PARTICULATE TOUGHENING OF UNSATURATED POLYESTER: EFFECT OF PARTICLE SIZE AND VOLUME FRACTION

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ABSTRACT

Micron- and nanometer-sized aluminum particles were used as reinforcements to enhance the fracture toughness of a highly-crosslinked, nominally brittle, thermosetting unsaturated polyester resin. Both particle size and particle volume fraction were systematically varied to investigate their effects on the fracture behavior and the fracture toughness. It was observed that, in general, the overall fracture toughness increased monotonically with the volume fraction of aluminum particles, for a given particle size, provided particle dispersion and deagglomeration was maintained. The fracture toughness of the composite was also strongly influenced by the size of the reinforcement particles. Smaller particles led to a greater increase in fracture toughness for a given particle volume fraction. Scanning electron microscopy of the fracture surfaces was employed to establish crack front trapping as the primary extrinsic toughening mechanism.

KEYWORDS

Fracture, nanocomposite, particulate reinforcement, thermosetting polymer, crack trapping.

INTRODUCTION

Thermosetting polymers, such as epoxy resins and polyesters, are used extensively as adhesives, potting and encapsulating materials, tooling compounds, and as matrix materials for reinforced composites. These polymers exhibit a very high degree of cross-linking between the individual polymer chains, which results in many useful properties including high specific strength, high stiffness, dimensional stability at elevated temperature, and good solvent resistance. Unfortunately, this cross-linking also makes these materials inherently brittle with poor resistance to crack initiation and propagation, in comparison to other engineering plastics.

Improving the fracture toughness of thermosetting resins has been the subject of considerable research. However, the conventional approach of introducing micron-sized particles (elastomeric, thermoplastic or ceramic) into the polymer matrix has failed to yield significant improvements in the fracture toughness of highly cross-linked thermosetting polymers. Furthermore, other mechanical properties are often compromised, or there are processing problems.

Recent research indicates that the dispersion of *sub-micrometer* and *nanometer* sized inorganic particles

presents a viable alternative for improving the mechanical properties of polymers. Such materials, which include polymer nanocomposites, have the potential for significantly enhanced and unique properties as compared to polymers reinforced with conventional microscale fillers [1].

Nanoscale reinforcements in thermoplastic and thermosetting polymers are formed either as inorganic-organic hybrids [2, 3], or as intercalated/exfoliated polymer-silicate structures [4-6]. These materials can exhibit substantial enhancements in the modulus, yield strength and heat resistance of the polymer. While these studies have not focused on fracture toughness as the primary issue, there are clear indications that reducing the size of reinforcement particles could lead to significant improvements in fracture toughness and resistance to crack growth. Despite these observations there is limited fundamental information regarding the effects of reinforcement size on fracture processes, toughening mechanisms and the resulting overall fracture toughness.

This investigation addresses these issues and presents a systematic characterization of the fracture behavior of a highly cross-linked thermosetting polymer reinforced with high-modulus inorganic particles, as a function of particle size and particle volume fraction. Such an understanding is essential for identifying parameters that will lead to the design and fabrication of optimally toughened thermosetting polymers.

SPECIMEN FABRICATION

Composite materials were fabricated by incorporating aluminum particles in MR 10790 unsaturated polyester resin at different volume fractions. Reinforcement quantities of interest were 1%, 2%, 5% and 10% of the particles by weight, which resulted in volume fractions of 0.5%, 0.9%, 2.3% and 4.4%, respectively. Three distinct sizes of aluminum particles were used: 100 nm, 3.5μm and 20 μm. A direct mixing approach was used to provide flexibility in exercising independent control over reinforcement material and reinforcement geometry (size, morphology and size distribution) [7]. Tables 1 and 2 provide details for the polyester resin and aluminum particles.

TABLE 1
PROPERTIES OF THE MR 10790 POLYESTER RESIN

Polymer	MR 10790 Polyester Resin
Curing Agents	Methyl Ethyl Ketone Peroxide (0.85% pph) Cobalt Octoate (0.03% pph)
Curing Cycle	48 hrs at 25°C; 4 hrs at 52°C; 5 hrs at 63°C
Young's Modulus	3.25 GPa
Fracture Toughness	0.64 $MPa.m^{½}$
Density	1160 kg/m^3

TABLE 2
PROPERTIES OF ALUMINUM PARTICLES

Property	Aluminum A	Aluminum B	Aluminum C
Nominal Diameter	20 μm	3.5 μm	100 nm
Diameter Range	17-23 μm	3-4.5 μm	100 nm
Young's Modulus	70 GPa	70 GPa	70 GPa
Fracture Toughness	30 $MPa.m^{½}$	30 $MPa.m^{½}$	30 $MPa.m^{½}$
Density	2699 kg/m^3	2699 kg/m^3	2699 kg/m^3

FRACTURE TESTING

Three-point-bend single-edge-notched (3PB-SEN) fracture specimens were machined from the cast polyester sheets for testing. The specimens had a nominal length, *L*, of 55.9 mm, a height, *W*, of 12.7 mm and a thickness, *B*, of 6.35 mm, as shown in Figure 1. A 4.25 mm deep notch was first cut into the center of the specimen using a diamond saw. A fresh razor blade was then tapped into the cut with a hammer to create a naturally sharp crack. The actual length of the overall crack, *a*, was measured after the fracture experiment by observation in an optical microscope equipped with a micrometer stage. All the specimens used for valid fracture tests had a nominal crack length to specimen width ratio, *a/W*, of ~ 0.5, as per ASTM standard 5045 [8].

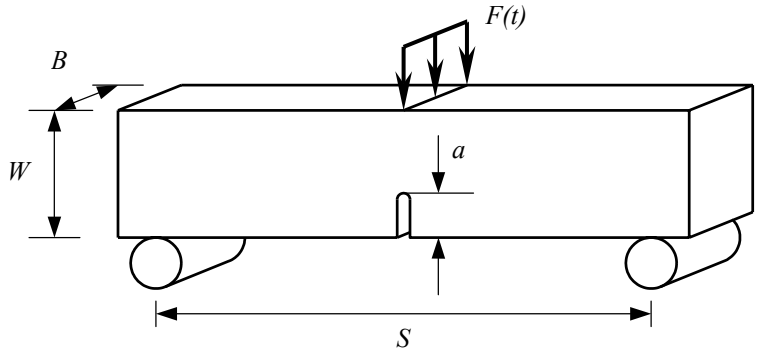

Figure 1: Three-point bend fracture specimen

The quasi-static fracture toughness of the polyester-aluminum composites was measured as a function of particle size and particle volume fraction. Single-edge-notched fracture specimens were loaded quasi-statically under three-point-bending until the initiation of fracture. The specimens were loaded in a displacement-controlled mode and the crosshead speed was fixed at 5 mm/minute to keep the loading rate constant. The maximum applied load at the point of failure was measured using a 500 N load-cell and then used to quantify the quasi-static fracture toughness of the composite being tested.

The mode-I stress intensity factor was determined from these measurements as per Eqn. 1 [9].

$$K_I(t) = \frac{3S\sqrt{a}}{2BW^2} Y\left(\frac{a}{W}\right) F_{\max} \tag{1}$$

Where, $F_{\max}$ is the force required for fracture, *B* is the specimen thickness, *W* is the specimen width, *S* is the span, *a* is the crack length and *Y* is a geometry factor [10].

Figure 2 shows the variation of composite fracture toughness as a function of the volume fraction of 20 μm, 3.5 μm, and 100 nm aluminum particles added to the polyester resin. For the case of 20 μm and 3.5 μm particles the fracture toughness of the polyester-aluminum composite increased monotonically with the volume fraction of aluminum particles. However, the relative increase in fracture toughness was significantly greater for reinforcement by 3.5 μm particles as compared to that observed for reinforcement by 20 μm particles. For reinforcement by 4.4% volume fraction of 3.5 μm aluminum particles the fracture toughness increased by 51%, which is more than twice the increase observed using 20 μm particles. When the size of the reinforcement aluminum particles was further decreased to 100 nm a different trend was observed, also shown in Figure 2. For this case the fracture toughness increased rapidly till a particle volume fraction of 2.3%. As the particle volume fraction was increased further the fracture toughness registered a sharp decrease. Thus, from Figure 2 it is evident that fracture toughness is strongly governed by the size of the reinforcement particles. Smaller particles lead to a greater increase in the overall fracture toughness for a given volume fraction. This trend is not observed only for the case of reinforcement by 100 nm aluminum particles in volume fractions greater than 2.3%.

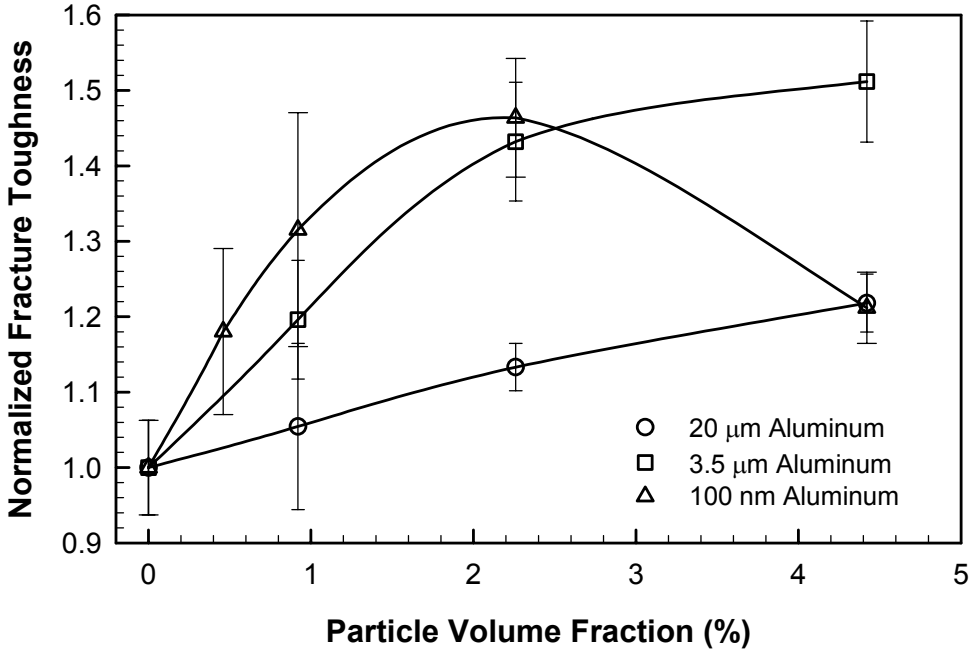

Figure 2: Effect of particle size and volume fraction of the fracture toughness of polyester resin reinforced with aluminum particles

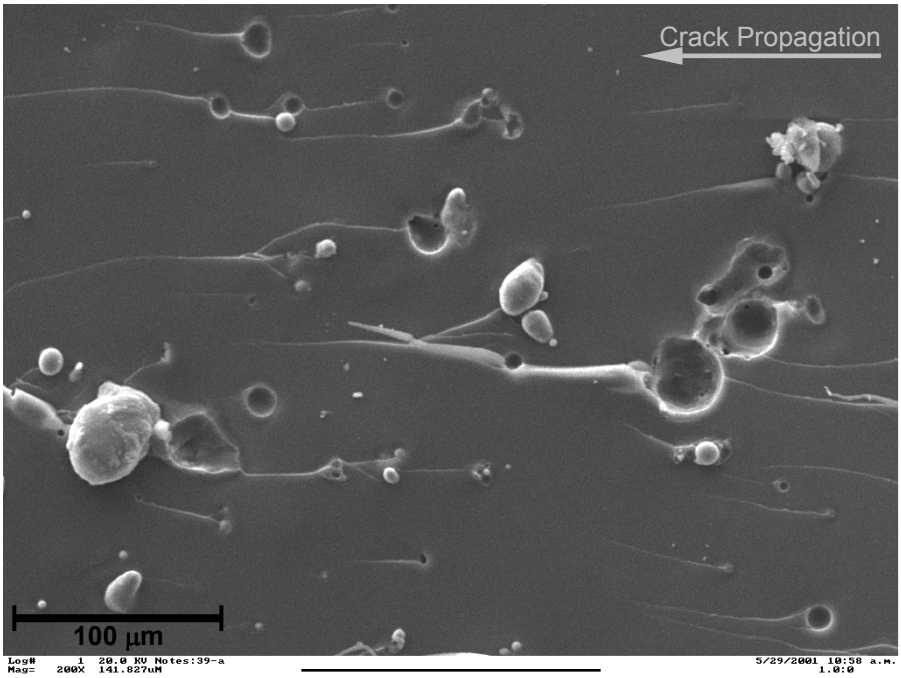

Figure 3: Fracture surface of polyester resin reinforced with 20 μm aluminum particles

Microscopic observations of the fracture surfaces were carried out using scanning electron microscopy (SEM) to characterize the interaction of the crack with the reinforcing particles and identify the extrinsic toughening mechanisms. Figure 3 shows an SEM micrograph of the fracture surface for polyester reinforced with 20 μm aluminum particles. The fracture surface showed evidence of crack front trapping [11] in the form of steps, or 'fracture tails', that emanated from the reinforcing particles along the direction of crack growth. Besides the formation of these steps, the fracture surface was fairly flat, which indicated that crack path deflection did not occur. Moreover, the aluminum particles appeared to be debonded from the polyester matrix and did not show any evidence of particle yielding and deformation. Thus, extensive crack face bridging did not occur either. Finally, microcracking of the polyester matrix was also not observed. In this manner, crack front trapping was established to be the primary extrinsic mechanism responsible for the increase in fracture toughness of polyester reinforced with 20 μm aluminum particles. These observations

were made for all particle volume fractions that were investigated. Similar observations were made using scanning electron microscopy of the fracture surface of polyester reinforced with 3.5 μm particles and crack front trapping was again identified as the primary toughening mechanism.

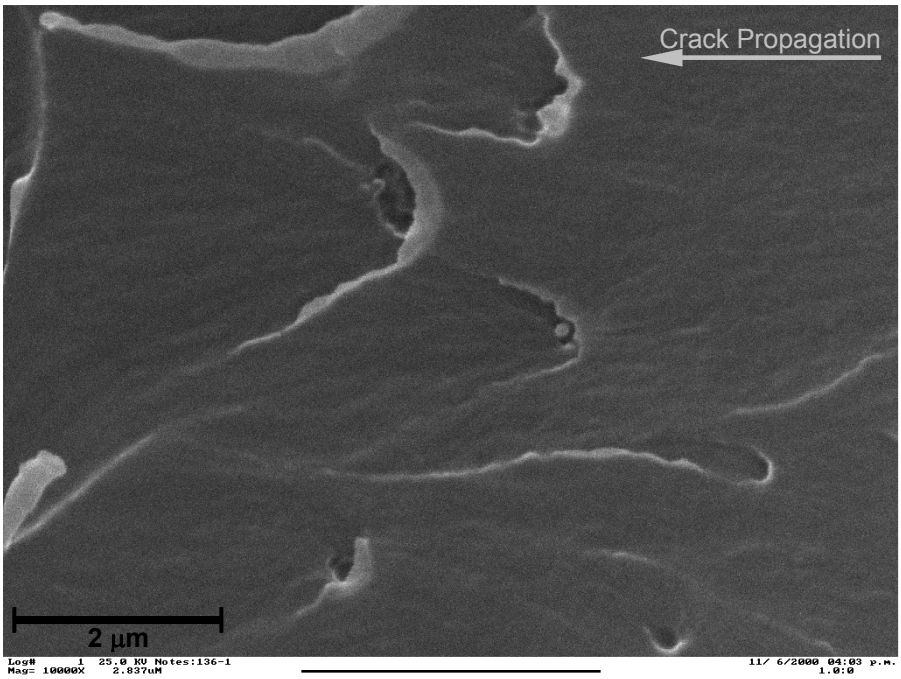

Figure 4: Fracture surface of polyester resin reinforced with 100 nm aluminum particles

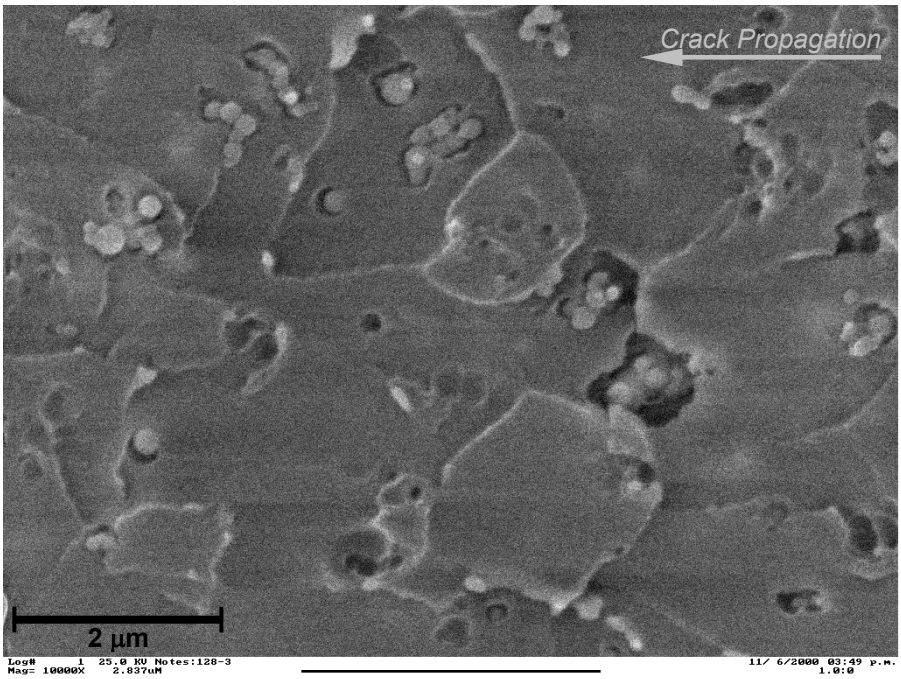

Figure 5: Fracture surface of polyester reinforced with 100 nm aluminum particles showing agglomeration

For the case of reinforcement by 100 nm aluminum particles fracture mechanisms were found to be dependent on particle volume fraction. For the case of low volume fractions (≤2.3%) the particles were uniformly distributed and contributed to crack front trapping, as shown in Figure 4. The fracture surface exhibited features similar to those observed for the case of 20 μm and 3.5 μm aluminum particles. In contrast, when the particle volume fraction was greater than 2.3%, the fracture surface exhibited marked differences, as shown in Figure 5. In this case, the aluminum particles tended to clump together and form agglomerates. These particle clusters inhibited proper wet-out, promoted the trapping of air and led to the

formation of voided spaces, which acted as damage initiation sites. As a result, the fracture surface appeared to be 'flaky' and no evidence of crack trapping was observed.

These observations of the fracture surfaces were consistent with the quantitative measurements of fracture toughness. Aluminum particles in the polyester matrix led to crack front trapping and hence an increase in the overall fracture toughness. This was observed for all the three sizes of aluminum particles except for greater volume fractions (≥2.3%) of 100 nm particles. In this case, the particles tended to agglomerate and were unable to promote crack trapping. The formation of these small agglomerates, at volume fractions greater than 2.3%, occurred despite the use of ultrasonic disruption. Thus, alternate chemical and/or mechanical treatments would be required to further disperse and deagglomerate 100 nm particles, which would probably lead to an enhancement in the overall fracture toughness.

SUMMARY

This investigation focused on the toughening of a highly cross-linked thermosetting unsaturated polyester by the incorporation of micron and nanometer sized aluminum particles. The effects of reinforcement particle size and particle volume fraction on the overall toughness and fracture behavior of polyester-aluminum composites was investigated by systematically varying the size (20 μm, 3.5 μm, 100 nm) and volume fraction (0.9%, 2.3%, 4.4%, 8.5%) of the aluminum particles. From experimental observations it was established that the enhancement of fracture toughness is strongly influenced by both these parameters. In general the fracture toughness increased monotonically with the volume fraction of aluminum particles, for a given particle size. Furthermore, it was observed that the increase in fracture toughness was significantly greater for smaller particles, for a given particle volume fraction.

Crack front trapping was established as the primary extrinsic toughening mechanism by conducting scanning electron microscopy of the fracture surfaces. It was observed that it is essential to maintain uniform particle dispersion and deagglomeration, and proper particle wet-out in order to ensure that the reinforcement particle promote crack trapping. While ultrasonic disruption has been found to be very effective in preventing the formation of large agglomerates [7], further chemical and/or mechanical treatments would be required to disperse and deagglomerate 100 nm aluminum particles at volume fractions greater than 2.3%.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the Ashland Chemical Company for supplying the polyester resin.

REFERENCES

[1]. Gleiter, H. (2000) *Acta Mat.* 48, 1.
[2]. Novak, B.M. (1993) *Adv. Mater.*. 5, 422.
[3]. Mark, J.E. (1996) *Poly. Eng. Sci.* 36, 2905.
[4]. Okada, A., Kawasumi, M., Kurauchi, T. and Kamigaito, O. (1987) *Abstr. Pap. Am. Chem. Soc.* 194.
[5]. Giannelis, E.P. (1998) *Appl. Organometal. Chem.*12, 675.
[6]. LeBaron, P.C., Wang, Z. and Pinnavaia, T.J. (1999) *Appl. Clay Sci.* 15, 11.
[7]. Singh, R.P., Zhang, M. and Chan, D. (2001) *J. Mat. Sci.* In Press.
[8]. ASTM Designation D5045-99, (1999) *Annual Book of ASTM Standards*.
[9]. Anderson, T. L., Fracture Mechanics: Fundamentals and Applications. CRC Press. Inc. 1991.
[10]. Srawley, J. E., (1976) *Int. J. Fract.* 12, 475.
[11]. Lange, F. F., *Philos. Magazine*, Vol. 22, pp. 983, 1970.