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**Chemical Treatment of Epoxy Resins to
I. Reduce Moisture Absorption and
II. Improve the Mechanical Properties**

Richard D. Gilbert and Raymond E. Fornes

September 15, 1989

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Statement of Problem

Epoxy resin/graphite fiber composites absorb significant amounts (~ 4%) of water which causes a decrease in the epoxy resin Tg, plasticization, micro-cracking, delamination, and resin-fiber debonding, resulting in a serious property loss.

The epoxy resin at its optimum degree of cure contains numerous functional groups (hydroxyl, amine, epoxide, sulfone) and the electrostatic attraction between these groups and water provide the driving force for water absorption. The amount of water uptake is determined by the unoccupied volume of the epoxy which is a function of the degree of cure. It was proposed to study the effect of blocking the functional groups, by chemical reaction with suitable reactants, on the moisture absorption. Reduction of the moisture absorption would improve mechanical properties. It was also proposed to study the use of carboxylic terminated elastomers to obtain a better property balance at higher degrees of cure.

Summary of Important Results

1. Employing thin films of the epoxy resin, it was shown by infrared spectroscopy and differential scanning calorimetry, that silylation, carbanilation, and/or cyanoethylation of residual hydroxyl, amine, and epoxy groups occurs.
2. Reductions in equilibrium moisture absorptions up to 75 percent were obtained.
3. Moisture uptake by the epoxy resin exhibits Fickian behavior at 30, 45, 55, and 70°C. The diffusion coefficient, D, increased from 30° to 55°C but decreased at 70°C, attributed to a reaction of water with residual oxirane groups.
4. Sorption of isocyanates essentially follows Fickian behavior.
5. Moisture diffusion of the films after blocking the residual functional groups by cyanoethylation or carbanilation exhibits Fickian behavior. At 30°C, D values are significantly higher for reacted films. At 70°C, the value of D is unchanged for cyanoethylated films, but D values are significantly lower for films reacted with isocyanate blocking agents compared with the epoxy resin.
6. Blocking the residual functional groups of the epoxy resin with fluorinated aromatic reagents reduced the equilibrium moisture absorption by as much as 75%. Pentafluorobenzoyl chloride is a more efficient blocking reagent than fluorinated isocyanates. 2,4-Difluorophenyl isocyanate is a more effective blocking reagent than the trifluoromethylphenyl isocyanates due to its higher reactivity.

7. Several masked isocyanates were synthesized with variations in both the isocyanate type and masking group and were characterized by elemental analysis and NMR spectroscopy and determination of their unblocking temperatures. Those with unblocking temperatures in the 120–130°C range were incorporated into the epoxy resin prior to curing to provide *in situ* blocking of residual function groups in the epoxy resin. Infrared spectroscopy and differential scanning calorimetry demonstrated the residual functional groups were reacted. Reduction in equilibrium moisture absorptions as high as 65% were obtained, depending on the masked isocyanate.
8. Dynamic mechanical analysis studies showed the T_g of the epoxy resin is lowered by incorporation of the masked isocyanate, but the elastic modulus is relatively unchanged at temperatures below T_g.
9. Stress-strain studies of the epoxy resins after curing in the presence of the masked isocyanates are relatively unaffected by incorporation of the masked isocyanate, demonstrating this approach is a practical technique for lowering the equilibrium moisture absorption of epoxy resins.
10. High resolution ¹³C-CP/MAS NMR was used to follow the reactions of the residual functional groups with the masked isocyanates and to identify intermediates and by-products.

Publications

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