

# **Toughening vinyl ester matrix composites by tailoring nanoscale and mesoscale interfaces**

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Polymer matrix composites are used in the aerospace, automotive, and infrastructure industries to reduce high weight associated with their metallic counterparts. Vinyl ester (VE) is an attractive class of matrix resins due to its high chemical and corrosion resistance, good thermal and mechanical properties, and utilization of low-cost composite processing techniques such as vacuum assisted resin transfer molding (VARTM). The drawback of these materials, however, is low fracture toughness that can potentially lead to composite delamination and limited durability. The overall goal of this work is to improve the fracture behavior of VE composites while maintaining thermal and mechanical properties, interfacial performance, and their ability to be processed. Elastomer modification of epoxy resins has shown a great deal of success for increasing fracture toughness. During cure, rubber phase separates from the epoxy matrix, inducing energy dissipating mechanisms during fractures such as increased matrix shear yielding and rubber particle cavitation. There are inherent characteristics of VEs, however, that make them less conducive for elastomer toughening. Therefore, the first objective of this work was to identify these characteristics. We found that the cure behavior and rubber-VE compatibility were the main contributors to the ineffectiveness of rubber toughening. Unlike epoxies, VE contain styrene and vinyl ester monomers that undergo free radical copolymerization. Free radical polymerizing resins gel at a much lower conversion of reactive groups than epoxies. Therefore, rubber is given less time for phase separation and the VE matrix becomes plasticized. Also, the compatibility of VEs with rubber modifiers is a complicated issue. On a macroscopic level, overall compatibility is limited to low molecular weight VE monomers and low rubber loadings. On an interfacial level, we discovered that styrene diffuses into and swells the rubber domains. After cure, this behavior is responsible for void formation around the phase separated rubber domains. The next objective of this work was to develop a toughening method that circumvents obstacles associated with rubber toughening. We proposed that by imbedding electrospun micro- and nano-fibers as toughening composite interlayers, we could avoid the dependence of the initial compatibility of the modifier and cure behavior of the VE. In theory, these interlayers could exhibit a co-continuous, fibrous morphology, reminiscent of morphologies shown to toughen epoxies. Varying electro spinning processing parameters could be employed to tailor fiber size, and thus the second phase morphology. As was found with rubber modified VEs, the diffusion of styrene into the electrospun fibers was observed, resulting in void formation around the fibers and reduced resin and composite properties. The final objective of this work involved designing the interface between the electrospun fibers and VE to mitigate this problem. Plasma radiation and organosilane grafting were utilized to yield a controlled, cross linked organo-functional polysiloxane “shell” around each fiber. We investigated the effects of a reactive and non-reactive “shell” to distinguish which mechanism, a cross linked or reactive interface, limits styrene diffusion. It was found that styrene was able to permeate the non-reactive cross linked polysiloxane. However, the reactive interface provided a chemical link between the two phases that did not allow for void formation. The final part of this work entailed evaluating the effects on composite properties of surface modified PS electrospun fiber mats used as interlayers in carbon fiber composites. The interlayer toughened composites were compared to rubber toughened composites. The resins and composites containing fibers

with surface treatments yielded the worst properties. The most significant losses included flexural and shear properties. The systems containing the reactive fiber surface treatment showed moderate levels of improvement in mode I fracture toughness. Additionally, these composites were able to maintain other properties such as flexural, shear, and glass transition temperature ( $T_g$ ). The rubber toughened composite yielded the toughest composite with respect to mode I fracture, but demonstrated a significant level of plasticization. It was found that the toughening mechanisms were different for the rubber and interlayer toughened systems. The rubber toughened composite experiences a crack-tip blunting and increased stress concentration zones during delamination. The interlayer composite proved to increase the surface area of fracture during delamination by deflecting the crack in multiple directions. Also, the increased interlayer thickness allowed for fuller development of the stress concentration around crack tip.