

Highly Fluorinated Epoxy Resin. II. Behavior in Blend Applications

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SYNOPSIS

The behavior of a highly fluorinated epoxy resin blended with Epon 828 was studied. The two resins are immiscible, resulting in 10–20- μm spherical domains and a surface layer of fluorinated resin. A B stage for the blend providing for good ply lamination is indicated. The mechanical properties of the blend were commensurate with the Epon phase.

INTRODUCTION

The desirable properties of fluoroepoxy resins synthesized by Griffith and Field,^{1,2} such as low surface tension and friction coefficients³ and low water uptake,⁴ have been demonstrated elsewhere. In the first paper of this series, some unusual properties were discovered in the fluoroepoxy designated C8¹ cured with a silicone diamine curing agent (C8/1SA), the system used as a model in characterization of the postcuring and transition behavior of these materials.⁵ Low glass and deflection temperatures and consequently rapid physical aging directed interest away from the use of these resins as pure materials, and led to investigations of model blends of C8 with the diglycidyl ether of bisphenol-A (DGEBA) type resins, specifically Epon* 828 (E828), in which it was hoped that the unique and valuable properties of the fluoroepoxy would be incorporated into a resin system of known and useful properties. The morphology of a 10% by weight of C8 blend with E828 was studied and the tensile properties were compared with pure E828.

EXPERIMENTAL

Ten percent C8 by weight was mixed with E828. This blend was stirred with a stoichiometric amount of 1SA hardener at a temperature of 50 to 52°C. This temperature range reflected a compromise between the compatibility windows (temperature

ranges at which the resin and curing agent are miscible) of C8/1SA (50–60°C) and E828/1SA (40–60°C), giving the maximum pot life. The reacting mixture was poured into silicone molds to cast free surfaces, films, and dogbone samples. Samples were out-gassed under vacuum for 20 min at room temperature. Two types of cure schedule were then applied, a slow route entailing a room temperature cure of 16 h, followed by a 3-h postcure at 120°C, and a fast route employing 1 h at 60°C, 15 h at room temperature (during which, presumably, no further reaction occurred), and 3 h of postcure at 120°C. Due to the slowing of cure by the presence of CO₂,⁵ an N₂ atmosphere was used for all curing schedules.

For electron microscopy, a bulk sample and a dogbone sample 2.5 × 0.5 × $\frac{1}{8}$ in (l × w × h) with a 1.5 × 0.25 in (l × w) gauge dimension were fast cured. The bulk sample was cleaved at room temperature with a razor blade and ion etched in an air molecule plasma for 1 h. The etched surface was coated with Au–Pd. An aged dogbone sample was fractured in flexure at room temperature. The fracture surface was shadowed with Pt–C and carbon coated. Both surfaces were examined using an Hitachi S570 SEM.

A Perkin-Elmer Φ 5400 XPS was used to investigate the surface properties of the blend. A fast-cured free surface, fast-cured molded bottom surface (against the silicone mold), and fast- and slow-cured “free” surfaces were examined. Here, a free surface indicates the surface of a large film, while a “free” surface is the open surface of a molded dogbone sample, which has a much greater chance of contamination with silicone release agent.

XPS spectra were taken at 15 and 75° to enhance

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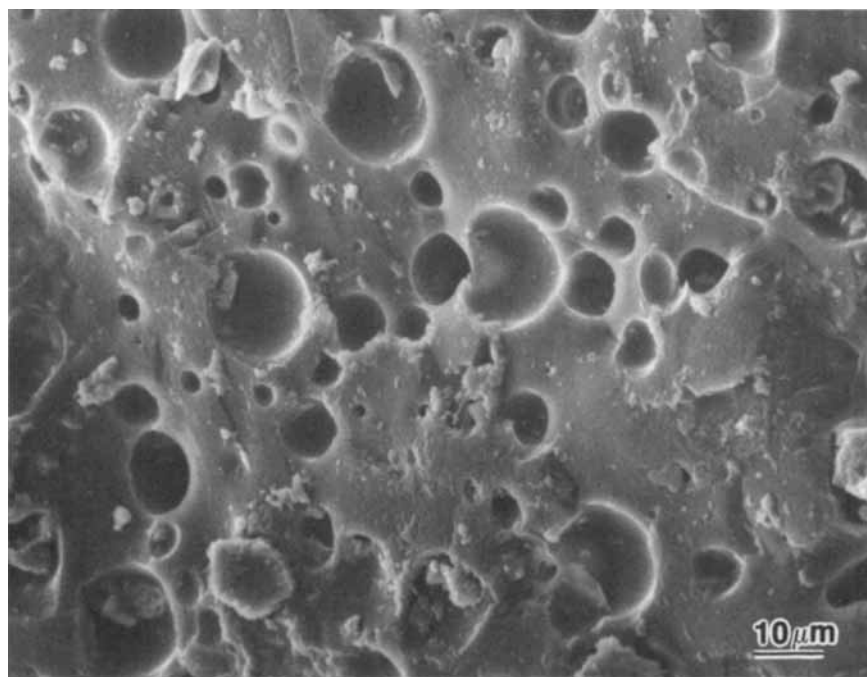


Figure 1 Micrograph of cut, etched surface of blend.

the surface and the bulk chemistry, respectively. The beam always penetrates 60 \AA , but when the sample is tilted at a greater angle relative to the beam the true sampling depth is decreased. In this manner, a depth profile could be obtained. Scans of neat C8/1SA and E828/1SA were run for comparison.

To test the weldability of the B stage of the blend, dogbone samples $2.5 \times 0.5 \times \frac{1}{8}$ in with 1.5×0.25 in gauge dimensions were prepared as before. After the initial room temperature cure, two samples were placed, variously, bottom surface (silicone molded surface) to bottom surface, top surface to top sur-

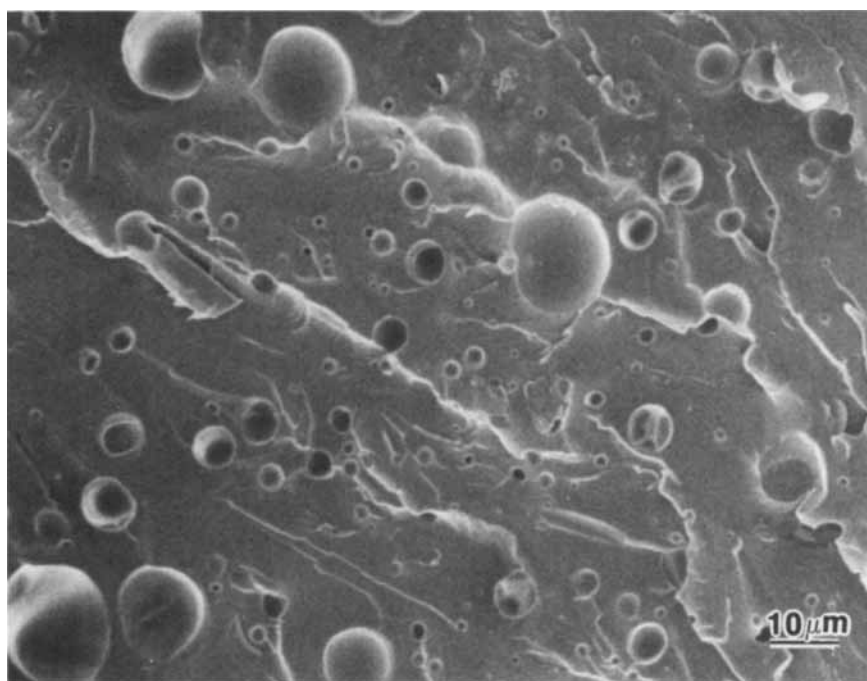


Figure 2 Micrograph of fracture surface of blend.

face, and bottom surface to top surface in a hot press. Postcuring was conducted for 3 h at 120°C in the press under contact pressure.

Using an Instron 1331, dogbone samples $2.5 \times 0.5 \times \frac{1}{8}$ in with 1.5×0.25 in gauge dimensions, which had been heated for over $\frac{1}{2}$ h at 120°C to remove aging history, were tested in tension. E828/1SA samples of the same dimensions and cured in the same way were also run for comparison.

RESULTS AND DISCUSSION

The etched surface in Figure 1 shows predominantly 10- to 20-micron diameter spherical domains where fluoroepoxy has etched out of the Epon matrix. (SEM of a replica of the surface shown in Figure 1 substantiated this.) The spherical domains are the logical consequence of the immiscibility of the C8 and E828 components.

In Figure 2, the unmodified fracture surface is seen. Again, the spherical domains are observed. These domains should be bound to the matrix by the common curing agent. Because of their ductility, at least before aging, they could serve as toughening agents by arresting cracks. However, since the domains are immiscible in the matrix, the crosslinking agent joining the materials should, hopefully, be located in a nearly monomolecular layer at the interface. The Si—CH₂ bonds are weak relative to any of the other types of bond in the materials, which might lead to a relatively low energy path of fracture through the interface around the domains. This interfacial fracture behavior may also serve to toughen the ordinarily brittle Epon by crack deflection in much the same way fibers toughen ceramic matrices. Indeed, in Figure 2 the fracture seems to have proceeded around the domains, indicating that adhesion is relatively weak at the interfaces. The interfacial nature of the fracture might separately be related to the specimen age of two weeks. Specimen aging was shown in the previous paper⁵ to cause a change from ductile to more brittle behavior in the C8/1SA resin, an effect that would result in brittle inclusions in the matrix.

Table I shows the 15 and 75° beam orientation results of XPS studies. First, there is an indication that there is a somewhat greater amount of fluorine functionality at the surface of the neat fluoroepoxy resin. This could be due to preferential segregation of the long fluorinated side chain (ca. 10 Å) at the surface of the specimen. However, the difference is not large and shall therefore be assumed for now to be due to experimental error.

The samples of neat E828/1SA were heavily contaminated by silicone release agents. No fluorine

activity was present, indicating that none of the propellents used in the mold release were retained. No measure of the percent elemental compositions were made due to the contamination. However, the presence of N_{1s} activity, an element present only in the curing agent, was noted.

Referring again to Table I, it is noted that the blend free surface is covered by a layer of fluoroepoxy at least 60 Å thick, i.e., the F_{1s} content of both the surface and bulk enhanced scans are identical to those of the neat C8/1SA resin. On the other hand, the scan of the bottom (silicone molded) surface shows a much reduced fluorine content. This indicates that the fluoroepoxy separated preferentially to the upper surface of the blend.

The presence of a large silicone content indicates heavy contamination by the silicone mold release agent on this surface. Here it is useful to note that the 75° orientations are most representative of the bulk and therefore are the most reasonable selection for a consistent comparison between different samples of differing surface contaminant levels.

The scan of the blend free surface revealed a chemical composition nearly identical to the neat fluoroepoxy resin, including equal N_{1s} activity (which is not detailed in the table). The N content indicated that the surface layer, and probably the subsurface domains, contained curing agent. Similar comparisons of the N_{1s} activity of pure E828/1SA and the bottom surface of the blend material showed that the E828 phase also contained curing agent. This laid to rest the fear that one or another of the resins was thermodynamically preferable for absorption of the curing agent.

The scans of the slow- and fast-cured "free" surfaces of the blends show no significant differences from the free surface scan. Both still show that there is a layer of fluoroepoxy over 60 Å thick at the surface; the rapid cure did not cause a thinning in the surface layer that was detectable by XPS.

The energy of formation for CF₂[•], CF₃[•], and related ions is very low and occurs under the X-ray beam. The time under the beam was therefore minimized to avoid sample damage with the concurrent change in surface chemistry, this change being similar to that occurring in ion etching of the material.

Figure 3 shows the interface region of two welded plies of the blend, in which the lower surfaces were placed in contact. One can see two types of region. The bulk region contains the characteristic 10- to 20-micron diameter domains that have been elongated in compression by the contact pressure applied during welding. In the interface region, there appears to be a lack of C8 domains. This indicates that the lower molded (vs. "free") surface is fluoroepoxy

Table I Peak Data for XPS Curves

Sample	Angle (°)	Element	Peak Area Counts	Corrected Peak Area ^a	Relative % Comp.
Neat C8/1SA	15	F 1s	10879	10879	26
		O 1s	2375	3770	9
		C 1s	4792	23376	56
		Si 2p	628	3694	9
	75	F 1s	10865	10865	23
		O 1s	3079	4887	10
		C 1s	5753	28063	60
		Si 2p	543	3194	7
Blend free surface	15	F 1s	15434	15434	27
		O 1s	3080	4889	9
		C 1s	6616	32273	57
		Si 2p	653	3841	7
	75	F 1s	11475	11475	26
		O 1s	2374	3768	9
		C 1s	5551	27078	57
		Si 2p	448	2635	7
Silicone molded blend surface	15	F 1s	2217	2217	13
		O 1s	1676	2660	16
		C 1s	1661	8102	48
		Si 2p	663	3900	23
	75	F 1s	2153	2153	28
		O 1s	4567	7249	9
		C 1s	4898	23893	56
		Si 2p	1826	10741	7
Slow-cured "free" surface	15	F 1s	11683	11683	22
		O 1s	2190	3476	9
		C 1s	4762	23229	63
		Si 2p	514	3024	6
	75	F 1s	11340	11340	22
		O 1s	2876	4565	9
		C 1s	6675	32561	63
		Si 2p	504	2965	6
Fast-cured "free" surface	15	F 1s	3337	3337	22
		O 1s	905	1436	9
		C 1s	1991	9712	63
		Si 2p	172	1012	6
	75	F 1s	9602	10879	22
		O 1s	2691	4271	9
		C 1s	6198	30234	63
		Si 2p	487	2865	6

^a Sensitivity factors*

Element	Sensitivity
F 1s	1.000
O 1s	0.630
C 1s	0.205
Si 2p	0.170

Used to calculate corrected peak area.

* From Wagner, Riggs, Davis, Moulder and Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, 1979.

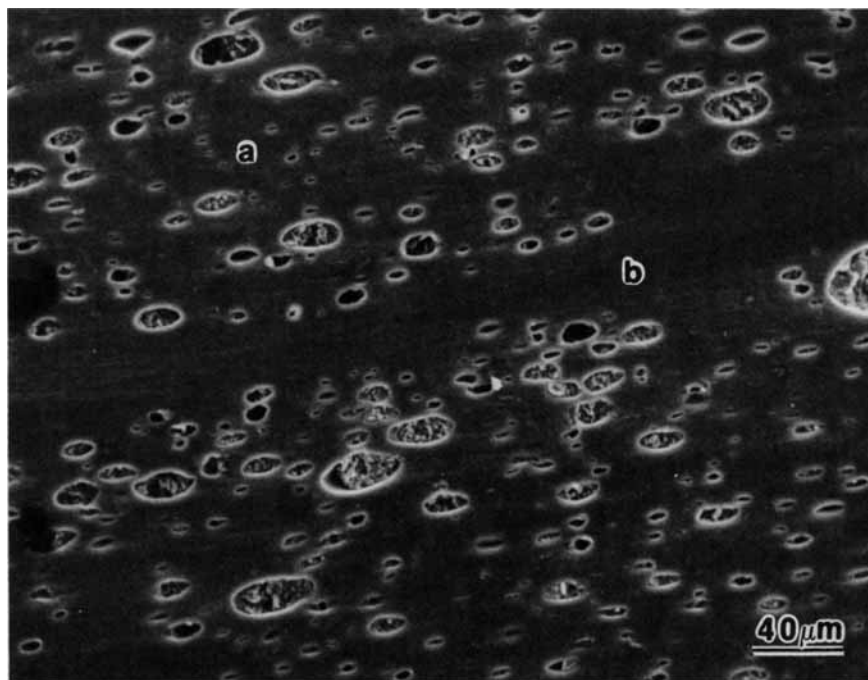


Figure 3 Micrograph of welded blend. Sample was fractured, polished, and etched. (a) bulk region with 10–20 μm pressure-elongated domains of fluoroepoxy and (b) resin-poor weld region.

poor, substantiating the findings using XPS. The surface layer is currently believed to be the result of gravitational forces and density differences, as surface effects are usually much weaker and would be expected to create a much smaller surface layer. The micrograph also shows that there is no separation between the two plies and no obvious weld line. The top-top and top-bottom welds also formed

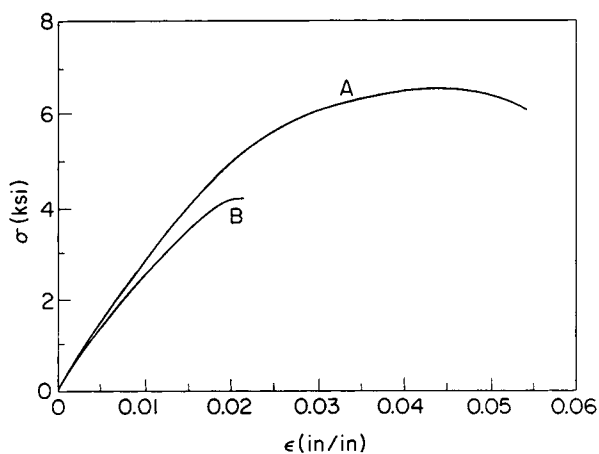


Figure 4 Stress-strain behavior of (A) E828/1SA and (B) E828/NC8/1SA blend material. The blend fractured at a void.

excellent welds. This indicates a B-stage material with good welding characteristics after room temperature cure.

The modulus of the blend was 290 ksi, comparable to that of E828/1SA, with a modulus of 347 ksi and noticeably greater than that of neat C8/1SA with a modulus of 194 ksi.⁵ E828 cured with a diamine hardener yields a material with a modulus of 477 ksi, a failure stress of 10 ksi, and an ultimate elongation of 0.024 in/in.⁶ The ultimate stress of the E828/1SA was 6.6 ksi while the elongation was 0.054 in/in. This indicates that either the E828/1SA is a weaker material or that it is not fully cured. The plastic yielding behavior reflected in Figure 4 indicates that both effects are probably present. Nevertheless, behavior in the region covered seems to be dominated by the Epon matrix rather than the fluoroepoxy resin, as was desired. All blend samples tested contained voids, so the ultimate properties have yet to be determined.

CONCLUSIONS

Using E828/C8/1SA as a model system, the fluoroepoxy resins appear to be useful in blends with DGEBA resins. The mechanical properties seem to be in line with the stronger, more mechanically use-

ful Epon component. XPS indicates that the fluoroepoxy is found preferentially at the upper surfaces of the material, potentially yielding a process-controlled method for coating plies for laminates. Welding experiments indicate that the material can have a B stage that can be laminated easily in various configurations. Fracture appears to occur along weak domain interfaces. Considering, however, that most experiments were conducted using fresh (or freshened) samples, the effects of aging might change the mechanical behavior significantly.⁵ As the blend ages, the ductile regions will become brittle and lessen the toughening abilities of the domains. Other fluoroepoxy systems are available,⁷ however, for which T_g is below room temperature, and for these systems, aging should not be a problem. Discussion of the results of using C8/1SA as a composite matrix or fiber coating will be presented in a future paper.

This research was supported by the Office of Naval Research through the University of Illinois National Center for Composite Material Research. T. T. acknowledges an

ONR Fellowship. Appreciation is also expressed to Dr. Carol Jones for her help with the XPS experiments.

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Accepted February 16, 1990