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SYNTHESIS AND STRUCTURE PROPERTY STUDIES OF TOUGHENED
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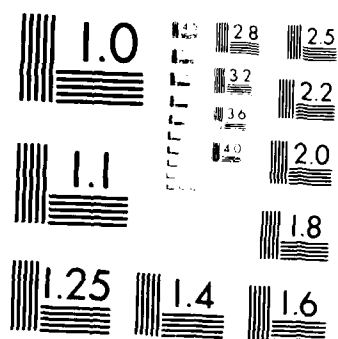
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Epoxy resins chemically modified with functionally terminated poly(dimethyl siloxane), poly(dimethyl-co-methyltrifluoropropyl siloxane) and poly(dimethyl-co-diphenyl siloxane) oligomers are described in terms of their synthesis, morphology, solid-state properties, and friction and wear properties. The compatibility between the epoxy resin and the siloxane modifiers can be enhanced by increasing the percentage of methyltrifluoropropyl (TFP) siloxane or diphenyl (DP) siloxane relative to dimethyl siloxane. The compatibility of the siloxane modifier with the epoxy resin subsequently controls the size and make-up of the phase-separated elastomeric domains. Fracture toughness of the epoxy resin can be improved by modification with siloxanes containing 40% or higher TFP content or 20 and 40% DP content. Both fracture toughness and modulus changes are given a morphological basis. Friction and wear properties in both fatigue and abrasive wear tests have been found to be related to changes in modulus, fracture toughness, and morphology in ways dependent on the particular modifier.					
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SYNTHESIS AND STRUCTURE PROPERTY STUDIES OF
TOUGHENED EPOXY RESINS VIA FUNCTIONALIZED POLYSILOXANES

SUMMARY

Epoxy resins are currently utilized widely as coatings, castings, adhesives and laminating materials. Their excellent chemical resistance, insulating and adhesive properties make them prime materials for these types of applications. In recent years, demand for "high performance" materials has heightened interest in these resins as structural adhesives and as matrix resins for high-strength composites. Such uses, however, require good fracture resistance and impact strength, properties which epoxy resins do not generally exhibit.

The most common route to toughening epoxy resins has involved the incorporation of elastomeric modifiers into the final glassy matrix. The principal objective has been the improvement of fracture properties with the smallest possible decrease in modulus and strength. The CTBN and ATBN (carboxyl and amine terminated butadiene) copolymers have done much towards accomplishment of this objective. Siloxane modifiers presented an attractive alternative to the butadienes due to the siloxane's superior thermal and UV stability. Moreover, it was anticipated that the unique surface properties imparted by the polysiloxanes might dramatically enhance the fatigue wear resistance of the epoxy systems.

The research done on this contract was an interdisciplinary effort encompassing three major areas. Synthetic investigations were conducted with the objective of preparing a series of appropriately functionalized, potential polysiloxane modifiers for epoxy resins. The materials were synthesized by the Polymer Chemistry Group at Virginia Polytechnic Institute and State University under the direction of J. E. McGrath. Additionally, subsequent reaction processes for covalent incorporation of those modifiers into the final epoxy networks were developed. Secondly, a detailed analysis of the mechanical and fracture properties of the resultant rubber-modified systems as a function of the domain size of the rubber particles and as related to the final morphology was done in the Chemical Engineering Department under the direction of Garth Wilkes. Finally, correlation of the surface compositions of the series of materials with their wear behavior was done principally in the Mechanical Engineering Department under Dr. N. S. Eiss.

The compatibility of the modifier with the resin system is an important factor in achieving quantitative reaction of the functional modifiers into the resin and in controlling the point in the reaction process where microphase separation occurs. In turn, this controls the size and dispersion of the rubbery domains. It was found that the solubility parameter of the polysiloxanes could be systematically controlled by co-reacting dimethylsiloxane units with either diphenylsiloxane or methyl-trifluoropropylsiloxane (TFP) units. Synthetic procedures were developed for making secondary amine terminated, precisely difunctional, polysiloxane oligomers wherein both the molecular weight and solubility parameter of the modifiers could be controlled. A series of the materials was prepared and reacted into bisphenol-A diglycidyl ether-based epoxy resins in varying amounts. Bis(4-aminocyclohexyl)methane was normally used as the curing agent for these materials. This series of modified epoxies was then used for the morphological, mechanical, and wear behavior investigations.

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Morphological characterization of the modified epoxy resins indicates that elastomer particle size decreases from 50 to less than 5 μm as the TFP content of the modifier is increased and that the same general trend exists for the dimethyl-diphenylsiloxane containing systems. This appears to be consistent with the fact that miscibility between the epoxy resin and the modifier is enhanced as TFP or diphenyl content is raised. As expected for the incorporation of any elastomer into a high modulus system, modification with the various polysiloxane oligomers causes the flexural modulus to decrease somewhat. However, the decrease was found to be substantially less severe as the level of TFP or diphenyl units was increased. Moreover, K_{IC} , the plane-strain fracture toughness, tends also to increase with increasing TFP or diphenyl content. This suggests that compatibility of the modifier and the resin is an important criterion for efficient rubber toughening to occur.

Because of their low surface energies and non-polar structure, the polysiloxane block segments of these epoxy networks tend to microphase separate and migrate toward the air-polymer surface. The influence of the resultant low energy surfaces on the friction and wear properties of the modified epoxies was measured using two test configurations, a steel ball sliding on a cast epoxy surface and an epoxy pin sliding on a glass or steel disk. Using the stationary steel ball on the rotating epoxy disk, the abrasive and adhesive wear mechanisms were minimized whereas the fatigue mode was emphasized. Wear results give a positive correlation with the elastic modulus of the epoxy materials. Thus, both the coefficient of friction and the wear were reduced by the addition of the polysiloxane. Using the trifluoropropyl-methyl co-dimethylsiloxane modified epoxies, it was found that the lowest wear rate occurred when 20% by weight of the siloxane was trifluoropropyl-methyl substituted and the total polysiloxane content was 10-15%. When all of the modifier was comprised of trifluoropropyl-methylsiloxane units, the domains were very small, and the wear rates were comparable to those of the unmodified epoxy. The path of the steel ball on the modified materials indicated that, when the elastomeric domains were small relative to the distance between them, the only damage was the tearing of the elastomer from the wall of its cavity. When the domains were large compared with the distance between them, the wear was initiated when the thin epoxy walls between domains cracked and were removed as loose wear particles. The wear of the modified epoxy pins on steel was found to be initially abrasive. In contrast to the results of the fatigue wear described above, the wear rates in this abrasive mode correlated with the inverse of the fracture toughness. Steady state wear resulted after the abraded polymer had transferred to the steel disk and smoothed the steel ridges. For sliding on both glass and steel, the compositions with the higher rubber concentrations exhibited higher steady state wear rates. It was concluded that the relative ranking of these modified epoxies based on wear rate depends on the dominant wear mechanism observed in the chosen wear test.

Finally, during the latter stages of this grant, novel amine and hydroxyl functional engineering thermoplastic oligomer modifiers based on poly(arylene ether sulfones) and poly(arylene ether ketones) were synthesized and utilized in epoxy toughening experiments. Very significant improvements were obtained, with minimal loss of stiffness. The investigation is summarized in several preliminary papers, the Ph.D. thesis of J. L. Hedrick and in a manuscript attached to this report.

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