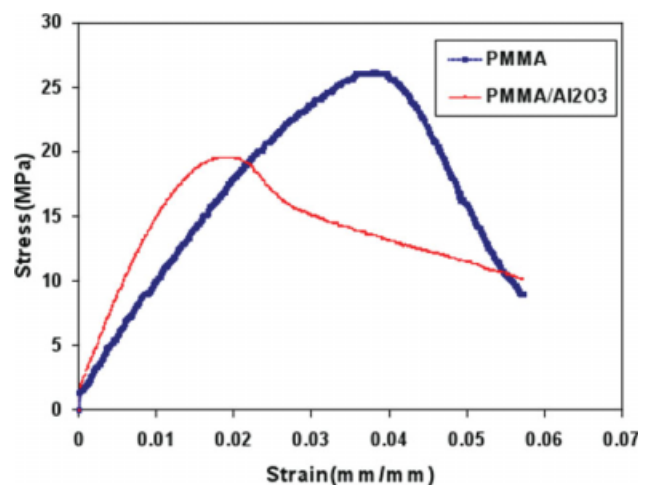
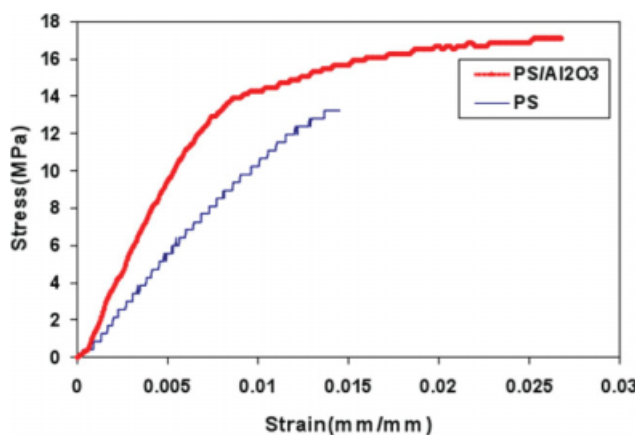


Figure 6 Tensile testing stress-strain curves for pure PMMA and PMMA- $\text{Al}_2\text{O}_3$  composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



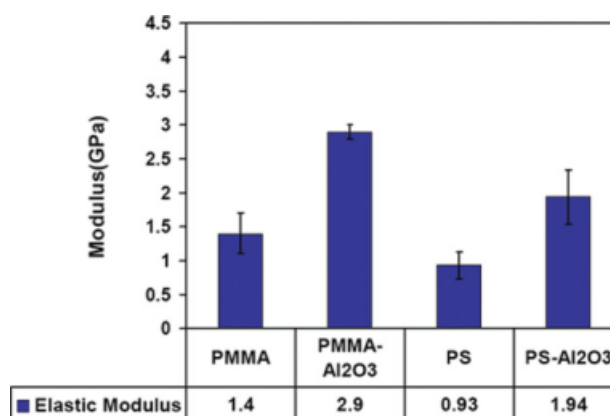
**Figure 7** Tensile testing stress–strain curves for pure PS and PS-Al<sub>2</sub>O<sub>3</sub> composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

nm which were prepared using urea to AA ratio about 3. XRD data from the flakes showed  $\alpha$  phase with broad peaks that is related to small crystalline size (Fig. 3). From width of the peaks and using Scherrer and Warren equation the average size of grains was deduced about  $26 \pm 4$  nm. Then we dispersed the grinded flakes in polymers to make composite sheets. Topography of the fracture surfaces, distribution of the Al<sub>2</sub>O<sub>3</sub> flakes in the polymeric matrixes and elemental composition were determined using SEM images and EDX analysis. As is shown in Figures 4 and 5, the images show a good dispersion of Al<sub>2</sub>O<sub>3</sub> flakes in both PMMA and PS polymeric matrixes.

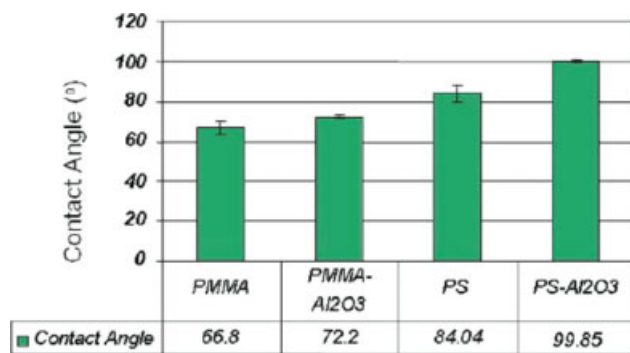
Alumina is known as a hard and high strength material. To compare the effect of alumina addition in polymers on mechanical properties, stress–strain curves of the pure PMMA and PS and also its composites are tested. The results are shown in Figures 6 and 7. Linear part of the curves was used to measure sample elastic modulus and their values are presented in Figure 8. Our data exhibited that the yield stress, maximum values of the curves in PMMA-Al<sub>2</sub>O<sub>3</sub> sample has decreased about 25% compared with pure PMMA polymer but the elastic modulus has increased. A decrease in yield stress is common in some filled polymers, due to de-bonding of the filler from the matrix polymer. This effect that occurs during the tensile process leads to formation of voids which reduces the apparent yield stress of the composites.<sup>13</sup> However, the mechanical behavior in PS-Al<sub>2</sub>O<sub>3</sub> samples presented differently. Figure 7 shows the stress–strain curves of pure PS and PS-Al<sub>2</sub>O<sub>3</sub> composite. In comparison with pure PS, the ultimate strain in PS-Al<sub>2</sub>O<sub>3</sub> composite is increased from 1.4 to 2.7% that shows an increment of about 93%.

In traditional composites, addition of rigid filler usually decreases the ultimate strain, but in these

systems, as shown in Figures 6 and 7, there is no decrement in the value of ultimate strain probably due to high aspect ratio of filler. In PS-Al<sub>2</sub>O<sub>3</sub> composite, the filler particles have increased the plastic deformation and this effect has delayed the failure mechanism. According to the calculated elastic modulus values, shown in Figure 8, addition of alumina flakes increased the elastic modulus in both of these systems. This increment is 107% in PMMA-Al<sub>2</sub>O<sub>3</sub> and 109% in PS-Al<sub>2</sub>O<sub>3</sub> composites. Although in the previous study, composites containing spherical alumina nanoparticles with 39 nm mean diameter showed a decrease in elastic modulus,<sup>8</sup> our data presents positive effect on mechanical properties perhaps due to the high aspect ratio of the fillers' configuration and bonding between polymer matrixes and filler particles. The chemistry of the interaction between PMMA and alumina surface has been reported.<sup>14–16</sup> Since metal oxide surfaces usually have charges due to higher concentration of oxygen, we expect the polar part of polymer to interact with the alumina surface. This effect results in non polar end to become free and therefore, hydrophobic property of the nanocomposites increases. Figure 9 shows better hydrophobic properties for the samples containing alumina flakes compared with pure polymer. Hydrophobicity of dielectric materials plays important role in organic thin-film transistors with gate dielectrics made from polymers such as PMMA,<sup>17</sup> and PS.<sup>18</sup> Also strong correlation between the dielectric constant and the field effect mobility has been observed i.e. the increment of dielectric constant increases the mobility of charge carriers. It is shown that filling the polymeric dielectric gates with inorganic nano-<sup>19</sup> or microparticles<sup>20</sup> can increase the dielectric constant which leads to reduction of the operation voltage and increment of charge mobility. On the other hand among the number of effective parameters in transistors'



**Figure 8** Elastic modulus of the pure polymer and composites samples. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 9** Contact angles of water droplet on the surface of pure polymers and polymers containing alumina flakes. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

performance, “hydrophobicity” and “less roughness” of the gate dielectric surfaces have important roles. The surface —OH groups (less hydrophobicity) and the rough surfaces result in an inferior channel/dielectric interface along with poor crystalline growth of the organic channel, and thus OTFTs fabricated on such dielectric surfaces usually exhibit undesirable device characteristics.<sup>21</sup> Within this study it might be concluded that using the alumina flake fillers in polymeric gates can be a good idea.

In summary, our results show that the mechanical properties of PMMA-Al<sub>2</sub>O<sub>3</sub> and PS-Al<sub>2</sub>O<sub>3</sub> composites which were prepared by solution method are improved.

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