



## Research paper

# Role of weak particle-matrix interfacial adhesion in deformation and fracture mechanisms of rigid particulate-filled poly(methyl methacrylate)



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## ABSTRACT

Toughening glassy thermoplastics such as poly(methyl methacrylate) (PMMA) without sacrificing modulus and thermomechanical stability is a valuable but challenging objective. Rigid particulate fillers have been found to improve toughness of some polymers with complex dependence on matrix ductility, particle size, and particle-matrix interfacial adhesion. We tested the effects of both strong and weak interfacial adhesion on deformation and fracture of a model system comprising PMMA filled with monodisperse 1  $\mu\text{m}$  diameter silica spheres. Fracture energy  $G_{IC}$  of PMMA was found to increase by over 50% when filled with 1 v% of weakly bonded particles, while the force observed during melt compounding increased by less than 15% and Young's modulus increased systematically with filler loading. However,  $G_{IC}$  decreased with filler loading above 1 v%. This behavior is consistent with a modified Kinloch-type model considering localized shear banding and plastic void growth around debonded particles at the crack tip. The ability of the matrix to deform via shear yielding and plastic void growth was confirmed by digital image correlation measurement of volumetric strain in uniaxial tension. We have extended Kinloch's model to account for shortening of the crack tip craze by the particles, which reduces the intrinsic toughness and toughenability of the PMMA matrix. Particles with strong interfacial adhesion generally reduced toughness. The experimental and modeling results suggest weakly bonded particles with size on the order of the crack-tip craze width may provide optimum toughening of glassy thermoplastics.

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## 1. Introduction

Glassy thermoplastics are important engineering materials used for a broad range of civilian and defense applications. Desirable properties of glassy thermoplastics such as poly(methyl methacrylate) (PMMA) include ease of processing and forming, low density, good optical clarity, high rigidity, and unique high rate impact performance (Moy et al., 2003). Owing to these advantages, PMMA and related linear acrylic polymers are employed in applications including lightweight armor, medical devices, electronics fabrication, transportation components, and glass replacement. However, the toughness and fracture resistance of PMMA are relatively poor, hindering implementation in emerging applications.

Polymers are traditionally toughened by addition of a dispersed rubber phase. In PMMA this approach usually requires high rubber loadings of 30v% or more (Jansen et al., 2001), considerably reducing modulus, thermomechanical stability, and ultimate strength.

Addition of rigid particles to polymers generally increases modulus and decreases thermal expansivity, yet can either improve or degrade toughness depending on a complex interplay of multiple phenomena (Fu et al., 2008; Bucknall, 1978). For example, Argon and coworkers (Bartczak et al., 1999) found that both modulus and impact toughness of high-density polyethylene were improved by incorporation of calcium carbonate particles. These authors presented evidence that toughness is enhanced by a similar mechanism for both rubbery and rigid particles, when fillers are weakly adhered to the matrix allowing matrix plastic deformation without adhesive constraint.

Thermosets such as epoxies are often toughened by microscale rigid particles, for which crack pinning is a primary toughening mechanism (McGrath et al., 2008; Spanoudakis and Young, 1984b). Other studies (Lee and Yee, 2000; Dittanet and Pearson, 2013; Johnsen et al., 2007; Hsieh et al., 2010; Wetzel et al., 2006; Bray et al., 2013; Liang and Pearson, 2009) have shown that rigid particles including nanoparticles can improve epoxy fracture toughness via particle-matrix debonding, plastic void growth, and localized shear banding in the matrix ligaments between particles, similar to classical rubber toughening. In such systems weak

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particle-matrix adhesion facilitates debonding under stress, which relieves triaxial constraint at a crack tip and initiates the major energy-consuming mechanisms of void growth and localized shear deformation.

Despite substantial research on toughening thermosets and semicrystalline thermoplastics with rigid fillers (Argon and Cohen, 2003), studies on glassy thermoplastics toughened with rigid particles are less prevalent. Glassy thermoplastics with low entanglement density such as PMMA and polystyrene (PS) are relatively brittle, tending to deform by crazing and fail at low tensile strains (Wu, 1990), thus making them intrinsically difficult to toughen. Nevertheless, a few studies have shown promising results. For example, ductility of PMMA has been significantly enhanced by incorporation of 38 nm diameter alumina particles into the matrix along with a small percentage of methacrylic acid as a dispersant (Ash et al., 2004a). At low loadings (1–2wt%) of alumina nanofiller, ultimate tensile strain increased by a factor of 6, while modulus and yield stress were reduced by 20–30%. Glass transition temperature was reduced by 20 °C, suggesting a large volume of interfacial phase with greater mobility than the bulk matrix (Ash et al., 2004b).

Toughening of PMMA was achieved in both quasistatic and high rate split-Hopkinson pressure bar testing by the addition of cyclohexyl-functionalized polyhedral oligomeric silsesquioxane (POSS), which crystallizes into rigid particulates ranging between 50 nm and several  $\mu\text{m}$ , and a methacryl-functionalized POSS which disperses molecularly and acts as a plasticizer (Kopesky et al., 2006). These two additives appear to facilitate ductility in the matrix following debonding at the weak interface between the rigid particulate POSS and the PMMA matrix. In another study (Lach et al., 2006; Kausch and Michler, 2007), fracture toughness of PMMA containing silica nanoparticles was found to increase concurrently with the modulus, peaking at a stress intensity factor  $K_{IC}$  1.7 times that of the neat matrix. This behavior was hypothesized to originate from an apparent critical value of the ligament thickness between particles. However, the nature of the particle-matrix interface, processing conditions, and behavior over a broader range of particle loading have not been fully explored or disclosed. In recent years, composites incorporating layered silicates (Pavlidou and Papispyrides, 2008), carbon nanotubes (Coleman et al., 2006), and graphene (Kuilla et al., 2010) into a variety of polymeric matrices including PMMA have been extensively studied. While these advanced nanocomposites offer potential for dramatic improvements of a range of thermomechanical and electrical properties, they remain difficult to disperse, high in cost, and difficult to analyze in terms of the mechanisms of property improvement.

In many of the cited examples above, toughening effects are attributed to weak interfacial adhesion between the matrix and filler. A weak interface allows particles to debond from the matrix under applied stress (Dekkers and Heikens, 1983) relieving constraint to deformation. Stress concentrations around voids can lead to large plastic deformations that consume energy and increase fracture resistance, similar to the effect of cavitation in rubber-toughened polymers (Huang and Kinloch, 1992a, Bain et al., 2015). On the other hand, strong particle-matrix interfacial adhesion facilitates efficient stress transfer between phases and is associated with toughening mechanisms such as crack pinning (Spanoudakis and Young, 1984b), crack deflection (Faber and Evans, 1983), and crack bridging (Pearson and Yee, 1993). Toughening mechanisms due to both strong and weak adhesion have been demonstrated for particle sizes from hundreds of  $\mu\text{m}$  to tens of nm. Due to the complexity of large strain deformations in heterogeneous materials and the variety of results in the literature, uncertainty still exists as to whether strong or weak interfacial adhesion provides better toughness improvements. Furthermore, while optimal particle sizes of 100 nm (Kopesky et al., 2006) and 250 nm (Wu, 1990) for tough-

ening of PMMA have been proposed, rigid particles with a narrow size distribution have rarely been systematically studied in PMMA, and thus the role of particle size is not yet fully understood.

In this study we have modified the surface chemistry of well-defined, monodisperse spherical 1  $\mu\text{m}$  silica particles to gain insight into the role of particle-matrix adhesion and particle size on the fracture resistance of PMMA-matrix composites over a range of particle loadings. Toughening mechanisms are modeled, including matrix shear banding and void growth within a plastic zone containing debonded particles with weak adhesion near the crack tip. Deformation and volumetric strain measurements in uniaxial tension support the model by demonstrating the ability of the composites to deform by shear yielding, void growth, and crazing. The results suggest toughening is possible within a window of filler loading and size defined by interactions between fillers and the crack-tip craze, the primary source of intrinsic matrix toughness.

## 2. Experimental

### 2.1. Materials

1  $\mu\text{m}$  silica spheres (AngstromSphere), prepared by the Stöber method, were obtained from Fiber Optic Center<sup>1</sup>. Prior to use, silica was etched with a 3:7 (v/v) mixture of 30% hydrogen peroxide and concentrated sulfuric acid (piranha solution – caution should be used with this mixture). Etched silica was washed with water until the effluent pH was neutral, then dried in a vacuum oven at 110 °C overnight and stored in a desiccator until use. Acrylite M30 grade pelletized PMMA was supplied by Evonik industries, and was dried under vacuum for several hours at 65 °C before processing. Additional information about PMMA can be found in Section S1 in the supporting information. Propyltrimethoxysilane (PTMS) was obtained from Sigma Aldrich and used as received. Deionized water (DIW) of 18 M $\Omega$  resistivity was produced by a Milli-Q filtration system (Millipore Corporation). All other chemicals were obtained from major suppliers such as Sigma-Aldrich, VWR, or Fischer Scientific, and used as received.

### 2.2. Differential scanning calorimetry (DSC)

Alternating heating/cooling cycles were run from 25 °C to 150 °C at 10 °C/min on 3–4 mg samples of each composition using a TA Instruments Discover Series Differential Scanning Calorimeter (DSC). The second and subsequent heating curves were analyzed to determine glass transition temperature ( $T_g$ ) for each sample. Good agreement, within the error estimated for the mathematical fit, was found for four samples of neat PMMA (one virgin and three extruded / molded), and for two samples each of 14 v% *p-1s* and 33 v% *e-1s* composites (see text for abbreviations).

### 2.3. Modification of silica particles with propyltrimethoxysilane (PTMS)

A solution containing 10v% PTMS, 85.5v% methanol, 4 v% DIW, and 0.5v% 1 M hydrochloric acid was stirred 4–5 h at room temperature to allow hydrolysis of PTMS. Etched silica was added 0.1 g/mL, and the suspension was sonicated 30 min, followed by 30 min of rapid stirring. The silica was separated by centrifugation, then added 0.1 g/mL to toluene in a round bottom flask and sonicated several minutes. A Dean-Stark apparatus was attached and

<sup>1</sup> Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the Army Research Laboratory, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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