The Thermooxidative Stability of Cured Epoxy Resins. I

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SYNOPSIS

Prior studies have shown that for many epoxy resin systems significant oxidative degradation occurs in air at temperatures as low as 100°C and that thin oxidized surface layers serve as crack initiators in flexural samples at low strains and can reduce flexural strengths to less than 25% of the original values. This study was undertaken in an attempt to identify predominant degradation pathways and cured resin systems that are thermooxidatively stable in 125°C air. Based on flexural property retention and IR spectral data, the thermooxidative resistance ranking of D.E.R.*332 epoxy resin polymerized with the following is p-toluenesulfonamide > 4,4'-diaminodiphenyl sulfone or sulfanilamide > methylene dianiline ≫ triethylenetetraamine > 2,5-dimethyl-2,5-diaminohexane. Oxidation of aliphatic amine-cured D.E.R.*332 epoxy resin is initiated by electrophilic attack of oxygen on the lone-pair electrons of the nitrogen to form an amine oxide. Polymer chain cleavage then occurs via Cope reactions. A newly proposed oxidative degradation pathway is described wherein the hydroxylamine products of Cope reactions are further oxidized to nitrones, which then decompose to amides via oxaziridine intermediates. Commercial antioxidants added to an aliphatic amine-cured epoxy resin were ineffective, supporting the conclusion that the predominant degradation mechanism is not free radical in nature. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Long-term thermal aging stability is required for many of the applications in which epoxy resins are used, such as for structural adhesives, coatings, and composites. Historically, most thermal aging/degradation studies have been performed in very high temperature nitrogen atmospheres while measuring only weight loss and volatiles composition.[1-5] Unfortunately, the conclusions drawn from the results of such high-temperature, accelerated aging studies may seldom be applicable at lower temperatures due to changes in the predominant degradation mechanism. Testing in nitrogen provides no information on thermooxidative degradation that can occur at much lower temperatures than that of simple thermal decomposition. Additionally, weight loss measurements may be particularly misleading since some resins may gain weight during oxidation. Although a few papers describe the oxidative instability of cured epoxy resins, most of these studies were limited to high temperatures (> 170°C).[6-13] One recent paper describes the thermooxidative degradation of a glass-reinforced polyamide-cured epoxy resin in oxygen at pressures of 3–5 atmospheres and concludes that the same degradation mechanism exists under these conditions as in air at 145, 160, 180, and 190°C.[14]

In two prior studies it was shown that for many epoxy resin systems significant oxidative degradation occurs in air at temperatures as low as 100°C.[15,16] One earlier study[15] showed that thin oxidized surface layers can serve as crack initiators in flexural samples at low strains and reduce flexural strengths to less than 25% of the initial values. The present study was undertaken in an attempt to identify (1) polymer structures that are most susceptible to oxidation, (2) how oxidation affects property degradation, (3) predominant degradation pathways, and (4) cured resin systems that are thermooxidatively stable at 125°C. Reported in this

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paper are some results on DGEBA-type resins cured with nitrogen-containing curing agents.

Undesirable changes in properties that have been reported in relation to resin oxidation may be summarized by applications area as follows:

1. Coatings: Oxidation of the top surface and of the coating's interior may cause increased chalking and microcracking, decreased abrasion resistance, color changes, increased moisture absorption (and therefore swelling), and embrittlement due to molecular weight changes. At the coating/substrate interface, resin oxidation may lead to adhesion loss and substrate corrosion. For coatings, oxidative degradation may be coupled with photooxidation processes[17-21]; thus, understanding the thermooxidation of cured resins could provide information useful in improving the "weatherability" of epoxy coatings.

2. Composites and electronics: In addition to the effects mentioned above for coatings applications, thermooxidation of resins can lead to decreased fatigue resistance, lower environmental stress crack resistance, lower strength, changes in modulus, and increased dielectric constant.

Earlier work[15] on rubber-modified epoxy resins described how air aging of flexural samples led to surface degradation that resulted in greatly reduced flexural strengths. Samples tested after removal of this surface layer showed no significant flexural strength losses. Additionally, no strength losses were seen for samples aged in nitrogen. Because of the potentially wide-ranging applicability of a resin's thermooxidative performance to its performance in many other areas, this earlier work was broadened to include a wider variety of hardeners and several "antioxidants." A variety of chemical structures were included in this study with hopes that comparison of the results might allow deduction of stability rankings for various polymer chain segments and provide insights into the degradation mechanisms. This goal has been achieved. It should be emphasized, however, that the stability rankings in this report only directly apply to resins aged at 125°C in air. In other environments and or at other temperatures, the stability rankings may drastically change as a result of changes in the relative rates of various degradation mechanisms that occur, even within the same sample.

EXPERIMENTAL

Chemicals were used as received from their manufacturers: D.E.H.[†] 24 epoxy hardener (triethylenetetraamine), D.E.R. 332 epoxy resin, D.E.R. 383 epoxy resin, and 4,4'-oxybis(benzenesulfonamide) from The Dow Chemical Co.; Ancamine®2006 epoxy hardener (2,5-dimethyl-2,5-diaminohexane) from Air Products and Chemicals; methylene dianiline (MDA), and p-toluene sulfonamide from Aldrich Chemical Co.; 4,4'-diaminodiphenylsulfone (DDS) from Ciba-Geigy; sulfanilamide from Napp Chemicals. D.E.R. 332 epoxy resin (epoxide equivalent weight = 174) and D.E.R. 383 epoxy resin (epoxide equivalent weight = 180) are predominantly the diglycidyl ether of bisphenol A (DGEBA) and contain a small fraction of higher molecular weight oligomers.

Casting components were heated to be of low enough viscosity that efficient hand-mixing was possible (usually from 60 to 150°C). After mixing by hand, the samples were vacuum-degassed (when time allowed) and poured into preheated glass molds that had been treated with a fluorocarbon mold-release agent. After baking was finished and the oven turned off, the castings were allowed to cool in the oven. The bake schedules of the individual castings were varied to obtain complete polymerization, while limiting the castings' exposure time at high temperatures to try to avoid any premature oxidative degradation. In general, castings were postcured for at least 2 h at a temperature somewhat higher than their glass transition temperatures.

Air aging was done in a Blue-M Stabil-Therm® forced-air convection oven at 125°C.

Calorimetry: Glass transition temperatures (T_g's) were determined using a DuPont 2100 differential scanning calorimeter (DSC). The scan rate was 10°C per min in a nitrogen atmosphere. The vertical half-height of the inflection resulting from the change in heat capacity was taken as the T_g. The pieces on which T_g's were measured were made by slicing pieces of the aged castings roughly in half and placing the air-aged surfaces in contact with the bottom of the aluminum DSC sample pans. Samples were generally stored in a "dry box" prior to running T_g's, but in one instance, a sample was exposed to humid laboratory air for weeks prior to T_g measurement. As expected, this sample showed a depressed T_g as shown in Fig. 1(C).

Flexural testing was done on a Model 1125 Instron Universal Testing Instrument equipped with a 1000 lb. load cell. ASTM Method D 790-86 Method 1 was followed using three-point loading of $\frac{1}{8} \times \frac{1}{2} \times 3$ in. specimens and a 2 in. support span. The crosshead speed was 0.05 in. per min. Flexural testing was used in this study since flexural strength may be more sensitive to thermal degradation than are tensile or compressive strength.[22]

Fourier transform infrared spectroscopy was done using a Nicolet 5DX-B FTIR. A saw blade was used to produce powder from the various samples, which was then mixed with KBr and pressed into pellets for analysis. Wavenumber assignment of the various peaks was done utilizing the spectrum expansion capabilities of the spectrometer's computer. To better characterize peak size and shape in Table I, the following abbreviations were used: br = broad, sh = shoulder, s = small, vs = very small, vvs = very very small, decr. = decreasing in size, and unres. = unresolved. "Unresolved" is used to indicate that a peak appears to be present but that a well-defined local maximum cannot be obtained using the computer. This occasionally happens with shoulders. The abbreviations described above are sometimes combined (e.g., vssh = very small shoulder).

Color changes in the samples during aging were followed by comparing the color of the casting pieces (nominally 0.125 in. thick) to Gardner color standards for liquids (Permanent) 1953 Series.

RESULTS AND DISCUSSION

Background: Oxidation of Amines and Amides

As with the oxidation of cured epoxy resins, the oxidation of amine compounds, in general, can be rather complex. For this reason, and as a guide for understanding the proposed degradation mechanisms, the following general discussion should be helpful:

According to Challis and Butler[23]:

The oxidation of amines is complicated by the operation of several reaction paths. Not all of these involve substitution on nitrogen, for both hydrogen abstraction from either carbon or nitrogen and addition of oxygen to carbon may occur. The predominant path seems to depend as much on the reagent as on the structure of the amine. Oxidative substitution of alkylamines results in the formation of either hydroxylamines or amine oxides. The hydroxylamines can oxidise further to nitroso and nitro derivatives. However, the lone-pair electrons activate the

α-hydrogens of aliphatic amines, and hydrogen is therefore removed by some reagents as easily from this site as from nitrogen. . . . The actual products depend on the amine structure and others may arise from subsequent hydrolysis, oxidation, condensation and dealkylation.

As far as reagents are concerned, substitution on nitrogen generally occurs with peroxides. . . . Despite the wealth of products formed by peroxidic reagents, most of their reactions can by understood in terms of an initial attack by the electrophilic peroxidic oxygen on the nitrogen lone pair. Since this leads to a quaternisation of the nitrogen atom, it is not surprising to find that steric congestion as well as electron withdrawal in the amine moiety inhibits the reaction rate.

It has been shown that electron-withdrawing substituents retard the oxidation rate of many tertiary amines.[24,25] For those amine groups that are oxidized to amides, further autooxidation to additional products can occur, the principal overall reactions having been described[26] as

1. formation of N-acylamides from N-n-alkylamides;
2. formation of N-formylamides from N-n-alkylamides or N-acylamides from N-s-alkylamides, via C—C bond cleavage;
3. oxidative dealkylation (C—N bond cleavage) to give carbonyl derivatives.

The initial steps in the autooxidation, which appear common to all three pathways mentioned above, are removal of the α_N-hydrogen atom followed by oxygen addition to give the peroxy radical, which may then decompose in various ways. These oxidations may be induced either thermally ($> 100°C$) or photochemically at lower temperatures.[26]

Triethylenetetraamine Cured Diglycidyl Ether of Bisphenol A: With and without "Antioxidants"

Because triethylenetetraamine (D.E.H. 24 epoxy hardener) cured D.E.R. 332 epoxy resin is a widely used system that showed poor stability in an earlier study,[15] it was reformulated with several different commercially available antioxidants to see if they would provide some protection from oxidation. Figures 1 (A–C) show the results of these experiments. None of the antioxidant systems used appeared to provide any protection of this cured resin under the test conditions [Fig. 1(A)]. This suggested that either the antioxidants were consumed by reaction with the components of the resinous mixture during polymerization or that free radical pathways did not
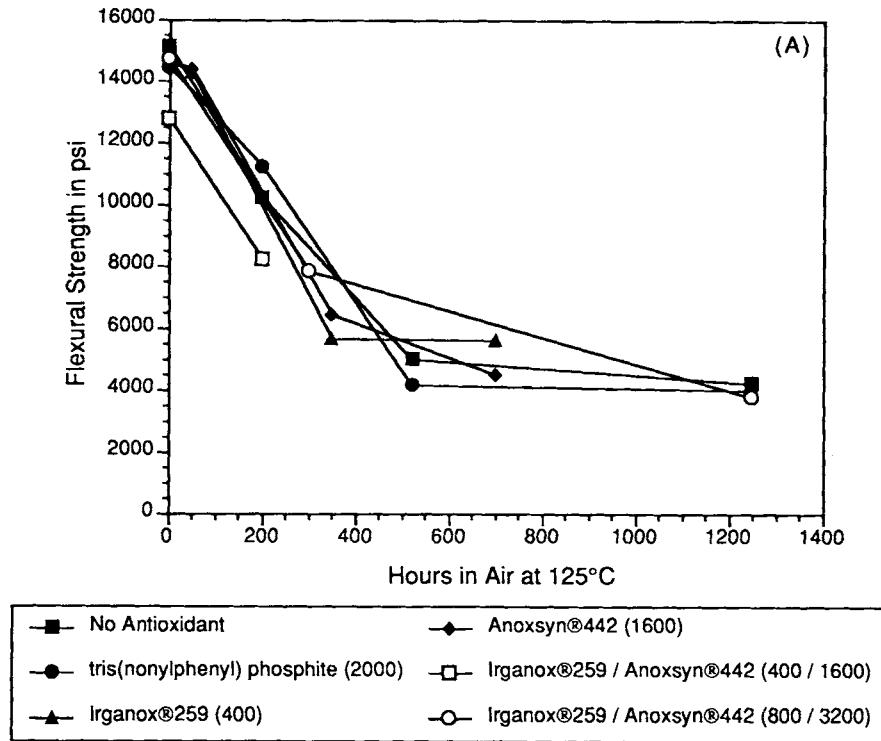
Table I FTIR Data on Various Cured Epoxy Resin Systems before and after Aging in 125°C Air

Wavenumber Ranges. Because of its great width, the original table is printed in three horizontal panels covering successive wavenumber regions; they are reproduced below as three sub-tables.

High-frequency region (≈2800–3600 cm⁻¹)

Epoxy Resin	Coreactant	Aging Time (h)										
D.E.R. 332	D.E.H. 24 hardener	0	3565sh	3422		3125vs	3096	3056	3035	2964	2931	2870	2827
		1250		3379		—		3059	3036	2963	2932	2874	
D.E.R. 332	Ancamine 2006	0	3569sh	3405		3133	3100	3055	3036	2966	2932	2873	
		1250		3366				3061	3034	2966	2932	2872	
D.E.R. 332	Methylene dianiline	0	3544	3416		3139	3098	3053	3034	2962	2928	2872	
		1250		3378		Covered		3059	3038	2966	2932	2872	
		3458		3385	3427	Covered		3061	3038	2966	2932	2875	
D.E.R. 383	Diamino-diphenyl-sulfone	0		3424	3402	3126vs		3055	3038	2963	2928	2871	
		1200		3429	3402	?		3060	3036	2963	2929	2870	
D.E.R. 332	Sulfanilamide	0	3530	3407		3126	3097	3057	3036	2964	2931	2872	
		1250	3471	3405		3123	3097	3056	3037	2962	2932	2872	
D.E.R. 332	p-Toluene sulfonamide	0		3425		3123vs	3096	3059	3038	2964	2927	2874	
		1250	3467		3434	"	3100	3061	3040	2966	2931	2870	
		4220	3503	3456	3430	"	3100	3060	3036	2964	2927	2871	

Mid-frequency region (≈1550–2770 cm⁻¹)

Epoxy Resin	Coreactant	Aging Time (h)											
D.E.R. 332	D.E.H. 24 hardener	0		1889	1735vvs			1700vvs		1655ssh	1607		1582	1559
		1250	2768ssh	1888				1701sh		1655		1609	1582sh	1560
D.E.R. 332	Ancamine 2006	0		1889	1759		1726sh	1701vs	1684vs	1655	1608		1581	1560s
		1250		1890	1736sh		1720sh	1701			1612	1599s	1583sh	1561
D.E.R. 332	Methylene dianiline	0		1888	1772vs		—	1720sh			1610		1584	1561ssh
		1250		1888	Covered		1720		1683sh	1655	1602		Covered	sh?
		3458		1888	Covered		1720			1654	1606		Covered	1560
D.E.R. 383	Diamino-diphenyl-sulfone	0		1893	1771vs		1720			1653ssh		1590		1560
		1200		1893	1771ssh		1741 / 1720	1700		1654ssh		1594		1560
D.E.R. 332	Sulfanilamide	0		1891	1736			1700		1654sh		1598		1560
		1250		1889	1735			1700		1652		1598		1558
D.E.R. 332	p-Toluene-sulfonamide	0	2757sm	1890	1749vs	1735sm				1653sh	1608		1581	1560vs
		1250	"	1889	1750vs	1735		1702		1655	1608		1582	1560vs
		4220	"	1889	1750vs	1735		1702		1655	1607		1583	1560s

Low-frequency region (≈1240–1540 cm⁻¹)

Epoxy Resin	Coreactant	Aging Time (h)											
D.E.R. 332	D.E.H. 24 hardener	0	1539	1510	1459	1445	1413	1384	1362	1331sh		1297	1247
		1250	1540	1509	1456		Covered	1383	1362	—		1296	
D.E.R. 332	Ancamine 2006	0	1539vssh	1509	1464sh / 1459		1428vs	1414	1385	1363	1337sh	1296	1250
		1250	1540	1510	1457	1447	1414	1383	1364			1297	1244
D.E.R. 332	Methylene dianiline	0	1540vssh	1512	1459	—	1414	1383	1361	1336vs		1297	1240br
		1250		1512	1459	1432	1410	1383	1364	Covered	1289sh		
		3458	1539	1508	1459	1432vvs	1414	1383	1364	1337vs	1289sh		

Table I (*continued*)

Infrared absorption bands (cm⁻¹). The page presents the data in three stacked sections; they are combined below by sample. Bold figures are reproduced in bold.

Section 1

Resin	Hardener	Treatment	Bands (cm⁻¹)
D.E.R. 382	Diamino-diphenyl-sulfone	0	1540vs, 1508, 1464ssh, 1458, (decr.), 1397 (—), 1384, 1363, (decr.), 1299, 1295, 1245br, 1239br
		1200	1540vs, 1510, 1464ssh, 1459, 1386, 1363, 1301, 1295, 1244br, 1242br
D.E.R. 332	Sulfanilamide	0	?vvssh, 1535, 1509, 1458, 1413, 1386, 1362, 1334sh, 1299, 1245br
		1250	1540ssh, 1508, 1458, 1411, 1384, 1361, 1334sh, 1301, 1244br
D.E.R. 332	p-Toluene sulfonamide	0	1540vvvssh, Unres., 1509, 1474br, 1459br, 1412, 1383, 1363, 1336, 1303, 1294sh, 1242br
		1250	1539vvs, 1509, ", 1458, 1414, 1385, 1363, 1338, 1305, 1294sh, 1243br
		4220	1539s, 1506, 1474br, 1459, 1438s, 1420, 1384, 1361, 1337, 1304, 1295, 1239br

Section 2

Resin	Hardener	Treatment	Bands (cm⁻¹)
D.E.R. 332	D.E.H. 24 hardener	0	1234, 1182, 1151, 1107, 1085, 1035, 1013, **963**, 937, **921**, 872
		1250	1179, 1103, 1085, 1037, 1013, **963sh**, 937
D.E.R. 332	Ancamine 2006	0	1231sh, 1183, 1157, 1121, 1109, 1085, 1037, 1013, 956, 934, 915
		1250	1232, 1181, 1154, 1104, 1083, 1040, 1015, 956, 936, 919, 887
D.E.R. 332	Methylene dianiline	0	1236br, 1183, 1104, 1085, 1036, 1013, 953, 938, 915
		1250	1236br, 1225, 1176, 1104, 1085, 1040, 1013, 953sh, 938, sh?
		3458	1236br, 1225, 1179, 1108, 1085, 1040, 1013, 953sh, sh?
D.E.R. 383	Diamino-diphenyl-sulfone	0	1181, **1144**, 1103, 1090, 1035, 1011, 955, 944, 918
		1200	1183, **1146**, 1104, 1090, 1036, 1011, 955, 940, 916
D.E.R. 332	Sulfanilamide	0	1183, 1150, 1119, 1090, 1036, 1012, **960**, 942, 915
		1250	1184, 1150, 1119, 1090, 1037, 1010, **960**, 938, 915
D.E.R. 332	p-Toluene-sulfonamide	0	1236br-doublet, 1184, 1155, 1118, 1108, 1086, 1035, 1019, 1010, 996, **959**, 933, 916
		1250	1184, 1155, 1119, 1108, 1090, 1039, 1020, 1009, **962**, 933, 914
		4220	1182, 1155, 1120, ", 1087, 1034, ", 1010, ", ", 915

Section 3

| Resin	Hardener	Treatment	Bands (cm⁻¹)
D.E.R. 332	D.E.H. 24 hardener	0	863, 808sh, 793vs, 760, 757, 735, 727, 718, **665**, 638, 558
		1250	829, ", ", 760, ", ", 729, 722, 684, 639, 556
D.E.R. 332	Ancamine 2006	0	864, 812sh, 769, 759, 735, 728, **665**, 639, **615**, 559
		1250	829, 762, 727, 654, 679, 641, 565
D.E.R. 332	Methylene dianiline	0	**865sh**, **805ssh**, 756, 737, 728, 696, 640vs, 637, 560
		1250	828, 768, 736, ?br, 696, —, 637, 571, 556
		3458	828, 764, ", 728, 670, 640, 561
D.E.R. 383	Diamino-diphenyl-sulfone	0	829, 789, 756sh, 718, 697, 668, 641, **593ssh**, 569
		1250/1200	831, 790, 761, 722, 679, —, 571
D.E.R. 332	Sulfanilamide	0	828, 793, 754, 735, 728, 706, 670, 639, 563, 565
		1250	829, 793, 755, 735, 727, 671, 639, 559, 565
D.E.R. 332	p-Toluene-sulfonamide	0	861, 815sh, **749br**, 735, 727, 706, 681sh, 655, **608**, 547, 566
		1250	863, 816sh, 754br, ", ", 707, ", 656, 550, 564
		4220	861, 814sh, 755br, ", 728, 708, 681, 658, 549, 561

See text for abbreviations.

Note: Antioxidant levels in ppm are in parentheses.
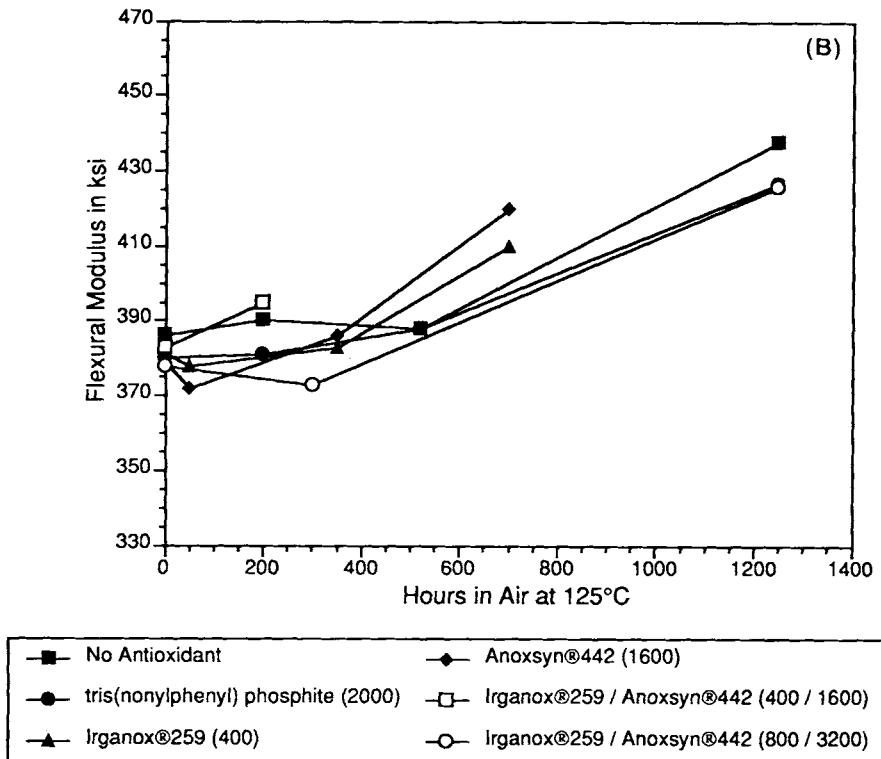
Note: Antioxidant levels in ppm are in parentheses.

Figure 1 D.E.R. 332 epoxy resin cured with triethylenetetraamine (D.E.H. 24). The effect of air aging on (A) flexural strength, (B) flexural modulus, and (C) glass transition temperature.
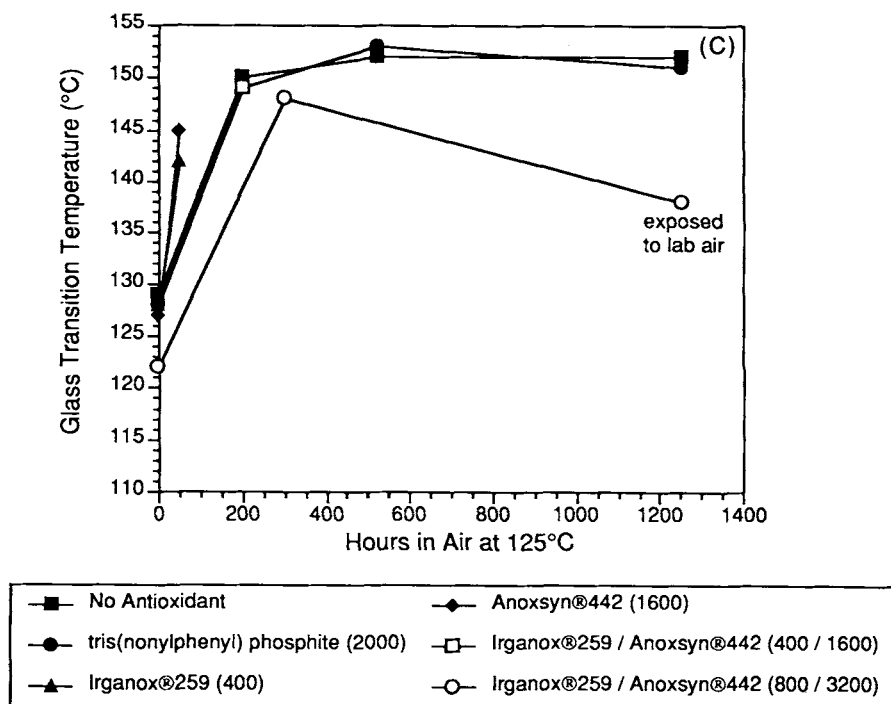
Note: Antioxidant levels in ppm are in parentheses.

Figure 1 (*Continued from the previous page*)

represent the predominant degradation route for this polymer. Differential scanning calorimetry of mixtures of D.E.R. 332 or D.E.H. 24 with either Anoxsyn™442 or Irganox®259 subsequently showed there to be no exothermic peaks from room temperature to 200°C. Degradation via free radical mechanisms has been reported for cured epoxy resins, but these studies were typically performed at much higher temperatures than those used here.[8,9,11,17,27-30] The closeness of the flexural strength plots for all of the D.E.R. 332 epoxy resin/D.E.H. 24 epoxy hardener castings, with and without added "antioxidants" [Fig. 1(A)], supports the assumption that the relative 125°C air-stability rankings obtained from Figure 2(A) will be reproducible with respect to flexural strength.

Other Nitrogen-Containing Hardeners Polymerized with D.E.R. 332 Epoxy Resin

Figure 2(A-C) shows the flexural and glass transition temperature data obtained for these other resin systems in addition to those for the D.E.H. 24-cured control resin discussed in the previous section.

Since several of the proposed degradation pathways[17,26,29,31] (both thermo- and photooxidative)

showed that methylene groups alpha to the nitrogen may be particularly susceptible to oxidation, 2,5-dimethyl-2,5-diaminohexane (Ancamine® 2006) was used to cure D.E.R. 332 epoxy resin in place of triethylenetetraamine. This substitution eliminates all α_N-hydrogens in the amine and reduces the total number of α_N-hydrogens from 13 to 6 for each three epoxy groups cured. Interestingly, the oxidative stability of the resin cured with this hardener was much worse than that cured with triethylenetetraamine. At the longest aging times, the surfaces of the 2,5 - dimethyl - 2,5 - diaminohexane - cured materials crumbled away when rubbed. Because cleavage of the nitrogen–carbon bond in this curing agent would generate a more stable radical than that formed by a similar bond cleavage in triethylenetetraamine, the possibility of radical pathways was explored but no satisfactory mechanisms were developed. Because of the greater energies of the carbon–carbon bonds compared to the carbon–nitrogen bonds, and because the IR spectrum showed large peaks at 1655 cm^{-1}, degradation of the interior hydrocarbon portion (away from the nitrogen atoms of the 2,5-dimethyl-2,5-diaminohexane) also seemed unlikely as the predominant degradation mechanism.

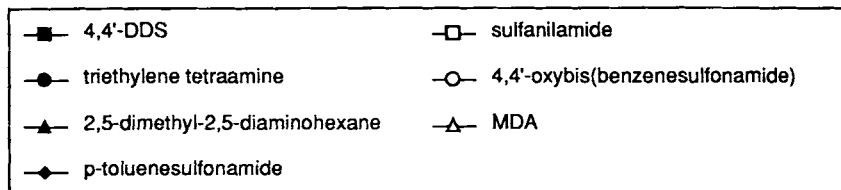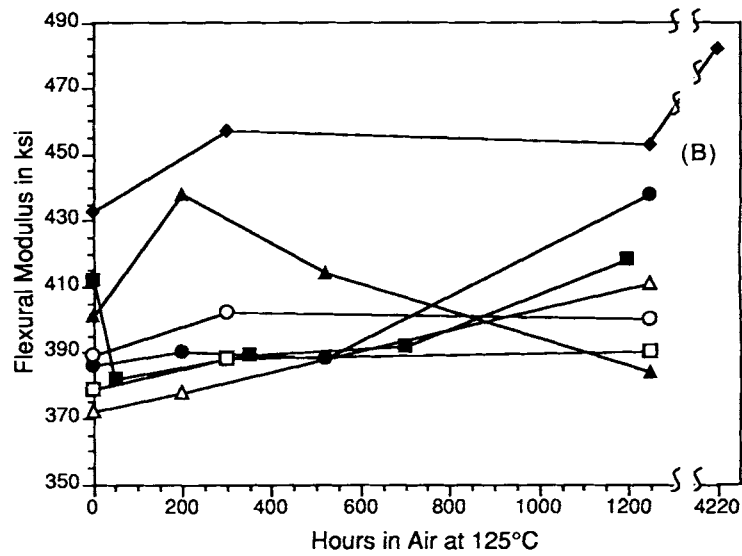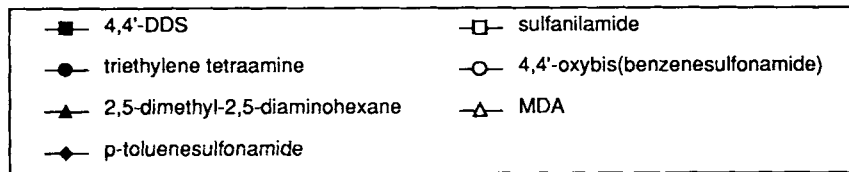The above-mentioned aliphatic amine-cured resin systems initially showed flexural strength degra-
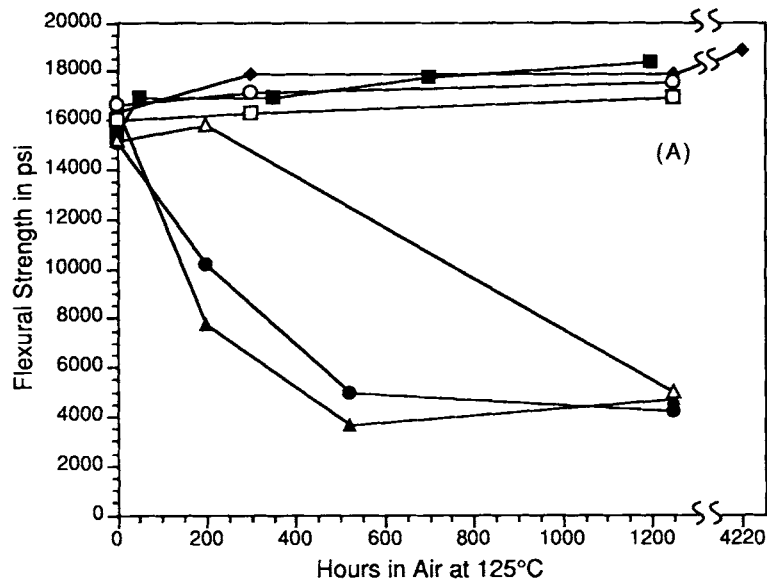
Figure 2   DGEBA-type resins/N-containing curing agents. The effect of air aging on (A) flexural strength, (B) flexural modulus, and (C) glass transition temperature.
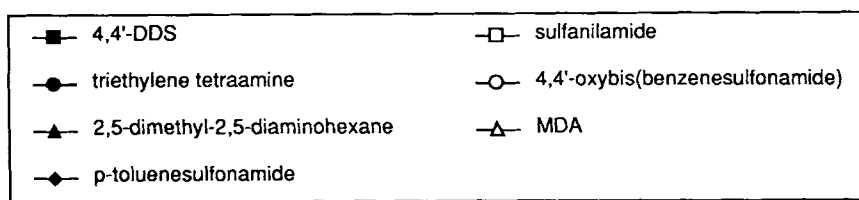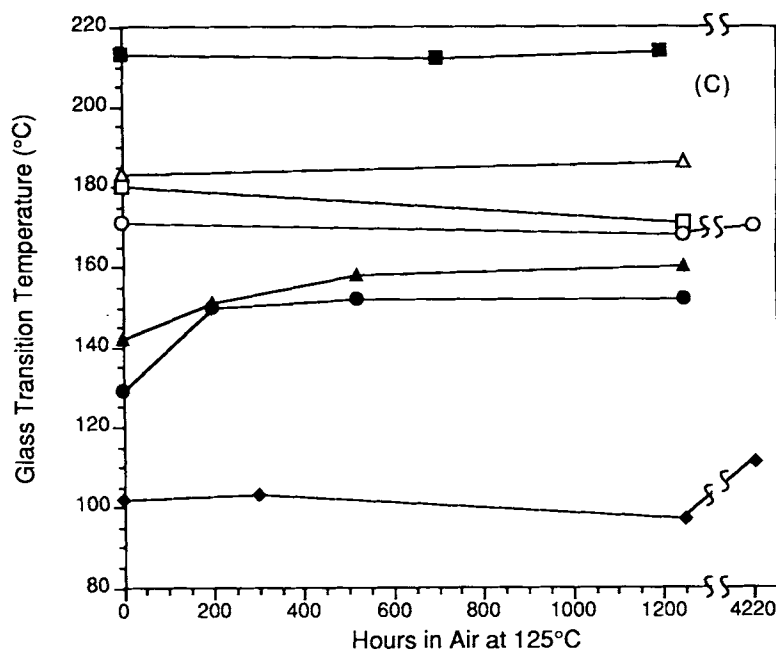
Figure 2 (*Continued from the previous page*)

dation much more quickly than did D.E.R. 332 epoxy resin cured with methylene dianiline (MDA), but by 1250 h, all of the flexural strengths had been reduced to roughly 5000 psi. It is unclear just which factors are affecting these results and to what degree each of them must be weighted in assessing the stability of the aliphatic amine-cured resins relative to MDA. As an example of the factors that complicate the analysis of these and other systems, MDA-cured resins are known[32] to undergo degradation at the aromatic methylene bridge of the MDA residue as well as at the aliphatic regions of the cured resin structure. The initial flexural strengths of these three resin systems are similar but the differing T_g's and moduli of these systems may lead to differences in their relative oxygen absorption rates. Additionally, contributions of residual thermal stresses and physical aging to embrittlement of the sample's interior, and subsequent increases in notch sensitivity, would also be expected to affect the retention of flexural properties. (Many of the differential scanning calorimeter traces made of aged resins showed

significant post-T_g endotherms that are indicative of physically aged materials.)

Figure 2(A–C) shows the results of aging DGEBA-type resins (either D.E.R. 332 or D.E.R. 383 epoxy resins) that have been polymerized with a wide variety of different nitrogen-containing hardeners. The resin systems that showed no significant flexural strength loss to 1200 or 1250 h aging time in 125°C air were those which used 4,4'-diaminodiphenyl sulfone (DDS), p-toluenesulfonamide, 4,4'-oxybis(benzenesulfonamide), and sulfanilamide as the hardeners. The p-toluenesulfonamide-cured resin was aged much longer without strength reductions and even showed small strength increases after 4220 h of aging.

To better understand the oxidative processes and the effect of any other processes (mentioned above) on polymer degradation, direct evidence of oxidation was sought using infrared spectroscopy. The infrared spectra of all cured resins were studied, both initially and after long-term thermooxidative aging, since resins might show spectral evidence of oxidation

Table II   Some of the New IR Absorbance Bands Found for Amine-Cured Epoxy Resins Aged 1250 h in 125°C Air

Ancamine 2006/D.E.R. 332	1736sh	1720sh	1701	—	1655
D.E.H. 24/D.E.R. 332	—	1726sh	1701sh	—	1655
MDA/D.E.R. 332	1735	1720	1702	1683sh	1654
4,4'-DDS/D.E.R. 383	1741	1720	1700	—	Unchanged

sh = shoulder.

without showing significant changes in flexural properties. Each of the amine-cured resin systems described above showed new bands or shoulders in the carbonyl regions of their IR spectra after aging for 1250 h at 125°C. These bands were roughly centered at the wavenumbers (cm^{-1}) shown in Table II.

D.E.R. 383 epoxy resin cured with 4,4'-diaminodiphenylsulfone and aged 1200 h showed no significant increase in a small peak initially present at 1654 cm^{-1}. As shown, however, other peaks did develop at 1741 (largest peak), 1720, and 1700 cm^{-1}. The small peak initially present at 1654 cm^{-1} may have formed during the high-temperature curing of this system. Several reports in the literature have referred to the peaks around 1655 cm^{-1} as "amide" peaks, amides being products of their proposed degradation mechanisms. Peaks due to oximes and imines also fall in the same general region but should not be as strong as amide peaks.

The peaks in the first three columns of Table II are attributed to esters (first column) and ketones rather than to aldehydes since the C—H stretch bands expected for aldehydes were not seen to develop near 2750 and 2850 cm^{-1}. The height of peaks near 1103 cm^{-1} increased in the aged triethylenetetraamine-cured D.E.R. 332 epoxy resin (Fig. 5). These peaks may be due to the C—O stretching or to C—N stretching (discussed later).

The only change in the carbonyl region of the IR spectrum of D.E.R. 332 epoxy resin cured with sulfanilamide, after aging 1250 h, was a very small increase in the peak at 1735 cm^{-1}. A similar small increase in the 1735 cm^{-1} peak was the main change noted in the spectrum of p-toluenesulfonamide-cured D.E.R. 332 epoxy resin, even after aging for 4220 h. A peak at 1749 cm^{-1} in this system showed no change with aging.

A consistent trend seen for oxidation of the cured resins above is that as the nitrogen in the curing agent becomes more nucleophilic the thermooxidative stability of the polymer decreases. The nucleophilicity of nucleophiles whose attacking atoms are in the same row of the periodic table falls in

about the same order as their basicity. Reported pK_a values for the curing agents used could not be found, but those of similar compounds are shown to illustrate this point:
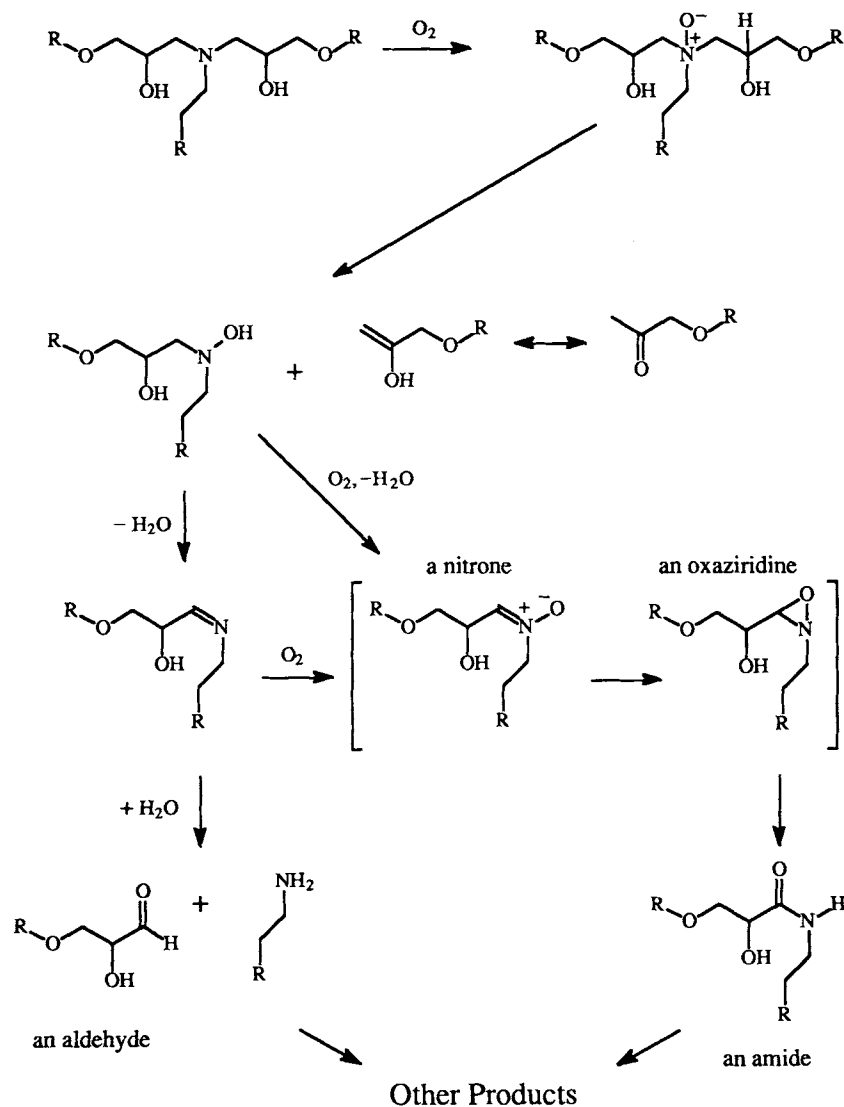
	pK$_a$
Benzenesulfonamide	10
4,4'-Diaminodiphenyl sulfone	—
Aniline	27
Aliphatic amines	35

For the curing agents used, the relative rate of their reaction with epoxy resins is D.E.H. 24 > methylene dianiline > 4,4'-diaminodiphenyl sulfone > p-toluenesulfonamide. The pK_a of DDS was unknown but should fall between that of benzenesulfonamide and aniline.

This apparent correlation of nucleophilicity with oxidative stability is logical if the initial step in the degradation process is an electrophilic attack by atmospheric oxygen on the more electron-rich regions of the polymer, specifically, the amine nitrogen atom as suggested by Dante and Conley.[33] Bellenger et al.[28,29] reported an influence of amine nitrogen nucleophilicity on the nonoxidative dehydration of the hydroxypropyl group in three aromatic amine-cured epoxy resins. For oxidative conditions, they propose that an increase in the nucleophilicity of the amine nitrogen increases the rate of radical abstraction of hydrogen atoms from the methylene group alpha to the amine. They do not discuss the possibility of a direct oxidation of the amine to an amine oxide.

Paterson-Jones et al. simulated the degradation of aromatic amine-cured resins at 180°C using 1-(N-ethylanilino)-3-phenoxypropan-2-ol and reported that identical results were obtained in air as in nitrogen.[34] Since the 125°C air used in the present study only discolored the outer surfaces of the aromatic amine-cured resins, and since this layer grew with time, it appears that at 180°C the oxidation pathway that occurs at 125°C is no longer the predominant degradation pathway for these materials.

In the polymers of the present work, it is reasonable that increased electron withdrawal by substituents on the nitrogen atoms could decrease the rate of amine-oxide formation until at some point this step no longer initiates the predominant degradation route. If oxidation of some aliphatic amine-cured D.E.R. 332 epoxy resin systems occurs via electrophilic attack of oxygen on the lone-pair electrons of the nitrogen to form an amine oxide, this is only the start of the polymer degradation process that at some point should involve chain cleavage and/or cross-linking. For polymers containing N-oxides in the backbone, chain cleavage can occur via a Cope reaction that produces enamines, methyl ketones, imines, and hydroxylamines (Figs. 3 and 4). The Cope reaction is known to occur under mild conditions (110–150°C) with few side reactions and usually without rearrangement of the olefins formed.[35,36] "With simple alkyl-substituted amine oxides the di-

rection of elimination seems to be governed almost entirely by the number of hydrogen atoms at the various β positions."[36] (Significant variations from this rule have been shown in which the relief of steric interactions and acidity of the β-hydrogen atoms are factors favoring elimination of some groups.) The occurrence of the Cope reaction would explain why Ancamine 2006 (containing eight hydrogens beta to the nitrogen) showed much poorer thermooxidative stability than triethylenetetraamine amine (containing only two hydrogens beta to the nitrogen) when used to cure D.E.R. 332 epoxy resin. It would also explain the ineffectiveness of free-radical inhibitors in slowing the degradation.

For the aliphatic amine-cured resins used in this work, the initial degradation products of such a Cope reaction would be hydroxylamines and either alkenes or methyl ketones (rearranged from the enols) depending upon which of the possible Cope reactions

Figure 3 Proposed degradation of an amine-cured epoxy resin via a cope reaction.

Figure 4   Proposed degradation of an amine-cured epoxy resin via cope reaction loss of a methyl ketone.

occurs (Figs. 3 and 4). If a Cope reaction occurs after the oxidation of an aromatic amine-cured resin, hydroxylamines and methyl ketones are expected to be the primary degradation products (Fig. 4). Dante and Conley,[33] the only researchers found to suggest a Cope reaction, further suggest that this step is followed by dehydration of the hydroxylamine to yield an aldimine that is subsequently hydrolyzed to amine and aldehyde. Conley later suggests[37] that further oxidation of the formed amine will yield nitro compounds. Since no nitro groups were apparent in the IR spectra, reasonable alternative pathways were sought.

Pathways similar to those proposed by Dante and Conley are illustrated on the left sides of Figures 3

and 4 for various cured resins. Three questions were of particular concern: (1) If hydroxylamines (and perhaps, subsequently, aldimines) form should not these undergo direct oxidation given the conditions employed? (2) If dehydration of the hydroxylamine occurs at these temperatures, should dehydration of the starting amino-alcohol also occur (as suggested by others) and give a wider distribution of products including new alkenes? (3) Since hydroxylamines are rather reactive, might they react in some manner other than oxidation or dehydration? These questions led to the proposal of the alternative degradation pathways, which are illustrated on the lower right sides of Figures 3 and 4. Direct oxidation of hydroxylamines to nitrones has been described[38] as

have thermal rearrangements (as well as photo-rearrangements) of nitrones to amides via oxaziridine (a.k.a. oxazirane) intermediates.[39] In addition, aryl hydroxylamines are known to condense, even at room temperature, with some aldehydes and ketones to give nitrones and water.[40-42] Boyland and Nery[42] reported that the infrared spectra of a number of nitrones show strong N → O bands at 1555–1534 cm^{-1} and they attribute a band at 3378 cm^{-1} to the N-hydroxyl group of a secondary hydroxylamine. Although no nitrone bands were seen in the FTIR spectra taken, nitrones, if formed at 125°C, may only exist as transient intermediates in the polymer degradation mechanism. As seen in Table I, the resin systems containing resolvable bands close to 3378 cm^{-1} were thermally aged samples of D.E.R. 332 epoxy resin cured with either Ancamine 2006 (3366 cm^{-1}), D.E.H. 24 (3379 cm^{-1}), or MDA (3378–3385 cm^{-1}). (The bands at 3378 cm^{-1} are part of the broad hydroxyl stretch region.) The three amine-cured resins mentioned above are those that showed the greatest degradation of flexural strength and sample integrity.

Regarding the stability of oxaziridines, the following generalizations have been made[39]: When two alkyl substituents, one on the nitrogen and one on the carbon, are present, the oxaziridines are reasonably unstable and thermally decompose, even at room temperature. If the nitrogen substituent is aromatic, the oxaziridines are too thermally unstable to be isolated. Two ionic mechanisms have been proposed for the spontaneous rearrangements of oxaziridines, each of which lead to either N-substituted alkylamides or N,N-disubstituted formamides depending upon the ring substituents and the conditions of degradation.[39] These mechanisms can account for the relative stabilities of D.E.R. 332 epoxy resin cured with aliphatic amines, aromatic amines, and sulfonamides.

In Figure 5, the absorption peak at 2827 cm^{-1} in the unaged spectrum of triethylenetetraamine-cured D.E.R. 332 epoxy resin is attributed to C — H stretching of the methylene group α to the amine nitrogen that was originally part of the curing agent. Triethylenetetraamine is the only curing agent used in this study that has such a group and that shows a peak at 2827 cm^{-1} in the spectrum of the cured polymer. Its disappearance upon aging, coupled with the absence of any new methylene C — H stretching peaks, suggests that Cope reactions that occur during the oxidative degradation of this system will tend to cleave the polymer in such a way as to produce enamine fragments (Fig. 3) rather than

methyl ketone fragments (Fig. 4). The increase in absorption of the band near 1103 cm^{-1} may be due to C — N stretching or to the C — O stretch bands of esters that may form subsequent to the primary degradation process.

Descriptions of the FTIR spectra of unaged and air-aged epoxy resins cured with various hardeners are shown in Table I. Spectrum expansion was done using the computer associated with the FTIR. Peaks that fell into similar wavenumber ranges were grouped in the same columns. For the sake of compactness, some differing peaks were merged into the same columns. In these cases, the peak numbers of the least similar values were put in bold print to highlight the difference. Also, the regions of a given sample's spectrum that changed during aging were also printed in bold numbers. Very small peaks and shoulders were very reproducible. The wavenumber assignments of peaks from separate KBr pellets of the same sample never varied by more than two or three wavenumbers, which is about the same variation that occurred due to remeasuring the same peak at different degrees of spectrum expansion using the computer. "Covered" is used in the table to indicated that as aging proceeded, a given peak area was covered up by a new peak, making its continued presence uncertain. A lack of the abbreviations "s" or "vs" in describing a peak listed in Table I does not mean that the peak is not small. In some spots, arrows have been added to the table to indicate how some peaks are shifting from one region to another, due either to aging or as a result of compositional changes in the starting formulation. Certain peaks are common to nearly all of the formulations, whereas other peaks are present only in those formulations that contain a specific component, such as p-toluenesulfonamide residues. The FTIR spectra of D.E.R. 332 epoxy resin cured with either triethylenetetraamine, 2,5-dimethyl-2,5-diaminohexane, methylene dianiline, or sulfanilamide are shown in Figure 5, before and after aging, to better illustrate the spectral changes that occur in the first three of these resins.

Color Development

As the air-aging times were increased, the outer portions of the samples usually became more colored. However, the interior portions of the castings appeared to retain their original color, as was observed in an earlier study.[15] Also, the outer, oxidized layers of the samples became thicker with increased aging time and well-defined boundaries existed between
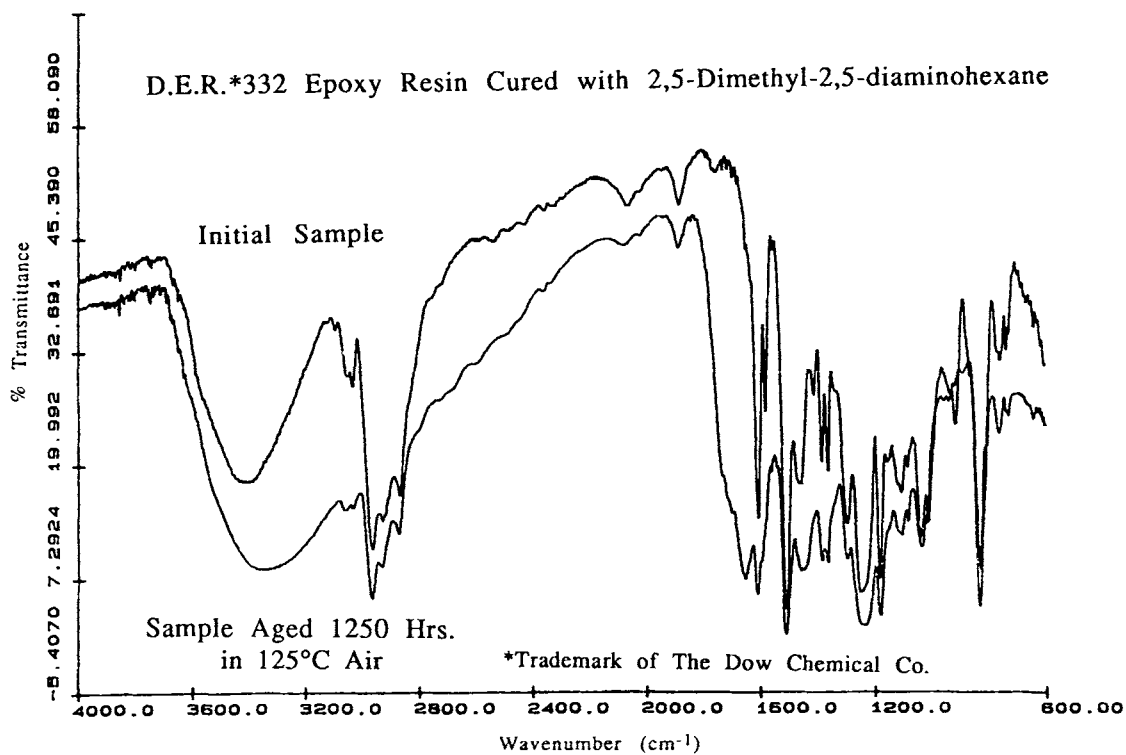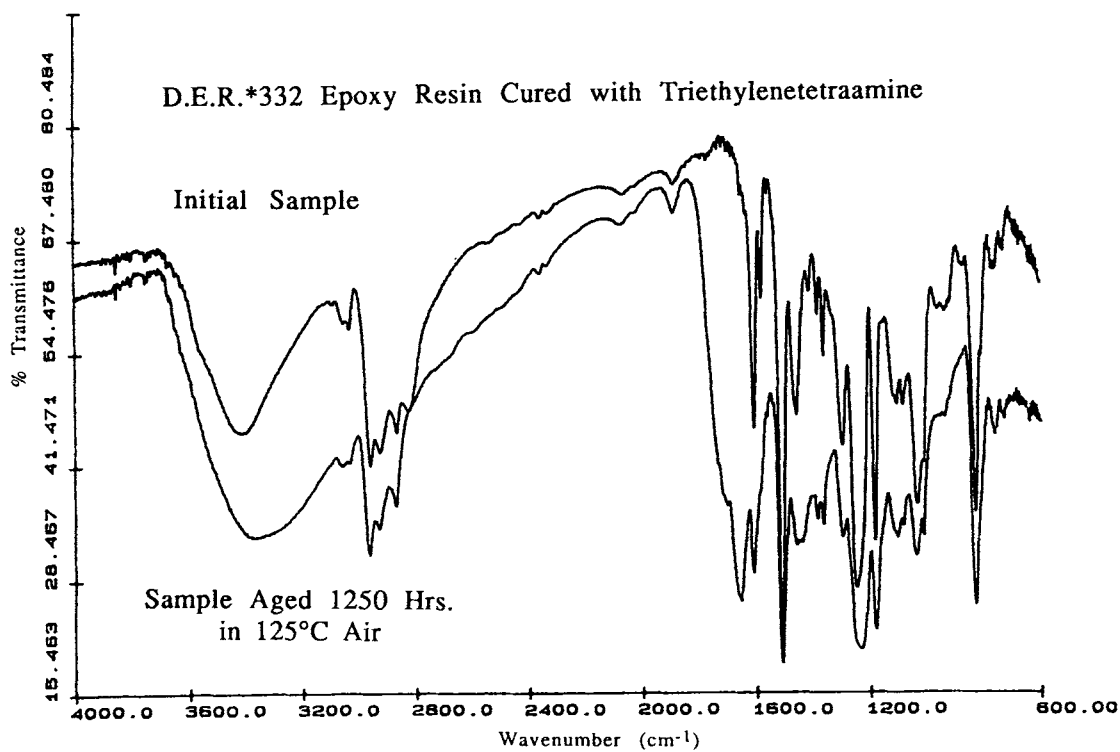
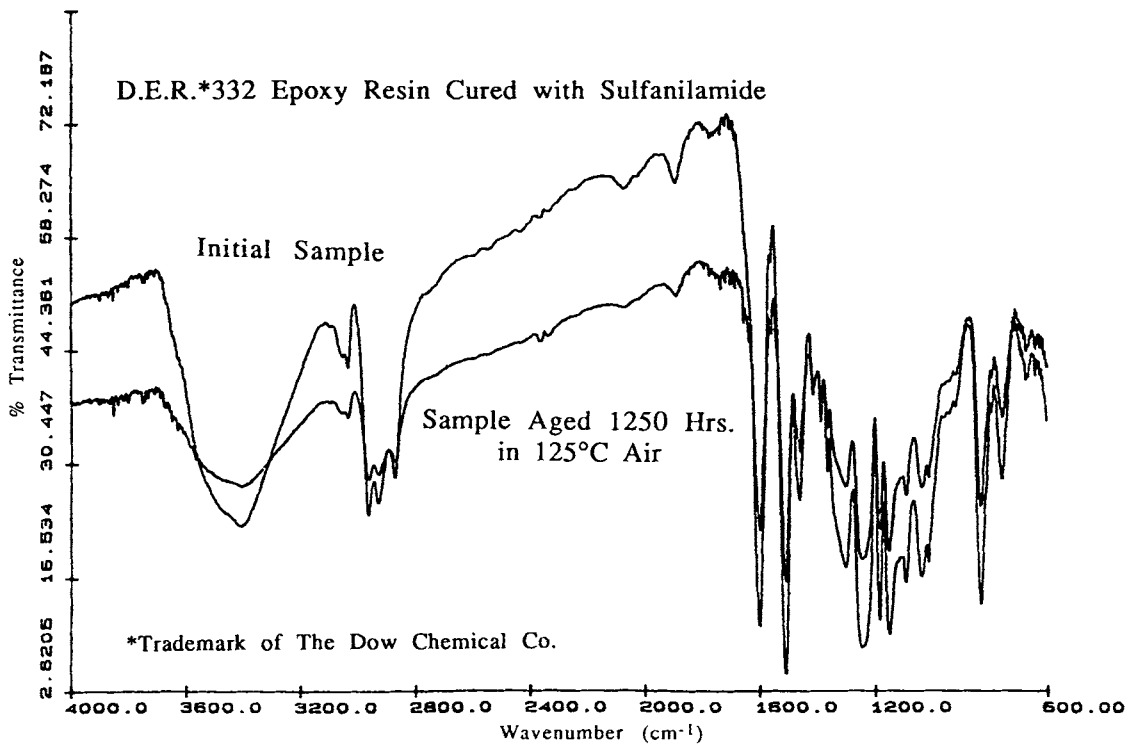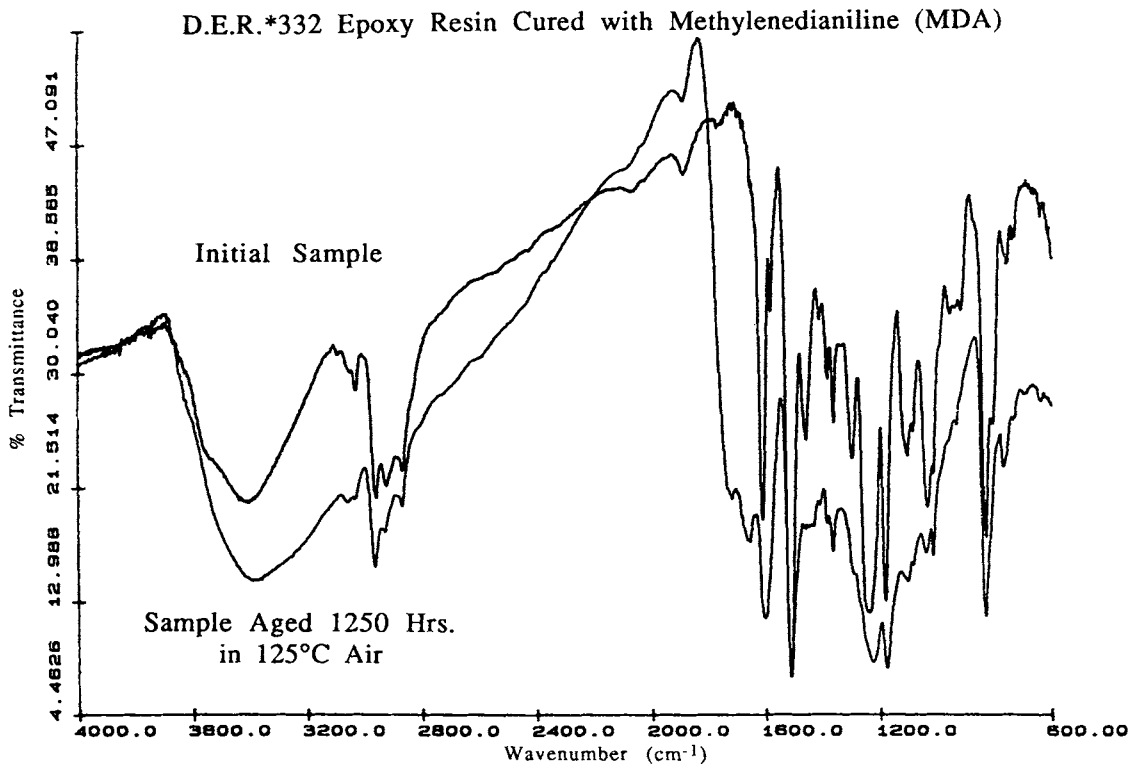**Figure 5** Examples of FTIR spectra taken before and after aging.

Figure 5   (*Continued from the previous page*)

Table III   Gardener Color of the Cured Resins at Various Aging Times

Resin Type	Hardener Type	Hours in 125°C Air								
		0	50	200	300	350	700	1200	1250	4220
D.E.R. 332	D.E.H. 24	3							15	
	Ancamine 2006								≫ 18	
	MDA	9		14					"Black"	
	Sulfanilamide	1			4				10	
	4,4'-Oxybis(benzenesulfonamide)	4			4				"10"	
	p-Toluene sulfonamide	1			4				14	18
D.E.R. 383	4,4'-Diaminodiphenylsulfone	3	4			9	11	13		

this discoloration and the samples' interiors. This is expected for degradation reactions that are limited by rate of oxygen diffusion. (Samples aged in 149°C nitrogen did not darken in color.[15])

Although all samples became more colored with increased aging time, the degree of color increase provided no real clues as to strength performance, as can be seen by inspection of Table III. Table III lists the Gardener color values for some of the resins tested. The color measurements were taken from broken flexural test specimens. One sample's color was of such a different tint (nonyellow/brown) that the value could only be estimated. This value, given in Table III has quotation marks around it. The color value given as "black" was determined by looking at the surface in normal room light.

The development of color during the degradation process allowed estimates to be made of the degraded layer thickness by observing the fracture surfaces of the flexural specimens. The minimum layer thickness at which the maximum decreases in flexural strengths were first observed was about 0.003 in.

SUMMARY AND CONCLUSIONS

At 125°C in air:

1. Based on flexural property retention and changes in the infrared spectra, the thermooxidation resistance ranking of curing agents for D.E.R. 332 epoxy resin is as follows: p-toluenesulfonamide > 4,4'-diaminodiphenyl sulfone or sulfanilamide > methylene dianiline ≫ triethylenetetraamine > 2,5-dimethyl-2,5-diaminohexane.

2. Oxidation of aliphatic amine-cured D.E.R. 332 epoxy resin is initiated by electrophilic attack of oxygen on the lone-pair electrons of the nitrogen to form an amine oxide. Polymer chain cleavage then occurs via Cope reactions.

3. It is proposed that the hydroxylamine products of Cope reactions are further oxidized to nitrones, which then decompose to amides via oxaziridine intermediates.

4. Commercial antioxidants added to an aliphatic amine-cured resin were ineffective in preventing air oxidation, supporting conclusion 2 in that the predominant propagation steps leading to chain cleavage are not free radical in nature. These antioxidants did not appear to react with either the epoxy resin or the amine hardener.

5. When used with DGEBA-type resins, p-toluenesulfonamide, 4,4'-diaminodiphenylsulfone, and sulfanilamide-curing agents provide good flexural strength retention after 1200 h exposure time.

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