Effects of Skydrol (A Hydraulic Fluid) on the Network Structure of TGDDM/DDS-Based Resins

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ABSTRACT: The effects of Skydrol 500B-4 upon the physical and mechanical properties of the final network structure of a DDS-crosslinked TGDDM resin were investigated using conventional thermal analysis techniques. The chemical system studied was I.C.I's Fiberite 934 epoxy resin. The characteristic thermal transitions associated with epoxy networks were correlated with the structure, employing dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA). A decrease in the temperature location of the glass/rubber and vitreous transitions, accompanied by a reduction in the peak height and area beneath the β transition, were observed in cured systems incorporating the hydraulic fluid. An increase in the elastic modulus was also noted in the contaminated networks. Solvent extraction, using a Soxhlet apparatus, was performed to further characterize the role played by the Skydrol. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2025–2030, 1997

Key words: network structure; epoxies; hydraulic fluid; thermal transitions

INTRODUCTION

The effects of Skydrol 500B-4 upon the cure characteristics of a commercial TGDDM/DDS-based formulation were previously reported.[1] The incorporation of the hydraulic fluid within the crosslinking resin diminished the overall heat of reaction and delayed the onset of vitrification. Diminished molecular mobility within the gel, caused by the presence of Skydrol, was advanced as a plausible mechanism. The scope of the present study was to characterize the effects of the hydraulic fluid on the physical and mechanical properties of the final network structure, using thermal analysis techniques, and to elucidate further the nature of the role played by the contaminant. Skydrol 500B-4 is a standard fire resistant-based hydraulic fluid, composed of alkyl aryl phosphate esters and additives, which is presently employed within the aircraft industry.

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Dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA) are both forms of relaxation spectroscopy which permit changes in molecular motions and structural transitions to be detected and quantified as a function of temperature. The dynamic mechanical and dielectric spectra of amine-cured epoxy resins are well established and thus permit correlation of microscopic characteristics, which, for epoxy systems, include crosslink density, free volume, and thermal transitions with macroscopic properties such as the Young's modulus.[2–8]

EXPERIMENTAL

Materials

The materials employed in this study were I.C.I's Fiberite 934 epoxy resin and Skydrol 500B-4. The chemical constituents of these formulations were previously outlined.[1]

Sample Preparation

The commercial 934 resin was heated to 100°C for 10 min before the hydraulic fluid was added at 2.5, 5.0, 7.5, and 10.0% by weight of formulation. These samples were subsequently cured in a vacuum oven in accordance with the recommended curing schedule: 121°C for 2 h, 177°C for 2.5 h (allowing 0.5 h for the oven to reach the upper temperature), followed by slow cooling to room temperature. Rectangular DMTA specimens, of nominal dimensions 31 × 11 × 2 mm, were cut and machined from sheets employing a Buehler Isomet 2000 precision saw and a Microcut grinding wheel. Disk DETA specimens, with nominal thicknesses of 1.0 mm and diameters of 30.0 mm, were cut from rods using the same saw.

Methods

DMTA was employed to observe any variations in the temperature location and, where feasible, the intensity and transition width of the thermal transitions resulting from Skydrol addition. Dynamic storage moduli (E'), dynamic loss moduli (E''), and damping ($\tan \delta$) were measured in a Polymer Laboratories Mark II dynamic mechanical thermal analyzer fitted with a torsion head. Dynamic analyses were performed at a heating rate of 2°C/min over the range −140 to 300°C. The multiplexing capabilities of the instrument allowed measurement of the sample response at three discrete frequencies: 0.1, 1.0, and 10.0 Hz.

To complete the rheological study, DETA was used to determine any effects the hydraulic fluid played on the extent of dipole relaxation. The relative permittivity, ε', and the damping, $\tan \delta$, were obtained in a Polymer Laboratories Mark II dielectric thermal analyzer, fitted with parallel plates. Scans were carried out at 2°C/min over the range 50 to 300°C. The selected frequencies of measurement were 0.5, 1.0, and 5.0 kHz.

DMTA and DETA analysis were performed on each of three specimens, so that, for each state of contamination, three damping curves were obtained. The most representative curve was plotted for each level of contamination.

Cured 934 + 10 wt % Skydrol resin samples were subjected to solvent extraction to determine whether the hydraulic fluid had become chemically bonded to the polymer network during the cure cycle. Cured samples were pulverized in a Giromill (Glen Creston Ltd), passed through a 150 μm sieve, dried for 24 h at 80°C, extracted with methanol and ethanol[9] for 1 week, and redried at 80°C for 48 h. A Soxhlet apparatus was employed for the extraction process. The sample weights before and after extraction, obtained on an Sartorius electrobalance (precise to 10^{-5} g), were employed to determine the mass extracted.

Cured 934 resin samples were immersed in Skydrol to estimate the maximum uptake. Samples were firstly vacuum-dried at 80°C for 48 h and subsequently weighed. They were mounted so as to ensure sorption at all sample faces and edges and stored at ambient. Sample weight increases were recorded by removing the sample from the hydraulic fluid, drying the faces and edges thoroughly with tissue paper, and weighing on a Sartorius electrobalance. The uptake was averaged from the results recorded for three samples taken at each aging period. At each aging period, a single dynamic DMTA scan was performed on a sample in accordance with the procedures outlined above, allowing any possible effects due to absorbed Skydrol to be observed.

RESULTS

Mechanical Relaxations

The dynamic mechanical spectrum of amine-cured epoxy resins is well established and is characterized by three loss peaks labeled α, ω, and β, in decreasing order of temperature. The most prominent relaxation in the damping trace is the α transition, which is synonymous with long range cooperative motion of the crosslinked network, i.e., the glass transition temperature.[10] Incorporation of the hydraulic fluid into the matrix suppressed the α peak temperature significantly, in a decreasing monotonic function of percentage Skydrol added, as shown in Figure 1.

The glassy-state relaxations proved to be equally susceptible to the inclusion of the contaminant. The temperature location of the β transition (T_β), generally attributed to the rotation of the flexible —CH_2—CH(OH)—CH_2—O— crosslinking segments formed during the curing process decreased in parallel with a reduction in the peak value ($\tan \delta_{max}$) and area beneath the curve (A_β).[2–8,11,12] These effects of Skydrol addition, shown in Figure 2, were accompanied by a narrowing of the trace on the high-temperature side.

The multiplexing capabilities of the analyzer permitted the activation energy, $E_{a\beta}$, to be calculated using an Arrhenius law:

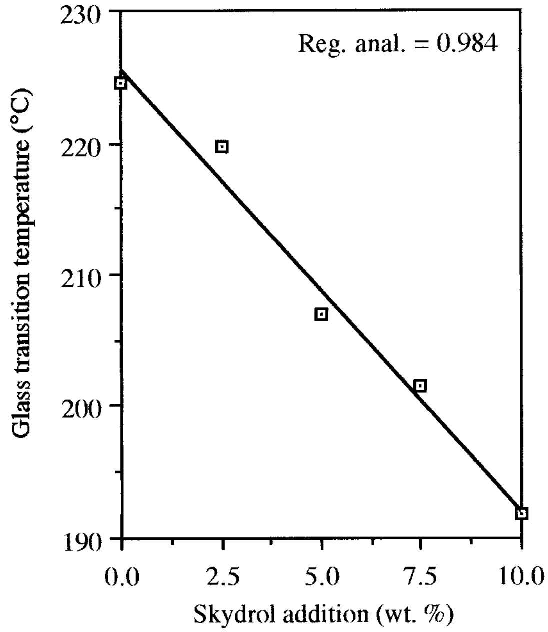

Figure 1 Plot of the shift in T_g of I.C.I's 934 epoxy resin as a function of weight percent Skydrol addition (frequency = 1 Hz).

$$\ln f = \frac{-E_a}{RT_m} + K \tag{1}$$

where R is the universal gas constant and T_m is the temperature location of the peak maximum (damping, in this case) at a given frequency. The activation energy for the transition of the neat 934 resin diminished by approximately 19% from 72 to 58 kJ/mol upon addition of 10 wt % Skydrol.

Unreacted molecular segments and/or inhomogeneities in the material arising from regions of dissimilar crosslink density give rise to the ω transition.[3] This second glassy relaxation, shown in Figure 3, became appreciably more predominant as the percentage Skydrol added to the reactants was increased. The presence of Skydrol also appeared to shift the transition to lower temperatures.

DMTA was also used to determine the possible effects of absorbed Skydrol on the thermal transitions of noncontaminated 934 cured samples, in order to elucidate whether the effects of Skydrol noted this far occurred simply from its presence during the crosslinking reactions. Outlined in Table I are the masses absorbed and variations in

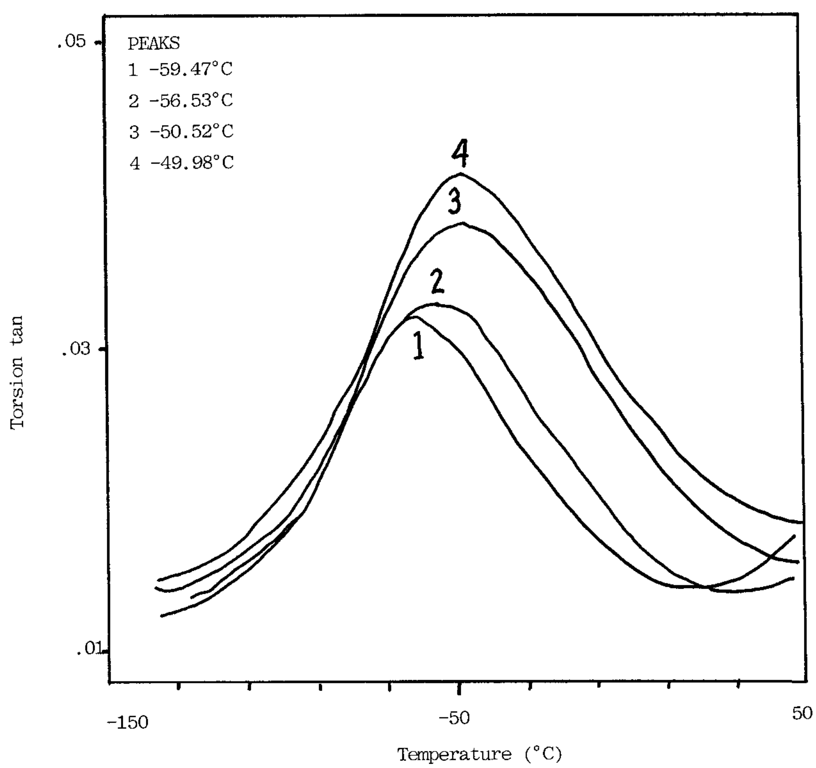

Figure 2 Changes in the characteristics of the β transition of I.C.I's 934 epoxy resin. Curve (4) is that of the neat resin, whereas curves (3), (2), and (1) represent the same resin system contaminated with 2.4, 7.5, and 10.00 wt % Skydrol.

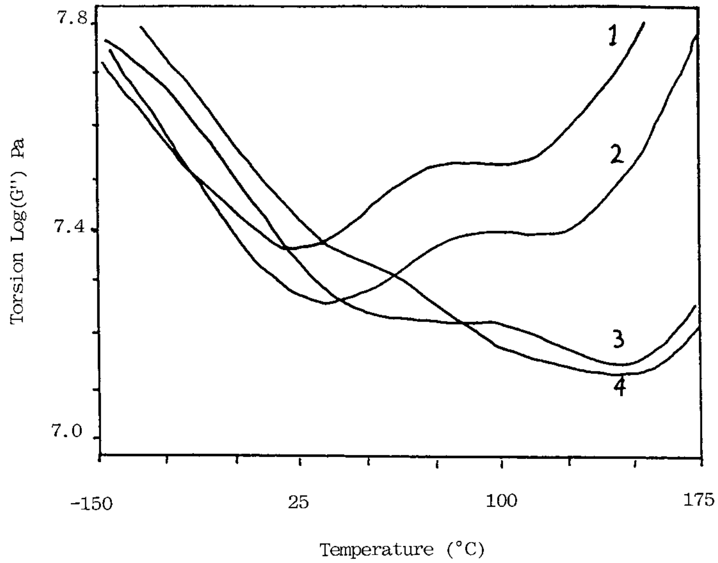

Figure 3 Development of the ω transition of I.C.I's 934 epoxy resin. Curve (4) is that of the neat resin, whereas curves (3), (2), and (1) represent the same resin system contaminated with 2.5, 7.5, and 10.0 wt % Skydrol.

the glass transition temperature resulting from prolonged absorption times in Skydrol. In contrast to the reductions in temperature location of the α transition resulting from the physical premixing of Skydrol within an unreacted system, absorbed Skydrol did not alter the glass transition temperature of the final network structure, determined again as a peak in the damping trace. However, the masses absorbed are not comparable with the quantities of Skydrol physically premixed, suggesting that insufficient contamination may be the cause of the constant T_g values observed.

Dielectric Relaxations

The dielectric spectrum of amine-cured epoxy resins is characterized by the same loss peaks previously observed mechanically. The systematic decrease in T_g was again observed as a downward shift in the peak temperature of the tan δ curves. However, the interesting feature of the DETA curves is the accompanying reduction in relaxation strength, numerically determined by subtracting relaxed permittivity values, log ε'_r, from unrelaxed permittivity values, log ε'_u, as outlined in Table II.

Modulus

The modulus–temperature curves showed clearly a glassy region, a transition region, and a rubbery region which are characteristic of highly crosslinked polymeric systems. The reduction in T_g observed in the damping curves mirrors the reduction in temperature location of the transition region. However, the most striking effect of incorporating Skydrol in

Table I Percent Mass Uptake and Resulting T_g Following Prolonged Absorption Times in Skydrol of I.C.I's 934 Resin

Absorption Time (Weeks)	Absorbed Mass (%)	T_g (°C)
Reference	—	222.9
12	0.54 ± 0.03	221.3
24	1.09 ± 0.05	222.6
36	1.46 ± 0.05	221.7

Table II Strength of Relaxations of I.C.I's 934 Resin as a Function of Weight Percent Skydrol Addition

Content (wt %)	log ε'_r − log ε'_u
0.0	0.87
2.5	0.79
5.0	0.69
7.5	0.38
10.0	0.46

Table III Change in Modulus in the Glassy and Rubbery States of I.C.I's 934 Resin as a Function of Weight Percent Skydrol Addition

Content (wt %)	E' at 25°C (MPa)	E' at 250°C (MPa)
0.0	1196	30
2.5	1223	18
5.0	1199	18
7.5	1533	17
10.0	1659	23

the resin systems is an increase in the elastic modulus, meaning that, in this temperature region, the contaminated systems can accommodate less strain under a fixed stress than can the neat resin formulations (Table III).

Solvent Extraction

The neat, powdered reference sample and the Skydrol-contaminated, powdered sample had negligible weight loss upon solvent extraction, indicating that the hydraulic fluid is retained by the network under the chosen conditions.

DISCUSSION

Both the glass/rubber and vitreous transitions depend on molecular mobility, which, in turn, is a function of the chemical and/or physical nature of each molecule and its local environment. In principle, then, the degree of crosslinking can affect the T_g and/or relaxations in the glassy state since the creation of network junctions can alter chain mobility and vary the free volume available for the relaxational motion. The notable decrease in T_g for Skydrol-contaminated systems suggests increased ease of movement of the polymer backbone made feasible by an increase in the free volume of the final network structure. A parallel decrease in the temperature location of the β and ω transitions would therefore also be expected and was subsequently observed.

Various characteristics of the β relaxation have been related to the degree of crosslinking within a specific amine-cured resin.[3,7,8,12,13,14] The accompanying reductions in intensity and area beneath the DMTA tan δ curves exhibited by this glassy relaxation, as it shifts to a lower temperature, suggest a decrease in the number of mobile groups giving rise to this transition. Such manifestations are indicative of a decrease in the number of epoxy groups opened by the DDS hardener in the contaminated system, relative to the neat resin, both formulations having been exposed to the same cure profile. Furthermore, the developing dominance of the ω transition suggests an increase in unreacted molecular segments, implying that the crosslink density indeed diminished. An increase in the molecular weight between crosslink points (M_c) within the contaminated systems is further supported by the observed decrease in activation energy associated with the β transition, in accordance with the conclusions of former investigations, which state that $E_{a\beta}$ is a decreasing function of crosslink density.[8,14]

Recalling the prominent role played by the epoxy–hydroxyl reactions (E–OH) following gelation, the secondary alcohols should be particularly attractive sites for hydrogen bonding with the Skydrol (an alkyl aryl phosphate ester), thus isolating potentially reactive centers. The retention of the hydraulic fluid by the network during extraction supports the proposal that chemical bonding is occurring between the contaminant and component(s) of the 934 system and is a natural progression from the thermogravimetric results previously reported.[1] Furthermore, the passive nature of absorbed Skydrol upon the fully cured three-dimensional structures suggests that the presence of the hydraulic fluid during the crosslinking process is indeed fundamental to the origin of the noted effects.

The DETA results, which indicate a decrease in the extent of dipole relaxation, do not appear to support the concept of an increase in free volume arising from a decrease in the degree of cure. However, in epoxy resin systems, previous investigations agreed with the conclusion that as the crosslink density increases the packing efficiency decreases.[15–17] Upon cooling, a matrix with a high crosslink density will have a more restricted molecular mobility and thus be less able to closely pack in the glassy state. A reduction in the extent of crosslinking caused by the presence of Skydrol within the gel would therefore give rise to increased compactness and reduce the extent of dipole relaxation while shifting the T_g to lower temperatures.

Numerous mechanical changes parallel the changes in thermal relaxations upon augmenting the free volume of a polymer system. The addition of Skydrol to the 934 formulation resulted in, contrary to that expected of a plasticized system, a monotonic increase in the glassy modulus. The low-temperature β transition is a stress-relaxation process which contributes to the outstanding toughness of amine-cured epoxies. Any decrease in the extent of crosslinking upon contaminant addition reduces the number of these flexible, energy-dissipating segments, arising from the opening of epoxy rings by amines and thus increases the rigidity of the resulting structure. This interpretation of modulus being a decreasing function of crosslink density is well established.[8,16,17]

CONCLUSIONS

The physical and mechanical properties of the final network structure of I.C.I's 934 epoxy resin are susceptible to the presence of Skydrol. The incorporation of the hydraulic fluid within the epoxy system diminishes the temperature location of the rubber/glass and vitreous transitions, reduces the intensity and area beneath the β transition, and augments the glassy modulus. An increase in the molecular weight between crosslink points is advanced as the cause of these observations.

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