

Preparation, mechanical properties and fracture of the optimal surface modified alumina silicate based ceramic particles reinforced polymer composites

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Abstract

Polyester resin was replete with a high percentage of surface-modified fly ash ceramic particles using a combination of sol-gel and handlay-up techniques. The characterizations of the fly ash powder showed that the ceramic particles were the spherical solid type and composed of both the glass and crystal phases. The composites were subjected to the mechanical and Charpy impact tests as well as the fracture studies. Consequently, the hardness was found to increase linearly. The required results derived from both the mechanical and impact tests indicated that a positive correlation was obtained. The tensile strength of the higher percentage was lowered due to the existence of large size particles and the elongation at break was decreased due to the restriction of the polyester molecular chain flexibility. Finally, the fracture surfaces of the excellent compositions indicated that the particles had strongly bonded with the polyester matrix. This is mostly due to the existence of reasonable (-OH) groups on the particle surfaces.

Keywords: *Filler; Polymer; Fracture; Tensile strength; Impact strength*

1. Introduction

Nowadays filled polymer composites are finding a growing demand in various engineering applications. The improvement of the mechanical, electrical, thermal and optical properties of the polymers, while reducing their costs through the addition of the filler materials and utilizing advanced processing routes, has become an extremely popular research interest [1]. Among the commonly used polymers, include thermoplastic polyesters; usually, they are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements such as O, N, and Si. The polyesters are used in applications such as appliance parts, electric and electrical components, HVAC components, industrial light housings, and automotive. However, because of their excessive brittleness, these thermoset polyesters are being nearly useless if not combined with fillers. On the other hand, fly ash utilization has become a nuisance to governments as much more is produced each day. Fly ash inorganic components are finely divided residues, which are becoming one of the

principal raw materials. A fly ash has several advantages; it contains ceramic materials such as silica and alumina. Silica provides the highest hardness, while alumina is an electrical insulator with a relatively high thermal conductivity.

At present, works are being done to investigate the properties of the fly ash-reinforced polymers. Challenging efforts are being focused on treating the surface of the fly ash with chemical solutions to build a strong interface adhesion between the fly ash particulates and the selected matrix. There are reports made with the addition of unsilanized mica into unsilanized fly ash reinforced polyester, of which an increase of the tensile strength and elongation was reported [1]. The surface-coated fly ash used as filler in biodegradable polyvinyl alcohol (PVA) composite films showed 33% higher strength than those of unmodified fly ash [2]. A surface modified fly ash improved an interface adhesion between fly ash and polyether ether ketone (PEEK) with some improvements in the mechanical and Charpy impact strengths [3]. The study of the surface modification of

the purified fly ash and application in the polymer also showed that a rough surface of the composite fly ash in the $\text{Ca}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ system improved the interface when blended with polypropylene (PP) [4]. However, there are limited studies done on the fly ash-reinforced polyester resin matrix. There are efforts reported in the study of the polyester resin modified with maleated castor oil while filled with fly ash particles [5]. The polyester resin as an organic binder contained fly ash as a fine aggregate material replaced the normal river sand in polymer concrete systems [6].

In the present paper, the study of the polyester reinforced with different sizes of the fly ash particles of the previous work [7] was extended. The chemical and physical characterizations of the selected fly ash were carried out and applications in the unsaturated polyester were reported. Accordingly, the required properties derived from both the mechanical and Charpy impact tests of different compositions, using the surface-modified precipitated fly ash, were primarily chosen. From the fracture studies, a very distinguished interface for every particle was achieved. This advantage indicates that the methods of the fabrication are effective.

2. Materials and Methods

2.1 Materials and Sample Preparations

The poly(methyl methacrylate) (PMMA) orthophthalic unsaturated polyester (UP) resin was purchased from a company and the fly ash (FA) powder was collected from a Coal Power Plant located in Malaysia. The surface-modified fly ash was used to study various properties. The preparation of the fly ash by the sol-gel technique was as follows: 30 g of FA particles were mixed with 30 ml of ethanol solution ($\text{CH}_3\text{CH}_2\text{OH}$) and 20 ml of distilled water (H_2O). The mixture was stirred uniformly by using a hot plate stirrer at 70 °C for almost 30 min. The surface-modified FA was then dried in an oven at 110 °C for 1 h. Next, neat polyester and FA-reinforced polyester samples corresponding to the equation $UP-\alpha FA$ ($\alpha = 0-50$ wt.%) were prepared by the hand lay-up technique as follows: the α wt.% of the FA was mixed homogeneously together with the matrix system consists of polyester and 1% hardener. The mixture was poured into a mold fabricated for three specimens (tensile, Charpy impact and hardness tests). The mold was fabricated on a 20×12.7×1.6 cm aluminum block. The specimens were allowed to cure for about 1 hour at room temperature before removing them from the mold. They were then cured at room temperature for 24 h before post-curing them in an oven at 90 °C for 1 h.

2.2 Characterizations and Testings

Particle size distributions of the surface-modified FA particles were analyzed using Mastersizer 2000 particle size analyzer, Malvern Instruments Ltd. Consequently, the powder was pulled from the machine vacuuming system of the analyzer at a pressure of 1 bar and then a computer software was used to calculate the particle sizes. The as-received FA was used to determine the density using the Archimedes's method. The phase identification was performed by XRD analysis using the X'Pert PRO Diffractometer from Panalytical B.V Company. Thus, diffracted X-ray beams were collected and compared to the standard patterns available with expert high score computer software library. The hardness test was done with the Mitutoyo Vickers hardness tester. Accordingly, for each specimen, an average of 20 hardness values was taken at 9.81 N load applied for 12 seconds. The tensile specimens were prepared according to ASTM D-638-I standard, having a gauge length of 50 mm, a gauge width of 13 mm and a thickness of 3.2 mm. The tensile test was done on AG-1 100KN SHIMADZU tensile testing machine, applying an axial tension force gradually to produce an axial elongation rate of 0.2 mm/min. The Charpy impact test was done by using HT-8041A test model having the 7.5-Joule and the pendulum weighs 2.6 Kg. Consequently, each specimen was cast according to ASTM D-6110-10 standard. The samples are 80 mm in length, 10 mm width and 4 mm thickness. The fracture surfaces of the samples subjected to both tensile and impact tests were examined in the ZEISS EVO 50 SEM from Oxford Instruments. The samples were gold coated with an ion sputtering unit beforehand because FA particles contained in the fabricated composite are non-conductive materials. This gold layer serves as a conductor for the electron beam in order to be scanned.

3. Results and Discussion

Particle size distribution of the surface-modified FA particles (Fig. 1) lies in the range from 0.02 to about 600 μm . The figure indicates that both narrow size ranges (maximum 15 μm) and large size ranges (maximum 120 μm) are used. The mean value of the non-symmetric distribution was almost 60 μm . The density was measured at 1.12 g/cm^3 , which means that the fly ash was the solid type.

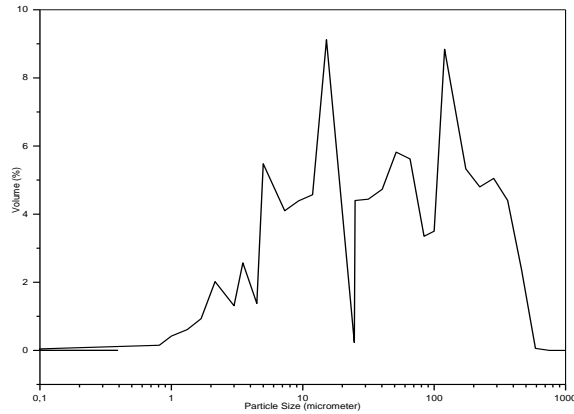
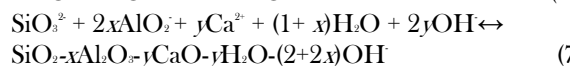
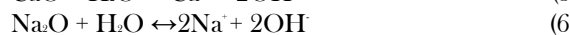
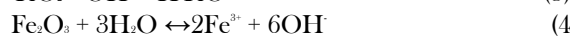


Figure 1. Particle size distribution of the modified fly ash particles

The crystal structure was analyzed by XRD. The XRD pattern of the as-received FA particles (Fig. 2) shows a mild hump ranging from 15° to 25° 2θ indicating the presence of the amorphous phase. From the percent mass composition of a FA taken from a nearby power plant station, the glass phase consists of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , TiO_2 , P_2O_5 , MgO , K_2O and MnO [8]. The percentage of the glass in a bulk FA ranges from 45% to 80%, while the remaining percentage is the crystallinity of the FA [9]. As for a chosen FA particle, it had a wide distribution of different carbonaceous materials richer in Si and Al and with minor concentrations of Fe, Ca, Ti, Mg, K, Mn, Na and carbon traces (Table 1). The composition of a particle such as Al_2O_3 means the major element is aluminum, but has a minority in any other elements. It is assumed in the hydration reactions that SiO_2 , Al_2O_3 and TiO_2 consume hydroxides; while Fe_2O_3 , the earth alkalis (CaO/MgO) and alkalis ($\text{Na}_2\text{O}/\text{K}_2\text{O}$) give them. Thus, the reactions of the glass FA are as given in the equations (1-6). Accordingly, a number of reactions can be produced in different existing conditions, depending on alkali content and temperature of the ambient solution. On account of the chemically activated FA, both the active silica and alumina react with hydrated lime and produce varieties of silicate and aluminate products, which deposit, nucleate and grow on the particle surfaces [04]. Therefore, the equation (7) is the major possible product that occurs thermodynamically.



Where x and y are the mole fraction ratio of the glass phases.

In addition, the XRD pattern of the FA particles shows the existence of the peaks of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), quartz (SiO_2), aluminum oxide (Al_2O_3), calcium aluminum oxide (CaAl_2O_6) and small amounts of hematite (Fe_2O_3). Hence, a part of the FA was crystalline (richer in quartz and mullite). This part is nonreactive and contains the crystalline SiO_2 (in quartz and in mullite) and crystalline Al_2O_3 (in mullite and other forms only). Mullite was formed by SiO_2 reacting with Al_2O_3 at the high temperature of $1200\text{--}1650^{\circ}\text{C}$ in the boiler of the power plant, which had a very stable crystalline form. In the modification, the conditions used were FA/(CH₂-CH₂-OH)/H₂O weight ratio of 1/1/0.5, $70\text{--}90^{\circ}\text{C}$ slurry temperature, 30 minute heating with constant rpm stirring speed and 1-hour isothermal heating at 110°C . Thus, the coating of the particles was partial to fully achieve. This was proven by XRD of which the intensity of many crystalline products was increased and the significant increase was seen in the peaks of Al_2O_3 , which means that crystalline spherical particles richer in Al reacted with the minor elements Ca/Si were formed through the chemical reaction (eq. 7). This is mostly due to the presence of (-OH) groups on the particle surface (eq. 4-7). This thin layer plays a significant role in the reduction of the attractive forces of particle-particle and helps to disperse in the matrix media. The orderly distributed filler in polymer composite attributes higher mechanical strength compared to neat polymer matrix [2].

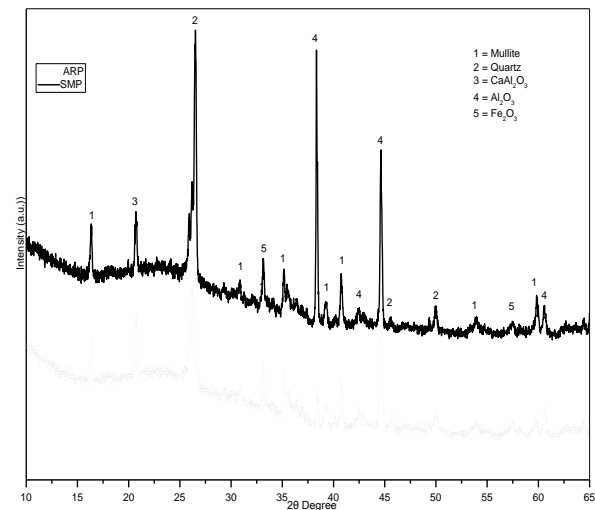


Figure 2. XRD pattern of the as-received (ARP) and surface-modified (SMP) fly ash particles

The microhardness of the samples prepared from the surface-modified FA particles and compared to the surface-original FA particles is given in (Fig.3). For the surface-modified FA, the hardness was increased with the increasing FA particles, which was similar to the hardness obtained in the original FA particles-reinforced polyester matrix.

The almost constant increase of the hardness implied that the particles of the FA were incorporated within the polyester constituents (C-O-H) with a uniform distribution of the particles. The higher hardness of the as-received FA may be due to the numerous existing functional hydroxide (-OH) ions. In general, the hardness depends on the modulus of elasticity.

The higher hardness is, the higher elastic modulus will be. Both hardness and modulus of elasticity (E) are related to porosity, and the total porosity is directly related to density (ρ). The density of UP (1.40 g/cm^3) is higher than the solid FA (1.12 g/cm^3) used in this research, which means a lightweight composite was obtained. It has been mentioned [08.] that at higher volume fractions of spherical particles moving relative to a continuous fluid, the particles interact with each other and reduce the velocity. The model used to describe the velocity is

$$V \propto d^2 (\rho_s - \rho) \quad (8)$$

Where d is the FA particle diameter ($60 \mu\text{m}$), ρ_s is the density of the FA spherical particles and ρ is the density of the polyester. In other words, due to the agglomeration which limited the reaction of the FA particles with the matrix when the amount of FA exceeded a limit, the velocity decreased due to the smaller density of the particles. It was also reported [2] that the decrease in the ultimate mechanical strengths was due to the formation of a cluster or agglomerate among the FA particles themselves, resulting in a filler-filler interaction and a poor interface bonding, due to the strong polarity of hydroxide groups on the FA surfaces. Hence, the reduction in the properties may occur at the higher volume of the FA particles.

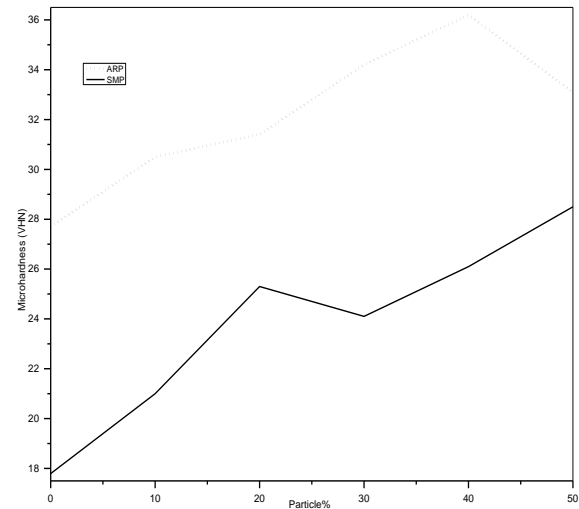


Figure 3. Micro-hardness of the as-received (ARP) and surface-modified (SMP) fly ash particles

The tensile details of the neat and FA-reinforced cured samples are shown in Fig. 4. The tensile strength increased by 8% when there was 20% FA while the lowest ebb of 38% was found when the amounts of FA are 50%. The σ -modulus was increased up to 40% FA with development by 112%. The elongation-at-break was found to decrease as compared to the average value of the neat polyester of 8%. The higher strength was due to the creation of stronger interface interactions between the polyester and FA particles. This leads to greater load transfer between the polyester and the filler and enables greater stress generated in the material before the failure [10]. The decrease of the tensile strength at higher filler contents is observed. The reason was largely because of the interactions between the filler and polyester matrix was impeded resulting in reduced strength of the composites [11].

The presence of the minor traces of the carbon impurities might be a cause of the reduction. The strain at failure decreased with increasing the filler addition of the FA due to the interface interaction, which restricted the flexibility of molecular chain of polyester.

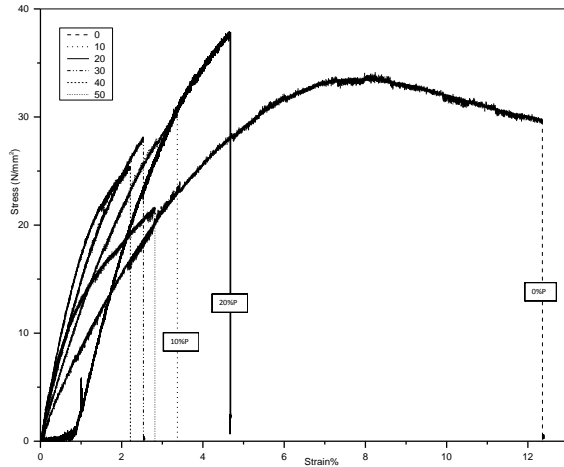


Figure 4. The mechanical properties of FA-UP composite

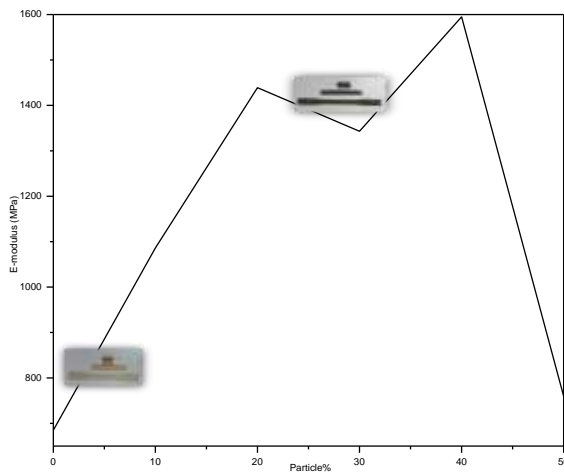


Figure 5. The e-modulus property of the FA-UP composite

The modulus data of the composites are given in Fig. 5. The modulus was increased with FA addition. Moreover, the extent of the increase was greater than the neat polyester. This was because the interaction hardly influences the strength of the modulus [12]. In other words, the modulus is a phenomenon involving the initial strain values that require the lower stress. The higher filler reduced the modulus due to super-saturation of the FA concentrations. Thus, the reduction in the intimate contact area between polyester and FA occurred [10].

Figure 6 depicts the Charpy impact strength of the polyester-FA composites. The figure shows the composites prepared from the surface-modified FA particles and compared to the surface-original FA particles. There was a considerable increase as the FA

content increased. The reduction was seen at 50% FA, which is in accordance with the ϵ -modulus. Both the tensile and impact properties indicated that there was an optimum interaction between the matrix and FA components. At 10% FA, the intercomponent bonding was slightly strong. At 20% FA, the increase was observed in all the properties, i.e. hardness, tensile strength, impact strength, modulus and tensile strain. At 30% FA, it is evident from some properties that the intercomponent bonding was lowered. At the points where there were higher amounts of FA particles, the increase in hardness was maintained while a good proportional trend can still be seen in hardness, modulus and impact strength. The impact resistance is the ability of a material to resist breaking under a shock loading. Since it is also defined as the ability to resist the fracture under stress applied at a high speed, it should be noted that the applied stress in the Charpy impact is limited under the yield point.

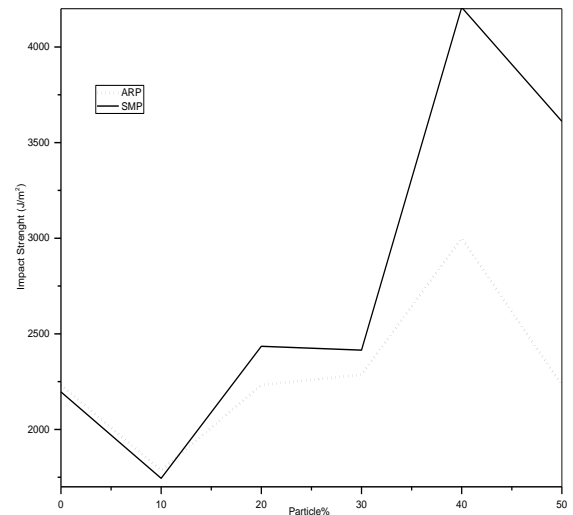


Figure 6. The impact strength of the as-received (ARP) and surface-modified (SMP) fly ash particles

The fracture morphology of the tensile tested specimens of UP-20% FA composite is shown in Fig. 7. It was observed that the fracture surface was not smooth, but slightly rough. The fracture morphology also shows small size voids seen well around the large particles. The void concentration can be increased with FA concentration, thus leads to reducing the strength and elongation at break. The SEM image of the impact-fractured surface of 40% FA (Fig. 7) also revealed that large sized FA particles played a significant role in bringing about the fracture. More voids can be expected at higher concentrations of the FA. Contrary to the impact-fractured sample of 40% FA filled HDPE [12], the evidenced crack formation at the fracture surface cannot be observed. The

decrease in the impact of 50% FA implied that possible cracks were rapidly propagated due to the large voids. Thus, contributing to the overall impact strength of the composites. Hence, the 40% FA represent the optimum composite for both impact and ϵ -modulus applications. It is mainly due to the lower pore content or higher hardness.

The further study of the SEM images is shown in Fig. 8. The fracture morphology showed that almost all FA particles remained intact in their places. This is the evidence for the existence of good interface bonding between the polyester matrix and FA particles. The SEM images also revealed that small sized FA particles did not play a significant role in bringing about the fracture. It was found that the composites with smallest size FA particles (less than about 3 μm) proved to be better in enhancing strength and relative elongation [12].

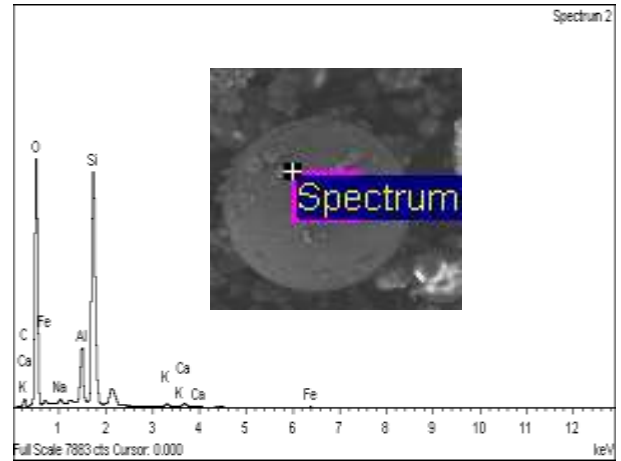
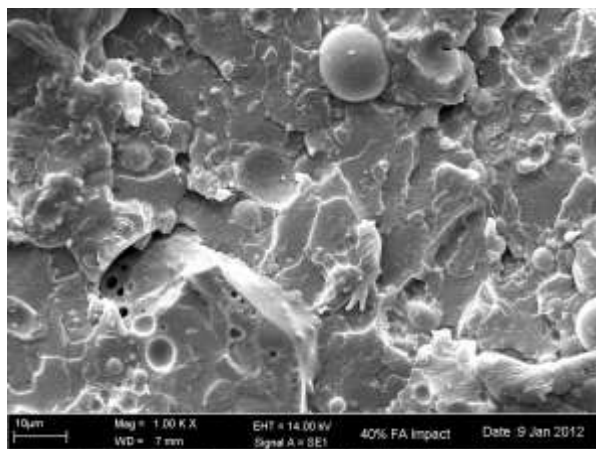
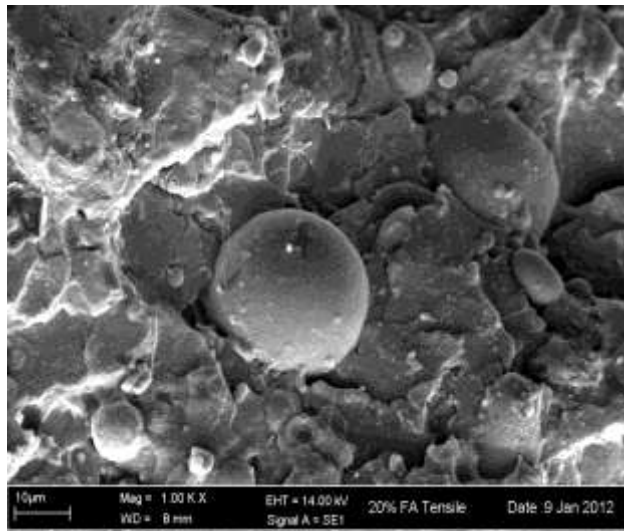
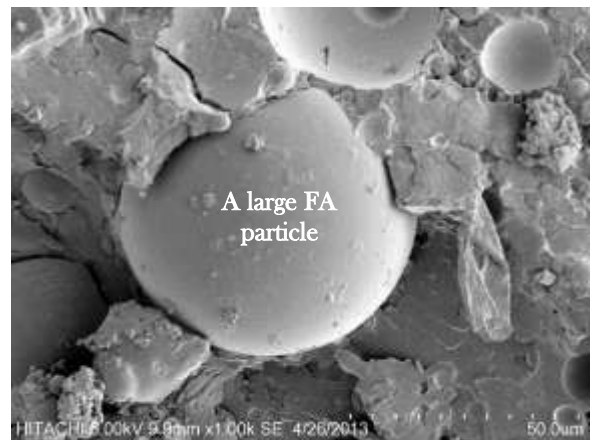


Figure 7. From first to last graph: (1) SEM image of 20% FA-UP tensile test specimen, (2) 40% FA-UP impact specimen, and (3) Fig. 2: SEM-EDX analysis of a chosen particle..



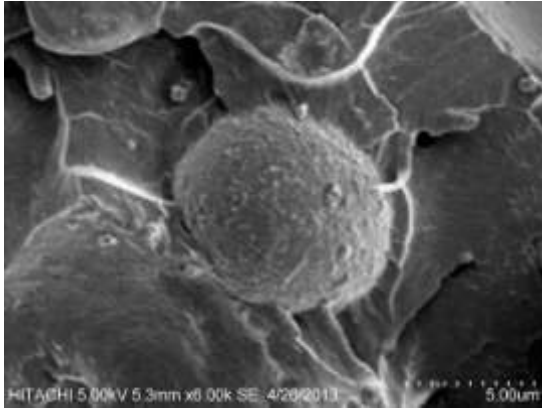


Figure 8: From first to last photo: (1) SEM images of 40 wt.% FA-UP tensile fracture morphology showing a uniform distribution of the particles, (2) spotted large FA particle, and (3) good attachment of small size FA particle

4. Conclusions

The reinforcing FA particles for UP matrix was proven in this study. The different phases of the FA incorporated into the UP matrix were well evidenced by XRD. This amount of FA into UP brought about the increase in hardness, ϵ -modulus, tensile and impact strengths. When 30% FA were added to the UP matrix, FA agglomerates might occur within the polyester matrix. However, the amounts of the UP still brought about the improvement in hardness and ϵ -modulus. Thus, the composite is an excellent for both impact and ϵ -modulus applications because the higher hardness.

Acknowledgements

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