UHMWPE as interface toughening agent in glass particle filled composites

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Abstract

UHMWPE was adsorbed from dilute solution onto glass beads surface modified with a copolymer of 0.5–1.2 mol% vinyltrimethoxysilane-ethylene (PE-silane). Functional methacrylate groups were introduced through treatment of the UHMWPE with octadecyltrimethoxysilane (OMS) followed by reaction with 3-methacryloxypropyltrichlorosilane (Cl-MPS). Composites were prepared with 20 vol% PE-silanated/UHMWPE glass and BisGMA/TEGDMA (60/40 wt/wt); Cl-MPS treatment did not affect the results. Toughness increased 40% compared with neat or glass-filled resin, consistent with the addition of the high toughness UHMWPE; moduli were intermediate between the neat resin and glass filled composites, consistent with the relative moduli of glass and UHMWPE; flexural strengths decreased in the order: neat resin > resin + glass beads > silanated/UHMWPE coated glass beads, suggesting that each interface negatively affected the flexural strength.
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1. Introduction

Inorganic fillers have been used extensively to enhance stiffness and to reduce the cost of polymer composites. The interface between the inorganic filler particles and the polymer matrix, possessing properties different than those of the bulk matrix, plays an important role in determining the mechanical properties of a composite. The compatibility between the rigid filler and the polymer matrix affects the dispersibility of the filler and the adhesion between the two components, which in turn determine the ultimate mechanical properties [1]. Interfaces can be the weakest part of a composite, but are also important in the transfer of stress between the matrix and the filler. Silane coupling agents have been most commonly used to improve compatibility between inorganic fillers and poly-

mer matrices [2–4], but grafting of polymers to inorganic surfaces has also been investigated [5–7]. Jerome et al. have used a technique consisting of fixing a catalyst for olefin polymerization on the filler surface and directing polymerization of a thin coating of polyethylene [8].

The buildup of stress results in the ultimate failure of materials through crack propagation. Stresses can occur either during polymerization of the matrix, when shrinkage produces both internal and interfacial stresses, or by subsequent use. Stress relief from contraction can be achieved through incorporation of matrix porosity [9] or by voids between the filler and resin matrix [10]. Since in composite materials one role of the interfacial region is to transfer stress between the matrix and the filler, the interface can modify the stress distribution in the vicinity of the filler and provide an energy absorption mechanism through large scale elastic or plastic deformation. Motivation for tailoring the molecular weight of the grafted chains or the modulus of the interface comes from modeling studies that suggest that the stress distribution around the filler

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and the bulk mechanical properties of the composite can be affected by changes in interfacial properties [11,12]. Improvements in the toughness of filler reinforced polymer composites can occur through increased interfacial adhesion, yielding or debonding mechanisms. Debonding can increase toughness by allowing plastic deformation of polymer segments between debonded filler particles [13].

Improvements in toughness through yielding at the interface can be achieved by encapsulation of the filler with a polymer to allow for a ductile zone for plastic deformation between the filler and resin. Glass particles coated with an amine terminated poly(butadiene/acrylonitrile) rubber increased the toughness of BisGMA/TEGDMA (60/40) resins without a large decrease in modulus [14]. In rubber modified glass–epoxy composites the effect of the rubber-coated particles was found to be critical in energy absorption at the interface by plastic deformation [15,16]. In the case of polymethyl-methacrylate (PMMA) non-covalently coated talc/polyvinyl chloride (PVC) composites, only slight improvements in toughening were observed [17], but greater toughening enhancement was observed for covalently attached polystyrene on glass used as a filler for polyphenylene oxide (PPO) [18]. Materials such as rubber or high density polyethylene, which can plastically deform, have also been added alone [19] or in addition to inorganic fillers [20], to toughen inorganic/matrix composites and reduce interfacial stress, with mixed results.

In the current work, we have investigated the use of UHMWPE, which has higher impact strength, elongation at break and yield strain than HDPE, but which is chemically inert and non-polar, to modify the interface at the surface of inorganic glass bead and fiber fillers, using a solution process. HDPE has previously been covalently attached to glass particles and used in composites of HDPE (20 wt% filled) [8]. A thin layer of PE was polymerized on the glass substrate that had been previously fixed with a metallocene-methalumoxane catalyst. The composites showed improved impact energy (by an order of magnitude), ultimate tensile strength, and elongation at break compared with composites prepared using unmodified beads [8].

UHMWPE has greater impact strength than HDPE (>1070 vs. 21–214 J/m measured by notched Izod impact test at 23 °C, 3.175 mm thick specimen) [21], but cannot be conveniently covalently attached to glass using a gas phase reaction. Therefore, a solution deposition process was employed in the current investigation. Dilute solutions of UHMWPE have previously been used to coat glass fibers, using a process in which the UHMWPE solution was mixed with cross-linkable silanes, although uniform coatings were not achieved and adjacent fibers could stick together [22]; neat UHMWPE solutions form thermoreversible gels upon evaporation of the solvent [23–25]. The high molecular weight and thus very small overlap concentration in solution of UHMWPE favors the undesirable formation of particles embedded in a film of UHMWPE, rather than individual particles coated with UHMWPE.

In order to achieve a coating of UHMWPE on individual micron-size glass particles, a procedure was adapted from one used to form micron-size droplets of UHMWPE. Micron-size droplet formation of both PE and UHMWPE has been observed from biphasic solutions of PE or UHMWPE [26–29] in poor solvents. In dilute solution, the polymer rich phase forms spheres in the solvent rich phase, and rapid cooling results in crystallization of the droplets and expulsion of the solvent. Crystallization of PE from the solvent rich phase onto the droplets has also been observed [3]. Therefore, an approach to coating UHMWPE onto glass was to use this same solution method but with the inclusion of glass beads hydrophobically modified with either a PE-silane or octadecyltrichlorosilane (OTS).

The UHMWPE coated glass was further surface modified to include the methacrylate functionality for better bonding to the resin, by swelling the UHMWPE with octadecyltrimethoxysilane in xylene; the methoxy groups of the silanes, after hydrolysis to form $-Si(OH)_3$, were reacted with 3-methacryloxypropyltrichlorosilane (Cl-MPS) to impart reactivity towards the resin. Previous micro-bond shear strength data for Spectra 900™ UHMWPE fibers indicated that this surface treatment gave the highest shear strengths [30] among the methods tested for introducing bonding to the resin. The resin system was a 60/40 wt% mixture of 2,2-bis [4-(2-hydroxy-3-methacryloxy propoxy) phenylene] propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA), which is used in dental and biomedical applications. Bonding between the glass and UHMWPE was measured using micro-bond shear tests with UHMWPE beads (prepared by melting) on treated (PE-silane or OTS) or untreated E-glass fibers.

The ultimate goal of this research was to evaluate the effects of a ductile interface on a glass-filled glassy composite, with the expectation that it would provide plasticity and enhance toughness, with minimal reduction in mechanical properties. The results indicate that addition of UHMWPE as a layer on the glass beads improved the fracture toughness (K_{IC}), and that covalent bonding of the UHMWPE to the resin, via inclusion of methacrylate functionality at the UHMWPE/resin interface, further increased K_{IC}, compared with composites prepared using neat or MPS-treated glass beads. However, the introduction of the lower modulus UHMWPE and additional interfaces resulted in decreases in composite moduli and strength.

2. Experimental

2.1. Materials

E-glass [SiO_2 (52–58%), Al_2O_3 (11–17%), B_2O_3 (6–7%), CaO (18–25%), MgO (0.5–1%)] beads (2.6 μm diameter) and fibers [chopped fibers ~3.6 μm (diameter) × 30 μm (length) and continuous 30 μm diameter fibers] were provided by MO-SCI Corp, Rolla, MO. PE modified