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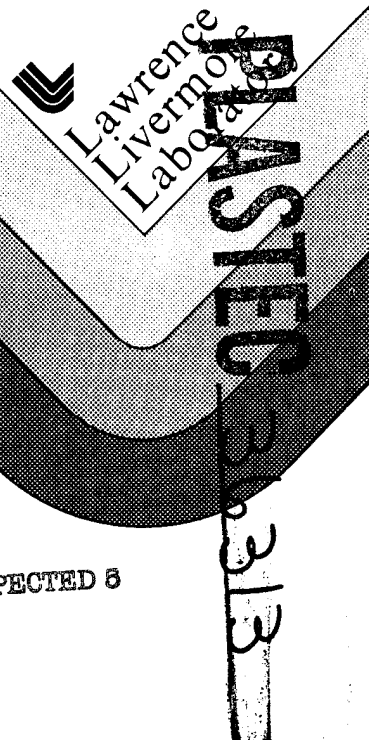
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# A Cycloaliphatic Epoxy Resin/Anhydride System Usable up to 150°C\*

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We determined the physical and mechanical properties of a cycloaliphatic epoxy resin that was cured using a liquid anhydride plus 1-methylimidazole as a catalyst. The resin system has a low viscosity and a long gel time, making it suitable for wet filament winding. The system cures at low temperatures (100-120°C) to yield strong, high modulus resins. High glass transition temperatures (>200°C) can be achieved with curing at 150°C. The cost of the resin system is low compared to other elevated-temperature resins. Data on aging at 150°C in air are presented.

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## Introduction

A fiber-reinforced epoxy resin composite with high tensile strength and light weight offers many advantages as a construction material for flywheels.<sup>1,2</sup> Filament winding is a convenient way to make such flywheels. The resin matrix selected for such an application should have good processing properties, such as low viscosity and long pot life; it should also be inexpensive. When cured it should have high strength and good strength retention up to 150°C in high vacuum.<sup>3</sup>

We chose and characterized a resin system based on a cycloaliphatic epoxide resin cured with a cycloaliphatic anhydride that meets the requirements of strength at temperatures up to 150°C and low cost.

## Experimental Details

The chemical structure and parts by weight of each component in the resin system are given in Table I. The relative weights of the epoxide resin (epoxide value 0.73 eq/100 g) and the anhydride provide about 82% of the anhydride needed for a 1:1 anhydride to epoxy group stoichiometry. A bisphenol A diglycidyl ether resin with an amine-promoted anhydride gives the best results at a 1:1 anhydride to epoxide ratio. However, cycloaliphatic epoxy resins give better results with about 0.85:1 stoichiometry because there is considerable epoxy to epoxy polymerization.

The viscosity of the freshly mixed components was measured with a Brookfield Model LVT\* rotating spindle viscometer. The pot life (i.e., time required for 30 g of the gelling resin mixture to support a 6-g weight for 15 s at 25°C) was determined with a gel timer.

Tensile, compressive, and torsional shear properties were determined from samples cut from cast sheets of the cured resin. Most of the test samples were taken from a single cure cycle (2 h at 90°C plus 4 h at 150°C). Tensile tests were conducted as described in Refs. 4-6. For compressive tests, solid cylinders 50.8 mm long by 12.7 mm in diameter were each fitted with two extensometers and tested on a universal testing machine (see Ref. 7 for test details).

For torsional tests, cylinders 127 mm long by 6.35 mm in diameter were mounted into end fixtures and the end of each specimen potted with adhesive in the fixture hole (33 mm long by 7.0 mm in diameter). To prevent slippage during loading, a 3-mm-diameter pin was slipped into a hole, machined to exact size, through both the diameter of each end of the specimen and the metal end-fixture located 6.35 mm from the end. Then, the center of the specimen was fitted with a torsion extensometer, placed where it would not experience end effects. The bottom fixture was rotated during the test to give a known stress; the top fixture was rotationally fixed but was allowed to float free vertically.

Heat capacity of the cured resin was determined with the DuPont differential scanning calorimeter, using sapphire as a standard. Thermal transition points (glass-transition temperatures) were determined by measuring the dynamic shear modulus at 0.1 Hz with a Rheometrics mechanical spectrometer. Heat distortion temperature was determined as per ASTM D648-72.<sup>5</sup> A modified version of the ASTM E228 test procedure was used for measuring the linear thermal expansion.<sup>8</sup> The interaction of the cured resin with water was checked on plate specimens measuring 25.4 by 25.4 by 2.85 mm as per ASTM D570.<sup>9</sup>

The thermal conductivity was measured using a double-stack axial heat-flow-system. A single measurement requires two specimens each with a diameter of 101.6 mm and equal thickness. Specimens are placed between auxiliary and main heaters, with insulators and cold plates. The auxiliary heaters control the base temperature of each specimen and the main heater maintains the temperature gradient. Two type-K thermocouples are needed. One is placed between each specimen surface and a 1.54-mm-thick copper plate. The

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copper plate is grooved to match the length and width of the thermocouple, i.e., 12.7 mm wide and 50.8 mm long. The voltage across the main heater is monitored at its leads, and current is determined from the voltage drop across a precision series resistor. Good thermal contact was made under a load of 10 psi (0.07 MPa) and measurements were then taken.

Infrared spectra were obtained using a Nicolet Model 7199 FTIR with NaCl plates. For this curing study, the mixed resin was placed between the salt plates and the first spectrum run at room temperature. A total of 100 scans was recorded for all spectra. After the first spectrum was recorded, the sample cell was placed in a 90°C forced-air oven for 0.5 h and then cooled to 23°C before the second spectrum was recorded. This process was repeated three more times so the sample was exposed to 90°C for a total of 2 h. The sample then was additionally cured for 0.5 h at 150°C followed by 0.5 h at 190°C.

Dielectric analyses were performed on an Audrey Model 202 dielectric spectrometer in the frequency range 100-1000 Hz. Samples were placed in an oven at 23°C and the temperature programmed through the cure cycle.

## Results and Discussion

The cycloaliphatic epoxy resin used in this formulation offers the advantages of low viscosity, low cost, and high glass-transition temperature when properly cured. Because cycloaliphatic epoxy resins cannot be cured with amines, they are generally cured with anhydrides. The particular anhydride we chose to use has the following favorable features: it is a liquid at room temperature, it provides good high-temperature performance, and it is inexpensive. In addition to the epoxy resin and anhydride, we added a small amount of liquid rubber (CTBN, carboxy-terminated butadiene acrylonitrile) to decrease brittleness but not to lower the glass-transition temperature significantly.

The catalyst was an imidazole to allow curing at relatively low temperatures and yet achieve high glass-transition temperatures. We evaluated several catalysts for this resin system before we selected 1-methylimidazole. The first catalyst we used was a chromium compound that yielded glass-transition temperatures  $T_g$  equal to  $T_c + 15^\circ\text{C}$ , where  $T_c$  is the maximum cure temperature and is greater than  $140^\circ\text{C}$ . Because imidazoles are also known to catalyze this reaction, we tested the well-known imidazole 2-ethyl, 4-methylimidazole, EMI-24, and found that it gave  $T_g = T_c + 60^\circ\text{C}$ . This had the advantage of allowing lower cure temperatures and yet achieving a high glass-transition temperature. A high  $T_g$  was also obtained with each of the other imidazoles; of these, the 1-methylimidazole (IMI) produced the fastest cure at  $60^\circ\text{C}$ , shown by the viscosity increase vs time plot (Fig. 1). We also used methyl-hexahydrophthalic anhydride (MHHPA) and a higher level of CTBN than in our standard formulation. Equivalent results for methyl-tetrahydrophthalic anhydride (MTHPA) are shown in Fig. 2. In this figure we see that hydroxyl-containing compounds are not necessary for rapid reaction at  $60^\circ\text{C}$ . The gel time for the system CY179/CTBN/MTHPA/IMI at various temperatures and imidazole concentrations is given in Table 2. The cycloaliphatic epoxy-anhydride reaction rate can be further increased by increasing the concentration of catalyst. The time to reach viscosity of  $1.0 \text{ Pa}\cdot\text{s}$  at  $25^\circ\text{C}$  can be reduced from 14 h for 1 part IMI to 3.5 h for 8 parts. Viscosity vs time for these data are shown in Fig. 3. The viscosity of the freshly mixed components of the system finally chosen (Table 1) is only  $0.38 \text{ Pa}\cdot\text{s}$  and this increases to  $0.72 \text{ Pa}\cdot\text{s}$  after 8 h at  $25^\circ\text{C}$ . Gel time at  $25^\circ\text{C}$  is 43.7 h.

The curing reaction of CY179/CTBN/MTHPA/IMI (100/5/100/1, parts by weight) was studied and curing measured by infrared spectroscopy (IR) and dielectric analysis. The IR spectra yield quantitative information on the consumption of epoxy and anhydride, whereas the dielectric analysis yields qualitative information on the state of cure and resin flow properties. The results from both methods were consistent with each other. The infrared spectra were obtained using a high-resolution FTIR (Fourier transform infrared)

spectrometer from 580 to 4000  $\text{cm}^{-1}$ . Spectra of the uncured and cured resins are shown in Fig. 4, these spectra show that several peaks could be used to follow the reaction. However, only the anhydride peak at 1778  $\text{cm}^{-1}$  is both strong and not interfered with by another peak. The CY179 has a very strong peak at 1728  $\text{cm}^{-1}$  that could be very useful for following the epoxy reaction. However, in this case, a peak develops at 1733  $\text{cm}^{-1}$  due to the ester from the anhydride epoxy reaction that is not resolved from the 1728- $\text{cm}^{-1}$  peak. By measuring the area ratio  $A/A_0$  of the 1778- $\text{cm}^{-1}$  peak, we can follow the epoxy anhydride reaction and find that after 1 h at 90°C, 94% of the anhydride has reacted (Figs. 5 and 6). After additional cure of 0.5 h at 150°C, all the anhydride has reacted. Other measurements using the weak epoxide peaks at 1309 and 789  $\text{cm}^{-1}$  yield qualitative results consistent with those from the 1778- $\text{cm}^{-1}$  peak. We see that this resin system is very reactive at 90°C and that complete reaction is achieved quickly at 150°C or less. The standard cure cycle we used, 2 h at 90°C plus 4 h at 150°C, is very conservative, and shorter cycles can be used without decrease in physical or mechanical properties.

Dielectric analysis was used to confirm the curing of this resin system using the standard cure cycle. The data yielded (Fig. 7) show that an essentially complete cure is achieved after 2 h at 90°C, with only a small amount of curing at 150°C and no further curing at 200°C. Because the procedures in the infrared and dielectric tests are different, the times are not directly comparable.

The test results for the cured resin system are summarized in Table 3. Most of the values are self-explanatory but some require further explanation and elaboration. Tensile properties were used to follow the effects of several variables on the cured resins, namely temperature, CTBN flexibilizer concentration, anhydride stoichiometry, cure cycle, and aging at 150°C. The effect of temperature on tensile strength is illustrated in Fig. 8 for temperatures from -40 to 150°C. These tests were performed on the standard formulation with 5 parts CTBN. Some preliminary tests at elevated temperatures were also performed on resin formulations at 10 and 15 parts CTBN; the data are shown in Table 4. The decision to characterize the resin system with 5 parts CTBN was based on the higher tensile strength and modulus of this formulation at 150°C. This formulation does not experience any decrease in strength or modulus until the temperature exceeds 100°C, when the stress at maximum begins to decrease and the failure strain increases (Table 3). Increasing the amount of CTBN, which is in the formulation to increase fracture toughness, lowers the modulus and the maximum stress at elevated temperatures. It also lowers the heat distortion temperature—170°C with 5 parts CTBN and 161°C with 10 parts.

The effect of further increasing the CTBN content is shown in Fig. 9, where the stress-strain curves at 25°C are plotted for 5, 15, and 30 parts CTBN. The higher CTBN levels increase the toughness of the resin system.

The effect of curing the resin at a lower temperature for a longer time on the tensile properties of the system is shown in Table 5. The long cure at lower temperatures slightly increases the modulus, the maximum stress, and the maximum strain. These results demonstrate the effectiveness of IMI to catalyze the cure of this resin system at these low temperatures and still achieve a high glass-transition temperature.

The effect of anhydride concentration on the tensile properties is shown in Table 6. At 25°C, no differences are discerned because of the brittle nature of the resins; however at 150°C trends are noted. As the MTHPA concentration is increased from 90 to 110 parts, the strength and modulus increase and the failure strain decreases.

It is estimated that during a 10-y period a flywheel may be at 150°C only for short periods, but this adds up to a total of about 3 mo at 150°C. Consequently, we determined the effect of aging up to 3 mo in a forced air oven at 150°C. Samples were tested at both 25 and 125°C after various periods of aging at 150°C; tensile properties and glass-transition temperatures are shown in Table 7.

On aging in air at 150°C, the modulus and  $T_g$  increase slightly, and the maximum stress and maximum strain drop when tested at 25 and 125°C. Most of this degradation is probably the result of oxidation

and not thermal instability.<sup>10</sup> In the flywheel application the degradation should be much less because of the vacuum and if care is taken to assure that the residual gas present is inert, e.g., helium.

While this system has many desirable properties—low viscosity, long pot life, strength, and high heat distortion temperature—it has one potential negative feature. Water absorbed during the filament winding process can adversely affect the curing process by reacting with the anhydride and converting it to a dibasic acid. In its cure by the anhydride, the epoxide group is essentially difunctional, i.e., when the epoxide group reacts with the anhydride or homopolymerizes, it is connected in the crosslinked network by two covalent bonds. If the epoxide group is cured by reacting with a dibasic acid, however, it is monofunctional, i.e., it is connected in the crosslinked network by only one covalent bond. Thus, any water absorbed during processing can result in a lower crosslink density for the cured system. In an experiment using MHPA, measured amounts of water were added to the system before curing and the glass-transition temperatures were measured on the cured resin. The results are plotted in Fig. 10. If no water was added, the glass-transition temperature was 185°C; if 1% water was added, it was 160°C; and if 2.3% was added, it fell to 137°C. There was a 20-25°C reduction in  $T_g$  for each 1% water added. In Fig. 6, we also see the reduction in crosslink density resulting from the presence of water. The shear modulus at temperatures above  $T_g + 40^\circ\text{C}$  is directly proportional to the crosslink density (from the theory of rubber elasticity). In this series, the dynamic shear modulus at  $T_g + 40^\circ\text{C}$  with 0, 1, and 2.3% water are 9.0, 4.0 and  $1.2 \times 10^6$  Pa, respectively, showing a decrease in crosslink density with increasing water content.

The effect of added water was also determined on the MTHPA-cured system. For this resin system, we added 1% water to the standard formulation and cured the resin for 2 h at 90°C plus 4 h at 150°C. Tensile tests at 25°C showed a reduction in modulus, maximum stress, and strain at maximum, while specimens tested at 125°C showed no reduction in maximum stress, an increase in strain at maximum, and a reduction in modulus (Table 8).

While the water pickup during processing is a problem, it can be handled. (Filament wound systems cured with anhydrides are used successfully in several commercial operations.) All contact with water must be avoided and the humidity in the process area must be controlled. Even if the water absorption is not reduced to zero, it should be controlled so that the effect is consistent.

We measured the dynamic shear modulus on the cured resin from -150 to 250°C. These measurements confirmed the trends of the tensile results and extended the temperature range over which we observed these trends. The shear modulus is approximately constant, decreasing by about a factor of two from -50 to 150°C. This range is the region of most interest to flywheel designers. Results of these shear modulus measurements are presented in Fig. 11. We see that the glass-transition temperature for this resin cured at 150°C is above 200°C. The moderate size of the modulus peak loss from -110 to -50°C shows that this resin is more brittle than typical amine-cured epoxy resins.

The coefficient of thermal expansion was measured by the method, ASTM-228 modified, from -50 to +175°C. Over this range, the expansion is nearly linear from -25 to 70°C and has a value of  $6.4 \times 10^{-5}$  cm/cm/°C. Over the entire range from -50 to 175°C the average value is  $7.4 \times 10^{-5}$  cm/cm/°C (Fig. 12).

One interesting aspect of this resin system is shown by the density data for the uncured and cured resin (Table 2). The density difference is less than 1%. This shows that the resin has very low shrinkage compared to amine-cured epoxy resins; normal shrinkage is on the order of 5-7%. This low shrinkage probably results from opening of the anhydride ring on curing which leads to a much lower reduction in volume. A resin system with such low shrinkage can be very useful in some applications, such as potting resins.

The thermal conductivity was measured from -40 to 180°C. Results present in Fig. 13 show that although the first test run differed from the second and third, overall the data is consistent.

## References

1. R. F. Post and S. F. Post, "Flywheels," *Sci. Amer.* **229**(6), 17 (1973).
2. *Proc. 1977 Flywheel Technology Symp., October 1977, San Francisco, CA*, U.S. Department of Energy, CONF 771053 (1978).
3. M. Baer, "Aerodynamic Heating of High-Speed Flywheels in Low-Density Environments," *Proc. Mech. Magn. Energy Storage Contractors Rev. Meet., October 1978, Luray, VA*, U.S. Department of Energy, CONF 781046
4. T. T. Chiao, A. D. Cummins, and R. L. Moore, "Fabrication and Testing of Epoxide Resin Tensile Specimens," *Composites* **3**(10), 10 (1972).
5. "Standard Method of Testing for Tensile Properties of Plastics," in *1973 Annual Book of ASTM Standards*, Part 27, ASTM D638-72.
6. "Standard Method of Test for Flexural Properties of Plastics," in *1973 Annual Book of ASTM Standards*, Part 27, ASTM D790.
7. "Standard Method of Test for Compressive Properties of Rigid Plastics," in *1973 Annual Book of ASTM Standards*, Part 27, ASTM D695-69
8. "Standard Test Method for Linear Thermal Expansion of Rigid Solids with a Vitreous Silica Dilatometer," in *1979 Annual Book of ASTM Standards*, Part 41, ASTM E228-71.
9. "Standard Test Method for Water Absorption of Plastics," in *1979 Annual Book of ASTM Standards*, Part 35, ASTM D570.
10. "Cycloaliphatic Epoxide Systems," Union Carbide brochure (1978), page 14.

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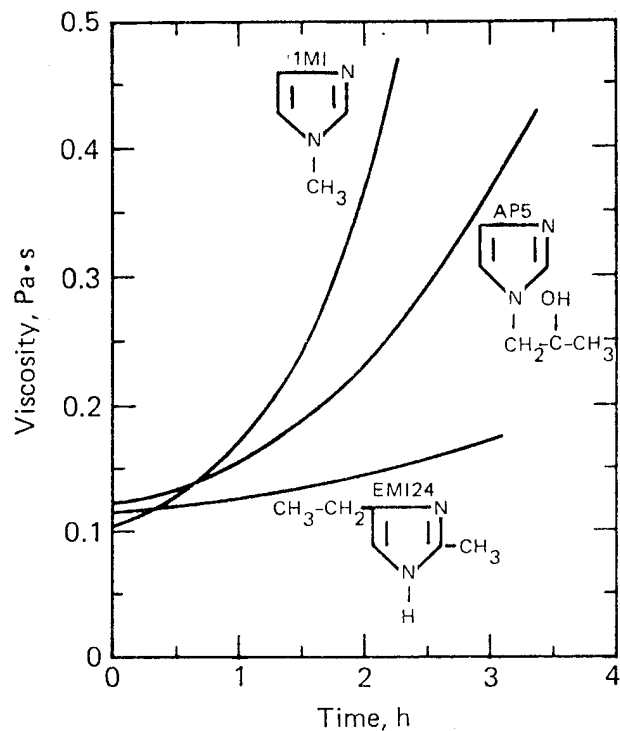


Fig. 1. The rate at which the imidazole catalysts 1-methylimidazole, 1-(2-hydroxypropyl)imidazole, and 2-ethyl-4-methylimidazole each promote the cure of the matrix resin system at 60°C indicates that the more complex the compound, the slower the rate of cure.

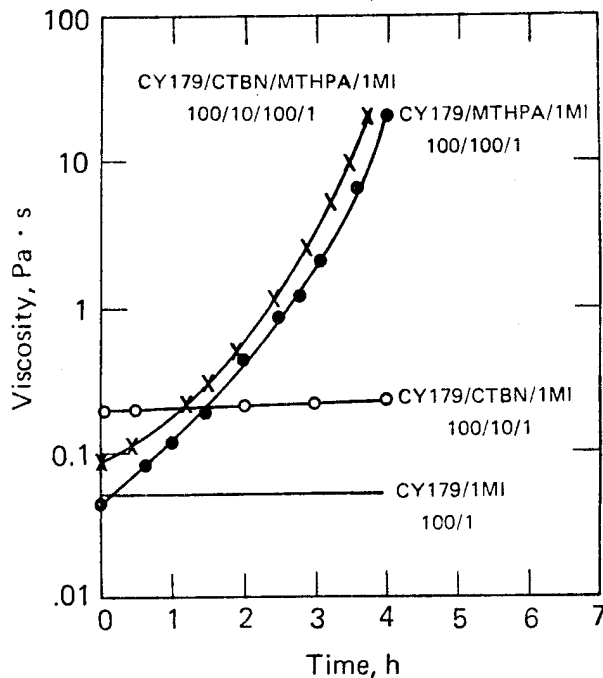


Fig. 2. The rate viscosity increases at 60°C for various cycloaliphatic resin systems catalyzed with 1-methylimidazole (1MI). The fast rate occurs in the presence of all four components, i.e., CY179, CTBN, MTHPA, and 1MI. The addition of CTBN minimally increases the rate.

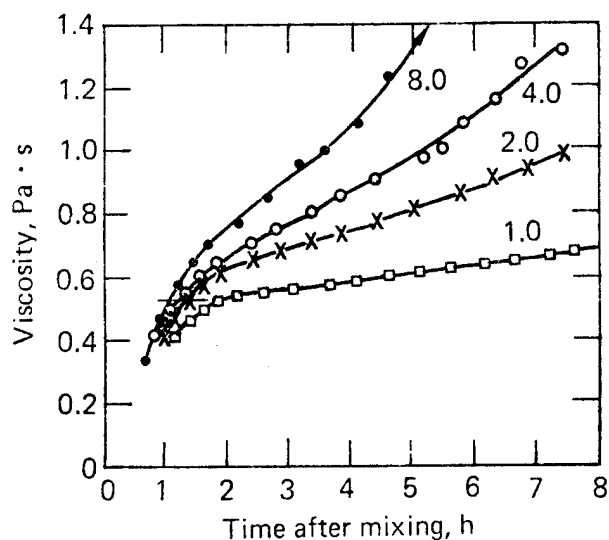


Fig. 3. The viscosity increases at 25°C for the matrix resin system, in which the catalyst is varied, as a function of catalyst concentration. The time to reach a viscosity of 0.7 Pa·s can be reduced from 8 to 1.65 h or by  $\approx 74\%$ .

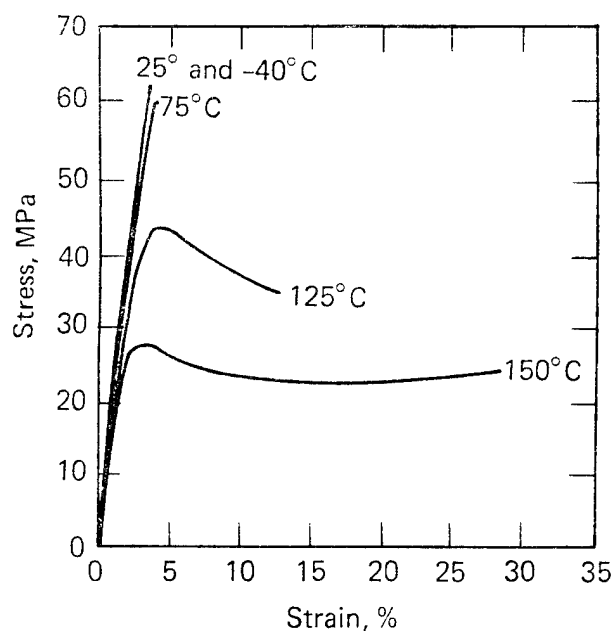


Fig. 4. Infrared spectra of the cured and uncured matrix resin systems enable us to follow the curing reaction as the anhydride peak at  $1778\text{ cm}^{-1}$  disappears.

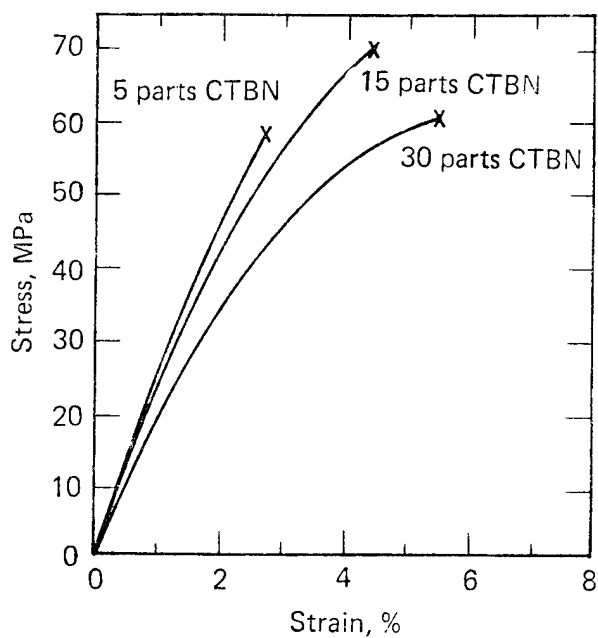


Fig. 5. The change in the infrared spectrum enables us to follow the curing reaction as it proceeds in the matrix resin system. The anhydride and epoxy peaks are in the region  $1500\text{--}2000\text{ cm}^{-1}$ , and the changes in the peaks between these wavelengths are clearly seen.

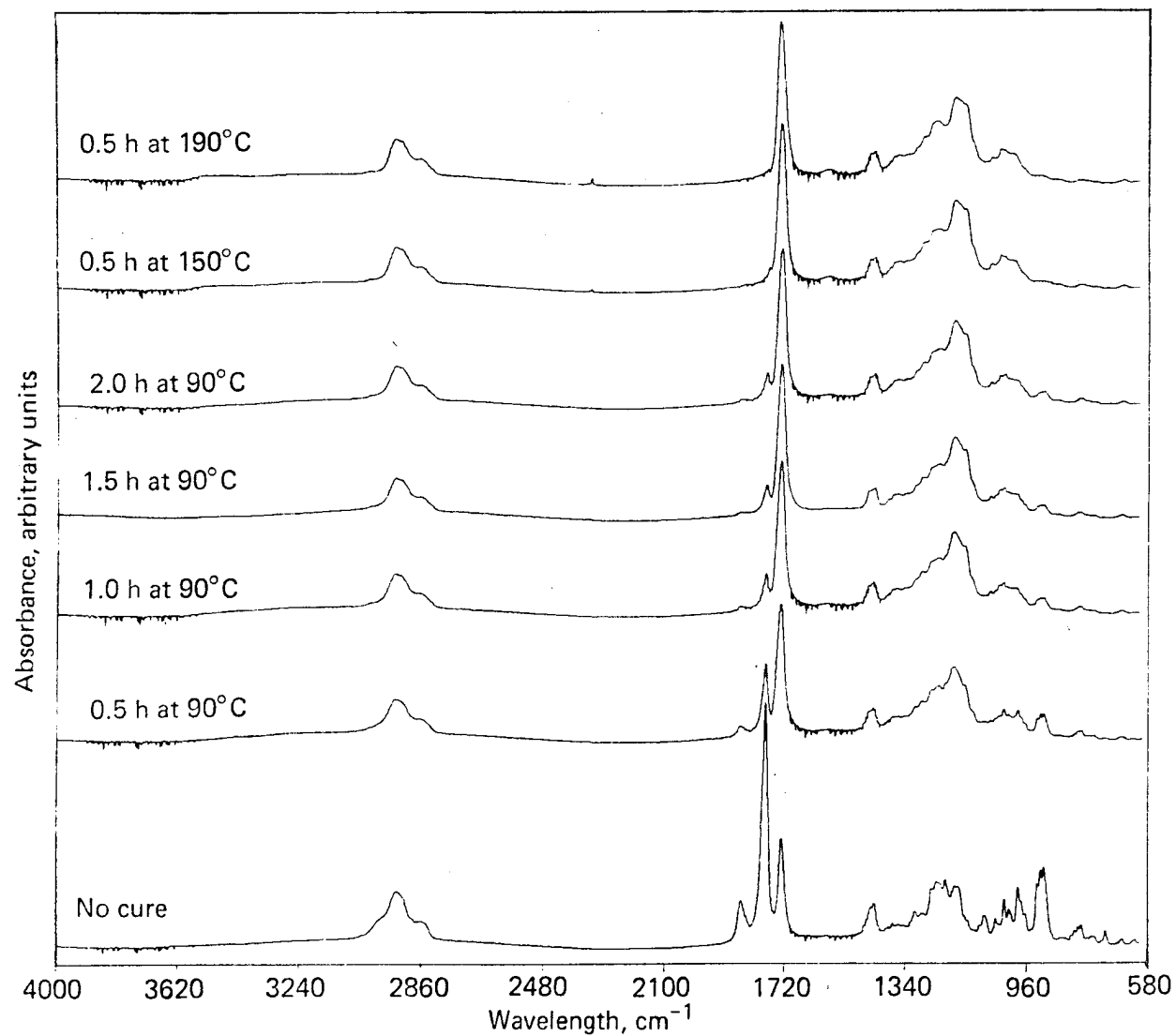


Fig. 6. The curing rate of the matrix resin system can be measured by determining the percentage of unreacted anhydride over time. This corresponds closely to the change in the infrared spectrum over time.

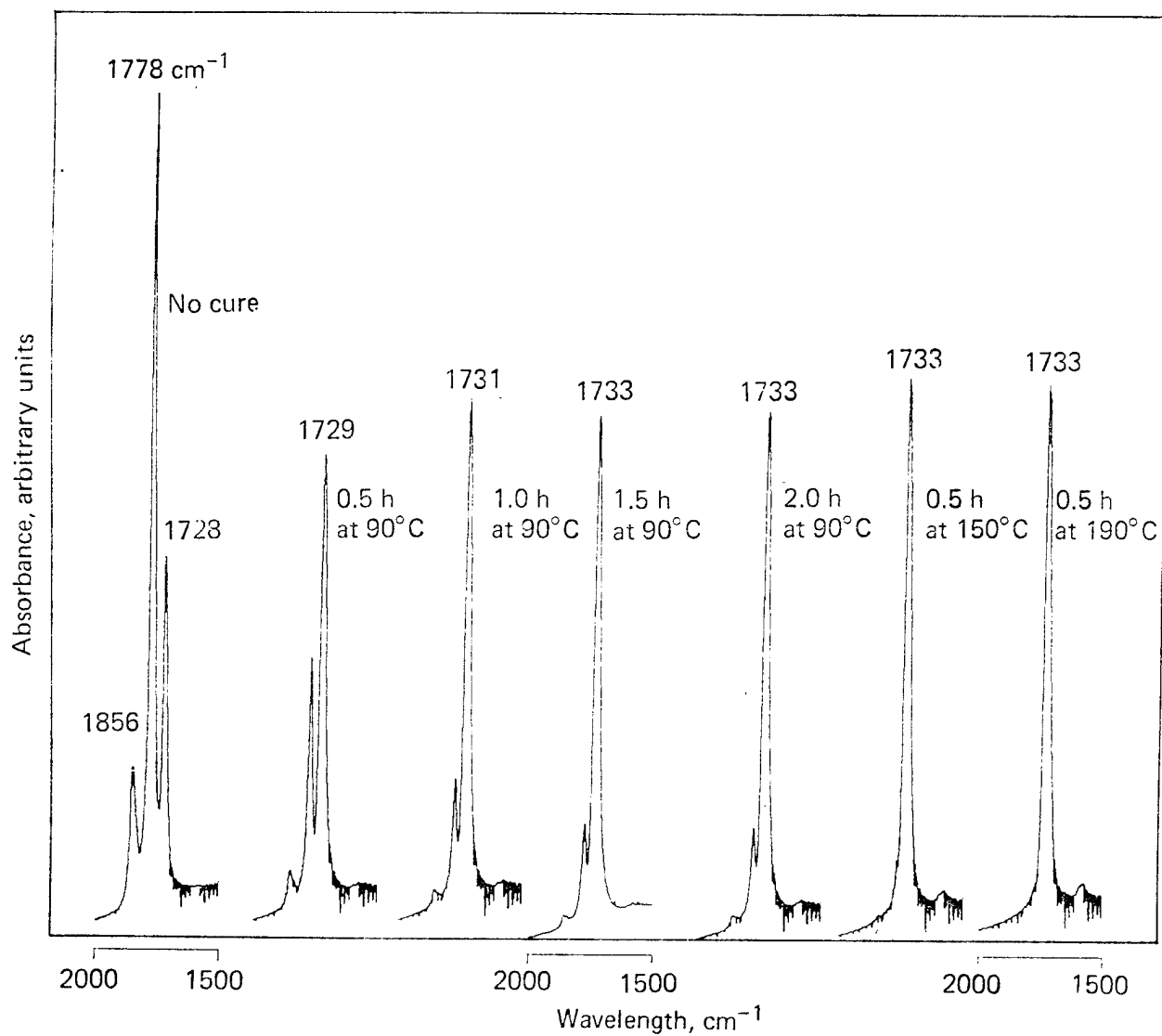


Fig. 7. The curing of the matrix resin system can be followed by plotting dielectrometer curves under standard conditions 2 h at  $90^\circ\text{C}$  plus 4 h at  $150^\circ\text{C}$ .

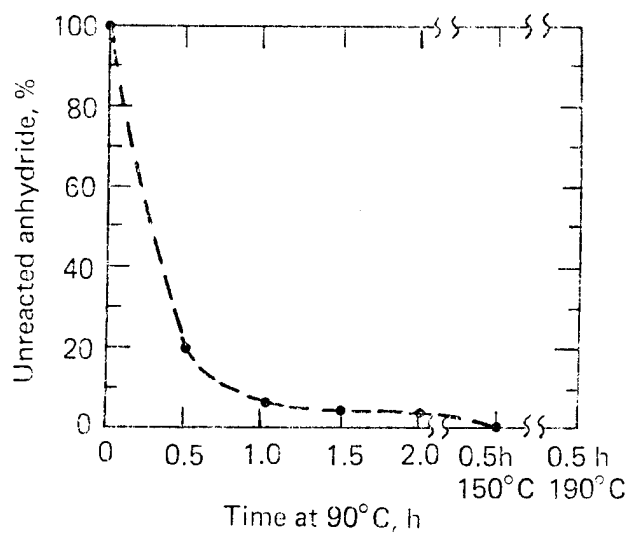


Fig. 8. Tensile strength of the matrix resin system at temperatures from  $-40$  to  $150^{\circ}\text{C}$  indicate that below  $75^{\circ}\text{C}$  there is essentially no change in tensile properties.

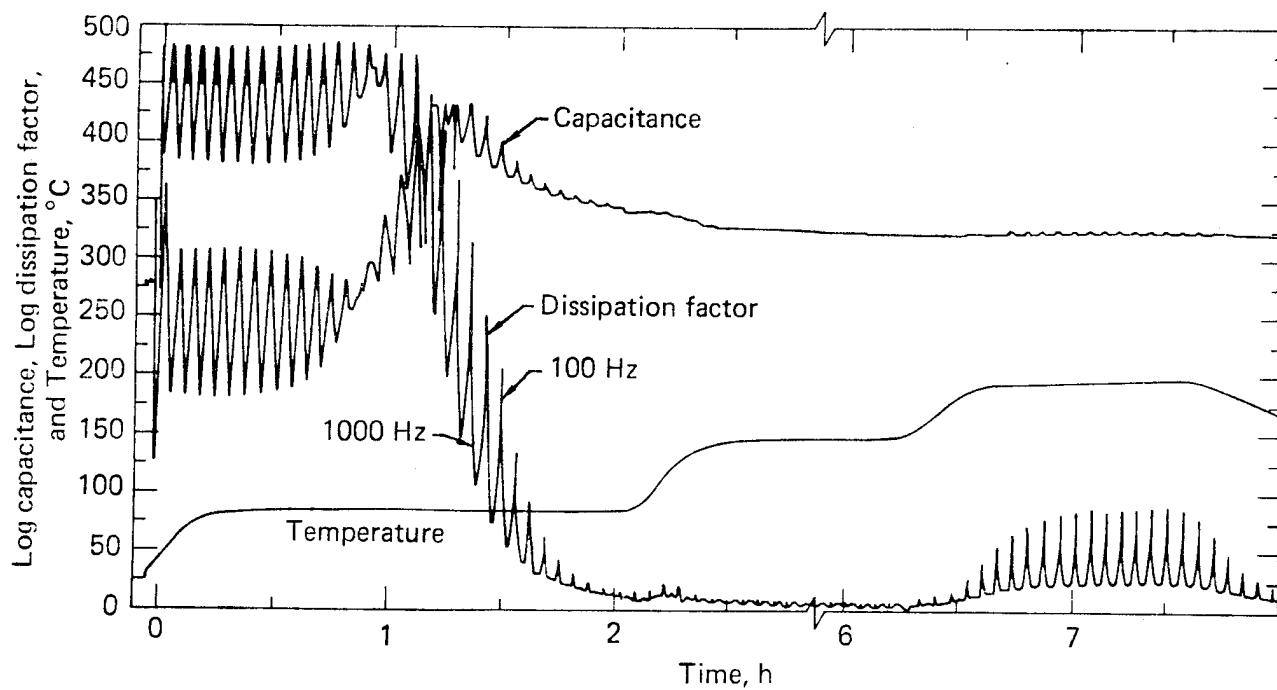


Fig. 9. The tensile test at  $25^{\circ}\text{C}$  for the matrix resin system cured at 2 h at  $90^{\circ}\text{C}$  plus 4 h at  $150^{\circ}\text{C}$  with varied amounts of CTBN indicate that higher CTBN levels increase the toughness of the resin system.

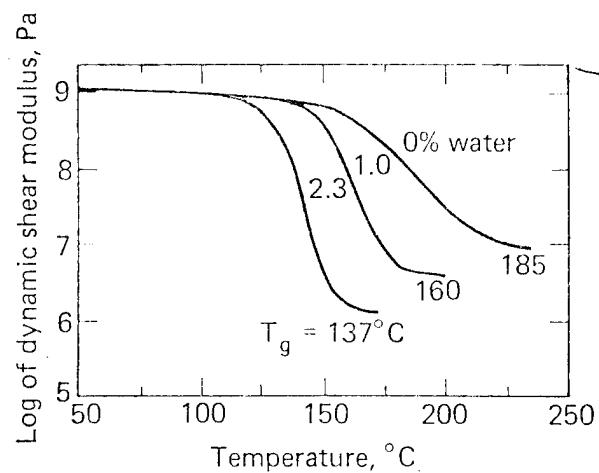


Fig. 10. The effect of water content on the dynamic shear modulus and glass-transition temperature for an anhydride-cured epoxy resin CY179/CTBN/MHHPA/EMI24 (100/10/100/2 parts by weight) cured for 24 h at 125°C.

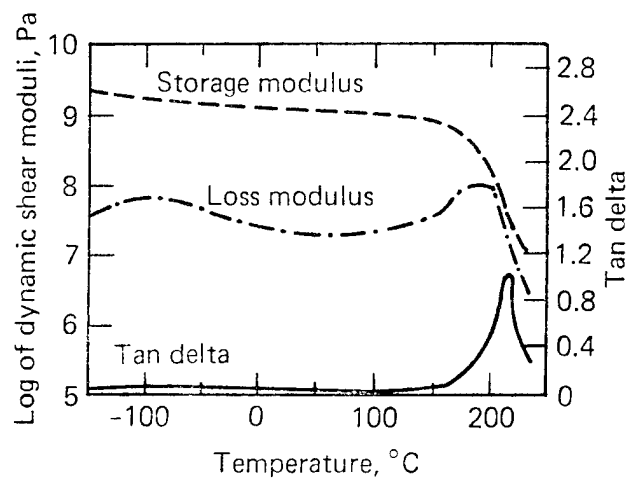


Fig. 11. The dynamic shear moduli of the matrix resin system at 1 Hz.

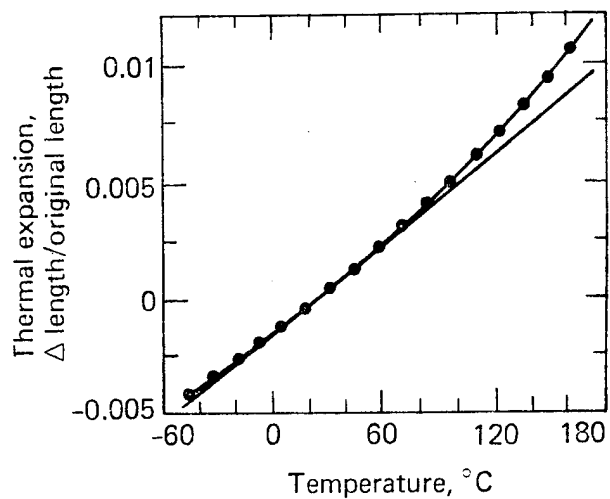


Fig. 12. The thermal expansion vs the temperature of the matrix resin system cured for 2 h at 90°C plus 4 h at 150°C.

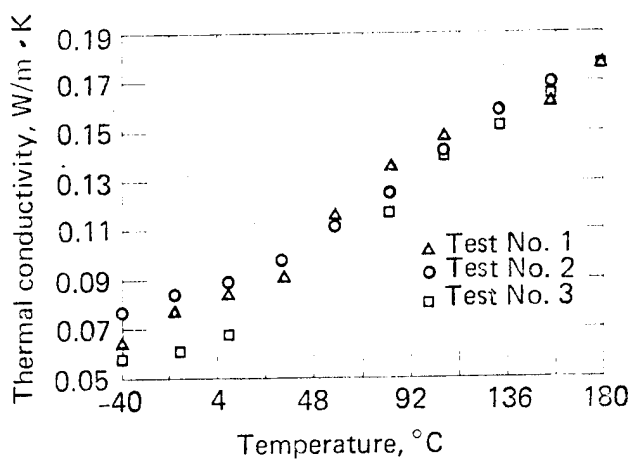
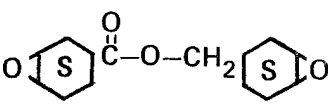
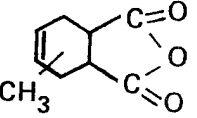
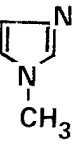


Fig. 13. Thermal conductivity vs temperature for the matrix resin system cured for 2 h at 90°C plus 4 h at 150°C.

Table 1. Components of the matrix resin system formulated for high-temperature use. It is designated CY179/CTBN/MTHPA/1MI (100/5/100/1).

| Component  | Parts by weight |
|--|-----------------|
| Cycloaliphatic epoxy resin: CY179  | 100             |
|   |                 |
| Flexibilizer: CTBN rubber (HYCAR 1300 X 8 <sup>a</sup> )   | 5               |
| $\text{HOOC} - \left[ (\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2)_x - (\text{CH}_2 - \underset{\text{CN}}{\text{CH}})_y \right]_m - \text{COOH}$ |                 |
| Curing agent: methyltetrahydrophthalic anhydride (MTHPA)   | 100             |
|   |                 |
| Catalyst: 1-methylimidazol (1MI)   | 1               |
|    |                 |

<sup>a</sup>HYCAR 1300 X 8 is a CTBN rubber manufactured by Goodrich Chemical Co.

Table 2. Gel time for the matrix resin system CY179/CTBN/MTHPA/1MI at different temperatures and concentrations 1MI. The concentration of CY179/CTBN/MTHPA is 100/5/100 parts by weight.

| Concentration<br>of 1MI,<br>parts by weight | Gel time at temperature, h |      |                 |      |
|---|----------------------------|------|-----------------|------|
|   | 25°C                       | 60°C | 75°C            | 90°C |
| 1   | 43.7                       | 5.4  | 1.7             | 0.3  |
| 2   | 37.5                       | 3.0  | NA <sup>a</sup> | NA   |
| 4   | 26.6                       | 1.9  | NA              | NA   |
| 8   | 21.9                       | 1.2  | NA              | NA   |

<sup>a</sup>Not available.



Table 3. Summary of physical properties of the resin system CY179/CTBN/MTHPA/1MI (100/5/100/1 parts by weight), cured at 90°C for 2 h plus 150°C for 4 h.

| Property  | Value                                 |
|---|---------------------------------------|
| Viscosity: at 25°C                                  | 0.38 Pa·s                             |
| after 8 h at 25°C                                   | 0.71 Pa·s                             |
| Time to reach 1.0 Pa·s                              | 14.4 h                                |
| Gel time for 30-g mass at 25°C                      | 43.7 h                                |
| Exotherm of 500-g mass from 25°C                    | None                                  |
| Density at 25°C: uncured resin                      | 1.18 Mg/m <sup>3</sup>                |
| cured resin   | 1.19 Mg/m <sup>3</sup>                |
| Tensile properties: stress at maximum               | 58.1 MPa                              |
| stress at failure                                   | 58.1 MPa                              |
| strain at maximum                                   | 2.8%                                  |
| strain at failure                                   | 2.8%                                  |
| modulus   | 2.4 GPa                               |
| Compressive properties: maximum strength            | 120.2 MPa                             |
| strain at maximum strength                          | 8.4%                                  |
| secant modulus                                      | 2.54 GPa                              |
| Shear properties: stress at failure                 | 27.5 MPa                              |
| modulus   | 0.47 GPa                              |
| Water absorption for 24 h at 100°C                  | 2.07% gain                            |
| Glass transition temperature                        | 210°C                                 |
| Heat distortion temperature at 1820 kPa             | 170°C                                 |
| Heat capacity: at 308 K                             | 1268 J/kg·K                           |
| 323 K   | 1344 J/kg·K                           |
| 348 K   | 1443 J/kg·K                           |
| 373 K   | 1547 J/kg·K                           |
| 398 K   | 1652 J/kg·K                           |
| 423 K   | 1765 J/kg·K                           |
| 448 K   | 1840 J/kg·K                           |
| Thermal coefficient of linear expansion (250–342 K) | $6.4 \times 10^{-3}/^{\circ}\text{C}$ |
| Thermal conductivity: at 298 K                      | 0.085 W/m·K                           |
| 348 K   | 0.12 W/m·K                            |
| 398 K   | 0.16 W/m·K                            |
| IZOD impact (ASTM D256, method A)                   | 8.5 J/m                               |

Table 4. Tensile properties of CY179/CTBN/MTHPA/1MI at several temperatures and CTBN concentrations.

| CY179/CTBN/<br>MTHPA/1MI,<br>parts by weight | 25°C                 |                              |                       |  | 100°C                |                              |                     |                       | 125°C                |                              |                     |                     | 150°C                |                              |                     |                     |
|--|----------------------|------------------------------|-----------------------|--|----------------------|------------------------------|---------------------|-----------------------|----------------------|------------------------------|---------------------|---------------------|----------------------|------------------------------|---------------------|---------------------|
|  | Modu-<br>lus,<br>GPa | Stress<br>at<br>max.,<br>MPa | $\epsilon_m^a$ ,<br>% |  | Modu-<br>lus,<br>GPa | Stress<br>at<br>max.,<br>MPa | $\epsilon_m$ ,<br>% | $\epsilon_f^b$ ,<br>% | Modu-<br>lus,<br>GPa | Stress<br>at<br>max.,<br>MPa | $\epsilon_m$ ,<br>% | $\epsilon_f$ ,<br>% | Modu-<br>lus,<br>GPa | Stress<br>at<br>max.,<br>MPa | $\epsilon_m$ ,<br>% | $\epsilon_f$ ,<br>% |
| 100/5/100/1.0                                | 2.4                  | 58                           | 2.8                   |  | 2.1                  | 56                           | 5.2                 | 10.6                  | 1.6                  | 43                           | 4.4                 | 13                  | 1.5                  | 28                           | 3.4                 | 28                  |
| 100/10/100/1.0                               | 2.4                  | 69                           | 4.2                   |  | 2.0                  | 50                           | 4.8                 | 12                    | 1.6                  | 37                           | 4.2                 | 15                  | 1.2                  | 23                           | 3.6                 | 22+                 |
| 100/15/100/1.0                               | 2.1                  | 72                           | 5.0                   |  | 1.7                  | 46                           | 4.9                 | 11                    | 1.5                  | 33                           | 4.2                 | 23                  | 1.2                  | 22                           | 3.5                 | 20+                 |
| 100/30/100/1.0                               | 1.84                 | 60                           | 5.4                   |  | NA <sup>c</sup>      | NA                           | NA                  | NA                    | NA                   | NA                           | NA                  | NA                  | NA                   | NA                           | NA                  | NA                  |

<sup>a</sup>Strain at maximum.

<sup>b</sup>Strain at failure.

<sup>c</sup>Not available.

Table 5. Effect of cure cycle on the tensile properties of CY179/CTBN/MTHPA/1MI (100/5/100/1) tested at 25°C.

| Cure cycle, h/°C | T <sub>g</sub> , °C | Modulus, GPa | CV <sup>a</sup> | Maximum stress, MPa | CV    | Maximum strain, % | CV    | Number of tests |
|------------------|---------------------|--------------|-----------------|---------------------|-------|-------------------|-------|-----------------|
| 2/90 + 4/150     | 210                 | 2.39         | 0.174           | 58.1                | 0.120 | 2.78              | 0.201 | 6               |
| 2/90 + 24/120    | 213                 | 2.60         | 0.066           | 65.8                | 0.141 | 2.80              | 0.193 | 9               |
| 2/90 + 24/100    | 214                 | 2.97         | 0.062           | 72.7                | 0.094 | 2.85              | 0.140 | 9               |

<sup>a</sup>Coefficient of variation.

Table 6. Effect of anhydride concentration on tensile properties of CY179/CTBN/MTHPA/1MI cured for 2 h at 90°C plus 4 h at 150°C and tested at 25 and 150°C. The concentration of CY179/CTBN/1MI is 100/5/1 parts by weight.

| Tensile properties             | Concentration of MTHPA, parts by weight |      |      |
|--------------------------------|---|------|------|
|                                | 90                                      | 100  | 110  |
| Modulus, GPa: at 25°C          | 2.24                                    | 2.39 | 2.30 |
| at 150°C                       | 1.16                                    | 1.51 | 1.47 |
| Maximum strength, MPa: at 25°C | 68.5                                    | 58.1 | 66.4 |
| at 150°C                       | 19.3                                    | 28.0 | 29.8 |
| Maximum strain, %: at 25°C     | 3.5                                     | 2.8  | 3.3  |
| at 150°C                       | 3.0                                     | 3.4  | 3.6  |
| Failure stress, MPa: at 25°C   | 68.5                                    | 58.1 | 66.4 |
| at 150°C                       | 15.9                                    | 24.4 | 24.7 |
| Failure strain, %: at 25°C     | 3.5                                     | 2.8  | 3.3  |
| at 150°C                       | 32.2                                    | 27.4 | 20.4 |
| Number of tests: at 25°C       | 4                                       | 6    | 2    |
| at 150°C                       | 5                                       | 8    | 4    |

Table 7. Test results of aging the matrix resin, tested at 25 and 125°C.

| Time aged, mo | Temperature, °C | Modulus, GPa | CV, <sup>a</sup> % | Maximum stress, MPa | CV, % | Maximum strain, % | CV, % | T <sub>g</sub> , °C | Number of tests |
|---------------|-----------------|--------------|--------------------|---------------------|-------|-------------------|-------|---------------------|-----------------|
| 0             | 25              | 2.39         | 17.4               | 58.1                | 12.0  | 2.78              | 20.1  | 210                 | 6               |
|               | 125             | 1.61         | 18.9               | 43.0                | 3.2   | 4.40              | 6.9   | 210                 | 8               |
| 0.25          | 25              | 2.91         | 3.3                | 53.9                | 16.0  | 2.08              | 20.0  | 211                 | 5               |
|               | 125             | 1.92         | 8.4                | 39.9                | 10.4  | 2.28              | 11.7  | 211                 | 4               |
| 0.5           | 25              | 2.70         | 2.6                | 46.2                | 11.0  | 1.84              | 14.0  | 214                 | 5               |
|               | 125             | 1.83         | 13.7               | 38.4                | 6.3   | 2.27              | 19.7  | 214                 | 3               |
| 1.0           | 25              | 2.82         | 4.7                | 41.7                | 6.7   | 1.54              | 5.4   | 215                 | 5               |
|               | 125             | 2.01         | 8.9                | 36.6                | 3.5   | 1.99              | 13.1  | 215                 | 4               |
| 1.5           | 25              | 2.90         | 3.7                | 43.7                | 2.2   | 1.54              | 4.4   | 209                 | 5               |
|               | 125             | 1.70         | 46.9               | 29.1                | 29.0  | 1.64              | 46.1  | 209                 | 4               |
| 2.0           | 25              | 2.82         | 3.7                | 38.3                | 10.0  | 1.39              | 11.0  | 208                 | 5               |
|               | 125             | 1.73         | 14.3               | 24.7                | 29.0  | 1.27              | 32.4  | 208                 | 5               |
| 3.0           | 25              | 2.02         | 6.1                | 34.7                | 13.0  | 1.80              | 19.0  | 210                 | 5               |
|               | 125             | 1.60         | 3.2                | 27.0                | 14.0  | 1.76              | 17.0  | 210                 | 4               |

<sup>a</sup>Coefficient of variation.

Table 8. Effect of added water on the tensile properties of CY179/CTBN/MTHPA/1MI (100/5/100/1 parts by weight) tested at 25 and 125°C.

| Tensile property    | Test temperature, °C | Presence of water |      |
|---------------------|----------------------|-------------------|------|
|                     |                      | No                | Yes  |
| Modulus, GPa        | 25                   | 2.39              | 2.02 |
|                     | 125                  | 1.61              | 1.19 |
| Maximum stress, MPa | 25                   | 58.1              | 34.7 |
|                     | 125                  | 43.0              | 46.5 |
| Maximum strain, %   | 25                   | 2.78              | 1.80 |
|                     | 125                  | 4.4               | 7.0  |
| Failure stress, MPa | 25                   | 58.1              | 34.7 |
|                     | 125                  | 35.0              | 41.7 |
| Failure strain, %   | 25                   | 2.78              | 1.80 |
|                     | 125                  | 13.3              | 11.6 |