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Development of Al-Cu-Fe Quasicrystal-Poly(*p*-phenylene sulfide) Composites

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ABSTRACT

Quasicrystalline Al-Cu-Fe powders were used as a novel filler material in poly(*p*-phenylene sulfide) (PPS). These polymer/quasicrystal composites showed useful properties that may be beneficially exploited in applications such as dry bearings and composite gears. Al-Cu-Fe quasicrystalline filler significantly improved wear resistance to volume loss in polymer-based composites. In addition to improving the composite wear resistance, the Al-Cu-Fe filler showed low abrasion to the 52100 chrome steel counterface. Furthermore, mechanical testing results showed a two-fold increase in the storage modulus of the reinforced composites compared with the polymer samples. In addition, the Al-Cu-Fe filler was compared to its constituent metals, aluminum oxide, and silicon carbide in PPS. Chemical analysis of the wear interface by X-ray spectroscopy indicated the generation of a third body oxide layer during wear. The fabrication in addition to the thermal, mechanical, and wear properties of these unique materials is described.

INTRODUCTION

Fillers and additives play an important role in the production of polymeric materials. The term filler is a generic label used for solid materials added to plastics. Fillers are often incorporated into plastics in large volumes. Plastics additives encompass other materials usually used in lower concentrations than fillers such as plasticizers, flame retardants, lubricants, and biocides. Both fillers and additives improve certain aspects of the end polymeric product.

Historically, fillers are used to reduce the cost of plastics by replacing the more expensive resin with inexpensive materials such as calcium carbonate, kaolin clays, silicas, and talc. However, other value-added properties are gained through the use of fillers. Fillers can improve the physical, rheological, chemical resistance, thermal, optical, and electrical properties of a polymeric material. For example, talc can be defined as a reinforcing filler. In addition to reducing cost, talc-filled plastics have higher stiffness and better creep resistance than plastics containing other inexpensive fillers like calcium carbonate. Metallic fillers are used to increase the electrical and thermal conductivity of plastic materials. Metal-filled plastics have more specific uses such as anti-fouling compounds, corrosion-resistant paints, maintenance and repair products such as “cold-poured steel” and tooling [1].

New filler materials are continuously being investigated with the premise of combining the properties of the filler and the processibility, adhesive properties, and high strength to weight ratios of the polymer matrix. Quasicrystals, first discovered in 1984 [2], are complex metal alloys that are most comparable to ceramic particulate fillers in polymer composites. Bulk quasicrystalline materials have useful properties including low surface energy compared to most metals, low wettability in contact with most aqueous solutions, low coefficients of friction, low thermal conductivity [3], high hardness, and high softening temperatures [4]. The major drawback in quasicrystal applications is in the brittle nature of the materials up to a few hundred degrees Celsius. Quasicrystal applications include coatings prepared by thermal spray or thin-film growth, precipitation-strengthened bulk materials, and Al-matrix quasicrystal composites [5,6]. The use of Al-Cu-Fe quasicrystals to improve the mechanical properties of polymeric materials is reported in our previously filed patent [7]. The results indicate that these new polymer/quasicrystal composites are a means of enhancing the properties of certain organic polymers while providing a new means of processing quasicrystals. In addition, Al-Cu-Fe quasicrystals are projected to be economically attractive with a relatively low cost of $ 10.00 / lb [6]. Specifically, the thermal, mechanical, and wear properties of Al-Cu-Fe filled poly(*p*-phenylene sulfide) composites are investigated in this paper.

EXPERIMENTAL DETAILS

Materials. Quasicrystalline Al-Cu-Fe icosahedral phase rich powders, QC powder, with the composition $Al_{65}Cu_{23}Fe_{12}$, were prepared at Ames National Laboratory [8]. Al-Cu-Fe powder was chosen based on several factors including its potential low cost, low toxicity, and availability. These powders were used as prepared by gas atomization with an approximate composition of 60 percent icosahedral phase and 40 % cubic phase [9]. Quasicrystalline powder was classified by sieve analysis to achieve various size fractions. The morphology of the resulting powder was determined to be spherical by scanning electron microscopy. PPS powder, Ryton-PR6, was provided by Phillips Petroleum Company.

Composite Fabrication. Desired amounts of PPS and quasicrystal powders were weighed, added together and shaken vigorously in a sealed container for ten minutes to provide optimum mixing. The volume fraction of the quasicrystals in the composite materials studied was in the range of 10 to 60 percent. The resulting QC/polymer powder mixture was placed in a die mold with a diameter of 2.50 cm and a final volume of 1.58 cm^3 when fully compressed. The mold was equipped with a thermocouple to monitor temperature during the compression molding process. The filled mold was heated in a variable temperature hydraulic press (Carver) under a pressure of 7 MPa to 310 °C. The samples were held at the set temperatures for ten minutes before cooling under pressure to room temperature. The resulting composite surfaces were polished with 320-grade emery paper followed by washing with deionized water. The same procedure was used to prepare compression-molded samples of neat PPS.

Characterization. Differential scanning calorimetry was performed on a Perkin-Elmer DSC 7 under a nitrogen purge at a heating and cooling rate of 20 °C/min. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA 7 in air with a heating rate of 20 °C/min. Measurements of storage modulus were obtained using a Perkin-Elmer DMA 7e equipped with a three-point bending measuring system with a 15 mm span length. Rectangular bars of the polymers and composite samples were machined to dimensions of 17 mm wide, 1.00 mm high and 3.25 mm in depth from compression molded disks. The scan rate was set at 5 °C/min with a static force, dynamic force and frequency of 110 mN, 100 mN and 1 Hz, respectively. Wear tests were performed using a pin-on-disk type configuration. The wear testing analysis for polymer and composite disks were run using a Falex Friction and Wear test machine Model # ISC450PC. A linear speed of 0.15 ms^{-1}, a 10 N load, and a total linear distance of 1 km were used in the wear testing. Chrome steel 52100 balls with a diameter of 0.635 cm were used as the stationary pin materials. After a wear test was performed, a profilometer (Hommelwerke) was used to determine the amount of volume loss from the composite sample. The weight loss of the sample and the counterface pin were also measured. The composite samples and counterface pins were then evaluated by scanning electron microscopy (SEM) (Hitachi). X-ray analysis of the samples was performed in the scanning electron microscope using an energy dispersive spectrometer (Oxford). A second pin-on-disk configuration was used with a PPS pin (3 mm x 3 mm x 20 mm) filled at 30 vol. % with Al-Cu-Fe powder (45-53 μm) on a molybdenum disk (diameter of 25.4 mm). A linear speed of 0.3 ms^{-1}, a 5 N load, and a total linear distance of 2.5 km were used in the wear testing. Analysis of the transfer film on the molybdenum disk was performed by X-ray photoelectron spectroscopy (XPS) to determine the changes in chemical composition resulting from wear.

The samples were analyzed by XPS with mono-chromatized Al X-rays. The system used was a 5500 Physical Electronics multi-technique system with 0.50 eV resolution on the Ag 3d peaks. The spatial resolution is 1.8 x 1 mm. The spectra obtained on the pin have charging artifacts and were corrected for it by shifting all spectra such that carbon 2s peak is at 284.5 eV. The spectra for the tracks on the Mo disk were not corrected. The "scraped" track had the topmost transfer material scrapped off using a Mo sharp edge.

DISCUSSION

Poly(*p*-phenylene sulfide) is a semi-crystalline high performance thermoplastic with excellent thermal and mechanical properties, including continuous usage temperatures of 200 °C to 240 °C [10]. The grade of PPS used, Ryton PR6. was a light tan powder. The PPS powder was classified by sieve analysis and the 45-53 μm fraction was used in the production of all composite samples. The Al-Cu-Fe quasicrystalline powder was also classified, reserving the 45-53 μm fraction for composite fabrication. The equal particle size of the polymer and the quasicrystals improved the dispersion of the Al-Cu-Fe particles in the final composite.

The thermal properties of PPS and the PPS / Al-Cu-Fe composites were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). No adverse interactions or notable differences between the PPS and PPS / Al-Cu-Fe composite were observed in the DSC thermograms shown in figure 1. The thermogram results showed a glass

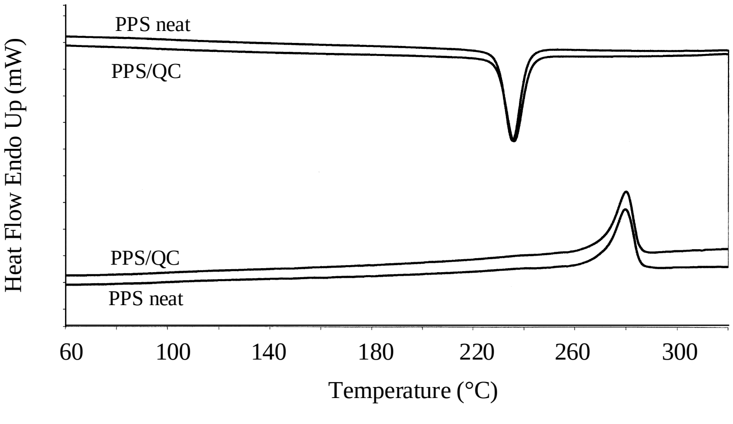

Figure 1. DSC thermograms of PPS and PPS/QC composite upon heating (bottom) and cooling (top) at 20.0 °C/min.

transition temperature of 85 °C and a melting temperature of 280 °C for neat PPS. Furthermore, 5 % weight loss temperatures of the PPS and PPS / Al-Cu-Fe composites in air were nearly identical at 530 and 533 °C, respectively. Thus, the useful temperature limit of the PPS / Al-Cu-Fe composite were dictated by the PPS matrix.

Storage modulus (E'), which is a measure of the stiffness or rigidity of a material, of the PPS / Al-Cu-Fe composite samples increased with increasing volume percent of Al-Cu-Fe filler. The magnitude of the storage modulus, measured by dynamic mechanical analysis (figure 2), increased in the PPS/QC composite with increasing Al-Cu-Fe filler content above a critical volume fraction of 10 %, especially below the glass transition temperature of the polymer matrix. The increase in E' with additional filler was expected and is a common trend when solid fillers are used in a polymeric matrix [1]. A comparison between Al-Cu-Fe and aluminum at 30 vol. % was made in PPS (Figure 3). While storage modulus did increase in the Al-Cu-Fe composites, the magnitude of the increase was very similar to that for aluminum. Therefore, while increasing the modulus of the composite material, Al-Cu-Fe quasicrystalline powders showed no advantage over aluminum in improving the stiffness of the PPS composites.

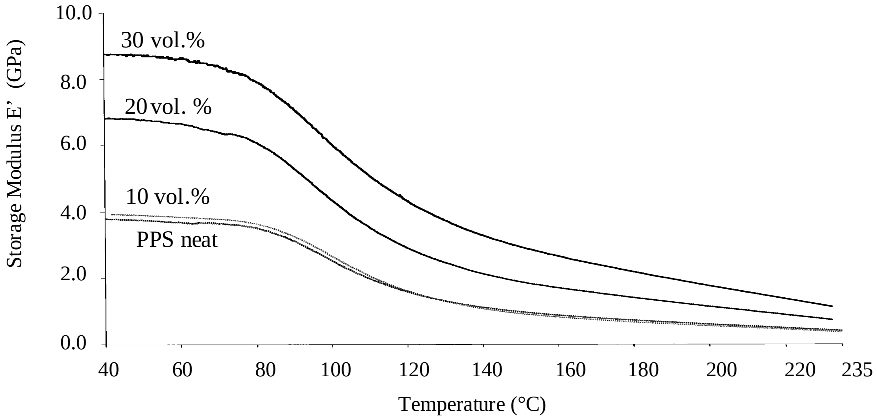

Figure 2. Dynamic mechanical analysis of PPS composite samples filled with Al-Cu-Fe (45-53 μm) quasicrystalline powders at various loading levels. The stiffness of the composite increased with increased Al-Cu-Fe loading.

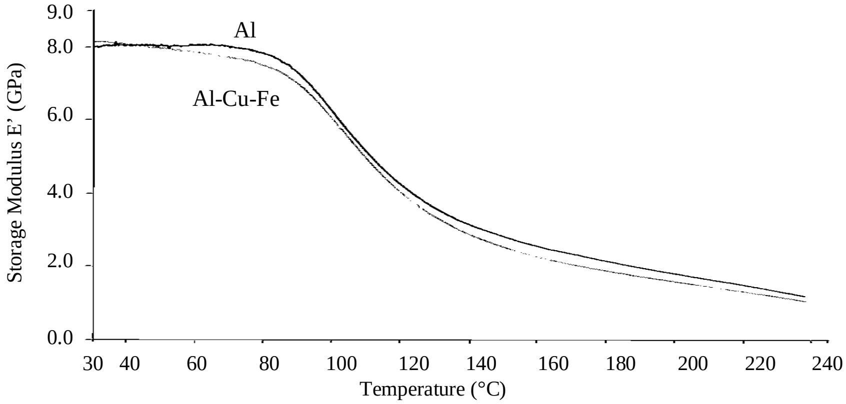

Figure 3. Dynamic mechanical analysis of PPS composites filled at 30 volume percent with Al (-45 μm) and Al-Cu-Fe (-45 μm).

The main focus of this study was to evaluate the wear properties of Al-Cu-Fe quasicrytal-polymer composites. Wear testing of the PPS-Al-Cu-Fe composites was performed in a pin-on-disk configuration. Composite disks were produced by compression molding; 52100 chrome steel balls (diameter = 0.635 cm) were used as the counterface pin. Other materials including mild steel (iron), copper, aluminum, aluminum oxide, and silicon carbide were used, tested, and compared to the Al-Cu-Fe quasicrystalline filler in PPS. During a wear test, the composite disk was rotated on a turning platform while the pin was held in contact with the disk by an arm with an applied load. Volume loss of the composite samples was measured with a profilometer. Mass loss from both the steel pin and composite disk was recorded.

Wear tests were initially performed on PPS samples filled at 30 volume percent with aluminum, mild steel, and Al-Cu-Fe quasicrystal powder. An unfilled sample of PPS was also tested. The test conditions were set at a normal load of 10 N, a total linear distance of 1000 m, and a linear speed of 0.15 m/s. Under these conditions, the role of the filler upon composite wear was apparent (figure 4). Aluminum filled PPS had the highest volume loss. The addition of mild steel powder also caused the wear of the PPS composite to increase compared to the neat PPS sample. Similarly, Bahadur and Gong [11] have shown that the addition of iron (35 volume percent) to increase the wear of poly(ether ether ketone) (PEEK), a high-performance thermoplastic. This effect was explained based on the relationship of the shear strength to the heterogeneous structure of metal-filled polymer composites. The shear strengths of polymers were shown to increase with the addition of a strong filler particle. However, the heterogeneous structure of the composite, created by the addition of a filler, increased the number of sites available for crack initiation. Therefore, in strong polymers such as PEEK, the heterogeneous nature of the composite outweighed the increase in shear strength which lead to an increase in

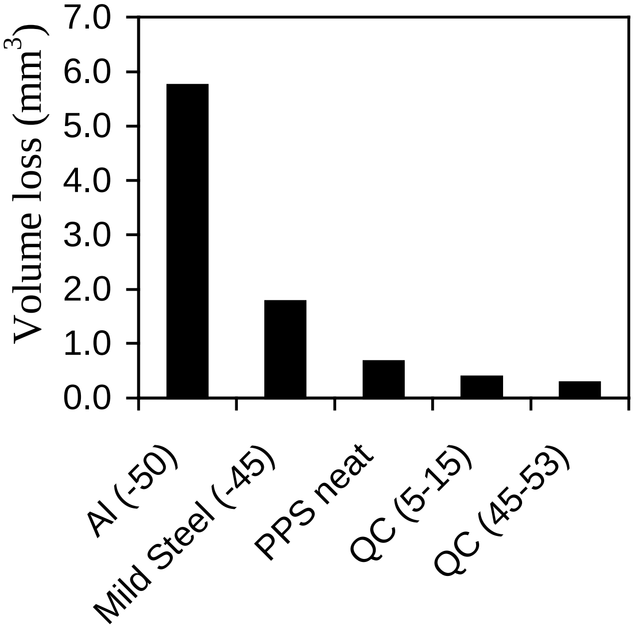

Figure 4. Volume loss from PPS composites filled at 30 volume percent (size fraction in microns). Wear tests were performed with a 10 N load, linear distance of 1000 m and linear speed of 0.15 m/s against a 52100 steel pin.

wear. In the PPS composites studied here, the aluminum filled sample showed higher wear than the mild steel sample. In both cases, the weakening effect was greater than any strengthening effects which resulted in increased wear compared to unfilled PPS. In contrast to aluminum and iron, the addition of Al-Cu-Fe quasicrystals at 30 volume percent decreased the wear of the PPS / Al-Cu-Fe composite compared to unfilled PPS. In this case the strengthening effect of the quasicrystalline Al-Cu-Fe was greater than the weakening effects of the heterogeneous composite structure. In addition to the high hardness of Al-Cu-Fe, the low surface energy and coefficient of friction of this mater compared to its constituent metals may have been partially responsible for the decreased composite wear.

Examination of the composite wear tracks, by scanning electron microscopy, further showed the role of filler hardness upon wear behavior. In the micrographs, metallic particles of the composites appeared lighter than the PPS matrix due to atomic number contrast. Aluminum and mild steel particles appeared to be deformed and smeared in the wear tracks in figure 5a and 5b. In contrast, Al-Cu-Fe particles retained their spherical shape (figure 5c). The Al-Cu-Fe particle showed minor abrasion resulting in flattened areas of contact with the pin.

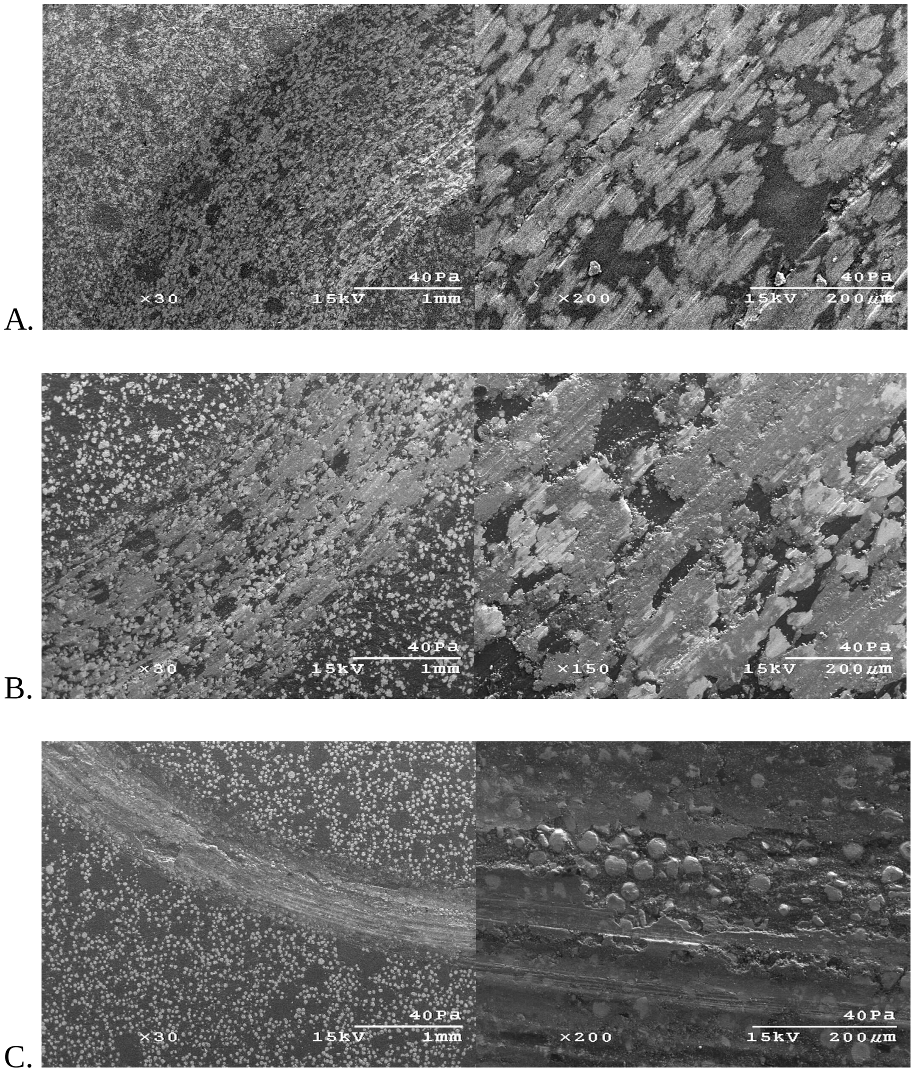

Figure 5. Wear tracks of PPS composites containing aluminum (A), mild steel (B), and Al-Cu-Fe (C) (SEM micrographs using a backscattered electron detector).

In addition to metallic fillers, Al-Cu-Fe powder was compared to silicon carbide and aluminum oxide in PPS. Aluminum oxide and silicon carbide powders were irregularly shaped with sharp angled edges. Angular Al-Cu-Fe powders, were used in addition to the spherical powder to evaluate particle morphology. Al-Cu-Fe quasicrystalline powder outperformed other fillers in preventing composite wear as shown in figure 6. Wear tracks on aluminum oxide and silicon carbide composites were notably different than those for the aluminum and mild steel samples. Mild steel and aluminum composites had wear tracks that appeared to be smooth, deep and widened from the removal of material by the spherical 52100 chrome steel pin. The wear tracks on aluminum oxide and silicon carbide samples were wide, rough and shallow. SEM micrographs of the wear tracks showed that material from 52100 steel pin was imbedded in the polymer composite (figure 7). This effect was due to the high wear of the 52100 steel ball by the abrasive aluminum oxide and silicon carbide fillers. The removal of steel from the ball produced a flattened region on the ball that resulted in increased contact area between the composite and pin resulting in higher wear. In addition, the steel removed from the ball was imbedded in the polymer matrix. This further increased the heterogeneity of the composite wear track, thus increasing wear. In contrast to the aluminum oxide and silicon carbide, both angular and spherical Al-Cu-Fe powders showed little wear on the composite and the pin. The wear track for the Al-Cu-Fe (angular) sample appeared smooth and was similar in contrast to the PPS matrix, which suggested a low content of high atomic number elements and low wear of the Al-Cu-Fe filler and 52100 steel pin.

A second set of tests were performed on the aluminum oxide and silicon carbide filled composites in which the pin load was reduced from 10 N to 5 N. The results now showed similar volume losses for aluminum oxide and Al-Cu-Fe composites after a 1000 m test (figure 7). SEM analysis of the wear tracks again showed that material from the 52100 steel pin was imbedded in the ceramic filled polymer composites. Supporting this observation, the 52100 pin loss was much higher when in contact with aluminum oxide and silicon carbide than Al-Cu-Fe powder (figure 9).

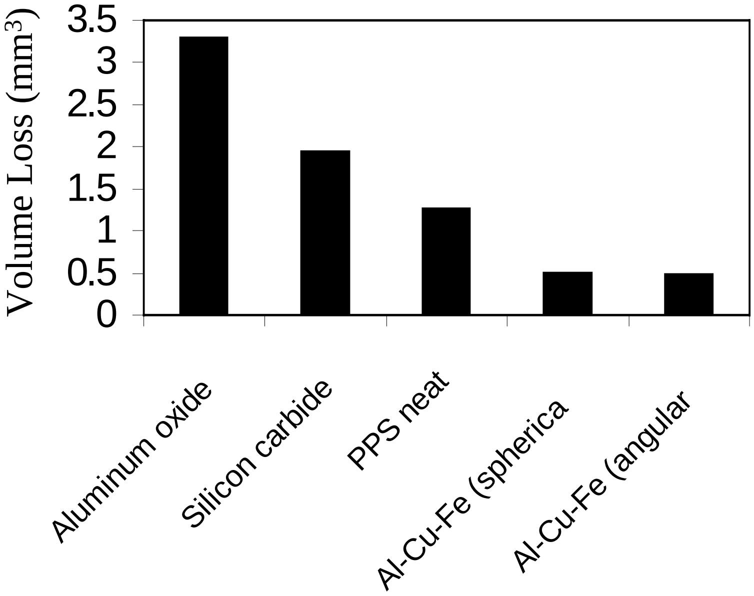

Figure 6. Volume loss from PPS composites filled at 30 volume percent with 45-53 μm particles. Wear tests were performed with a 10 N load, linear distance of 1000 m and linear speed of 0.15 m/s against a 52100 steel pin.

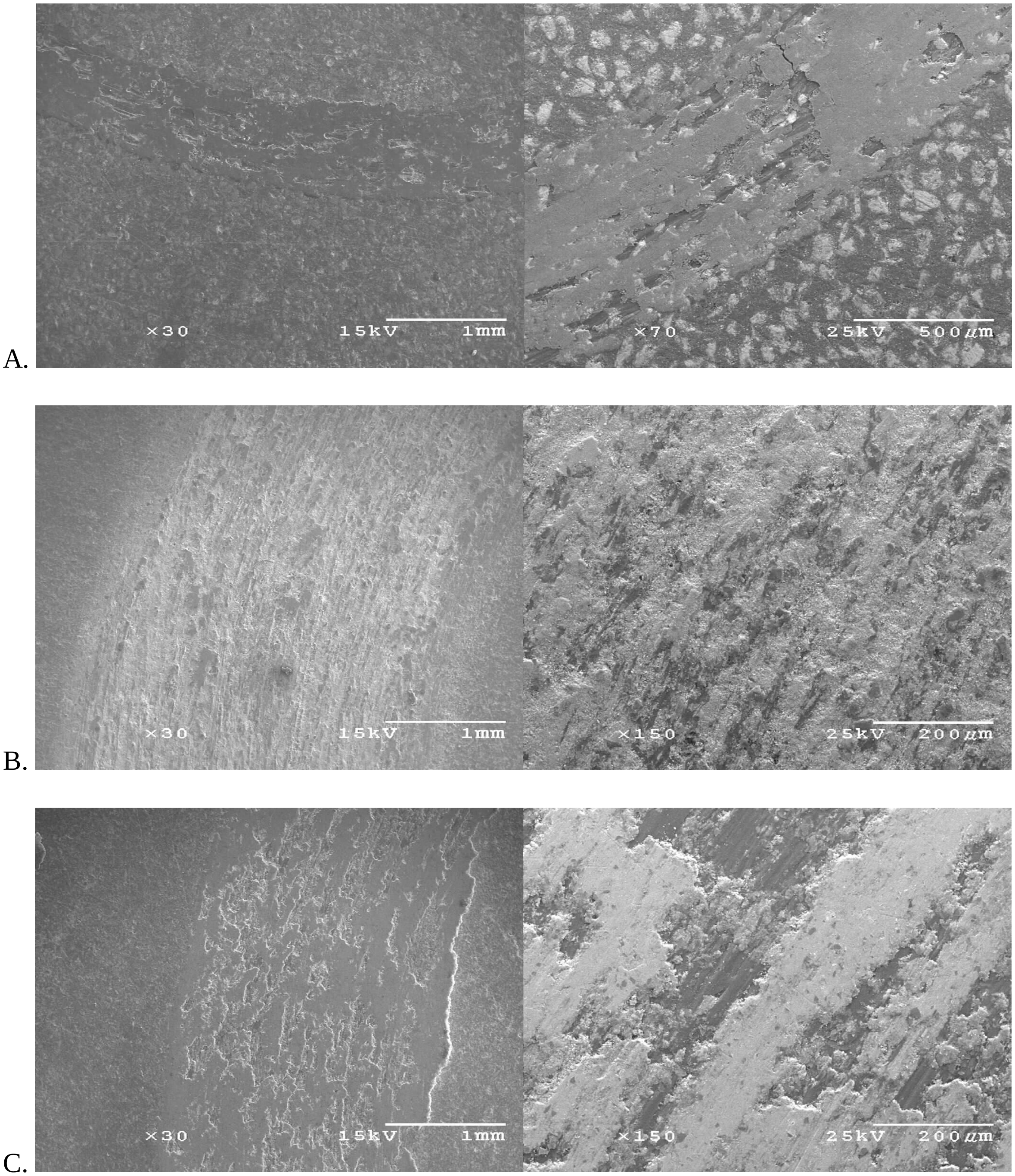

Figure 7. Wear tracks of PPS composites containing Al-Cu-Fe (angular) (A), aluminum oxide (B), and silicon carbide (C) (SEM micrographs). Images in the right column were collected with a backscattered electron detector. Metal rich areas appeared lighter than the PPS matrix due to atomic number contrast.

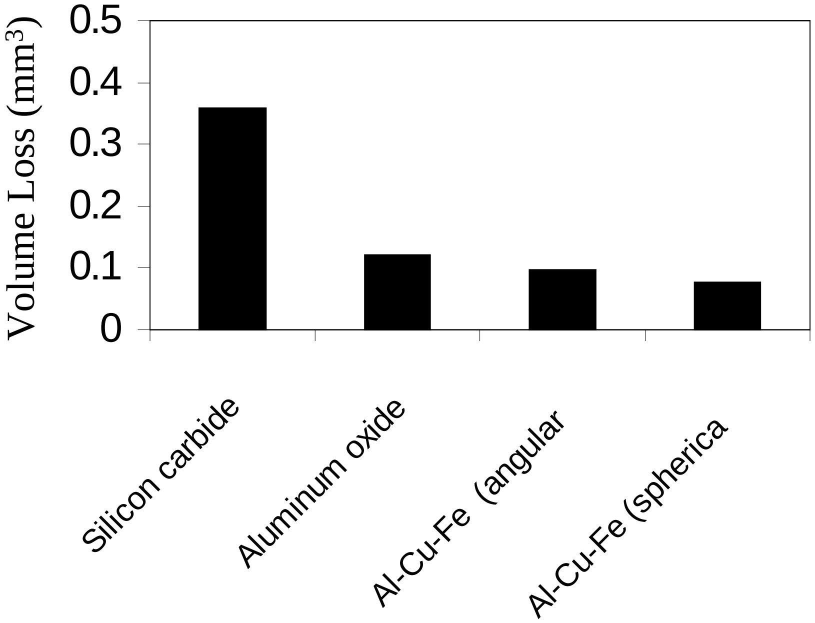

Figure 8. Volume loss from PPS composites filled at 30 volume percent with 45-53 μm particles. Wear tests were performed with a 5 N load, linear distance of 1000 m and linear speed of 0.15 m/s against a 52100 steel pin.

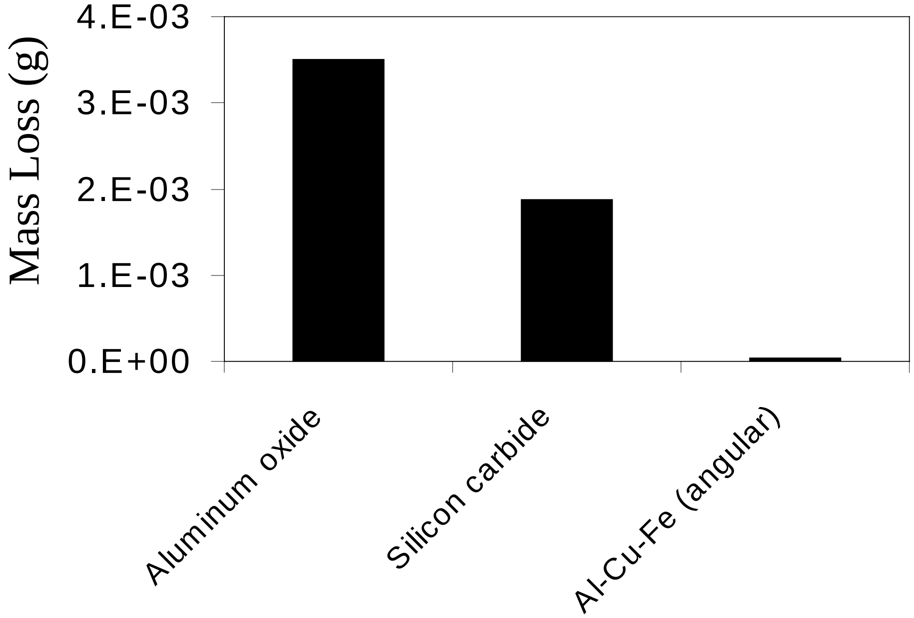

Figure 9. Mass loss from 52100 steel pin during wear testing with PPS composites. Wear tests were performed with a 5 N load, linear distance of 1000 m and linear speed of 0.15 m/s.

The aluminum oxide and silicon carbide fillers were more abrasive to the steel pin than Al-Cu-Fe particles of similar morphology. Overall, Al-Cu-Fe filler helped to reduce wear in a two-fold fashion. The Al-Cu-Fe particles decreased composite volume loss and were much less abrasive to the counterface pin.

The composition of the wear track on the Al-Cu-Fe (angular) composite sample was investigated with X-ray mapping. The X-ray map of the wear track and surrounding area is shown in figure 10. A secondary electron image is displayed in the upper left-hand corner of the figure. Elemental mapping was performed for carbon, oxygen, iron, copper and aluminum. The wear track was indistinguishable from the surrounding area in the carbon map. Higher levels of oxygen were found in the wear track than in areas of no wear. Similarly, both iron and aluminum appeared to match the map of oxygen. The presence of both aluminum and iron in a similar pattern to oxygen suggested the presence of metal oxides derived from the mechanical breakdown of quasicrystalline Al-Cu-Fe particles.

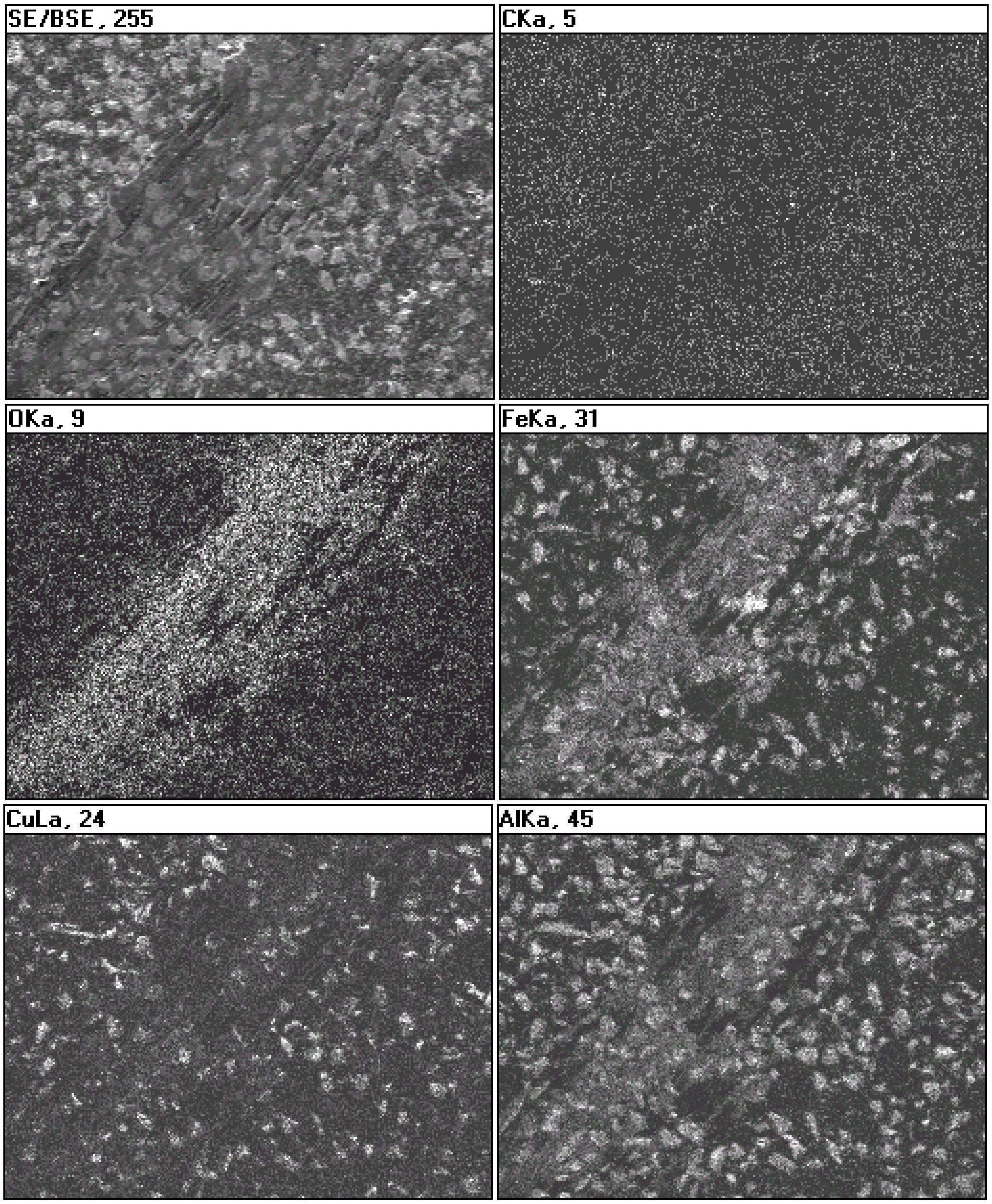

Figure 10. Elemental map of PPS / Al-Cu-Fe (angular) composite for carbon, oxygen, iron, copper, and aluminum.

Further pin-on-disk studies were performed to evaluate the mechanical breakdown of the Al-Cu-Fe filler and the simultaneous development of a polymer-rich metal oxide layer at the wear interface. A rectangular PPS composite pin filled at 30 volume percent with Al-Cu-Fe powder (45-53 μm) was held in contact with a rotating molybdenum disk under a load of 5 N. The test was allowed to proceed at 300 rpm for 100,000 cycles. During the test, the contact region became visible to the eye. The pin gained 1.5786 x 10^{-3} weight percent (actual mass gained of 0.01 mg) during wear and the disk showed a loss of 1.2051 x 10^{-4} weight percent (actual mass lost of 0.02 mg). The volume loss of the disk could not be determined by profilometry. XPS analysis of the wear track on the molybdenum disk showed the breakdown of Al-Cu-Fe quasicrystalline powder into metal oxides and buildup of a carbon rich transfer film (figure 11a). The deposited film was scraped to expose the underlying transfer layer and analyzed by XPS (figure 11b). The underlying film was very similar to the topmost transfer film. Further analysis of the pin showed the presence of metal oxides and the transfer of molybdenum to the polymer composite. XPS analysis confirmed the suspected mechanical breakdown of Al-Cu-Fe at the wear interface. The combination of XPS and x-ray mapping data indicated that the wear resistance of Al-Cu-Fe filled composites may be due to the smooth oxide-rich polymeric layer created during sliding.

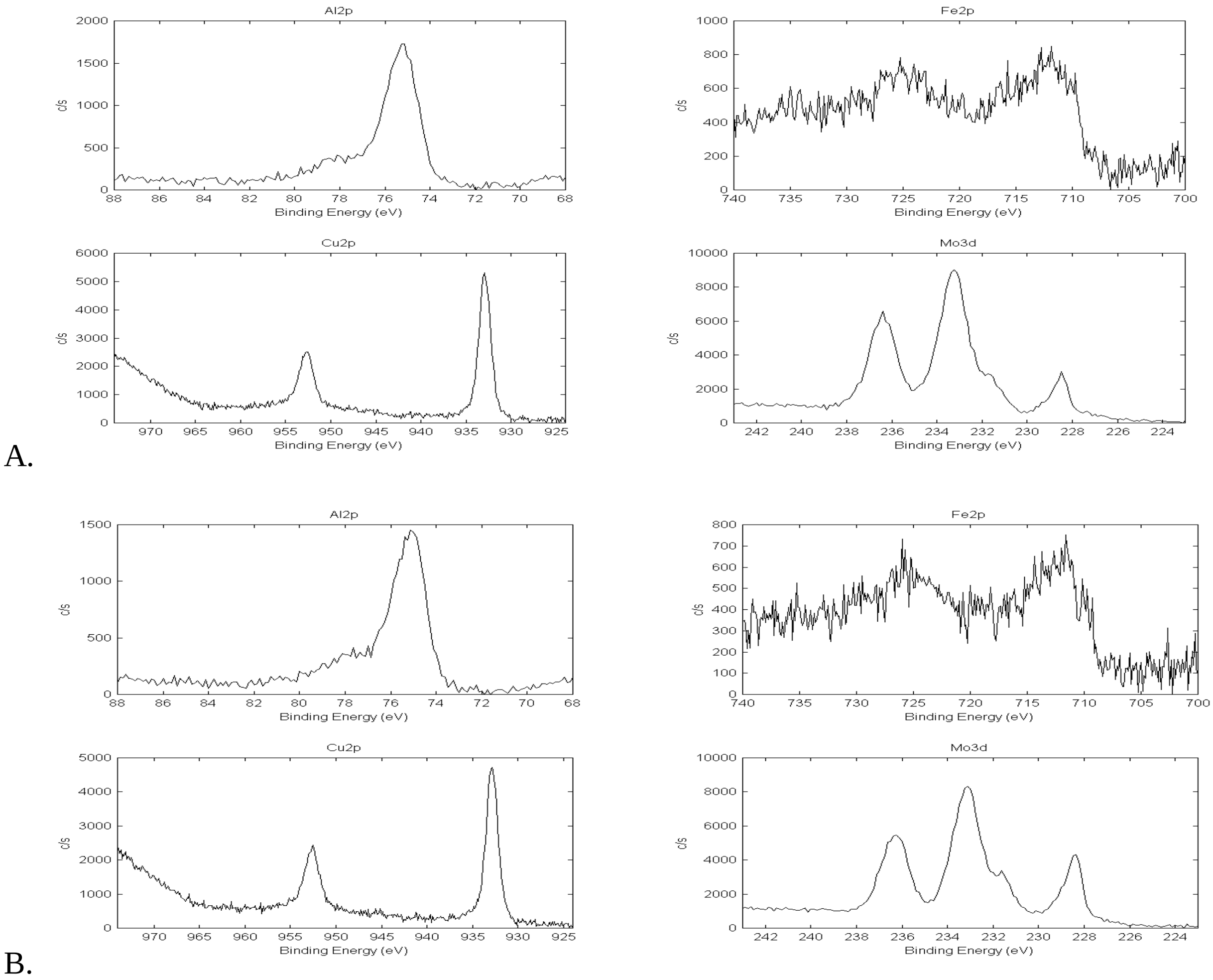

Figure 12. XPS spectra of the topmost (A) and scraped (B) transfer films formed on the molybdenum disk during sliding against the PPS / Al-Cu-Fe pin.

CONCLUSIONS

Al-Cu-Fe quasicrystals were used as a filler in poly(*p*-phenylene sulfide) to improve wear resistance. In addition to the improved composite wear, quasicrystals showed low abrasive wear on the 52100 steel counterface material compared to other hard fillers such as aluminum oxide and silicon carbide. Particle morphology of the quasicrystals did not influence abrasion. The high hardness, low surface energy and the mechanical breakdown of the Al-Cu-Fe filler into a smooth metal oxide layer was responsible for the enhanced wear resistance of the quasicrystal-polymer composites. The non-abrasive nature of quasicrystals should allow them to be compounded with plastics producing little wear on an extrusion system. These high-performance composites could find applications in the aerospace and automotive industries. Quasicrystal-polymer composites could replace heavier metal parts such as gears and bearings. Furthermore, the corrosion resistant properties of quasicrystals could lend themselves to be a useful filler in corrosion/solvent resistive polymers for adverse environments. Future work will center on thermal conductivity of quasicrystal-polymer composites, comparison of Al-Cu-Fe quasicrystals and its approximates, and a more detailed analysis of the wear mechanisms in both thermoplastics and thermosets.

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