TOUGHENING OF CARBON FIBER-REINFORCED EPOXY POLYMER COMPOSITES VIA COPOLYMERS AND GRAPHENE NANOPATELETS

By

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Carbon fiber-reinforced epoxy composites currently play a significant role in many different industries. Due to their high cross-link density, aromatic epoxy polymers used as the matrix in composite materials are very strong and stiff however they lack toughness. Toughness is the material’s ability to absorb energy prior to fracturing. This dissertation investigates three areas of the carbon fiber-reinforced composite, which have the potential to increase toughness: the carbon fiber surface; the fiber/matrix interphase; and the matrix material. Approaches to improving each area are presented which lead to enhancing the overall composite toughness without reducing other composite mechanical properties.

One approach to toughening the aromatic epoxy matrix is by increasing the amount of energy the material can absorb before fracturing. Diglycidyl ether of bisphenol A (DGEBA) has a large and stiff backbone and is a common di-functional epoxy resin used in structural applications. Di- and tri-functional epoxy copolymers with a flexible aliphatic backbone have been used to toughen DGEBA, however always at high concentrations (>7wt%). Low concentrations (<2.5wt%) of aliphatic epoxy were found to
increase the notch Izod impact toughness by 60% for di-functional and 80% for tri-
functional epoxy without reductions in static-mechanical properties or glass transition
temperature ($T_g$). This toughening mechanism at low concentration is attributed to the
added flexibility of the aliphatic epoxy in the cross-linked polymer matrix that will allow
more energy absorption by polymer chain movement.

The toughened fiber/matrix requires the matrix and fiber to be strongly adhering
to yield a tough composite. Treatment of the AS4-12k carbon fiber surface with high-
intensity ultra violet light in the presence of ozone was used to reduce defects from the
fiber surface and to increase the amount of reactive oxygen groups on the fiber surface. In
a composite using neat DGEBA/mPDA matrix this UVO-treatment enhanced the Mode I
fracture toughness by +32% over the as-received carbon fiber by enhancing fiber/matrix
bonding.

In addition to the UVO-treatment, fiber sizing (coating) using two different
epoxies was also investigated. An aromatic epoxy sizing, same as the matrix material,
enhanced the composite Mode I fracture toughness by +50% over the as-received,
unsized fiber composite by increasing the modulus at the fiber/matrix interphase. A
sizing of flexible di-functional aliphatic epoxy increased the composite Mode I fracture
toughness by +84% over the as-received, unsized fiber composite. This increased
toughness at the fiber/matrix interphase also has been shown to increase the transverse
flexural strength. (+59%) All increases in fracture toughness were achieved without
reducing the static-mechanical properties of the composites.

Toughening of the composite matrix with 1wt% di-functional aliphatic epoxy,
that showed good increases in impact toughness, was investigated in conjunction with the
UVO fiber surface treatment and epoxy fibersizing. For the lowest toughness case, as-received, unsized fiber, the Mode I fracture toughness increased by +35%. The matrix toughening was most effective due to the low fiber/matrix adhesion that makes matrix fracture a more important toughening mechanism. As the fiber/matrix adhesion increased with the UVO-treated, unsized and the UVO-treated, aromatic sized fiber composites, matrix toughening resulted in smaller levels of enhancement of +13% and +17%, respectively. The improved fiber/matrix adhesion played a larger role for these composites. However, combining the aliphatic fiber sizing, that was the most effective modification with the neat matrix, with the 1wt% aliphatically toughened matrix a reduction of Mode I fracture toughness of -30% was measured. This reduction results from the concentration gradient produced by the addition of aliphatic epoxy to the matrix leading to a more compliant, lower strength interphase. With the exception of the aliphatic sized composite, all improvements were achieved without significant reductions in static-mechanical properties.

An alternate toughening approach for the matrix material is the dispersion of graphene nanoplatelets (GnP) throughout the matrix to act as crack arresting agents. GnP with different platelet sizes and aspect ratios were investigated. To enhance the filler/matrix bonding, amine groups were grafted to the GnP platelet edges by reaction with tetraethylenepentamine (TEPA). GnP enhanced different mechanical properties, depending on their aspect ratio and edge area. GnP C750, with a nominal platelet diameter of 1-2µm, showed slight increases in flexural properties (+1 to +5%) but did not have any influence on fracture toughness because the platelet aspect ratio is too small to be an effective crack arresting agent. GnP M5, with a 5µm nominal platelet diameter,
showed good improvements in fracture toughness (+22 to +31%) due to the larger aspect ratio of the platelet-like particle. The flexural moduli were similar for all GnP treatments and flexural strength was found to be dependent on TEPA-grafting and additional DGEBA reaction. The GnP M25, with a nominal particle diameter of 25µm, showed the highest increase in fracture toughness (+32 to +43%) due to the larger aspect ratio being superior at crack deflection. While the flexural modulus was increased (+6% to +9%) due to platelet stiffness, flexural strength was decreased by about 15% due to low filler/matrix adhesion.

An effective way of adding GnP M5 both heat-treated and TEPA-grafted to the composite, was by applying it as a sizing onto AS4-12k carbon fiber in low GnP sizing bath concentrations (0.1 & 0.5wt%). For an aromatic epoxy fiber sizing, the composite fracture toughness increased for all GnP concentrations and treatments: +61% with 0.5wt% heat-treated GnP M5, +23% with 0.1wt% TEPA-grafted GnP M5 and +37% with 0.5wt% TEPA-grafted GnP M5. Flexural properties were statistically the same or better for aromatic fibersizing, with TEPA-grafted GnP having better flexural properties than heat-treated only GnP. For the aliphatic fibersizing, the addition of 0.5wt% TEPA-grafted GnP showed reductions in flexural properties and no change in fracture toughness over the aliphatic only sized composite, resulting from the changes in diffusion of the aliphatic epoxy from the fiber surface. The additional amine groups grafted to the GnP are hypothesized to produce additional cross-linking, increasing the concentration of aliphatic epoxy on the fiber surface and leading to a weaker, more compliant interphase.

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