

# Development of novel polymer/quasicrystal composite materials

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Received 3 September 1999; accepted 1 February 2000

## Abstract

We report on a new class of materials, polymer/quasicrystal composites with useful properties for beneficial exploitation in applications, such as dry bearings and composite gears. Our preliminary results indicate that our new composites are a means of enhancing the properties of certain organic polymers while providing a new means of processing quasicrystals. Al–Cu–Fe quasicrystalline materials significantly improved wear resistance to volume loss in polymer-based composites. Furthermore, mechanical testing results showed a two-fold increase in the storage modulus of the reinforced composites compared with the polymer samples. The fabrication in addition to the thermal, mechanical, and wear properties of these unique materials will be described. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Quasicrystal; Polymer; Composite; Filler; Additive

## 1. Introduction

Since the mid-1970s, the study of polymer additives has emerged as one of the most important fields of polymer science. Additives encompass a range of materials including plasticizers, stabilizers, flame-retardants, and fillers. The use of fillers in the plastics industry began when it was discovered that the cost of plastics could be reduced by the incorporation of inert materials to increase polymer bulk. Consequently, the production of plastic products became less expensive, earning fillers a low cost reputation which to date remains. More recently, active fillers have been employed which lead to improvements in certain mechanical and/or physical properties and, thus, are also known as reinforcing fillers. In practice, the term reinforcement is not specifically defined. It can mean an increase in tensile strength, flexural modulus, heat deflection temperature, etc. [1] all of which add value to the product for the supplier and the user. Here, we examine quasicrystals as a new additive to create a novel class of materials, polymer/quasicrystal composites [2]. The materials described here, along with other polymer/quasicrystal composites, have been described in our previously filed patent.

Quasicrystals, first discovered in 1982 [3], are complex metal alloys that are most comparable to ceramic particulate fillers in polymer composites [4]. The unique properties of the bulk quasicrystalline material include low surface energy

compared to most metals, low wettability in contact with most aqueous solutions, low coefficients of friction, high hardness, low thermal conductivity, and high softening temperatures. The major drawback in quasicrystal applications is in the brittle nature of the materials up to a few 100°C. Applications have been coatings prepared by thermal spray or thin-film growth, precipitation-strengthened bulk materials, and Al-matrix quasicrystal composites [5,6]. Our results have indicated that our new polymer/quasicrystal composites are a means of enhancing the properties of certain organic polymers while providing a new means of processing quasicrystals. Specifically, we have investigated a semicrystalline polymer poly(*p*-phenylene sulfide) PPS, an amorphous polymer bisphenol A poly(aryletherketone) PAEK, and two thermosetting polymers, novolac and diglycidyl ether of bisphenol A (DGEBA) epoxies in comparison to their polymer/Al–Cu–Fe quasicrystalline rich composites.

## 2. Experimental procedure

### 2.1. Materials

Quasicrystalline Al–Cu–Fe icosahedral phase rich powders, quasicrystal (QC) powder, with the composition Al<sub>65</sub>Cu<sub>23</sub>Fe<sub>12</sub>, were prepared at Ames National Laboratory [7]. 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%

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icosahedral phase and 40% cubic phase [8]. Quasicrystalline powder was air classified to achieve various size fractions. Morphology of the resulting powder was determined to be spherical by scanning electron microscopy. PPS powder, Ryton-PR6, was provided by Phillips Petroleum Company. PAEK was synthesized from bisphenol A (Aldrich) and 4,4'-difluorobenzophenone (Aldrich). The resulting PAEK had a number average molecular weight by gel permeation chromatography of 1,06,000 g/mol with polydispersity=1.93. Novolac resin D.E.N. 431<sup>TM</sup> and DGEBA epoxy resin D.E.R. 331<sup>TM</sup> were provided by Dow Chemical. Metaxylenediamine MXDA (Aldrich) and diethylenetriamine DETA were used with D.E.N. 431<sup>TM</sup> and D.E.R. 331<sup>TM</sup>, respectively, to produce thermoset epoxy formulations. Epoxy samples were formulated based on equivalent stoichiometry of amine and epoxy functionality.

## 2.2. Composite fabrication

Desired amounts of polymer and quasicrystal powders were weighed, added together and shaken vigorously in a sealed container for 10 min to provide optimum mixing. The volume fraction of the quasicrystals in the composite materials studied was in the range 10–60%. The resulting QC/polymer powder mixture was placed in a die mold that had a diameter of 2.50 cm and a final volume of 1.58 cm<sup>3</sup> 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 (American Steel Foundries Elmes Engineering Division) under a pressure of 7 MPa to 310°C. The samples were held at the set temperatures for 10 min 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. Disks of PAEK and PAEK/QC composites were compression molded at 250°C in a similar manner.

Epoxy samples were prepared from a two-part mix of epoxy resin and amine cure agent. Test samples were made as neat epoxy and at 30 vol.% of the QC powder in the epoxy matrix. The epoxy resin, cure agent, and Al–Cu–Fe icosahedral rich alloy were mechanically mixed together and poured into a Teflon mold. The mold was heated at 85°C for 4 h. The epoxy/QC composite was then removed from the mold and post-cured at 175°C for 2 h and 225°C for 2 h.

## 2.3. 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 for PPS samples and 2°C/min for epoxy samples with a static force, dynamic force and frequency of 110 mN, 100 mN and 1 Hz. 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 m s<sup>-1</sup>, a 10 N load, and a total linear distance of 1 km were used in the wear testing. Chrome steel 52,100 balls with a diameter of 0.635 cm were used as the stationary pin materials.

## 3. Results and discussion

TGA analysis of the neat PPS sample gave a 5% weight loss in air at 530°C. The PPS/quasicrystal composite material showed little change in thermal stability with a 5% weight loss in air at 533°C. The 5% weight loss temperatures of the PAEK and epoxy samples also showed little difference from their Al–Cu–Fe composites. The glass transition temperatures  $T_g$  of PPS and PAEK did not show any change upon quasicrystal addition. The thermal properties of the polymer in the composite samples were unaffected by the QC fillers, suggesting no adverse interactions between the filler and polymer.

Storage modulus ( $E'$ ), which is a measure of the stiffness or rigidity of a material, showed a two-fold increase in a 30 vol.% QC-enriched PPS sample. The magnitude of the storage modulus increased in the PPS/QC composite with increasing QC filler content above a critical QC volume fraction of 10%, especially below the glass transition temperature of the polymer matrix (Fig. 1). Comparison of the mechanical properties of D.E.R. 331<sup>TM</sup>/DETA-QC composites to unfilled D.E.R. 331<sup>TM</sup>/DETA epoxy thermosets showed an increase in storage modulus for the QC filled

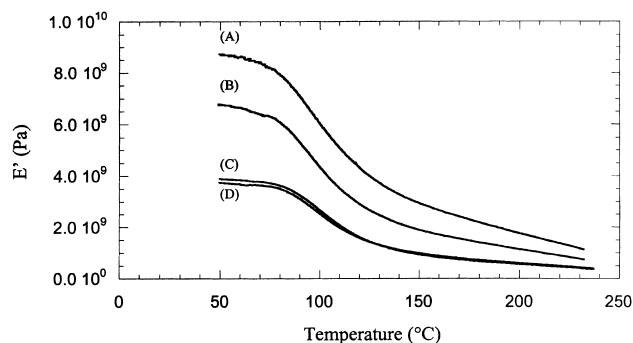


Fig. 1. Storage modulus curves for PPS filled with 5–15  $\mu\text{m}$  Al–Cu–Fe powder at (A) 30.0; (B) 20.0; (C) 10.0 and (D) 0.0 vol.%.

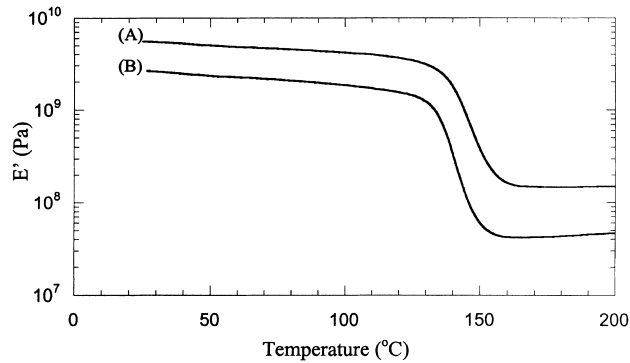


Fig. 2. Storage modulus curves for D.E.N. 331<sup>TM</sup>/DETA filled with 5–15  $\mu\text{m}$  Al–Cu–Fe powder at (A) 30.0 and (B) 0.0 vol.%.

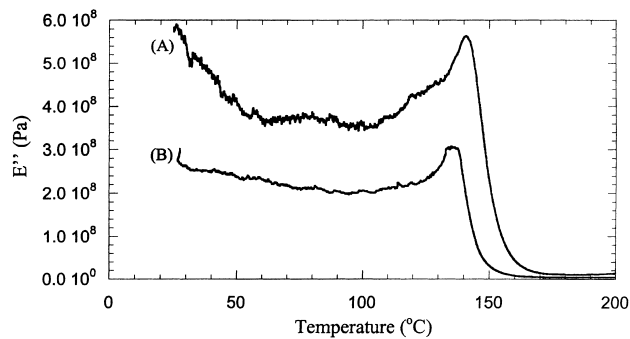


Fig. 3. Loss modulus curves for D.E.N. 331 filled with 5–15  $\mu\text{m}$  Al–Cu–Fe powder at (A) 30.0 ( $T_g=142^{\circ}\text{C}$ ) and (B) 0.0 vol.% ( $T_g=135^{\circ}\text{C}$ ).

samples (Fig. 2). The  $T_g$  of the D.E.R. 331<sup>TM</sup>/DETA/QC sample was also increased over the neat epoxy sample (Fig. 3). The storage modulus of D.E.N.431<sup>TM</sup>/MXDA and D.E.N. 431<sup>TM</sup>/MXDA/QC (30 vol.% loading) at 30 $^{\circ}\text{C}$  were  $3.5 \times 10^9$  and  $8.2 \times 10^9$  Pa, respectively.

Pin-on-disk wear testing results showed that the quasicrystalline reinforced composites exhibited enhanced wear resistance to volume loss. PPS/Al–Cu–Fe composites were evaluated at 30 and 60 vol.% loading levels versus unfilled PPS. The quasicrystalline filled PPS samples showed less volume loss due to wear than did the unfilled PPS (Fig. 4). In addition to wear testing done on semi-crystalline PPS, an amorphous polymer PAEK synthesized in our laboratory was blended with quasicrystals in solution and then precipitated. The resulting composite material was compression molded into disks and wear properties were evaluated. PAEK/Al–Cu–Fe quasicrystalline composites, filled at 30 vol.%, displayed  $0.47 \text{ mm}^3$  less volume loss to wear than the unfilled PAEK. Dow epoxies were used to formulate the QC-filled composites. Dow epoxy D.E.N. 431<sup>TM</sup> (novolac resin) was cured with metaxylenediamine. The results show that the novolac epoxy/QC composites had better wear resistance than the neat D.E.N. 431<sup>TM</sup> formulation. The addition of 30 vol.% QC in the novolac formulation resulted in an improvement in the

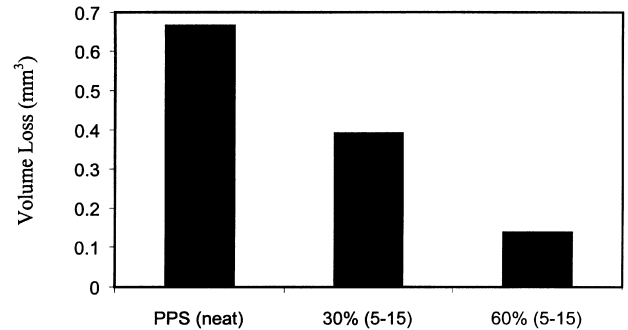


Fig. 4. Volume loss results of PPS composite wear at various volume percentages of QC powder from pin-on-disk testing. Particle size fraction in microns listed in parenthesis.

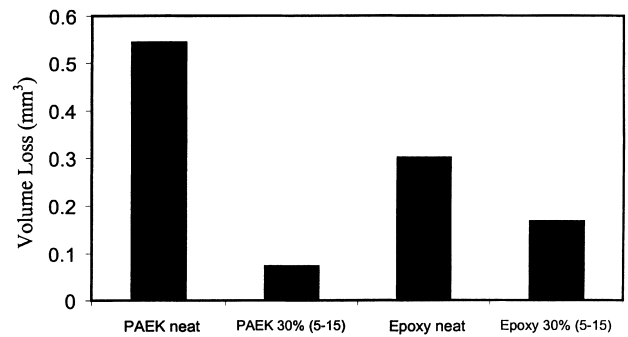


Fig. 5. PAEK and D.E.N. 431<sup>TM</sup>/MXDA composite volume loss results from pin-on-disk wear testing. Samples were tested neat (unfilled) and filled at 30 vol.% Al–Cu–Fe powder. Particle size fraction in microns listed in parenthesis.

wear resistance (Fig. 5). This result is similar to that displayed by the thermoplastic PPS/QC composites described earlier.

#### 4. Conclusions

Al–Cu–Fe gas atomized powder was used as reinforcing filler in the polymer matrices of this study. The addition of Al–Cu–Fe quasicrystal rich powder to amorphous, semicrystalline, and thermosetting polymers showed improved wear resistance to volume loss compared to the unfilled polymers. The corresponding reduction in wear was attributed to the low coefficient of friction and high hardness of the quasicrystal rich powders. The storage modulus ( $E'$ ) of the composite materials was found to increase with increasing volume fraction of the QC powder, as expected for a filled polymer composite containing rigid fillers [9]. In the thermoplastic polymers, the glass transition temperatures were unaffected by the addition of the QC filler. However, QC powder caused the  $T_g$  of the D.E.R. 331<sup>TM</sup> epoxy composite to increase by 7 $^{\circ}\text{C}$ , slightly extending the useful temperature range of the epoxy. Based on these results, polymer/QC composites

may find applications as dry bearing materials [10]. In addition, polymer/QC composites may find uses as other high wear components, such as composite gears. Future studies will include more detailed investigation of composite wear, thermal conductivity, and other composite properties of the interesting and technologically relevant materials described in this paper.

### Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the US Department of Energy under contracts No. DE-AC03-765F00098 and W-405-Eng-82 and Iowa State University. The authors would also like to thank Dr. Daniel Sordelet and Mr. Matt Besser of Ames Laboratory and Ms. Melissa McConnell of Iowa State University.

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