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CHARACTERIZATION AND CURE MONITORING OF STRUCTURAL ADHESIVES

WALTER X. ZUKAS, HOWARD H. WONG, DAVID A. DUNN, and STANLEY E. WENTWORTH
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ABSTRACT

Two potential replacement adhesives for a discontinued commercial adhesive were investigated. The composition and curing behavior of the replacements were compared to the commercial system utilizing a number of analytical techniques. High performance liquid chromatography, size exclusion chromatography, and thermogravimetric analysis were applied to establish the lot-to-lot consistency of the adhesive component composition. The thermal, dynamic mechanical, rheological, and dielectric properties, as a function of cure, were monitored by differential scanning calorimetry, torsional braid analysis, parallel plate rheometry, and microdielectrometry, respectively. Correlations between the various techniques and the state of cure of the adhesive were made. The glass transition temperature of the adhesive was observed to be a very sensitive measure of the state of cure.

CONTENTS

INTRODUCTION

The production of a commercial structural adhesive, Hysol EA934, was recently discontinued due to the hazards associated with its asbestos content. This adhesive had been used to bond the epoxy-Kevlar composite thread ring to the fused silica ceramic radome on the PATRIOT missile. Replacement adhesive systems were investigated to meet the processing and physical property requirements of this application.

In preliminary screening studies, carried out by Raytheon Co.,*[1] 35 adhesives were narrowed to 2. The criteria for suitability were primarily the lap shear strength as a function of temperature, the sag/flow characteristics, and pot life.

The objective of this work was to characterize and monitor the cure of the two replacement systems and compare them to EA934. These adhesives are ambient temperature cured, two-part systems. An aluminum-filled epoxy component was mixed with a nonaromatic amine component just before use.

EXPERIMENTAL

The two candidate adhesives will be referred to here as adhesives XX and YY. A single lot of Hysol EA934, one experimental lot and three lots of adhesive XX, and three lots of adhesive YY were obtained from Raytheon Co. for analysis. The aluminum-filled epoxy component is referred to as part A and the amine component is referred to as part B. The notation used in this study consists of the adhesive type followed by lot number and component, if necessary. For example, XX refers generally to a mixed adhesive XX, XX-A refers generally to part A of adhesive XX, XX-1 refers specifically to a mixed lot 1 of adhesive XX, and XX-1-A refers specifically to part A of lot 1 of adhesive XX. The experimental lot of adhesive XX is referred to as XX-0. Mixing of adhesive formulations was carried out on room temperature stored materials at weight ratios of 100:33 A:B for EA934 and 100:26 A:B for all other formulations. Approximately 5-gram samples were mixed by hand for five minutes before sampling.

High performance liquid chromatography (HPLC) and size exclusion chromatography (SEC) analyses were carried out on the soluble portions of both parts A and B of the adhesives. The nonsoluble portions, filtered from the solutions, appeared to consist of only the inorganic filler content. HPLC was run using a Waters Resolve column (5 μm, C18) with an acetonitrile/water mobile phase at a flow rate of 1.7 ml/min. SEC was run using IBM SEC A, C columns (5 μm) with THF at 40°C at a flow rate of 1.0 ml/min. An ultraviolet (UV) detector at 214 nm was used for HPLC and at 254 nm for SEC. A refractive index (RI) detector was also used for the SEC analyses.

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGS-2 Thermogravimetric System using a heating rate of 10°C/min. The atmosphere was flowing dry air at 50 ml/min. The weight loss as a function of temperature was monitored for both parts A and B.

Differential scanning calorimetry (DSC) analyses were carried out on a Perkin-Elmer DSC-2 equipped with an Intercooler II. Typically, samples of 10 to 30 mg were cured in open stainless steel pans at room temperature (22 °C to 25°C) for 0, 2, 4, 24, 48, and 72 hours. The pans were then sealed with an O-ring top and scanned at 10°C/min from -23°C to 227°C under nitrogen. Samples were also cured for seven days in both open and sealed pans and similarly scanned. All samples were then cooled at 40°C/min to -23°C and rescanned. An additional sample of YY-1 was cured for six to eight hours. Approximately five minutes were required to start the scan for the zero time sample.

*Private communication with EKSTEIN, C. J., and BAKER, T. E., ARDEC, November 4, 1987.

1. PATTERSON, D., and BOYCE, D. *Development of an Alternative Adhesive System for a Tactical Missile Radome Joint* in Proceedings Fifth International Joint Military/Government-Industry Symposium on Structural Adhesive Bonding, p. 309, 1987.

Torsional braid analysis (TBA) was performed on an automated system from Plastics Analysis Instruments, Inc. The mixed adhesive was coated on a glass braid and suspended in the system oven chamber at room temperature under helium. The time required for the adhesive to reach gelation and vitrification, as indicated by peaks in the log decrement trace, were recorded. After five to seven days, the TBA sample was cooled to approximately -50°C and subsequently heated to 230°C at 1.5°C/min, cooled at 40°C/min to -50°C, and reheated to 230°C at 1.5°C/min. The first heating scan revealed two peaks in the log decrement trace. The first peak was associated with the glass transition temperature, T_g, of the partially cured material (TG1) and the second with the fully cured material (TG2). Only one peak was observed in the second scan and was also associated with the fully cured sample (TG3).

Parallel plate rheometry (PPR) was carried out on a Rheometrics RDS-7700 at 24°C to 27°C at 1 Hz. Samples approximately 1 mm thick between 25-mm diameter aluminum disposable disks were oscillated with a 10% strain and the complex viscosity and modulus values obtained as a function of time. Approximately five minutes was required to introduce a sample for measurement.

Microdielectrometry (MDE) measurements were made using a Eumetric System II Microdielectrometer from Micromet Instruments, Inc. Isothermal cures of XX-1 and YY-1 were carried out at 25°C by placing a drop of the mixed adhesive on the dielectric sensor under nitrogen. Values for the dielectric constant and dielectric loss factor were monitored as a function of time at frequencies of 1, 10, 100, 1000, and 10,000 Hz.

RESULTS AND DISCUSSION

Typical HPLC traces of the A components are illustrated for XX-A and YY-A in Figures 1a and 1b, respectively. The formulations of XX-A and EA934-A appear to be similar, both quite different from the YY-A formulation. The HPLC peak areas are related to the amount of a particular component present in a formulation. Comparisons of the relative amounts of the components were made by taking ratios of the peak areas associated with the formulations. For EA934-A and XX-A, the ratio (I) of the sum of the peak areas at elution times (min) of 4.23, 4.56, and 4.88 to 2.36 and the ratio (II) of the sum of 7.09 and 7.24 to 2.33, and for YY-A the ratio (III) of 5.08 to 2.35 are shown in Table 1. These values reflect the average of duplicate runs for all samples. Negligible sample variation was observed. Only small lot-to-lot differences were observed for XX-A and YY-A. Both XX-A and YY-A appear to contain a common component, as indicated by the single peak at approximately 2.3 min.

Table 1. HPLC AND SEC ANALYSIS OF ADHESIVE COMPONENTS

Adhesive Component	HPLC Results			SEC Results (Area %)				
	I	II	III	9.54	9.86	10.41	10.94	11.51
EA934-A	0.429	0.315	–	5.76	6.63	17.73	6.85	63.03
XX-1-A	0.393	0.291	–	3.99	5.34	17.44	6.38	66.85
XX-2-A	0.388	0.292	–	3.58	5.14	17.52	6.36	67.40
XX-3-A	0.389	0.286	–	3.97	5.50	18.25	5.68	66.60
YY-1-A	–	–	2.40	5.49	11.49	11.52	39.34	32.16
YY-2-A	–	–	2.33	5.61	10.87	11.47	39.40	32.65
YY-3-A	–	–	2.43	4.74	11.42	11.59	39.91	32.34

An SEC trace for a sample of YY-1-A is shown in Figure 2. Similar elution times were also observed for the SEC peaks associated with XX-A samples. The SEC peak areas, as a percent of total area, are listed in Table 1. Similar to the HPLC data, these values reflect the average of duplicate runs for all samples where negligible sample variation was observed. SEC analysis similarly showed negligible lot-to-lot differences and a similar formulation for XX-A and EA934-A. The elution times are associated with molecular size

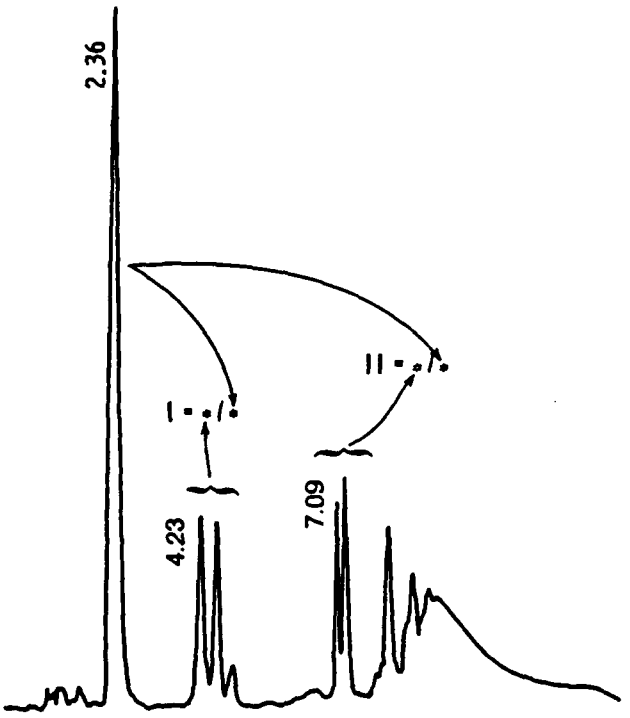

Figure 1a. HPLC of XX-A.

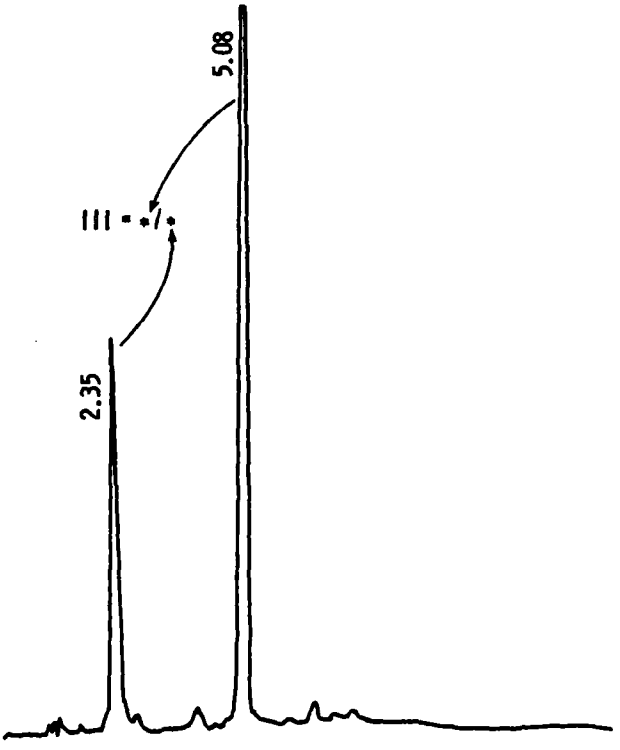

Figure 1b. HPLC of YY-A.

in solution, and similar elution times and number of peaks are observed for all samples. This is quite different from the HPLC results which showed quite a number of peaks for XX-A and only two significant peaks for YY-A. The difference in the UV detector wavelength used would account for some of these differences. The common, most-polar HPLC peak at 2.3 min is probably associated with the longest elution time SEC peak at 11.51 min. The other significant HPLC peak for YY-A samples at 5.08 min would appear to be related to the SEC peak at 10.94 min.

Accurate determination of the components in part B by either HPLC or SEC was not possible due to the insensitivity of both UV and RI detectors to the materials present.

Typical TGA traces for the A and B components are shown in Figures 3a and 3b for XX-3-A and YY-1-B, respectively. The TGA results are summarized in Table 2. Some duplicate sample runs showed slight sample variation. The filler content, indicated as the final plateau value in Figure 3, of the series XX-0-A, XX-1-A, XX-2-A, and XX-3-A was found, within experimental error, to be the same and only minor differences were found in the filler content of the series YY-1-A, YY-2-A, and YY-3-A. Periodic determination of filler content from the surface of a sample of YY-1-A over a period of two months showed no significant settling of filler. A small amount of silica filler content was observed in part B. The series XX-1-B, XX-2-B, and XX-3-B showed negligible batch-to-batch differences, while the series YY-1-B, YY-2-B, and YY-3-B showed small differences. The amount of initially stable thermal decomposition products formed in part B (and indicated in Figure 3b) was also determined. The only significant batch-to-batch variation was observed for YY-3-B which contains iess of this material than YY-1-B and YY-2-B. Overall, adhesive YY formulations represent a more highly filled system.

A typical DSC scan for a partially cured adhesive, YY-1 after six hours at room temperature, is shown in Figure 4. The residual heat of reaction values were calculated from the area under the exotherm and T_g's were determined from the onset of a baseline deviation occurring before the exotherm. The residual heat of reaction values and exotherm peak temperatures are shown in Table 3. The extent of reaction of the epoxy groups is proportional to the heat of reaction.[2] So the residual heat of reaction from the DSC scans represents the amount of cure which does not take place during ambient temperature cure. The extent of reaction at ambient is calculated assuming the residual heat of reaction from the uncured sample represents 100% of the epoxy groups. These values are listed in Table 4 and are shown for samples of EA934, XX, and YY in Figure 5. The glass transition temperatures obtained are listed in Table 5, with Figure 6 illustrating the increasing T_g with time for samples of XX-1 and YY-1.

Generally, adhesive XX appears to cure faster than YY, when the extent of reaction values are compared, and faster than EA934 and YY when the T_g values are compared. Most of the reaction in all samples appears to occur in the first 24 hours and all samples exhibit approximately 30% unreacted material after curing for seven days. The exceptions are EA934 and YY-3, which show approximately 20%. All samples have a T_g from 55°C to 60°C after seven days. Sealing a sample appears to have no significant effect on the DSC results. Lot-to-lot comparisons show XX-3 to react slower than XX-1 or XX-2 with XX-2 somewhat faster than XX-1 when based on the T_g advancement. YY-1 was observed to react somewhat slower than YY-2 and YY-3.

Isothermal and the first and second dynamic scans by TBA are shown, respectively, in Figures 7a, 7b, and 7c for a sample of YY-1. Gillham[3] has shown the usefulness of this technique in studying thermosetting systems. Times to gelation and vitrification and values for TG1, TG2, and TG3 are listed in Table 6. These values represent the average of a minimum of two separate experiments. The TBA results also indicate that XX reacts faster than EA934 and YY, as indicated by the shorter times to gelation and vitrification. However, the variation in the average gel times between XX and YY is only slightly larger than the sample variation observed. Comparison with the extent of reaction by DSC shows that gelation occurs in the 20% to

2. PRIME, R. B. *Thermosets* in Thermal Characterization of Polymeric Materials, Ch. 5, E. A. Turi, ed., Academic Press, New York, 1981.
3. GILLHAM, J. K. *Characterization of Thermosetting Materials by Torsional Braid Analysis*. Poly. Eng. Sci., v. 16, 1976, p. 353.

30% range. The exception to this is EA934 which gels at somewhat higher values. The average gelation times may correspond to a slightly lower extent of reaction for YY, when compared to XX, but more detailed DSC data would be required to confirm this.

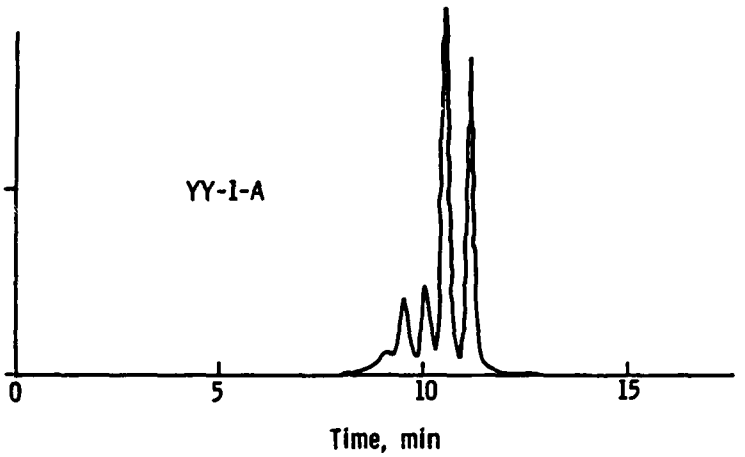

Figure 2. SEC of YY-1-A.

Table 2. THERMOGRAVIMETRIC ANALYSIS (TGA) OF ADHESIVE COMPONENTS

Adhesive Component	Filler (wt%)	Thermal Decomp. (wt%)
EA934-A	40, 40	–
XX-0-A	44	–
XX-1-A	43	–
XX-1-B	3	62
XX-2-A	43	–
XX-2-B	3	62, 57
XX-3-A	43	–
XX-3-B	3	62
YY-1-A	50*	–
YY-1-B	6	52
YY-2-A	52	–
YY-2-B	4	51
YY-3-A	51	–
YY-3-B	4	45, 39, 41

*Settling experiment values of 50, 50, 48, 49, 50

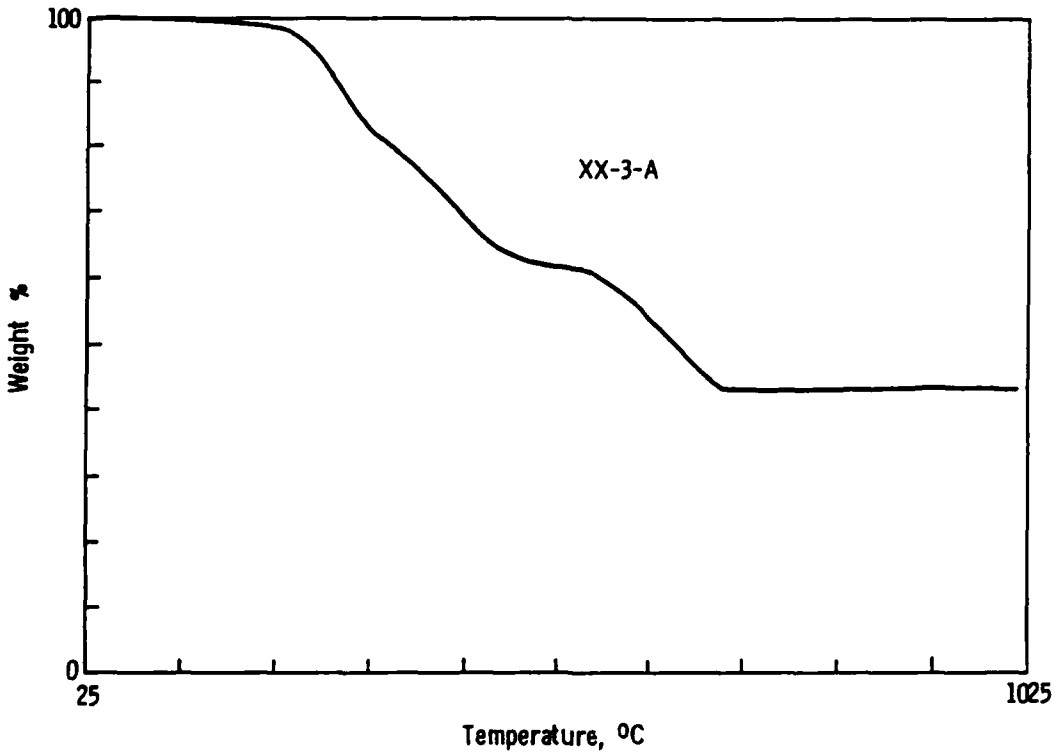

Figure 3a. TGA of XX-3-A.

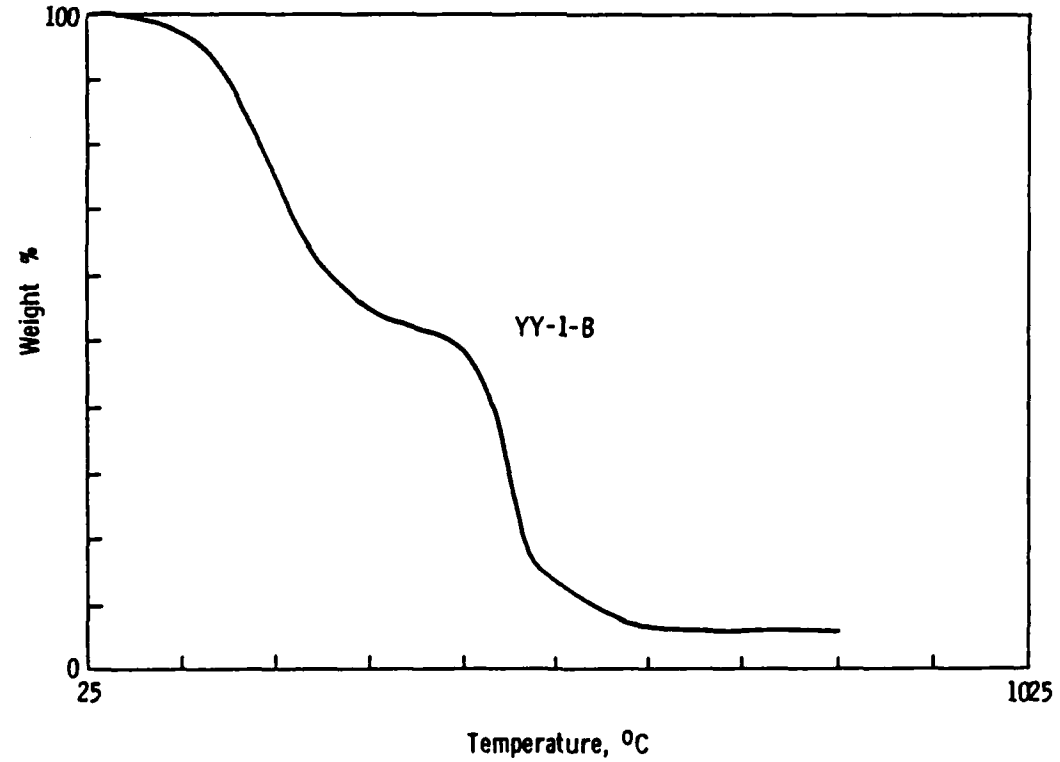

Figure 3b. TGA of YY-1-B.

Table 3. DIFFERENTIAL SCANNING CALORIMETRY (DSC) ADHESIVE EXOTHERM RESULTS

RESIDUAL HEAT OF REACTION, CAL/G
(EXOTHERM PEAK, °C)

Adhesive	RT Cure Time									
	0 hr	2 hr	4 hr	6 hr	8 hr	24 hr	48 hr	72 hr	7 Day	7 Day*
EA934	75.2 (100)	50.1 (104)	34.5 (108)	–	–	18.0 (116)	15.2 (118)	14.4 (116)	14.8 (118)	14.3 (117)
XX-0	83.7 (108)	61.1 (109)	46.3 (108)	–	–	31.2 (107)	30.2 (106)	28.8 (106)	27.1 (106)	27.9 (105)
XX-1	85.4 (104)	57.3 (106)	37.4 (108)	–	–	26.8 (107)	26.8 (106)	22.3 (104)	22.2 (105)	26.6 (106)
XX-2	83.9 (102)	56.8 (103)	39.7 (103)	–	–	24.8 (103)	28.9 (103)	27.1 (104)	25.3 (102)	26.4 (102)
XX-3	85.5 (108)	70.7 (109)	54.0 (109)	–	–	32.2 (108)	31.1 (106)	30.6 (107)	28.6 (105)	30.8 (106)
YY-1	85.2 (115)	69.1 (114)	52.9 (115)	–	–	32.4 (115)	27.5 (114)	27.0 (113)	24.2 (110)	27.2 (111)
YY-1	85.3 (114)	69.6 (113)	53.4 (112)	45.9 (113)	40.2 (112)	31.3 (112)	28.2 (112)	26.0 (112)	25.2 (109)	24.2 (110)
YY-2	82.7 (116)	64.1 (114)	49.9 (114)	–	–	29.7 (111)	25.9 (111)	24.1 (111)	22.3 (110)	22.3 (110)
YY-3	82.5 (115)	64.4 (115)	49.4 (115)	–	–	26.3 (114)	23.5 (114)	22.5 (113)	19.7 (109)	18.8 (111)

*Sealed for seven days

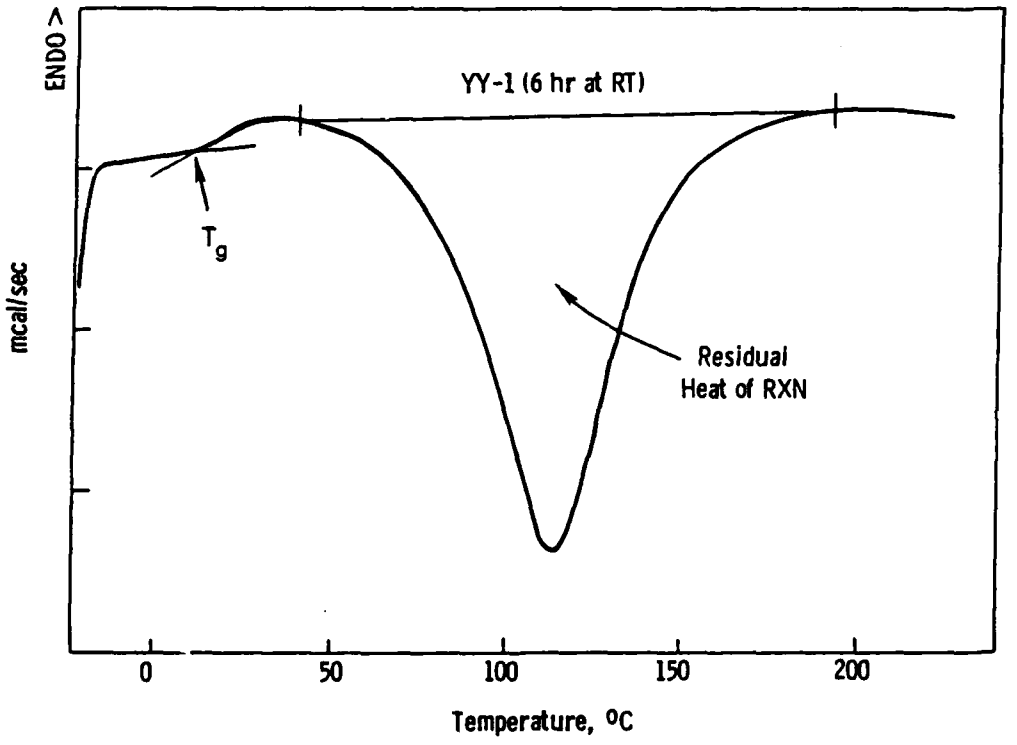

Figure 4. DSC scan.

Table 4. EXTENT OF REACTION BY DSC

Adhesive	RT Cure Time									
	0 hr	2 hr	4 hr	6 hr	8 hr	24 hr	48 hr	72 hr	7 Day	7 Day*
EA934	0	33%	54%	–	–	76%	80%	81%	80%	81%
XX-0	0	27%	45%	–	–	63%	64%	66%	68%	67%
XX-1	0	33%	56%	–	–	69%	69%	74%	74%	69%
XX-2	0	32%	53%	–	–	70%	66%	68%	70%	69%
XX-3	0	17%	37%	–	–	62%	64%	64%	67%	64%
YY-1	0	19%	38%	–	–	62%	68%	68%	72%	68%
YY-1	0	18%	37%	46%	53%	63%	67%	70%	70%	72%
YY-2	0	22%	40%	–	–	64%	69%	71%	73%	73%
YY-3	0	22%	40%	–	–	68%	72%	73%	76%	77%

*Sealed for seven days

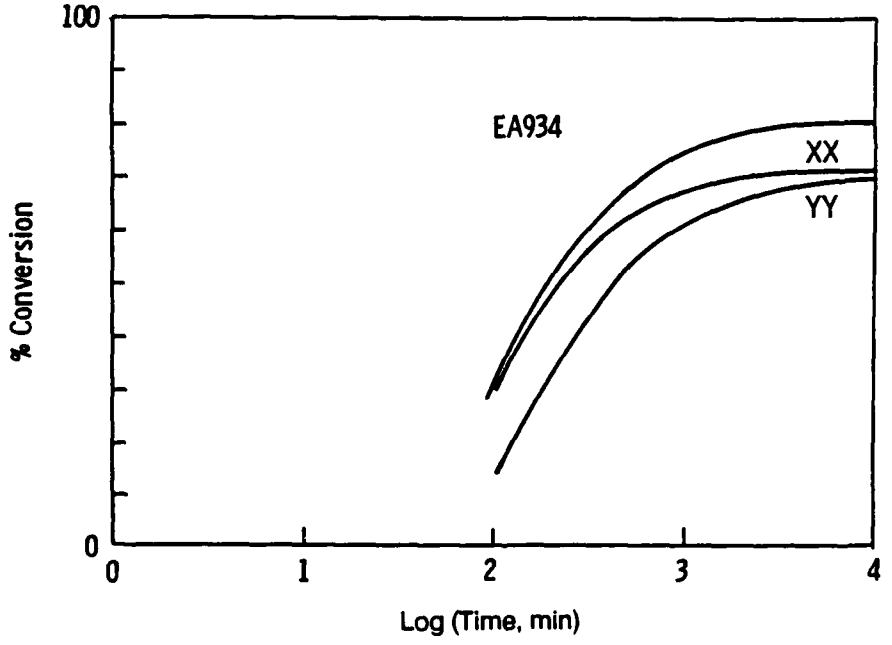

Figure 5. Extent of reaction by DSC.

Table 5. GLASS TRANSITION TEMPERATURES (°C) BY DSC

Adhesive	RT Cure Time 0 hr	2 hr	4 hr	6 hr	8 hr	24 hr	48 hr	72 hr	7 Day	7 Day*
EA934	†	-10	6	–	–	46	52	53	56	57
XX-0		-10	9	–	–	51	54	54	55	55
XX-1		-10	17	–	–	48	51	56	56	60
XX-2		-10	25	–	–	50	50	47	55	59
XX-3		†	11	–	–	47	52	55	57	58
YY-1			-7	–	–	46	51	56	56	59
YY-1			-3	10	23	44	51	53	56	58
YY-2			-2	–	–	45	52	56	59	58
YY-3			-1	–	–	42	50	50	56	55

*Sealed for seven days
†Not observed

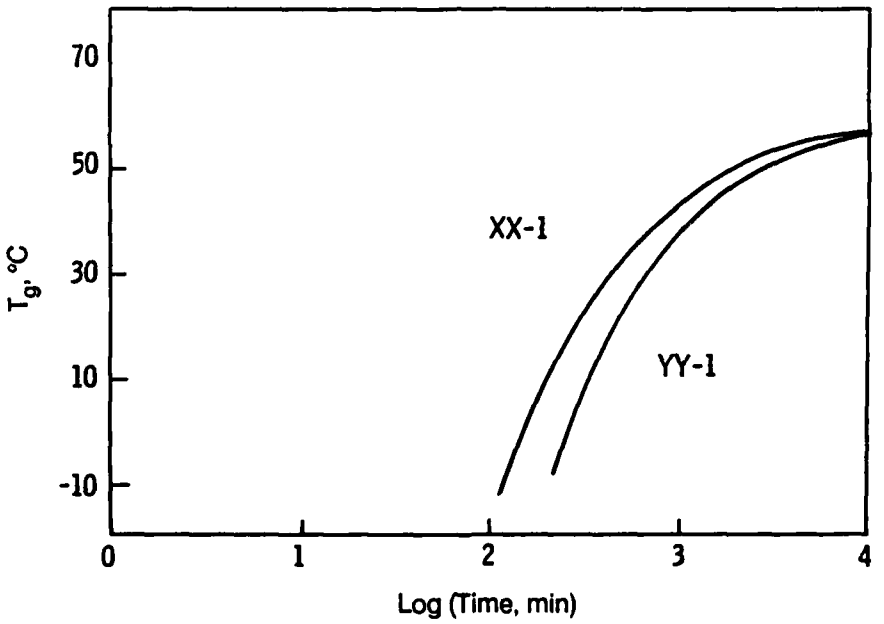

Figure 6. T_g by DSC.

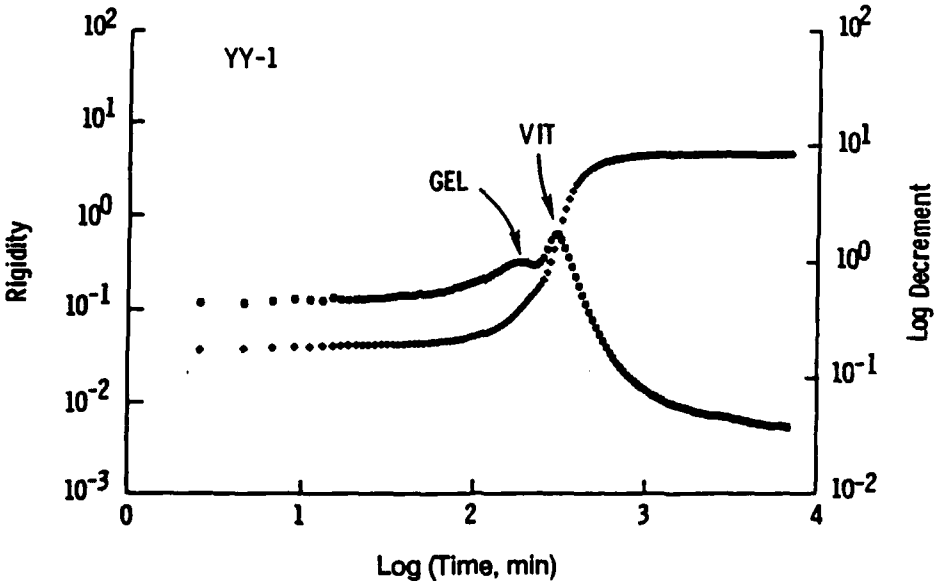

Figure 7a. TBA isothermal trace.

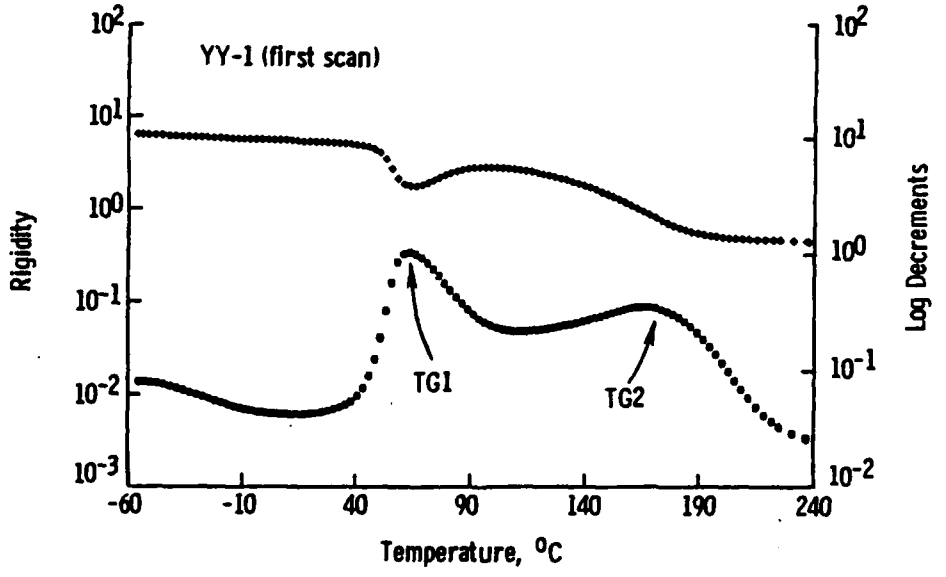

Figure 7b. TBA first heating scan.

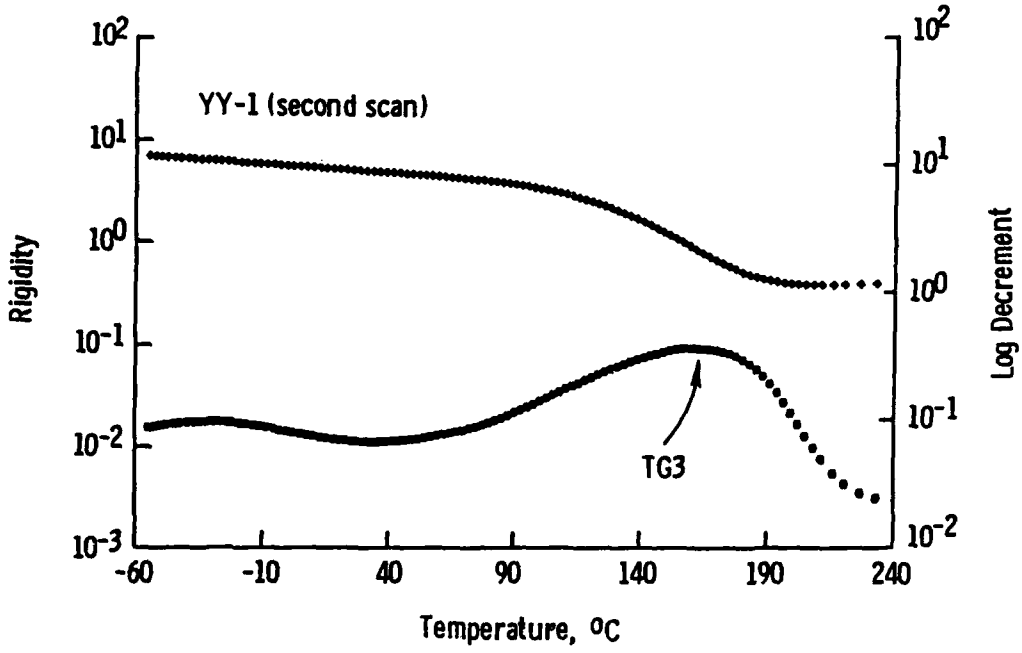

Figure 7c. TBA second heating scan.

Table 6. TORSIONAL BRAID ANALYSIS (TBA) RESULTS

Adhesive	Time to Gel (hr)	Time to Vit (hr)	TG1 (°C)	TG2 (°C)	TG3 (°C)
EA934	2.3	5.4	62	*	158
XX-0	1.7	2.9	66	152	155
XX-1	2.2	3.5	61	152	154
XX-2	*	2.2	62	173	166
XX-3	1.9	3.3	63	154	155
YY-1	2.9	5.1	64	181	178
YY-2	2.2	4.3	65	186	185
YY-3	2.0	5.1	67	196	195

*Not observed

All samples have essentially the same TG1 of 60°C to 65°C. These values appear to correspond to 40% to 50% conversion by DSC with YY again somewhat lower than XX. The exception to this is EA934 which occurs at a slightly higher value. These results indicate that vitrification begins to affect the cure behavior when less than half of the available functional groups have reacted. The XX adhesive has a lower TG2 and TG3 than YY, indicating the different fully cured networks formed by heating to higher temperatures. The glass transition temperatures are very broad and subject to some variation.

Batch-to-batch variations show no measurable gelation peak for XX-2 and XX-2 to vitrify sooner than XX-1 and XX-3. The gelation times indicate YY-1 reacts somewhat slower than either YY-2 or YY-3 and YY-2 to vitrify somewhat sooner than YY-1 and YY-3.

Typical viscosity vs time traces from PPR of XX-1, YY-2, and EA934 are shown in Figure 8. The initial viscosity values and the times to reach viscosities of 1,000 and 10,000 Pa-s are also shown in Table 7. The XX again appeared to react faster than the EA934 and YY, as observed by a faster increase in viscosity. The XX samples appear to have a slightly higher initial viscosity than the YY, but the differences can almost be attributed to the sample variation observed for duplicate runs. An investigation into the dependence of viscosity on frequency and strain, which would be necessary from a processing point of view, was not carried out. Batch-to-batch comparisons show XX-2 to react faster than XX-1 and XX-3 while YY-1 takes somewhat longer to reach higher viscosities than YY-2 and YY-3.

Table 7. PARALLEL PLATE RHEOMETRY RESULTS

Adhesive	Initial Visc (Poise)	Time to 10^3 Pa-s (min)	Time to 10^4 Pa-s (min)
EA934	1,700	62	118
XX-1	3,400	38	74
XX-2	3,400	27	66
XX-3	3,900	42	96
YY-1	3,500	66	141
YY-2	2,300	60	110
YY-3	3,000	55	106

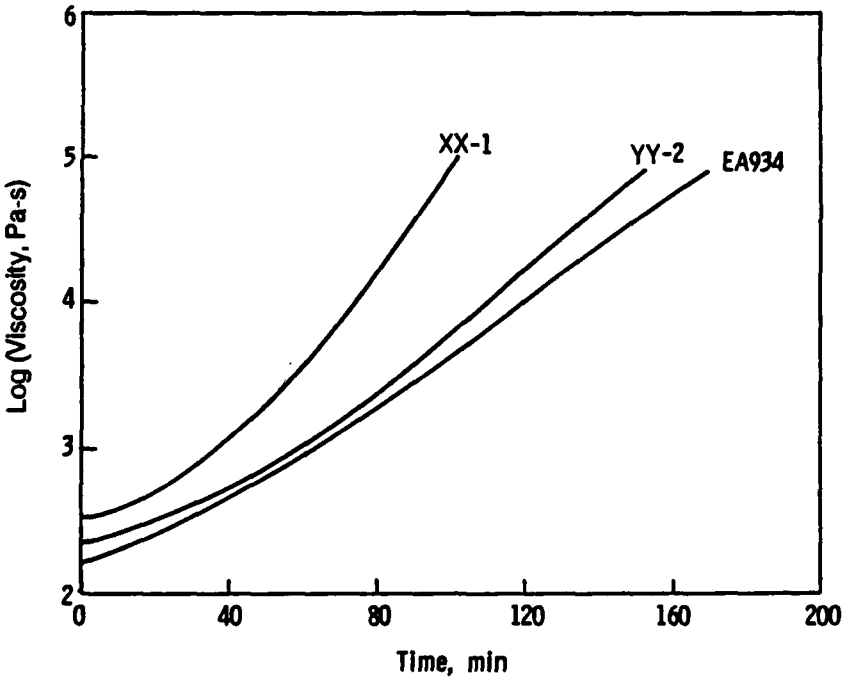

Figure 8. PPR of EA934, XX, and YY.

Microdielectrometry was also utilized to monitor the cure of XX-1 and YY-1. The dielectric loss factor versus time for samples of XX-1 and YY-1 is shown in Figures 9a and 9b, respectively. A faster initial decrease and approach to equilibrium in loss factor is observed for the XX-1 sample and indicates a faster cure. Duplicate runs showed only slight sample variation. Dielectric values were obtained from essentially the uncured through fully cured sample. This was a surprising result since the aluminum filler was expected to short the electrodes in the system. A significant amount of aluminum oxide was expected to be present. However, analysis of the filler from XX-2-A and YY-2-A revealed essentially all aluminum. The extremely thin layer of aluminum oxide on the surface of the filler is apparently enough to make dielectric measurements feasible.

In summary, DSC, TBA, PPR, and MDE all showed adhesive XX to cure faster than adhesive YY. TBA and PPR show EA934 and YY to have a similar cure behavior. DSC results indicate that XX cures at a similar rate as EA934 when comparing extent of reaction, and faster than EA934 when comparing T_g values. Adhesive YY cures slower than EA934 when comparing initial T_g values, but shows similar final values. Thus, the chemically similar adhesives XX and EA934 show some similarity in the extent of reaction and rate of T_g advancement behavior by DSC, but differ in the times to vitrification and the rate of viscosity rise. The chemically different YY and EA934 show similar times to vitrification and the rate of viscosity rise, but differ in the extent of reaction and rate of T_g advancement behavior by DSC.

The only lot-to-lot compositional difference observed for YY-3B did not appear to affect the curing behavior, but the YY-3 sample appeared to have somewhat less unreacted material after a seven-day cure than any other XX and YY. Generally, all the cure monitoring techniques showed XX-2 to cure faster and YY-1 to cure slower than the other respective lots. Only DSC showed XX-3 to cure slower.

All the cure monitoring techniques exhibited some scatter for duplicate runs with some of the scatter attributed to the small sample sizes utilized. Each technique is useful to the point where experimental error can account for the observed differences. All the techniques show relatively large initial changes before vitrification. After vitrification, continuing reaction can still be followed by DSC by monitoring the increasing T_g, where the change in extent of reaction is very small. TBA reveals a changing relative modulus and MDE experiments show changes in the dielectric properties which could be monitored well after vitrification. The parallel plate rheometry can only be utilized to approximately the gel point where the force generated in the geometry used begins to exceed instrumental limitation.

In all cases, vitrification appears to keep the adhesives from complete cure at room temperature. The similarity in the final T_g values for room temperature cures by DSC and TBA show little compositional effect. Only after a material was allowed to cure fully were compositional effects observed in the TG2 and TG3 values by TBA. The glass transition region of fully cured samples, as shown in Figure 7c by TBA, is apparently too broad and weak to be observed in a similar rescan by DSC.

Lot-to-lot differences were observed using the cure monitoring techniques when no compositional differences were revealed in the epoxy component. These differences appear greater than the variations observed due to mixing and room temperature. This suggests that differences in the amine component may account for the observations made. However, development of a technique to determine the amine composition would be necessary before this conclusion can be made.

This work also served to illustrate a variety of cure monitoring techniques and the stages of cure for which they may be useful. Figure 10 compares room temperature cure profiles for a sample of YY-1 from TBA, PPR, and MDE with the T_g data from the DSC scans. Information on the cure behavior can be obtained from TBA and MDE over the entire cure range. T_g development by DSC is observed to be a sensitive indicator of later stages of cure while extent of reaction by DSC and viscosity by PPR are more sensitive to the early stages. In addition, the frequency dependence of the MDE results can shift the greater rate of change of dielectric properties into the time range of interest.

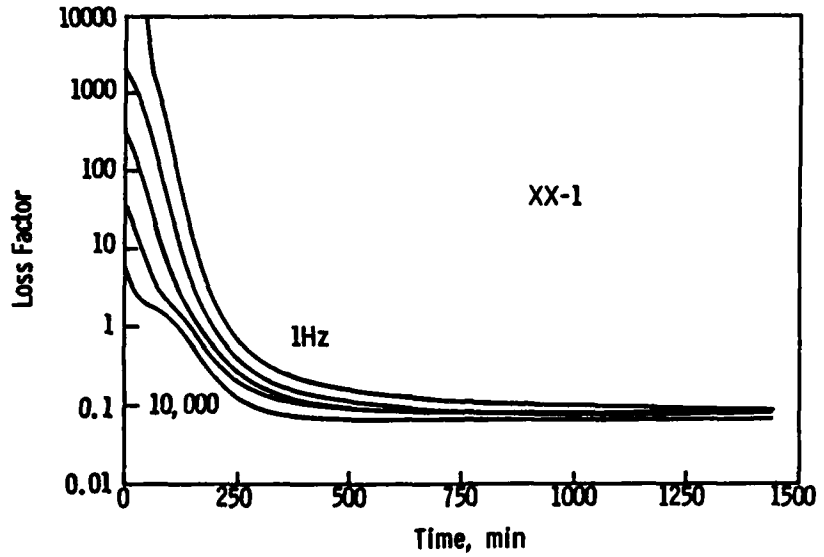

Figure 9a. Dielectric loss factor for XX-1.

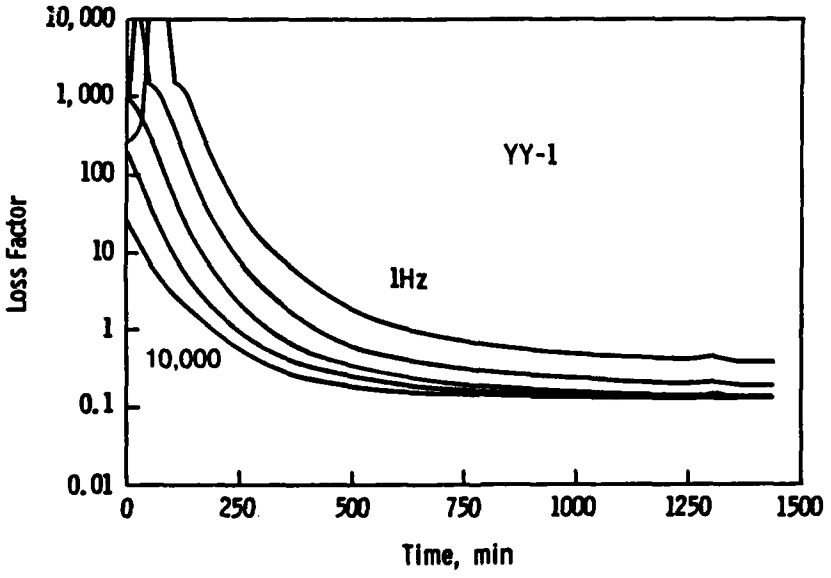

Figure 9b. Dielectric loss factor for YY-1.

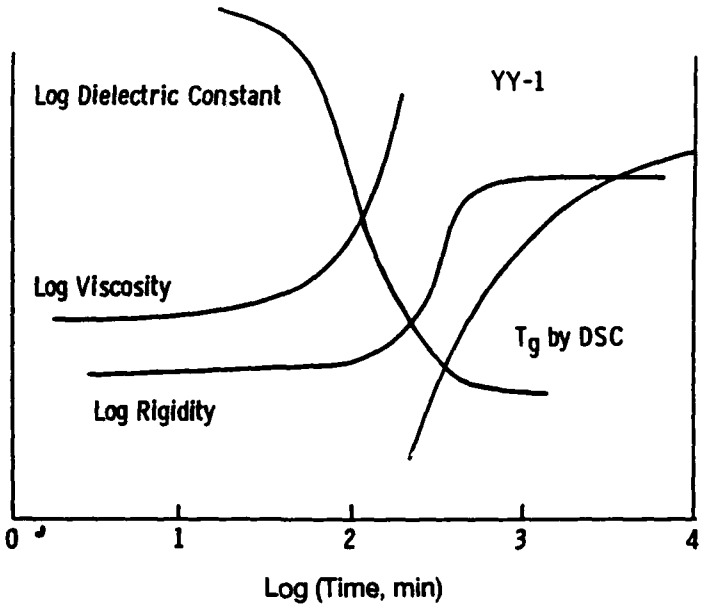

Figure 10. Cure monitoring techniques.

CONCLUSIONS

The composition and curing behavior of two adhesive formulations were compared to Hysol EA934 using a number of characterization techniques. HPLC, SEC, and TGA all show no significant lot-to-lot differences for the filled epoxy component of XX and YY. HPLC and SEC also show the soluble portion of XX-A to be quite similar to EA934-A and quite different from YY-A. Accurate determination of the composition of the amine component was not possible due to the insensitivity of the detectors used. Adhesive YY appeared to cure slower than the XX by DSC, TBA, and parallel plate rheometry, but showed similar cure behavior to the EA934 by the dynamic mechanical techniques used. Vitrification was observed to prevent any samples from completely curing at room temperature and the T_g of the partially cured systems was observed to be a sensitive measure of the advancing cure after vitrification. This work showed that some understanding of the cure behavior and variations in commercial systems could be developed through a choice of methods to measure the properties of greatest importance to a particular application or process.

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	Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
2	ATTN: SLCMT-TML
4	Authors

U.S. Army Materials Technology Laboratory
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