UCRL-52577

FILAMENT WINDING EPOXY RESINS FOR ELEVATED TEMPERATURE SERVICE

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October 9, 1978

Work performed under the auspices of the U.S. Department of Energy by the UCLLL under contract number W-7405-ENG-48.

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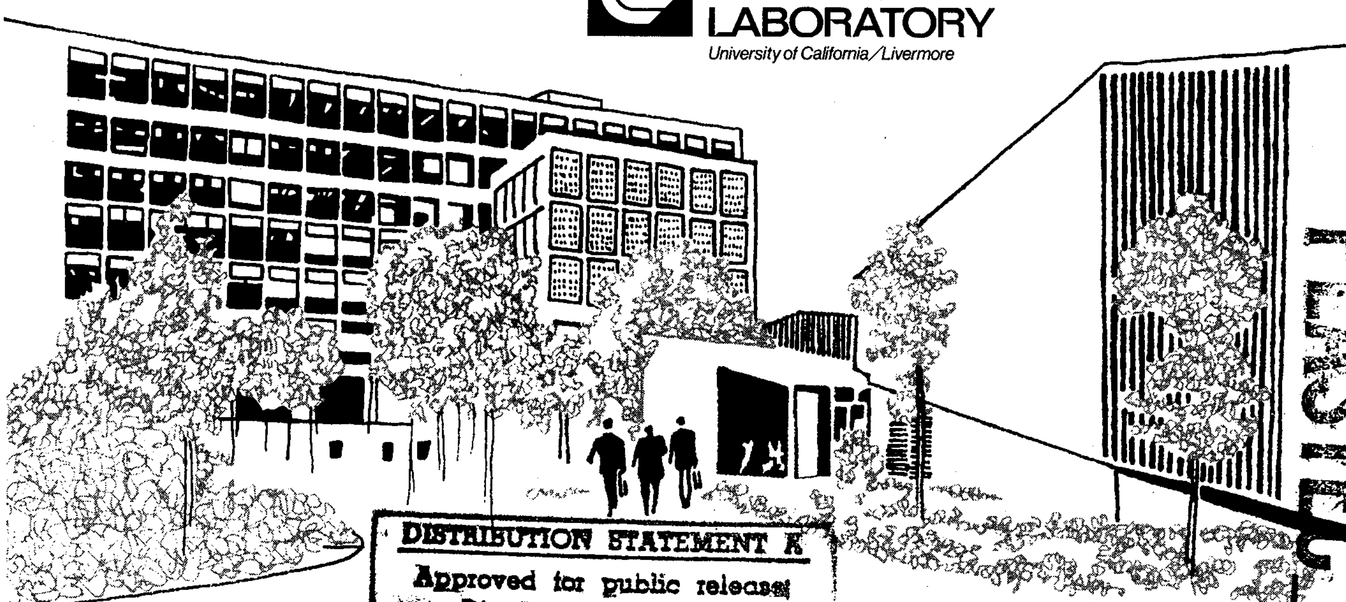

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Available from
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Springfield, VA 22161
Price: Printed Copy $; Microfiche $3.00

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ABSTRACT

We formulated and evaluated six epoxy resin systems suitable for wet filament winding of high-performance flywheels. We judged the resins on five criteria: (1) low viscosity (1.0 Pa·s at 25°C), (2) long gel time (⩾20 h for a 30-g mass at 25°C), (3) high glass transition temperature (⩾180°C), (4) high tensile strength with high modulus, and (5) good retention of mechanical properties upon accelerated heat aging (7 d at 175°C). From the results of mechanical and physical tests, we conclude that our resin 1 (Ciba 0510/RD-2/APCO 2330) is the best resin for the intended application. Our resin 2 (Ciba 0510/Tonox 60-40) is the second choice; it offers a lower tensile strength and a larger loss in strength upon heat aging than resin 1 but has the highest glass transition temperature.

INTRODUCTION

As part of the LLL fiber composite flywheel materials program, we have studied several matrix resins for advanced flywheels. A high-performance fiber composite flywheel that stores 0.3 MJ/kg (40 W-h/lb) of kinetic energy will spin at speeds as great as 40,000 rpm in a vacuum of 0.1 to 1 pa (1 to 10 μm) of mercury. Under these conditions, the outer surface of the flywheel will experience temperatures of 150°C as a result of aerodynamic heating. Therefore the fiber and resin matrix selected must be able to withstand these service conditions for several years. In addition, because flywheels are filament wound, and because filament winding is quite time consuming, the resin must have a low viscosity and a long gel time.

The epoxy resins and curing agents typically used for aerospace applications at high temperatures are very viscous materials. Also, the diluents used to lower resin viscosity usually lower the performance of the composite at elevated temperatures.

We approached this problem by formulating epoxy resin systems from some special epoxy resins and curing agents of low viscosity and by using little or no diluent. Presented here are the results of our evaluation of six of these epoxy resin systems formulated to meet the above service and processing requirements.

RESIN FORMULATIONS

The specific requirements for the resin systems studied are: (1) viscosity of about 1.0 Pa·s at 25°C, (2) gel time of 20 h or more for a 30-g mass at 25°C, (3) glass transition temperature T_g of 180°C or greater, (4) high tensile strength with high modulus, and (5) good retention of mechanical properties after 7 d of accelerated aging at 175°C. In Table 1, we list the resins and curing agents used. The resin systems formulated and some of their key characteristics are presented in Table 2.

Each material considered as a resin component has at least one drawback that limits its overall usefulness. For example, all resins formulated without a diluent have viscosities greater than our processing requirements. Therefore, even though diluents lower the resin performance at elevated temperature, some diluent had to be used to produce acceptable, low-viscosity resin systems. In addition, because of the toxicity of ERL 4206, we used RD-2 as the diluent in all formulations, except

Table 1. Resins and curing agents.

Component	Chemical description	Viscosity, Pa·s at 25°C	Drawbacks
Resins			
Ciba 0510	Molecular, distilled triglycidyl p-aminophenol	0.55 to 0.85	Costly and reactive
DEN 438	Polyglycidyl ether of phenol-formaldenhyde Novolac	200 to 500	Highly viscous
ERL 4206	Vinylcyclohexane dioxide	0.10	Toxic
APCO 2447	Mixture of DEN 438 and ERL 4206	4.0	Toxic
RD-2	1,4-butanediol diglycidyl ether	0.19	Lowers T_g
DER 322	Diglycidyl ether of bisphenol A	4 to 5	Crystalizes at room temperature
Curing Agents			
Tonox 60-40	60% methylene dianiline plus 40% m-phenylene diamine	15.0	Toxic
APCO 2330	Aromatic amine, no methylene dianiline	300 to 400	Highly viscous
APCO 2347	Modified imidazol, contains amine groups	0.34	Reactive

one, even though RD-2 gives a lower T_g than ERL 4206. (The resin that was the exception contained APCO 2447, a proprietary resin that uses ERL 4206 as one component.)

All formulations were cured for 3 h at 70°C plus 2 h at 120°C plus 2 h at 180°C to achieve a high T_g and to cure the resin at a temperature above the intended-use temperature (150°C). With the exception of the two resin systems cured with APCO 2347 (modified imidazol), these cure conditions produced a T_g greater than 185°C. Both the APCO 2347 systems, however, exhibited additional curing during the heat aging step (this shown in Table 2).

Table 2. Performance of the six epoxy resin systems formulated for elevated-temperature service.

Resin system No.	Resin components (parts by weight)	Viscosity, Pa·s	Gel time, h	Tensile Properties			T_g, °C	Density at 23°C, Mg/m
				Modulus, GPa	Stress, MPa	Strain, %		
1	Ciba 0510/RD-2/APCO 2330	1.05	21.1					1.292
	(100/20/43.1)[a]: Cured[b]			5.4	89.5	2.0	205	
	Aged[c]			4.8	84.7	2.0	220	
2	Ciba 0510/Tonox 60-40	1.33	25.1					1.271
	(100/49.8): Cured			4.1	86.8	3.2	210	
	Aged			4.1	73.4	2.2	226	
3	APCO 2447/ERL 4206/Tonox 60-40	1.08	38.6					1.232
	(100/20/39.9): Cured			3.9	83.5	2.4	190	
	Aged			3.9	71.4	2.0	215	
4	Ciba 0510/DEN 438/RD-2/Tonox 60-40	1.48	19.6					1.268
	(75/25/25/49.9): Cured			4.0	81.0	2.5	185	
	Aged			4.2	78.5	2.8	213	
5	Ciba 0510/DEN 438/RD-2/APCO 2347	0.88	34.4					1.260
	(75/25/20/12.2): Cured			3.1	74.8	3.7	115	
	Aged			3.4	73.2	2.8	170	
6	DER 332/RD-2/APCO 2347	0.90	48.5					1.194
	(100/15/9.5): Cured			2.8	59.8	2.7	115	
	Aged			2.6	53.7	2.5	145	

[a]Parts by weight.
[b]3 h at 70°C plus 2 h at 120°C plus 2 h at 180°C.
[c]7 d at 175°C

RESULTS

We found that the gel time of each of these resin systems is adequate for good filament winding (see Table 2). However, the viscosity of two of the resin systems (2 and 4) is a bit higher than desired and may be a problem in some winding applications. Warming these resins will reduce the viscosity, but because these formulations contain Ciba 0510, a very heat sensitive resin, warming may reduce the gel time too much.

The six resin formulations were also subjected to two mechanical properties tests and to thermal gravimetric analyses in both the as-cured and aged conditions. Samples were aged in a constant-temperature, forced-air oven at 175°C for 7 d. In general, aging causes the samples to darken and become brittle. The results of these tests are summarized in Table 2.

The tests revealed that resin system 1, cured with APCO 2330, meets our processing requirements of low viscosity and long gel time, and has the highest tensile strength and modulus, the second smallest loss in tensile strength upon heat aging, and the second highest T_g in both the as-cured and aged condition. Resin system 3 also meets the processing requirements, but has a lower T_g, a lower tensile strength, and a larger reduction in strength upon heat aging than resin 1.

Dynamic Shear Modulus

Dynamic shear modulus measurements were made on rectangular specimens (6.35 by 1.27 by 0.32 cm) from 25 to 300°C using a Rheometrics Mechanical Spectrometer, Model RMS-7200. For all samples, the shear strain was 0.05% in the glassy region and 0.10% in the rubbery region. Data were recorded at two frequency rates of 0.1 and 1.0 Hz.

Figures 1 and 2 present the 0.1-Hz data for samples of all six resin systems in the as-cured and aged conditions. These curves were used to determine the T_g values presented in Table 2. The T_g is taken to be the temperature at which the G′ curve has a value of 2.5×10^8 Pa (log G′ = 8.4). As shown in Table 2, heat aging at 175°C for 7 d increases the T_g of these resins by 15 to 55°C; those resins with the lower T_g values show the greatest increase.

Resin system 3 (see Table 2) has a relatively constant storage modulus from room temperature up to about 180°C and a sharp transition from the glassy to the rubbery state (Fig. 1). In contrast, resin systems 1, 2, and 4 first show a greater decrease in modulus from 25 to 180°C and then a more gradual change in modulus to the rubbery state. This difference in behaviors results from the higher crosslink density of resins 1, 2, and 4, as reflected by the G′ values in the rubbery state. However, resin system 3 is a high-molecular-weight rigid resin.

Resin systems 5 and 6 were incompletely cured, as shown by the large increase in T_g values after heat aging. In addition, the shape of the storage modulus curve changes for resin 5 (see Fig. 2) from a sharp transition (as-cured state) to a broad transition (cured condition). The crosslink density of resin system 3 increases on heat aging as does that of resin 6, whereas the crosslink density of resin 5 stays about the same.

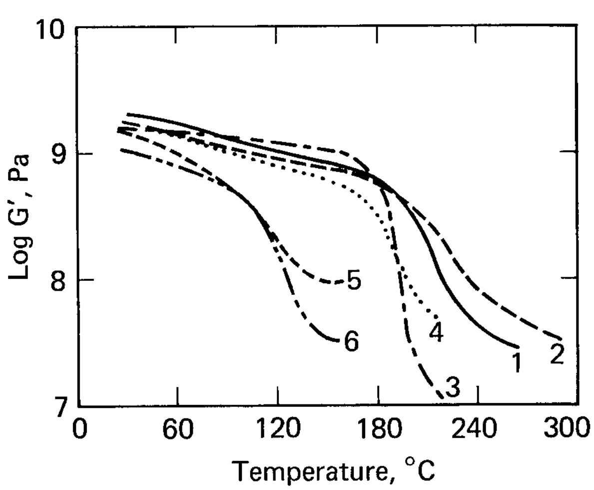

Fig. 1. Dynamic shear modulus for specimens of the six epoxy resin systems cured for 3 h at 70°C plus 2 h at 120°C plus 2 h at 180°C.

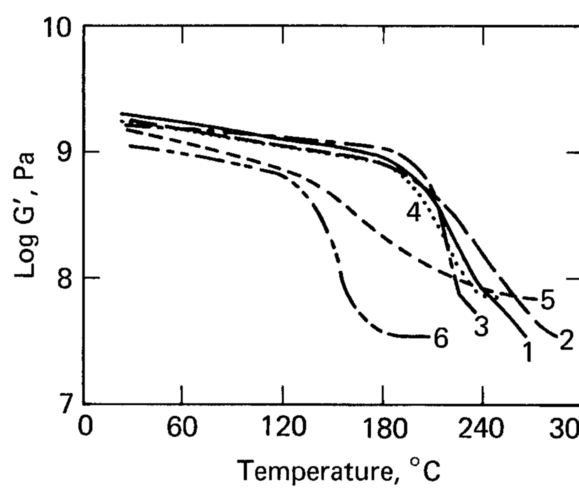

Fig. 2. Dynamic shear modulus for specimens of the six epoxy resin systems after aging for 7 d at 175°C.

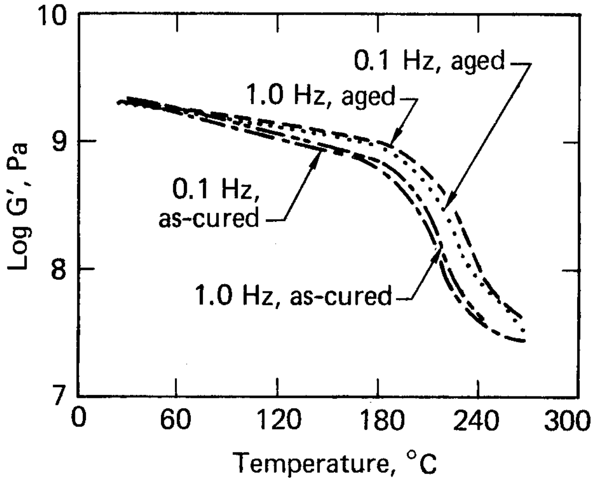

Fig. 3. Comparison of dynamic shear modulus for as-cured and aged specimens of resin 1 (Ciba 0510/RD-2/APCO 2330) at 0.1 and 1.0 Hz.

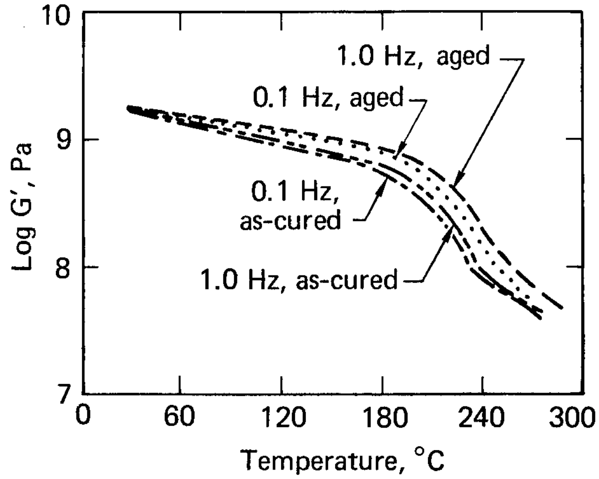

Fig. 4. Comparison of dynamic shear modulus for as-cured and aged specimens of resin 2 (Ciba 0510/Tonox 60-40) at 0.1 and 1.0 Hz.

Resins 1, 2, and 4 have approximately the same crosslink density; however, the scatter in the data at temperatures above 250°C make a good comparison difficult. Some decomposition is evident in the dynamic shear modulus tests.

The effect of heat aging is shown quite clearly in Figs. 3 and 4 for resin systems 1 and 2, respectively. The data show both the rate effect for each condition and the increase in T_g from aging. In both cases, the shape of the curve remains the same, but the actual curve is displaced along the temperature axis. Also, we note that for resin 1, the modulus of the heat aged sample is slightly lower than that of the as-cured sample; this behavior is also seen in the tensile test results (see Table 2). No explanation for this response is evident. The increase in modulus upon heat aging for resin system 2 (Fig. 4) represents the expected behavior.

Tensile Properties

Tensile stress-strain curves for the six resin systems are presented in Figs. 5 and 6, and the results are summarized in Table 2. The most notable change in the tensile properties of these resins is a decrease in the failure strain upon heat aging. This is especially true for resins 2 and 5.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were performed on samples of all six resins. We used a heating rate of 10°C/min in both nitrogen and air atmospheres. Some isothermal weight loss measurements were also made on selected samples at 175 to 275°C for short periods of time (⩾100 min). The TGA results are presented in Table 3 and Figs. 7

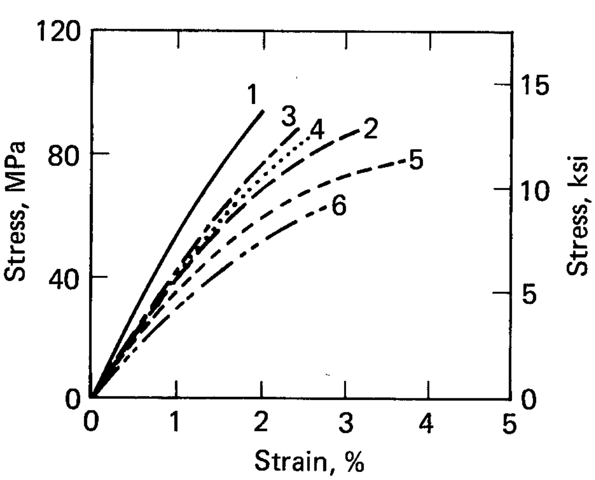

Fig. 5. Tensile stress-strain curves for as-cured specimens of the six epoxy resin systems.

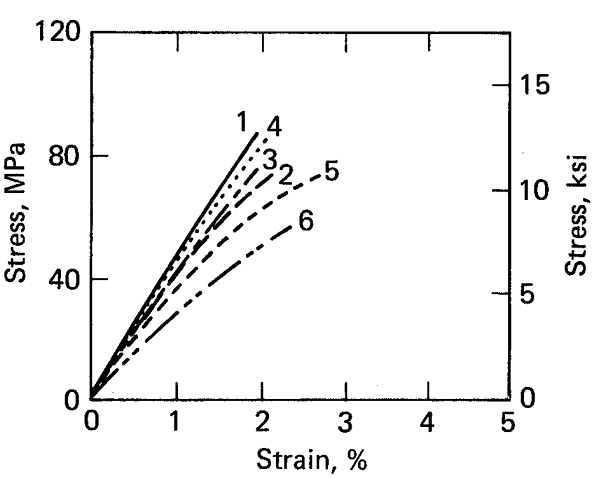

Fig. 6. Tensile stress-strain curves for aged specimens of the six epoxy resin systems.

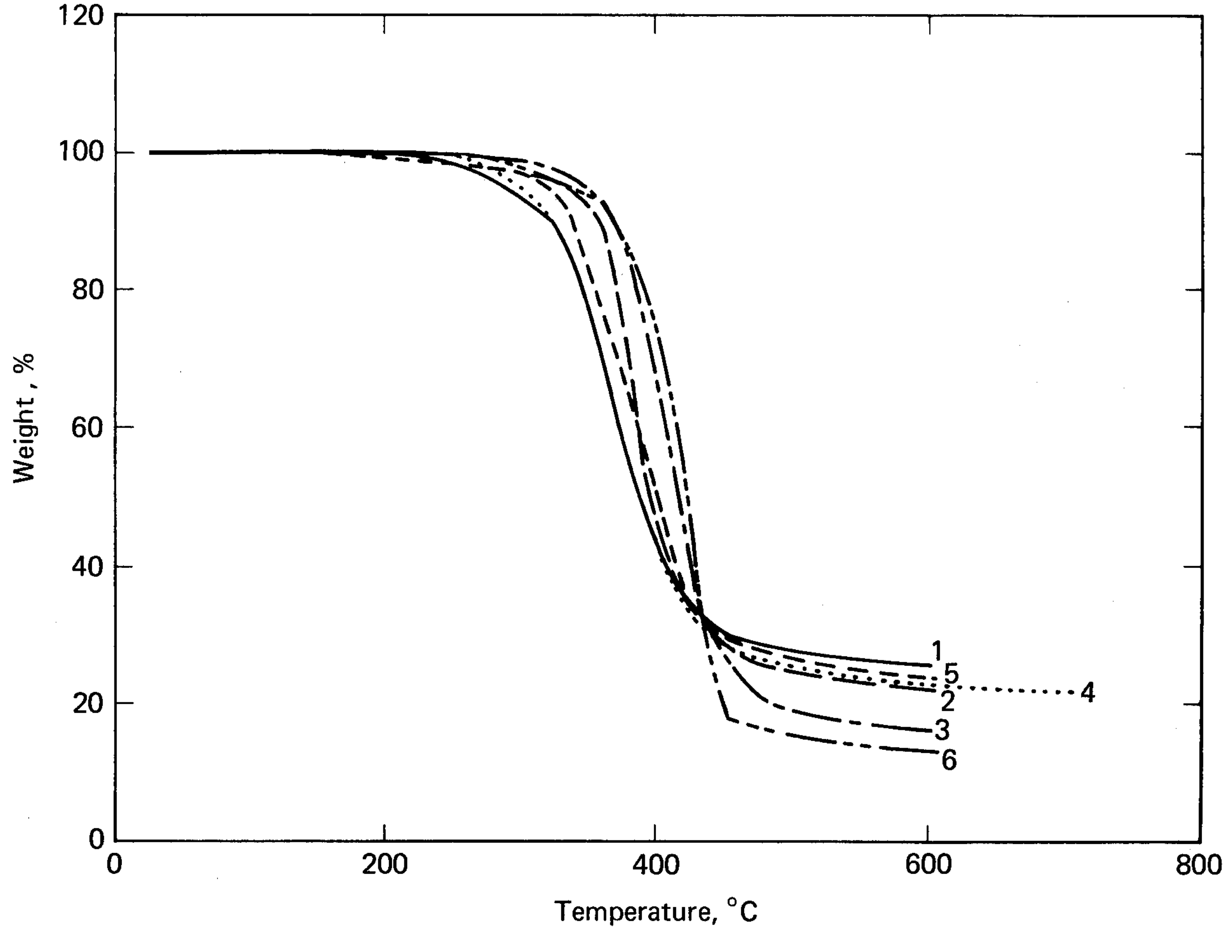

Fig. 7. Thermogravimetric analysis curves (% weight vs temperature) for specimens of the six epoxy resin systems tested in a nitrogen atmosphere.

Table 3. Results of the thermogravimetric analyses.

Resin system	Atmosphere	Temperature at which percent weight loss occurred, °C			
		2%	5%	10%	25%
1	Nitrogen	245	280	318	350
	Air	230	275	320	365
2	Nitrogen	295	330	355	370
	Air	280	320	350	370
3	Nitrogen	305	340	365	385
	Air	310	345	370	395
4	Nitrogen	270	290	318	350
	Air	250	285	320	360
5	Nitrogen	245	315	335	360
	Air	250	315	335	370
6	Nitrogen	265	335	365	395
	Air	245	315	350	405

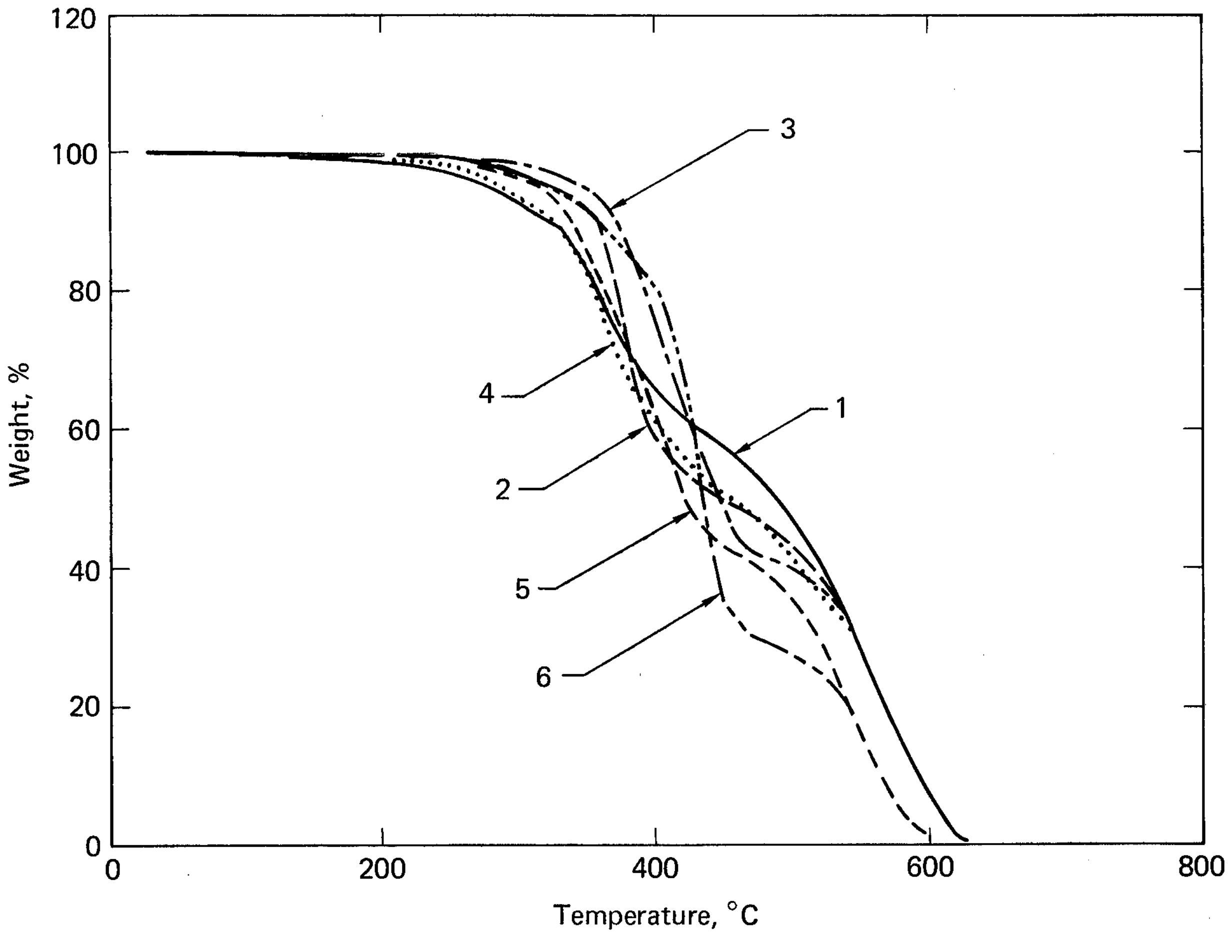

Fig. 8. Thermogravimetric analysis curves (% weight vs temperature) for specimens of the six epoxy resin systems tested in an air atmosphere.

and 8. By comparing the temperatures at which we observed a 2% weight loss for each resin sample, we see that resin system 3 is the most thermally stable, followed by resin 2. All four other systems contain RD-2; this resin probably is responsible for their lower performance at the elevated temperatures. We also note that weight loss up to 400°C is not greatly influenced by the presence of oxygen in these short-term tests.

The isothermal tests at 175°C for resins 1 and 4 reveal a 1.5 to 2.0% weight loss in the first 20 min, and then an approximately constant weight up to 100 min at which the time the tests were terminated. Figure 9 presents the isothermal weight loss curves for resin system 1 at temperatures from 150 to 275°C. At 150°C, the total weight lost after 1 h is 2.0%; the sample was losing weight at a rate of 0.4%/h. At 200°C, the resin sample had lost a total of 3.3% at 1 h and was losing weight at the rate of 1.0%/h. Tests at higher temperatures reveal an accelerating rate of decomposition with increasing temperature. Significant decomposition of our test specimens also occurred in the dynamic shear modulus tests at temperatures above 225°C; in a normal RMS test of dynamic shear modulus, the specimens spent about 30 min above 225°C.

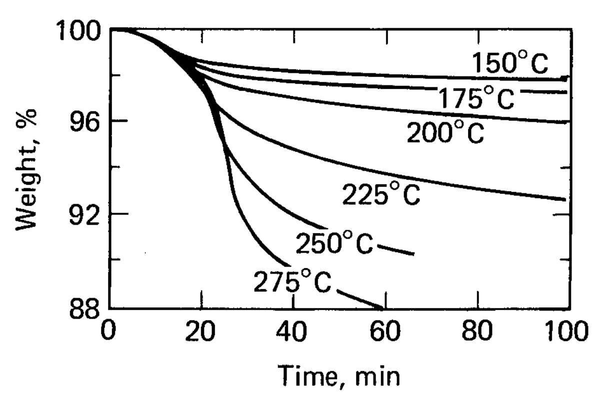

Fig. 9. Isothermal weight loss for resin 1 (Ciba 0510/RD-2/APCO 2330) at various temperatures in flowing air.

CONCLUSIONS

Resin systems 1, 2, and 3 are preferred over the other formulations. Although resin 3 is the most thermally stable according to the TGA tests, one of its components is ERL 4206 (vinylcyclohexane dioxide). The fact that vinylcyclohexane dioxide is listed as a carcinogen excludes resin 3 from consideration. Resin 2 is the second most thermally stable system by TGA but resin 1 offers the best tensile strength after 7 d of aging at 175°C. Considering all of the data, resin 1 (Ciba 0510/RD-2/APCO 2330) appears to be the best resin as the matrix for filament wound flywheels operating at surface temperatures of 150°C. Resin 2 (Ciba 0510/Tonox 60-40) is our second choice.

ACKNOWLEDGMENT

This work was supported by a contract with the Division of Energy Storage Systems, Physical Storage Systems, U.S. Department of Energy.

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