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NEW PROCESSABLE MODIFIED POLYIMIDE RESINS FOR ADHESIVE AND MATRIX APPLICATIONS

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A broad product line of bismaleimide modified epoxy adhesives which are cured by conventional addition curing methods are described. These products fill a market need for 232°C (450°F) service adhesives which are cured in a manner similar to conventional 177°C (350°F) epoxy adhesives. The products described include film adhesives, pastes and a primer. Subsequent development work has resulted in a new bismaleimide modified epoxy resin which uses an unique addition curing mechanism. This has resulted in products with improved thermomechanical properties compared to conventional bismaleimide epoxy resins. A film adhesive, paste and matrix resin for composites using this new technology is described. In all cases the products developed are heat cured by using typical epoxy cure cycles viz. 1 hour at 177°C (350°F) followed by 2 hours postcure at 246°C (475°F).

INTRODUCTION

Last year a broad product line of 232°-288°C (450-550°F) adhesives was described (ref. 1). These products process very easily using conventional epoxy curing conditions viz. 1 hour at 177°C (350°F) using minimum pressure (clamp or autoclave) followed by 2 hour postcure at 246°C (475°F). Two different chemistries have been used to develop these products although the base resin technology is bismaleimide modified epoxy. Table 1 summarizes some of the products which have been developed.

The "conventional BMI technology" in Table 1 refers to bismaleimide modified epoxy resins which are cured by addition methods as described in the literature (ref. 2). The "unique new BMI technology" in Table 1 refers to an addition curing mechanism which is not described in the literature and results in products with improved thermomechanical performance compared to other bismaleimide modified resins. We are still early in the development of a data base for these products, but from their neat resin properties, it is obvious that the unique new BMI technology has applicability to matrix resin for composites without attendant short out-life and volatiles/odor problems, as well as to adhesive applications.

The measurements and calculations were made in U.S. Customary Units.

RESULTS AND DISCUSSION

1. Hysol's Conventional BMI Technology Adhesives

The first film adhesive supported on a glass scrim fabric is EA9655. Table 2 shows some of its adhesive properties on various substrates. Some indication of thermal stability at 232°C (450°F) can be inferred from the tensile shear strength performance of EA9655 on aluminum substrates after 3000 hours at 232°C (450°F) as shown in Table 2. EA9655 has applicability in bonding honeycomb core materials and shows a moderate amount of peel strength (see Table 2).

The paste adhesives, EA9351 and EA9367 were developed for edge-filling and potting applications. EA9351 handles like a conventional epoxy paste which requires warming to about 49°C (120°F) for easy troweling. EA9367 is a syntactic paste version of EA9351 with a density of approximately 0.92 gm/cc. Table 3 shows some of the adhesive properties of these materials. Note that even with a cure of 2 hours at 177°C (350°F), EA9351 develops quite acceptable adhesive strength.

LR 100-581 was developed primarily as a protective coating which is applied by spraying. It is 20% by weight solids content, and is compatible with EA9655. Table 4 shows some of the properties of aluminum adherends treated with LR 100-581.

2. Hysol's Unique BMI Technology Adhesives

EA9673 is the designation for a film adhesive supported on a glass scrim fabric that is the unique bismaleimide modified epoxy which leads to improved thermomechanical properties. Table 5 shows some adhesive properties for EA9673 using different substrates. Basically, it gives good performance through the range 25°-287°C (77°-550°F). There also appears to be some limited strength characteristics at 360°C (680°F). In terms of thermal stability at 260°C (500°F) we have generated only one datum point after 700 hours. Further work on more suitable substrates is in progress. EA9673 also has remarkable outlife characteristics as shown in Table 6. A sample of the film adhesive was accidently left out on a benchtop and showed no loss of tack after 27 days in the open environment. Testing was carried out to 48 days with no loss of tack and retention of adhesive properties (Table 6).

A paste adhesive based on the unique bismaleimide modified epoxy chemistry has also been developed. LR 100-637 is a room temperture trowelable paste which has low slump during cure. Table 7 shows the adhesive properties of this material which should have similar outlife characteristics as for EA9673. In addition, a core splice (LR 100-633) material which expands 2.5 to 3.0 :1 during cure has been developed. The room temperature tube shear strength for LR 100-633 is 11.0 MPa (1.6 Ksi) when tested at room temperature. It would be anticipated that this strength would be maintained to 260°-287°C (500-550°F) based on results for EA9673 and and LR 100-637.

3. Bulk Resin Properties of EA9655 and EA9673

The Tg values for both EA9655 and EA9673 are shown in Table 8. These values were determined by thermomechanical analysis (TMA) on a Perkin-Elmer analyzer and by dynamic mechanical analysis (DMA) using a DuPont 981 DMA. Experience has shown that the DMA data is usually more reliable than TMA. Wet data refers to boiling castings of EA9655 and EA9673 in water for two days, and then rapidly carrying out the appropriate test.

Figures 1 and 2 show rheometrics plots for EA9655 and EA9673. EA9655 has a minimum viscosity of 41.6 poise at 177°C (350°F) and EA9673 has a minimum viscosity of 1.9 poise at 143°C (290°F). A lower viscosity version of EA9655 can be formulated, depending on application requirements. From this rheometrics data it is evident that EA9673 resin would be suitable for making prepreg materials.

Dog bone specimens for bulk tensile properties of EA9655 and EA9673 using the ASTM D638 testing procedure were prepared. Table 9 shows ultimate tensile strengths, modulus and elongation for these materials. As further confirmation of the EA9673 tensile property data, the variation of Young's modulus with temperature, both dry and wet, is shown in Figures 3 and 4. EA9673 appears to have dry properties suitable to at least 260°C (500°F) and wet properties to 210°C (410°F).

4. Matrix Resins

The resin used to make prepreg materials from EA9673 film adhesive is designated EA9102 as shown in Table 1. The chemistry of EA9102 is bismaleimide modified epoxy with the unique addition curing mechanism as noted earlier.

Table 10 shows short beam shear data obtained on unidirectional and woven graphite as well as Kevlar with EA9102 resin. The resin contents are a little high, but the main point is that the values obtained are consistent with use conditions as expressed for bulk castings. The 177°C (350°F) wet data on unidirectional graphite is lower than more recent data that has been generated at 32% resin content. This data suggest the short beam shear strength is closer to 63.4 MPa (9.2 Ksi). The woven graphite data shows little decrease in short beam shear strength in going from 177°C (350°F) dry to wet conditions.

Table 11 shows compressive data for EA9102 resin on woven Kevlar[R]. We believe that this data is very conservative due to difficulties in making good specimens for compressive tests. In addition, our compressive specimen jig was not absolutely true, so that some buckling deformation could occur. Nevertheless, the data probably represent the best compressive strengths reported for woven Kevlar[R] to date. We have reason to believe that our resin actually reacts with the surface of Kevlar[R] and therefore results in these improved compressive values.

A resin has also been developed for potential filament winding applications. This resin is still in preliminary evaluation and is denoted LR 100-617. The TMA data suggests that LR 100-617 has a Tg of approximately 274°C (525°F). Figure 5 shows a rheometrics profile for LR 100-617, and Figure 6 shows a time at temperature study for this material. This data suggests a reasonable winding temperature for LR 100-617 would be approximately 82°C (180°F). Further work on this resin is still in progress.

CONCLUDING REMARKS

A broad line of adhesives and resins which perform in the range of 232-287°C (450-550°F) have been developed. The new bismaleimide modified epoxy resin with the unique curing mechanism shows great promise for improved thermomechanical properties in such resins. This material is applicable to adhesive and matrix applications. Further work to define the long term thermal performance of these materials is in progress.

REFERENCES

1. Landman, D., "New Processable Polyimide Based Adhesives", First Technical Conference on Polyimides, SPE, Inc., Ellenville, NY (1982)

2. See for example: F. P. Darmory, "Processable Polyimides" in New Industrial Polymers, ACS Symposium, pp 124-44 (1974)

TABLE 1: Hysol's Bismaleimide Modified Epoxy Product Line

Conventional BMI Technology	New BMI Technology	Type of Product
EA9655	EA9673	Film Adhesive
EA9351	LR 100-637	Paste Adhesive
EA9367	———	Syntactic Paste Adhesive
———	LR 100-633	Core Splice
LR 100-581	———	Primer/Paint
———	EA9102	Matrix Resin
———	LR 100-617	Filament Winding Resin

TABLE 2: Some Adhesive Properties of EA9655 Film Adhesive at 488 gm/m^2 (0.1 psf) Weight

A. Tensile Shear Strength

Temperature/Condition, °C (°F)	Substrate	Tensile Shear Strength, MPa (Ksi)
25 (77)	Aluminum[a]	18.6 (2.7)
232 (450)	"	20. 2 (2.9)
232°C/aged 3000 hours @232°C	"	8.3 (1.2)
25 (77)	V378/graphite[b]	14.5 (2.1)
232 (450)	" "	13.0-16.5 (1.9-2.4)
25 (75)	PMR-15/graphite[c]	12.1 (1.8)
260 (500)	" "	10.3 (1.5)

B. Flatwise Tensile Strength

Temperature, °C (°F)	Substrate	Flatwise Tensile Strength, MPa (Ksi)
25 (77)	Aluminum	6.9 (1.0)
177 (350)	"	5.5 (0.8)
25 (77)	F178/graphite[d]	4.7 (0.7)
177 (350)	" "	4.8 (0.7)
25 (77)	F178/graphite	4.8 (0.7)
149 (300)	" "	4.8 (0.7)

C. Honeycomb Climbing Drum Peel at 25°C (77°F) on 2024 T3 aluminum face sheets (bare, FPL etched) and 5052 aluminum honeycomb core of 4.8 mm (3/16 in.) and 128 Kg/m^3 (8 pcf) density: 19 N-m/m (13.0 in. lbs./3 in. width)

NOTES:
(a) Adherends: 2024 T3 bare, FPL etched
(b) Product from U. S. Polymeric
(c) Product from NASA (Lewis)
(d) Product from Hexcel Corp.
(e) Cure cycle is 1 hour @177°C (350°F) with 0.17 to 0.34 MPa (25-50 psi) applied pressure, followed by postcure of 2 hours @246°C (475°F) with no applied pressure.

TABLE 3: Some adhesive properties of EA9351 and EA9367 on 2024 T3 bare FPL etched aluminum

Adhesive	Temperature, °C (°F)	Tensile Shear Strength, MPa (Ksi)	
		Cure A	Cure B
EA9351	25 (77)	16.0 (2.3)	13.8 (2.0)
"	177 (350)	--------	
"	232 (450)	14.0 (2.0)	--------
"	260 (500)	9.6 (1.4)	6.9 (1.0)
EA9367	25 (77)	13.8 (2.0)	--------
"	260 (500)	8.3 (1.2)	--------

NOTES: Cure A is 1 hour @177°C (350°F) with 0.17 MPa (25 psi) pressure, followed by 2 hours @246°C (475°F) postcure.

Cure B is 2 hours @177°C (350°F) with no postcure.

TABLE 4: Adhesive Properties of 2024 T3 bare FPL etched aluminum substrates primed with LR 100-581 and bonded with EA9655 at 488 gm/m^2 (0.1 psf) weight

Temperature, °C (°F)	Tensile Shear Strength, MPa (Ksi)		
	Primed		Unprimed
	Cure A	Cure B	
25 (77)	16.3 (2.4)	9.4 (1.4)	13.4 (1.9)
260 (500)	13.0 (1.9)	14.7 (2.1)	14.4 (2.1)

NOTES: Cure A - primer is cured 1 hour @177°C (350°F)

Cure B - primer is cured 1 hour @177°C (350°F) followed by 1 hour @246°C (475°F)

In both cases EA9655 is cured as shown in Table 2.

TABLE 5: Some Adhesive Properties of EA9673 Film Adhesive at 488 gm/m^2 (0.1 psf) Weight

A. Tensile Shear Strength

Temperature/Condition, °C (°F)	Substrate	Tensile Shear Strength, MPa (Ksi)
25 (77)	Aluminum[a]	13.8 (2.0)
232 (450)	"	13.1 (1.9)
232°C/aged 700 hours @260°C	"	12.4 (1.8)
260 (500)	"	15.2 (2.2)
288 (550)	"	13.1 (1.9)
316 (600)	"	3.4 (0.5)
25 (77)	V378/graphite[b]	12.4 (1.8)
232 (450)	" "	12.4 (1.8)
288 (550)	" "	12.4 (1.8)
22 (72)	PMR-15/graphite[c]	11.0 (1.6)
204 (400)	" "	11.0 (1.6)
260 (500)	" "	10.3 (1.5)
316 (600)	" "	2.1 (0.3)
360 (680)	" "	1.1 (0.16)

B. Honeycomb Climbing Drum Peel @25°C (77°F) on 2024 T3 aluminum face sheets (bare, FPL etched) and 5052 aluminum honeycomb core of 4.8 mm (3/16 in.) cell size and 128 Kg/m^3 (8 pcf) density:

19.4 N-m/m (13.3 in. lbs./3 in. width)

NOTES:
(a) Adherends: 2024 T3 bare, FPL etched
(b) Product from U.S. Polymeric
(c) Product from NASA, Lewis; postcure cycle in this case was 2 hours @288°C (550°F)
(d) Cure cycle is as shown in Table 2

TABLE 6: Outlife as a function of Tensile Shear Strength for EA9673

Conditions*	Tensile Shear Strength, MPa (Ksi)	
	25°C (77°F)	260°C (500°F)
Initial	13.8 (2.0)	15.8 (2.3)
After 27 Days	11.6 (1.7)	15.8 (2.3)
After 48 Days	15.0 (2.2)	15.8 (2.3)

* NOTES: Samples of tape left on bench at prevalent atmospheric conditions.
Substrates are FPL etched bare 2024 T3 aluminum.
Cure is as shown in Table 2.

TABLE 7: Some Adhesive Properties of LR 100-637 on 2024 T3 FPL etched bare aluminum

Temperature, °C (°F)	Tensile Shear Strength, MPa (Ksi)
25 (77)	11.7 (1.7)
232(450)	15.8 (2.3)
260 (500)	13.8 (2.0)
287 (550)	11.0 (1.6)

NOTE: Cure is 1 hour @177°C (350°F) with 0.17 MPa (25 psi) pressure, followed by 2 hours @246°C (475°F)

TABLE 8: Bulk Resin Tg Data for EA9655 and EA9673

Method	Tg, °C (°F)	
	EA9655	EA9673
TMA, Dry	253 (487)	299 (570)
TMA, Wet	109-118 (228-244)	
DMA, Dry	267 (512)	300 (572)
DMA, Wet		210 (410)

NOTES: TMA = Thermomechanical Analysis

DMA = Dynamic Mechanical Analysis

Wet = Casting immersed in boiling water for 2 days

TABLE 9: Tensile Properties for Bulk Casting of EA9655 and EA9673

Temperature, °C (°F)	EA9655	EA9673
Ultimate Strength, MPa, (Ksi)		
23 (75), dry	51.7 (7.5)	58.6 (8.5)
23 (75), wet	39.3 (5.7)	ND
177 (350), dry	26.9 (3.9)	43.4 (6.3)
260 (500), dry	ND	26.9 (3.9)
Modulus, GPa (Ksi)		
23 (75), dry	3.4 (493)	3.4 (493)
23 (75), wet	1.7 (247)	ND
177 (350), dry	1.6 (232)	1.8 (261)
Elongation (%)		
23 (75), dry	1.6	2.2
23 (75), wet	2.5	ND
177 (350), dry	2.2	3.3

NOTES: ND = Not Determined

Wet = 4 weeks @71°C (160°F) immersed in water.

TABLE 10: Short Beam Shear Data for Prepregs of EA9102 on unidirectional and woven graphite, as well as Kevlar R

Temperature, °C (°F)	Short Beam Shear Strength, MPa (Ksi)		
	Unidirectional Graphite	Woven Graphite	Woven Kevlar R
23 (75)	130.2 (18.9)	55.1 (8.0)	37.9 (5.5)
177 (350), dry	91.6 (13.3)	40.7 (5.9)	22.7 (3.3)
177 (350), wet	55.1 (8.0)	35.1 (5.1)	ND

NOTES: (a) Unidirectional graphite is Courtaulds E/XA-S, 6K high strain fiber with resin content 39.5%; void content, 0%; lay-up, $(0°)_{15}$

(b) Woven graphite is Celion 3K/8HS with resin content, 37.4%; void content, 1.0%; lay-up, $(0°)_8$.

(c) Woven Kevlar R is style 285 Kevlar R 49 with resin content, 45.Ø%; void content, 1.0%; lay-up, $(0°)_8$.

(d) Cure cycle: Heat up at 1-3°C (2-5°F) per minute to 113°C (235°F) with pressure of 0.7 MPa (100 psi); hold 1 hour @113°C (235°F); heat up at 1-3°C per minute to 177°C (350°F); hold for 1 hour at 177°C; cool to 66°C (150°F) and postcure in an oven at 246°C (475°F) for 2 hours.

(e) Wet = Sample immersed in boiling water for 2 days.

(f) ND = Not Determined.

TABLE 11: Compressive Strengths for EA9102 on woven Kevlar R

Temperature, °C (°F)	Compressive Strength, MPa (Ksi)
23 (75)	229.4 (33.3)
177 (350)	148.1 (21.5)

NOTES: (a) Woven Kevlar R as noted in (c) of Table 10

(b) Cure cycle as noted in (d) of Table 10

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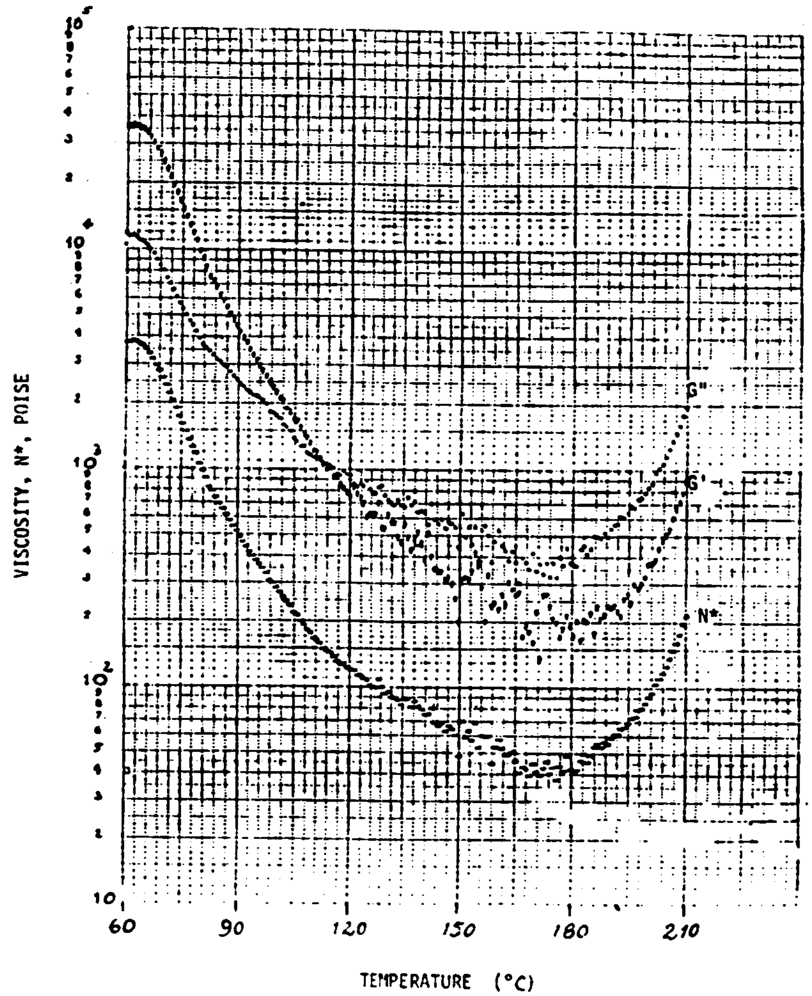

Figure 1. Rheometrics plot for EA9655 resin.

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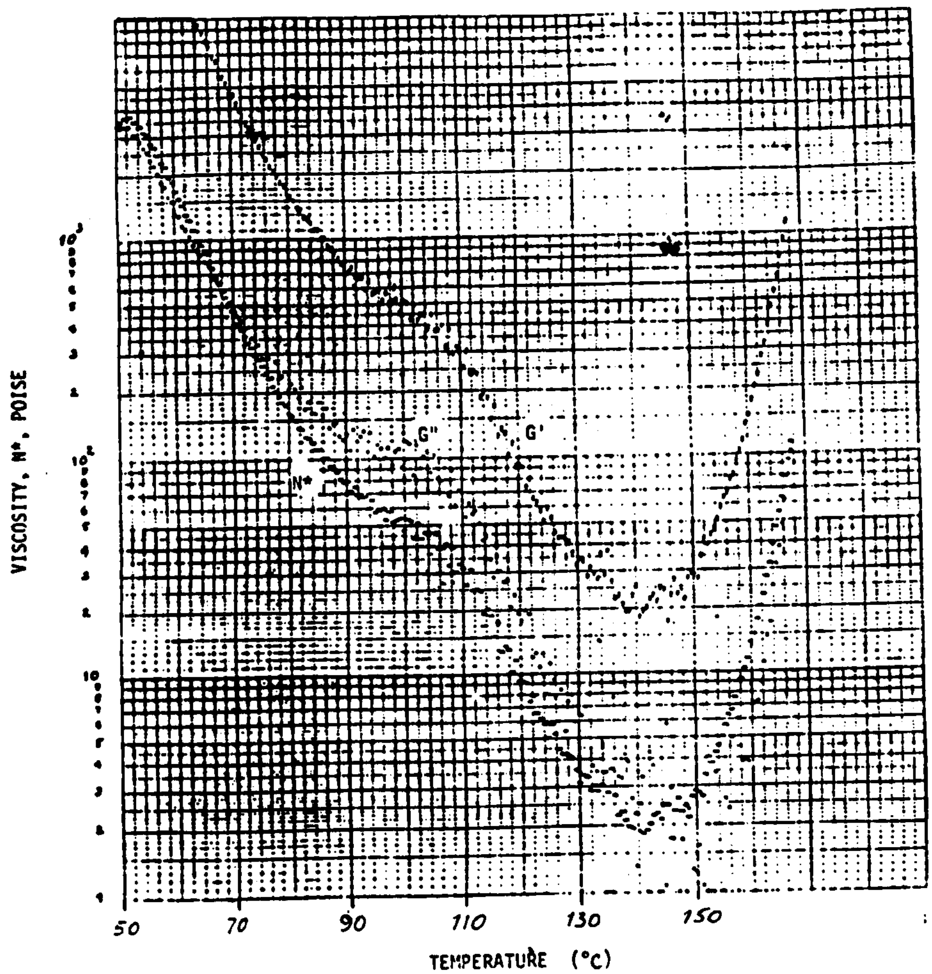

Figure 2. Rheometrics plot for EA9673 resin.

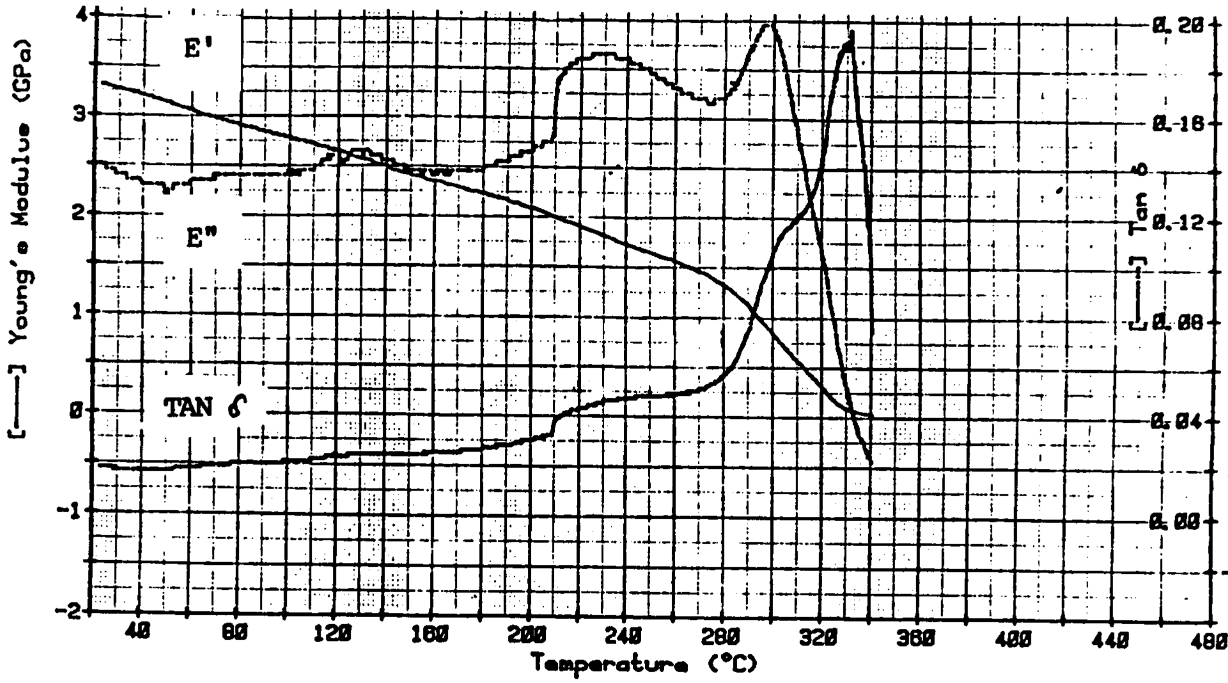

Figure 3. Dynamic mechanical analysis of EA9673, dry.

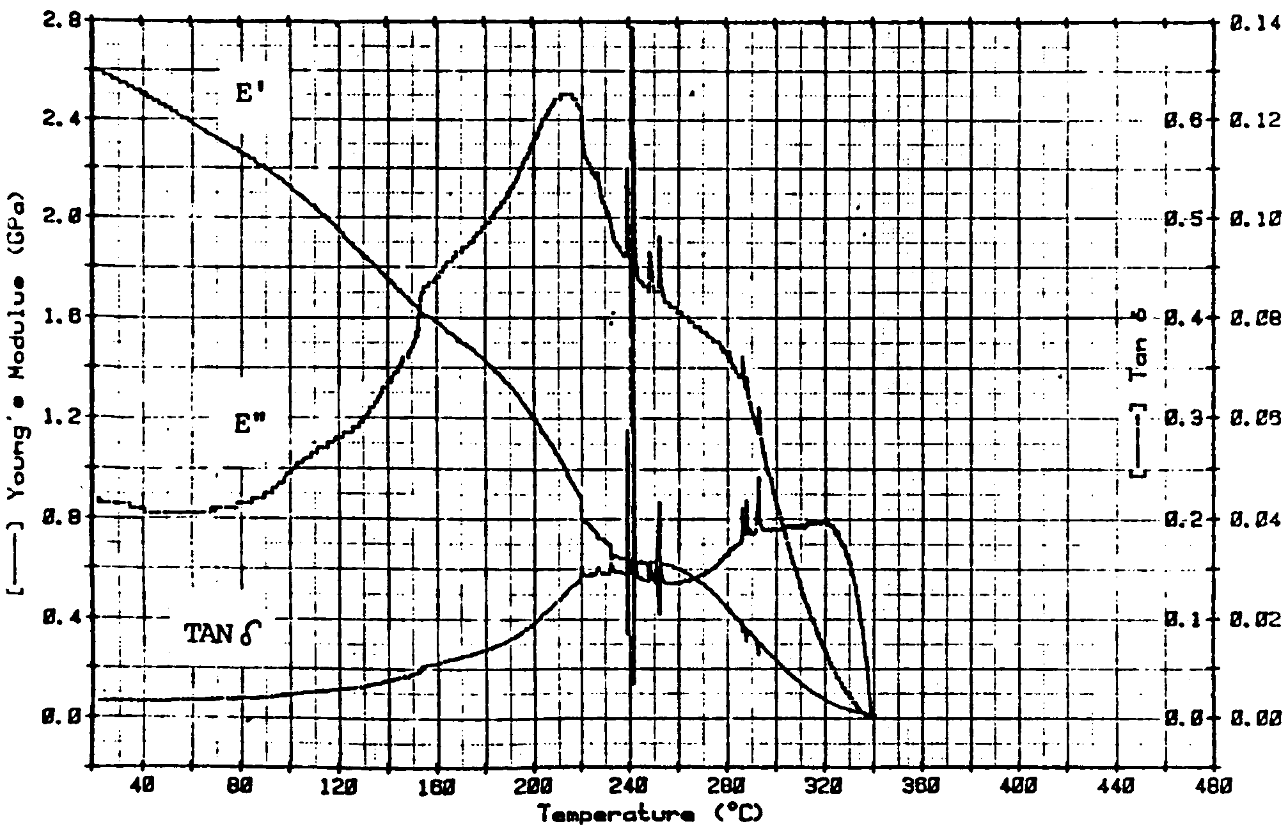

Figure 4. Dynamic mechanical analysis of EA9673, wet. Note, there is a scale difference for Young's modulus compared to figure 1.

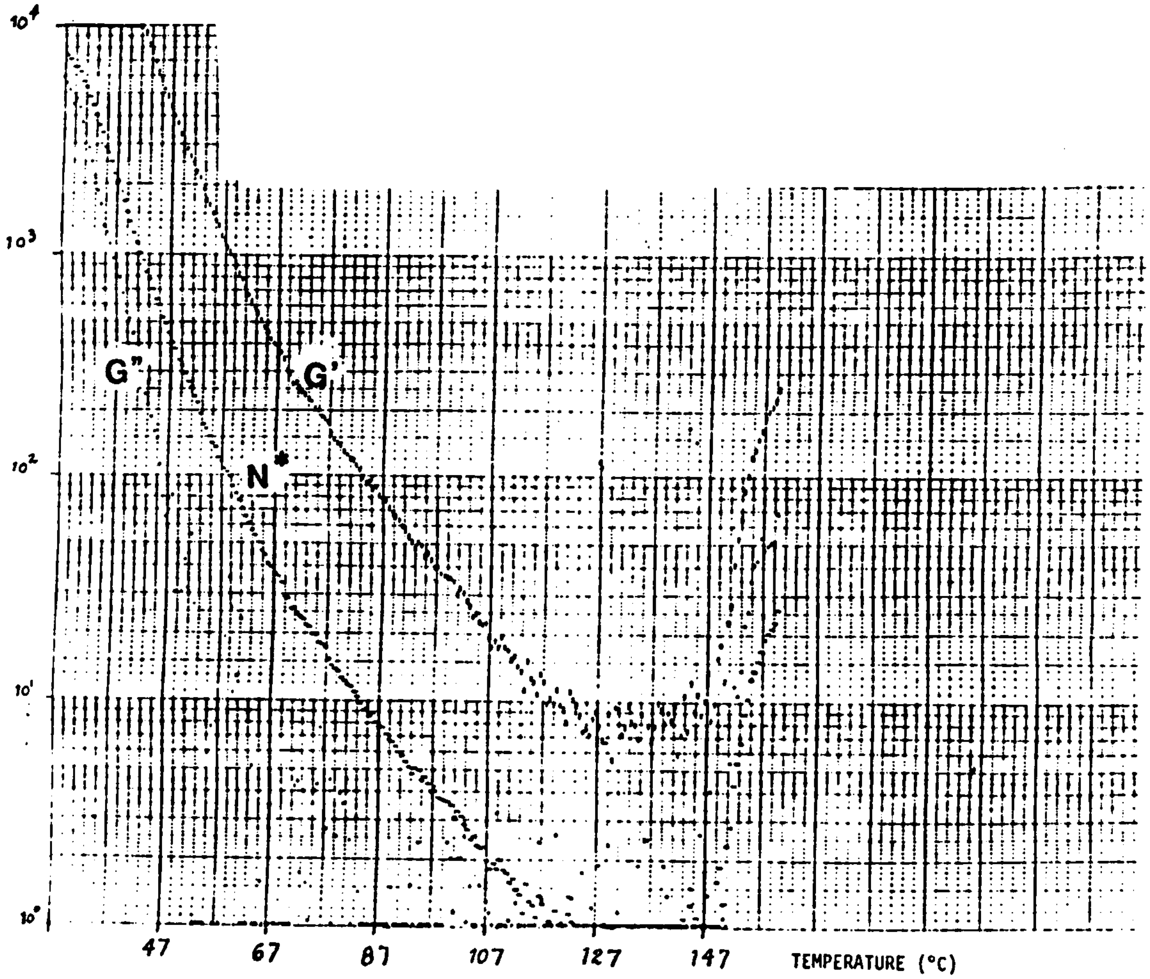

Figure 5. Rheometrics profile as function of temperature for LR100-617.

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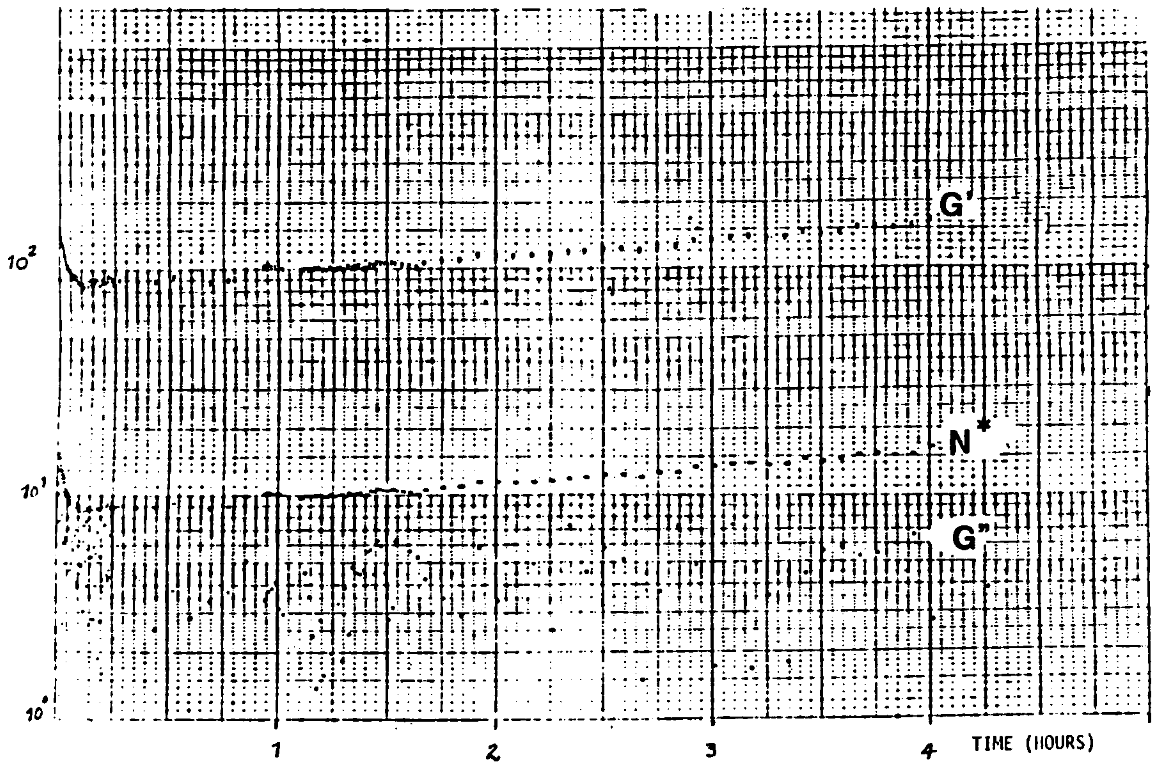

Figure 6. Rheometrics profile for LR100-617 kept at 82 °C.