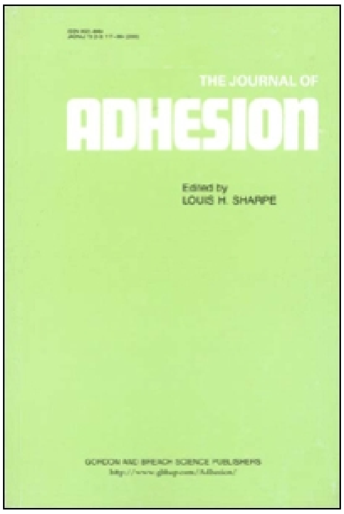

**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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**To cite this Article** Sharon, G. , Dodiuk, H. and Kenig, S.(1989) 'Effects of Loading Rate and Temperature on the Mechanical Properties of Structural Adhesives Containing a Carrier', The Journal of Adhesion, 31: 1, 21 — 31
**To link to this Article: DOI:** 10.1080/00218468908048211
**URL:** http://dx.doi.org/10.1080/00218468908048211

*J. Adhesion*, 1989, Vol. 31, pp. 21–31
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Printed in the United Kingdom

# Effects of Loading Rate and Temperature on the Mechanical Properties of Structural Adhesives Containing a Carrier

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*(Received December 23, 1989; in final form June 8, 1989)*

The viscoelastic related properties of four structural adhesives were studied in their bulk form. All four adhesives were based on rubber-toughened epoxy resin with a thermoplastic carrier. Two of the adhesives were commercial film adhesives (120°C curing systems) and the other two were formulated by us from commercially available constituents. The first formulation is a high-temperature-curing system based on cyclo-aliphatic resin and anhydride hardener, toughened with carboxy-terminated butadiene elastomer. The second self-prepared formulation is a special room-temperature-curing adhesive for elevated temperature service, based on a blend of trifunctional and tetrafunctional expoxies cured with triethylene tetramine toughened with amine-terminated butadiene elastomer. The latter formulation was also prepared, in addition to the carrier-containing composition, without the thermoplastic carrier.

As expected for viscoelastic materials, it was found that the yield stress and modulus decreased with temperature. The rate of loading had a pronounced effect on the yield stress which increased with increasing loading rates, and a negligible influence on the modulus. The rate-temperature effects on the yield stress were shown to obey the superposition as described by Eyring's theorem of viscosity. Consequently, the activation energy and activation volume were determined. The high-temperature-curing adhesives comprising a carrier exhibited higher activation energies compared with the room-temperature-curing formulation and other epoxy adhesives cured with aliphatic amines or polyamides reported in the literature.

KEY WORDS Structural epoxy adhesives; Eyring's theorem; yield stress; Young's modulus; loading rate; temperature.

## INTRODUCTION

Epoxy-based structural adhesives have become an industry standard in the design and manufacture of load-carrying structures. Advanced formulations include among the basic constituents a dispersed rubber phase for improved toughness.[1] Furthermore, for reasons of both mechanical properties and quality control of the bond line thickness, a thermoplastic carrier is incorporated into the epoxy system to form a supported film adhesive.

The mechanical properties of epoxy film adhesives have been the subject of numerous studies. Properties such as shear, tensile, peel and even fracture toughness are among those characterized to establish and consolidate the data base needed for the design of bonded structural components.

Viscoelastic properties of structural adhesives have not received a great deal of attention, even though the mechanical response of adhesively-bonded joints under sustained load, varying loading rates and temperature are of utmost importance for the designer and end-user.

Studies of epoxy adhesives with respect to viscoelasticity are commonly related to their stress-strain behaviour as a function of test temperature and loading rate.

Brinson *et al.*[2] studied the stress-strain and strain rate response of two commercial epoxy film adhesives. Based on the semiempirical approach proposed by Ludwik and reported by Thorkildsen,[3] their experimental results can be correlated using the following equation:

$$\sigma_y = \sigma' + \sigma'' \log(\dot{e}/\dot{e}') \tag{1}$$

where $\sigma_y$ is the yield stress, $\dot{e}$ is the strain rate and $\sigma'$, $\sigma''$ and $\dot{e}'$ are experimentally-determined material constants.

Sancaktar *et al.*[4,5] characterized the failure behaviour, in shear at constant strain-rate and constant stress loading modes, of four structural adhesives. They proposed an empirical modification of Eq. (1) to describe the temperature effects on the yield stress in shear, as follows:

$$\sigma_y = a_T\sigma' + \sigma'' \log(\dot{e}/\dot{e}') \tag{2}$$

where $a_T$ is a temperature shift factor.

The classical approach to describe failure mechanisms involving flow of solids and their correlation with temperature and strain rate is that of the Eyring theorem.[6,7] According to Eyring's theory, the mechanical response of the adhesive is described as a process that has to overcome a potential energy barrier, $\Delta E$. This barrier decreases as the applied stress is increased.

The relationship between the strain rate, $\dot{e}$, and the yield stress, $\sigma_y$, is given according to Eyring by:

$$\dot{e} = A \exp[(\sigma_y V - \Delta E)/RT] \tag{3}$$

where $A$ is a pre-exponential factor, $R$ is the gas constant and $V$ is the activation volume.

A logarithmic representation of Eq. (3) and further rearrangement leads to Eq. (4):

$$\sigma_y = \Delta E/V + [2.303RT \log(\dot{e}/A)]/V \tag{4}$$

The strain rate, $\dot{e}$, and the loading rate (cross-head speed), $\dot{Y}$, are related to the initial gauge length of the sample, $l_0$:

$$\dot{e} = \dot{Y}/l_0 \tag{5}$$

It should be noted that Eqs (1) and (4) are somewhat similar. The material parameters $\sigma'$, $\sigma''$ and $\dot{e}'$, in Eq. (1) are expressed by $(\Delta E/V)$, $(2.303RT/V)$ and $A$ in Eq. (4) respectively.

It has been suggested by Haward and Thackray[8] that the activation volume represents the volume of the polymer segment which has to move, as a whole, so that flow may occur. Bowden[9] has proposed that the product of $V$ and $\sigma_y$ represents the work done on a mobile segment during a jump. Moreover, according to him, the value of $\Delta E$ cannot be associated directly with a molecular relxation process. Bronstow and Corneliussen[10] studied the change of the yield stress over a wide range of temperatures and loading rates. Their conclusion was that Eq. (3) has to be corrected since $V$ and $\Delta E$ are not constants and they vary with temperatures and loading rates.

Using Eyring's Eq. (3), several workers studied the viscoelastic behaviour of some epoxy adhesives based on DGEBA (diglycidyl ether of bisphenol A) as function of test temperature and loading rate.

Kinloch, Shaw and Hunston[11] investigated the viscoelastic response of DGEBA cured with piperidine. They measured the compressive modulus and yield stress as a function of loading rate and temperature for the case of the neat epoxy adhesive as well as its CTBN-toughened modification. They found, as expected, that the compressive modulus and yield stress decreased as temperature increased. While the yield stress increased with increasing loading rates, no definite effect of loading rate could be discerned with respect to compressive modulus. The compressive yield stress results fit Eyring's theory and are summarized in Table I.

Sultan and McGarry[12] characterized the viscoelastic response of DGEBA, untoughened and toughened with 10% CTBN. Their experimental results fit Eyring's theory. As can be seen from Table I, the activation energy values are lower than those of Kinloch *et al.*[11]

TABLE I
Values of activation energy and activation volume for polymer and adhesives based on DGEBA (diglycidyl ether of bisphenol A)

| Activation energy $\Delta E$ [KJ/mole] | Activation volume $V$ [nm$^3$/molecule] | Material | Ref. |
|---|---|---|---|
| 350 | 2.0 | DGEBA + Piperidine + CTBN (100; 5; 15 phr) | 11 |
| 290 | 1.9 | DGEBA + Piperidine (100; 5 phr) | 11 |
| 242 | — | Epon 828 + Curing Agent D + CTBN (100; 5; 10 phr) | 12 |
| 234 | — | Epon 828 + curing Agent D (100; 5 phr) | 12 |
| 244 | 4.8 | Epon 815 + Versamid 140 (60/40 w/w) | 13 |
| 261 | 5.8 | Epon 815 + Versamid 140 (70/30 w/w) | 13 |

Ishai[13] measured the viscoelastic properties of another DGEBA derivative cured with different ratios of polyamide. His results are also given in Table I.

All previously-studied adhesives[8–15] did not contain a carrier, as is commonly the case in advanced structural adhesives. Consequently, the present study is aimed at characterizing carrier-containing epoxy adhesives with respect to their viscoelastic properties. Four adhesives were included in the investigation. Two were commercial 120°C curing film adhesives. The other two were formulated from commercial ingredients. One of the formulations was evaluated with a carrier as well as without a carrier.

## EXPERIMENTAL

### Materials

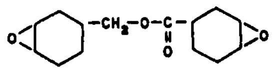
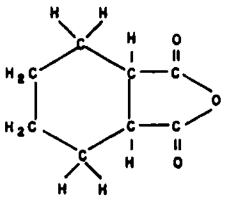
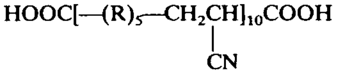
Two commercial structural film adhesives and two which we formulated were included in the present study. The commercial film adhesives were 120°C curing systems, FM-73[16] and MB-1137,[17] manufactured by American Cyanamid and BASF Structural Materials, respectively. Specimens were prepared by pressing 13 layers of adhesive in the mold and curing according to the manufacturers' specifications, at 120°C for 1 hour (FM-73) or 2 hours (MB-1137) under a pressure of 0.7 MPa.

The self-made formulations were based on high-temperature and room-temperature curing systems.

Formulation A was composed of cyclo-aliphatic resin (ERL 4221), anhydride hardener (HHPA) and carboxy-terminated butadiene elastomer (CTBN). Raw materials used in formulating composition *A* are given in Table II. Prior to mixing, HHPA was heated to 50°C and melted, ERL 4221 resin was heated to 50°C and CTBN was heated to 90°C. Materials were added to the epoxy resin in sequence according to Table II and then mixed for approximately 5–10 minutes. The felt carrier made of polyester was impregnated with the mixture and then degassed in vacuum at 65°C, for 15 minutes. Ten layers of impregnated carrier were then put into the mold, cured at 120°C for 2 hours under a pressure of 0.7 MPa followed by post-curing at 160°C for 4 hours.

Formulation B was a special room-temperature-curing system for elevated-temperature service, composed of tetra functional epoxy (MY 720) and trifunctional epoxy (ERL 510) resins, triethylene tetramine hardener (TETA) and amine-terminated butadiene elastomer (ATBN).[18] Raw materials used in formulating composition B are listed in Table III. After MY 720 resin and ATBN were heated to 50°C and melted, ERL 510 resin and ATBN were added to MY 720 and mixed for approximately 5 minutes. The mixture was then cooled down, and TETA hardener was added and well mixed. Specimens with carrier were prepared by impregnating the felt carrier with the adhesive and then degassing in vacuum for 15 minutes. Ten layers of impregnated carrier were then pressed in the mold.

TABLE II
Formulation A, raw materials and composition

| Component | Manufacturer | Chemical Structure | Composition [gr] |
|---|---|---|---|
| ERL 4221<br>(3,4 Epoxycyclo-Hexane Carboxylate) | Union Carbide Co., U.S.A. |  | 100 |
| HHPA<br>(Hexa Hydro Phtalic Anhydride) | Miller Stephenson Chem. Co., U.S.A. |  | 100 |
| CTBN 1330X8<br>(Carboxyl Terminated Acrylonitrile) | B. F. Goodrich Chemical Corp., U.S.A. |  $HOOC[-(R)_5-\underset{\mid \atop CN}{CH_2CH}]_{10}COOH$<br>$R = CH_2CH = CHCH$ | 60 |
| BDMA<br>(Benzyl Di Methyl Amine) | Miller Stephenson Chem. Co., U.S.A. | $C_6H_5CH_2N(CH_3)_2$ | 1 |
| EG<br>(Ethylene Glycol) | Frutarom Electro Chem. Ind., Israel | $HOCH_2CH_2OH$ | 1.5 |
| Fibermat I C-650 | 3M, U.S.A. | Polyester Felt | 113 |

Specimens without a carrier were prepared by degassing the adhesive in vacuum for 15 minutes and then casting it in a dumbell-shaped mold.

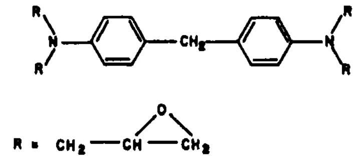
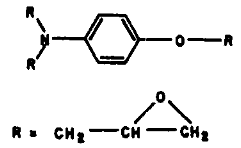
Both types of specimens were cured at *RT* for 7 days. Specimens with a carrier were cured under a pressure of 0.7 MPa.

## Mechanical characterization

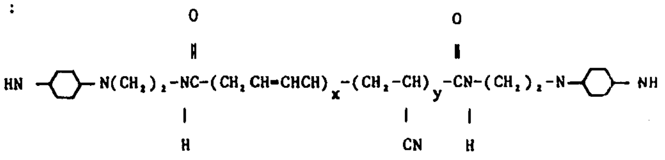
Yield stress, $\sigma_y$, and Young's modulus, $E$, were determined as a function of test temperature, $T$, and loading rate, $\dot{Y}$.

Tensile specimens, 190 × 12.5 mm, according to ASTM D3039,[19] were cut from the carrier-containing cured bulk laminates. Tensile specimens without a carrier were dumbell-shaped type I, according to ASTM D638.[20] $\sigma_y$ and $E$ were experimentally determined in tensile mode, using an Instron 1185 Mechanical Testing Machine including an extensometer. Tests were carried out at several temperatures (−30 to 120°C) and loading rates (2-200 mm/min).

TABLE III
Formulation B, raw materials and compositon

| Component | Manufacturer | Chemical Structure | Composition [gr] |
|---|---|---|---|
| MY 720 (Tetraglycidyl Ether of 4,4'Methylene Di Aniline) | Ciba-Geigy U.S.A. |  | 125 |
| ERL 510 (Triglycidyl Ether of *p*-Amino Phenol) | Ciba-Geigy U.S.A. |  | 100 |
| ATBN 1300X16 (Amino Terminated Butadiene acrylo Nitrile) | B. F. Goodrich Chemical Corp. U.S.A. | • | 90 |
| TETA (Tri Ethylene Tetra Amine) | Miller Stephenson Chem. Co. U.S.A. | $H_2N-(R)_2-NH-(R)_2-NH-(R)_2-NH_2$<br>$R = CH_2$ | 46.5 |
| Fibermat I C-650 | 3M, U.S.A. | Polyester Felt | 108 |

• ATBN :



## RESULTS AND DISCUSSION

The viscoelastic response, as manifested in the effects of temperature between −30°C to 120°C and loading rate in the range of 2 mm/min to 200 mm/min on the tensile yield stress and modulus was characterized for the two commercial and two self-formulated structural adhesives, containing a thermoplastic carrier. For reference, one formulation was investigated in its neat form.

Table IV summarizes one set of the mechanical properties of the adhesives at 25°C and at a loading rate of 2 mm/min. As can be seen from Table IV, the two commercial 120°C curing adhesives have similar properties at the ambient conditions exhibited in the strength, modulus and elongation. The high-temperature formulation possesses a higher modulus with somewhat higher yield

TABLE IV
Young's modulus, yield stress and yield strain of the investigated adhesives at $T = 25°C$ and $\dot{Y} = 2$ mm/min

| Structural Adhesive | Young's modulus $E$ [MPa] | Yield stress $\sigma_y$ [MPA] | Yield strain $\varepsilon_y$ [%] |
|---|---|---|---|
| FM-73 | $1507 \pm 37$ | $42 \pm 1$ | $3.7 \pm 0.3$ |
| MB-1137 | $1340 \pm 49$ | $38 \pm 2$ | $3.7 \pm 0.5$ |
| Formulation A | $2046 \pm 37$ | $42 \pm 2$ | $4.0 \pm 0.7$ |
| Formulation B (with a carrier) | $1336 \pm 74$ | $35 \pm 1$ | $4.8 \pm 0.4$ |
| Formulation B (without a carrier) | $1184 \pm 90$ | $29 \pm 2$ | $3.4 \pm 0.6$ |

elongation, while the room-temperature-curing formulation has a lower modulus and strength compared with the other adhesives. The effect of the carrier on the room temperature adhesive is evident, imparting higher strength, elongation and modulus to the adhesive.

The effect of loading rate on the tensile strength has been analyzed according to Eq. (4). Accordingly, the yield process is an activated rate process where a potential energy barrier has to be overcome and an applied stress reduces the energy barrier. First, the activation energy and activation volume were calculated for each adhesive studied using a correlation analysis. Subsequently, the experimentally-measured tensile strength values were correlated with the superimposed temperature rate variable, as indicated by Eyring's theorem.

Table V summarizes the activation energies and activation volumes calculated assuming that Eq. (4) describes the viscoelastic behavior of the adhesives. As could be seen from Table V, the carrier containing adhesives, FM-73, MB-1137 and formulation A, are characterized by relatively high activation energies (480–690 KJ/mole) compared with the ones obtained for the room-temperature-curing formulation B (330–360 KJ/mole), and the adhesives that contain no carrier reported in Table I (260–350 KJ/mole). No significance could be attributed to the calculated activation volumes which exhibit a large scatter. This was also the case for the previously-studied epoxy adhesives.[11,12,13] The lower activation energies typified by Formulation B and the DGEBA-based

TABLE V
Values of activation energy and activation volume for studied structural adhesives

| Activation energy $\Delta E$ [KJ/Mole] | Activation volume $V$ [nm$^3$/molec] | Structural adhesive |
|---|---|---|
| 482 | 3.7 | FM-73 |
| 688 | 7.6 | MB 1137 |
| 558 | 3.5 | Formulation A |
| 355 | 5.0 | Formulation B |
| 329 | 7.0 | Formulation B (without a carrier) |

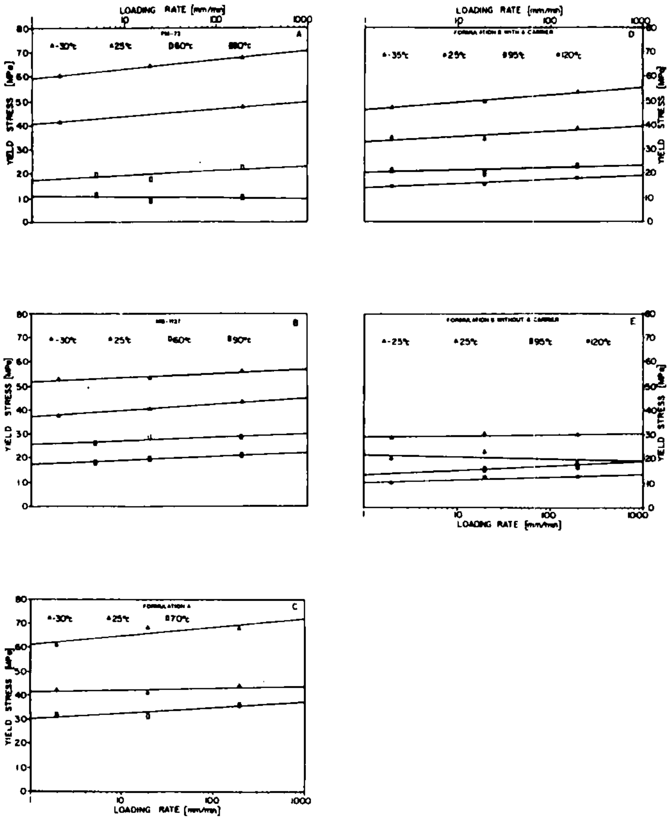


FIGURE 1 Yield stress–loading rate relationship for various temperatures of the structural adhesives studied.

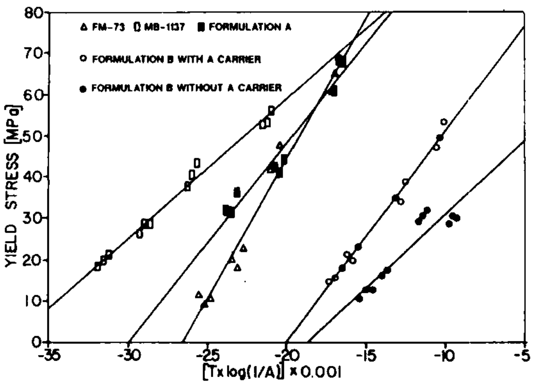


FIGURE 2 Rate–temperature superposition for tensile yield stress of the structural adhesives studied.

adhesives[11,12,13] could be attributed to the chemical composition of the curing agents. The lower activation energies obtained in the present study (Formulation B) and the ones obtained for the DGEBA systems are associated with aliphatic amines or polyamide curing agents. This may result in a different chemical network and cross-linking density.

The effect of loading rate on the yield stress of the studied adhesives, for various temperatures, are shown in Figure 1. The rate effect shown is similar in all the studied adhesives. The superposition of temperature and loading rate, and its effect on the tensile strength of the adhesives investigated, is illustrated in Figure 2. As can be concluded, Eyring's theorem of viscosity provides a useful phenomenological relationship for describing the yielding process of carrier-containing, and carrier-free, structural adhesives. However, since the structural adhesives studied are multi-phase and composite systems, care should be exercised as to the significance of the application of the traditional concept of activation energy to these systems.

The effect of loading rate on the measured moduli was found to be negligible in

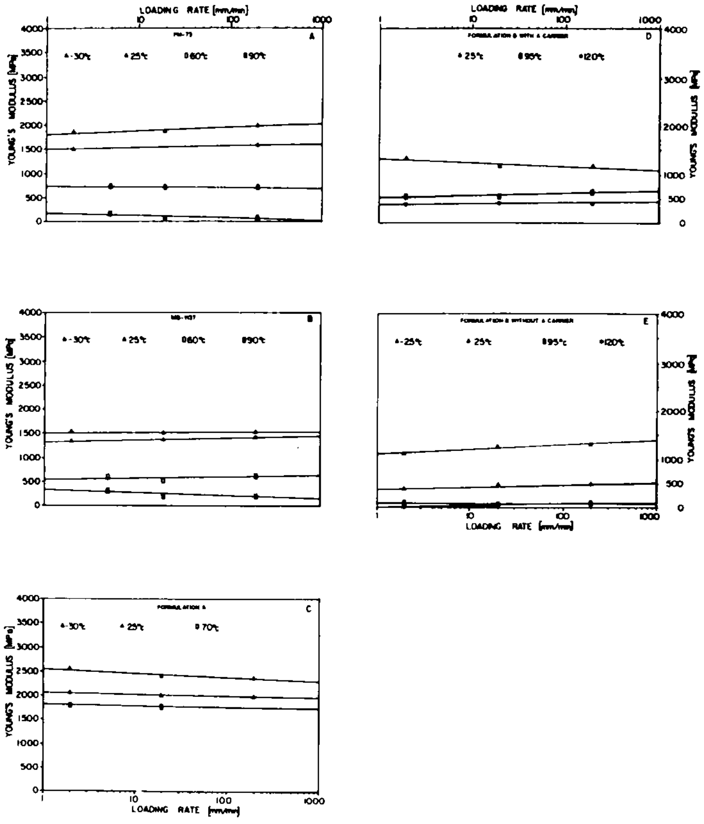


FIGURE 3 Young's modulus–loading rate relationship for various temperatures of the structural adhesives studied.

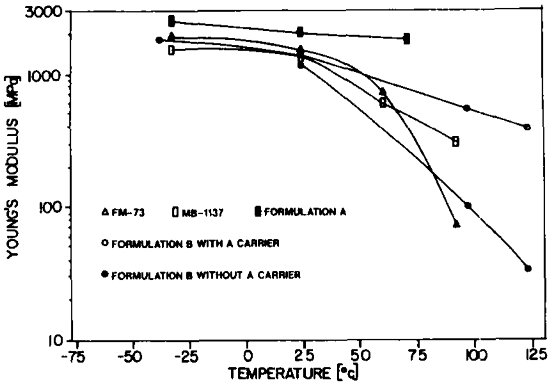


FIGURE 4 Young's modulus–temperature relationship for the structural adhesives studied.

the loading rates studied compared with the effect of temperature and the previously-discussed rate effect on the yield stress. Figure 3 correlates the Young's modulus of the studied adhesives with both the loading rate and temperature. As can be seen, no real variation of modulus occurred with increasing loading rate in the range of 2 to 200 mm/min, while the temperature effect is obvious. This result is in disagreement with the expected viscoelastic response of polymeric materials—an increase in modulus with increasing loading rates. Figure 4 describes the response of the elastic modulus of the adhesive with temperature in the range of −35°C to 120°C. The two commercial adhesives exhibited a similar response to temperature. Above 60–70°C a sharp decline in rigidity is evident.

The high-temperature Formulation A demonstrated an enhanced performance up to 70°C. Formulation B, even though it is designed to cure at room temperature, showed an improved rigidity at relatively elevated temperatures compared with the two commercial film adhesives. The effect of the thermoplastic carrier is clearly manifested for the case of Formulation B. The carrier is clearly manifested for the case of Formulation B. The carrier moderated the detrimental effects of temperature and contributed to the adhesive rigidity.

## CONCLUSIONS

The viscoelasticity-related characteristics of various epoxy film adhesives containing a thermoplastic carrier were studied.

The rate and temperature superposition, according to Eyring's theorem of viscosity, was shown to correlate with the bulk tensile strength of the adhesives studied. The activation energies determined for the high-temperature-curing, carrier-containing adhesives were found to be much higher then for the low-temperature-curing adhesives and the DGEBA-based, carrier-free epoxy formulations reported in the literature. The tensile modulus of the bulk adhesives was found to be independent of loading rate in the range of rates studied, contrary to the expected increase in modulus with increasing loading rates. However, as expected, the temperature has a pronounced effect on both tensile strength and modulus. Results indicated that, in the case of the room temperature formulation investigated, the inclusion of a carrier enhanced both the modulus and strength of the adhesive.

## Acknowledgment

To Ms. I. Liran, Mr. Y. Miller and Ms. S. Uziel, for preparing the adhesives specimens, and to Mr. E. Toledo for performing the mechanical testing.

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