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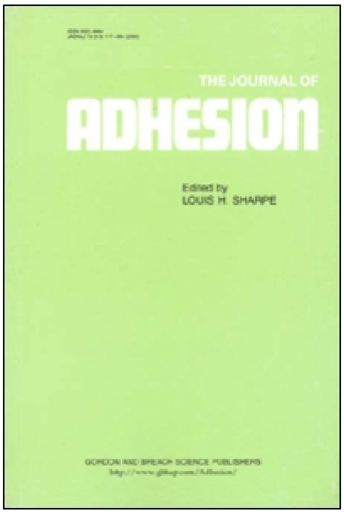

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A Thermo-Mechanical Study of Some Epoxy Adhesives Subjected to Combined Dynamic and Static Stresses

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A Thermo-Mechanical Study of Some Epoxy Adhesives Subjected to Combined Dynamic and Static Stresses

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The object of the present study was to investigate the effect of superimposed dynamic and static stresses on mechanical and thermal properties of some epoxy adhesives. It was found that combinations of shear creep and torsional oscillations, applied simultaneously to adhesive joints at temperatures within the glassy range of the adhesive, led to strengthening of the joints in shear and to an increase in the glass transition temperature of the adhesive. Similar loading stresses applied at temperatures close to the T_g of the adhesive, led to opposite effects on the above mentioned properties of the joints. The width of the glassy-rubbery transition of the adhesives increased, in the whole range of temperatures used in this study and for all epoxy compositions, as a result of subjecting the joints to superimposed dynamic and static stresses. The broadening of the glass transition was interpreted as a result of the stiffening of polymer network during the combined stressing experiments. A linear relationship was found between the area of endothermal peaks in the first DSC scan of specimens subjected prior to test to superimposed dynamic and static stresses at temperatures below T_g, and the shear strength of the joints. In agreement with this observation and with literature data, a linear relationship was revealed also between the glass transition temperature of the resins (measured in the first DSC scan) and the shear strength of the joints. Based on experimental observations and on some literature information, it was suggested that the strengthening of the joint, as well as the changes in thermal properties of the adhesives, are mainly due to physical processes, such as short-range orientation of network chains and an increase in intermolecular interaction between highly polar sites of the network. The possibility that superimposed stressing led to changes in chemical crosslinking was discussed but it seems that no such reactions occurred.

KEY WORDS mechanical and thermal properties; effect of superimposed static and dynamic stresses on adhesive joint strength; glass transition temperature; physical aging (ageing); shear creep stresses; glassy/rubbery transition region; DSC; moisture diffusion processes.

1. INTRODUCTION

The object of a previous study was to identify specific effects that the combined dynamic and static stresses may have on the mechanical properties of adhesively bonded joints, as compared with effects of single types of stresses applied separately.[1–3] We found that relatively mild combinations of dynamic and static stresses

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applied on Single Lap Joints (SLJ) had a considerable effect on their shear strength. The most surprising result was the strengthening of joints when different combinations of static and dynamic stresses were applied before the test, at temperatures lower than the T_g of the adhesive. On the other hand, combinations of stresses applied to temperatures close to, or higher than, T_g reduced the shear strength of the specimens, as compared with the shear strength of reference joints. It was assumed, based on the above observation and on some existing literature data,[4-6] that strengthening of the joint as a result of superimposed dynamic and static loading, is due mainly to short-range orientation of network chains and to an increase in intermolecular interactions between highly polar sites of the investigated network. The possibility of changes in chemical crosslinking should not be discarded.

An attempt to correlate the above-described findings with the microstructure of the adhesives was made. Thermal analysis of the resins was performed before and after application of superimposed stresses to the joint. The main data dealt with here refer to the effect of experimental conditions (including superimposed dynamic and static stresses) on the shape of Differential Scanning Calorimetry (DSC) thermograms, as well as on the glass transition temperature and on the glassy-rubbery transition zone width of the adhesives. These data were correlated with shear strength values of the same joints.

2. EXPERIMENTAL PROCEDURE

2.1. Instrumentation

2.1.1. Experimental Conditions. The static tensile load was applied vertically using either 0.8 kg or 6.4 kg dead weights per joint. Simultaneously, a dynamic load was applied horizontally as torsional oscillations of different amplitudes and frequencies. This was done by means of an electronically controlled DC motor, a variable cam and a system of arms connected through ball bearings to minimize the friction.[1-3] We believe that such a loading combination may serve as a model representing to some extent certain systems of stresses acting on real joints. Series of five specimens were simultaneously subjected to different combinations of stresses at ambient atmosphere with about 60% RH at various temperatures, for a period of 24 hours. The experimental temperatures were chosen in respect to the glass transition temperature of each adhesive, so that both the glassy and the transition regions would be investigated.

2.1.2. Specimens. The Single Lap (SL) type of joint was chosen. The specimens for DSC analysis were collected from the spew fillet of the joints, as suggested by Brett[7] (Fig. 1).

We are aware that both the effect of environmental conditions (such as relative humidity), and the state of stresses in the spew fillet, are not identical with those in the adhesive inside the joint. However, since measurements are only comparative and not absolute, we believe that this sampling location enables us to obtain data which may represent the processes taking place in the adhesive layer between the two aluminum substrates. An additional reason for this choice is connected with the

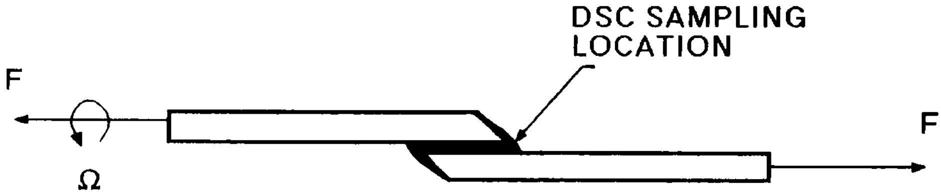

FIGURE 1 Schematic representation of the SLJ specimen and the location of the DSC sample.

TABLE I
Composition of adhesives (% weight)

	EV-1	EV-2	EV-3	E	ET
Epon Resin 828® (Shell Co.)	40	50	60	90.9	83.3
Versamid 140® (General Mills)	60	50	40	—	—
Thiokol LP-3® (Thiokol Co.)	—	—	—	—	8.3
TETA (Fluka A.G.)	—	—	—	9.1	8.3

difficulties encountered in taking samples from inside the joint: the layer of adhesive is very thin (approx. 200 μm) and strongly bonded to the substrate, so that only very small amounts (1–2 mg) can be collected. Therefore, even if we could collect "inside" samples, the DSC thermograms would be difficult to interpret because of the relatively low level of the signal-to-noise ratio (SNR). Moreover, since the distribution of stresses inside the SLJ is very complex and spatially dependent,[12,16] the accuracy by which these samples may represent the average effect of applied stresses on the adhesive behavior is also questionable.

2.1.3. Materials and Curing Conditions were as specified in Ref. 3 and a short extract of the Table 1 from that reference is presented in Table I. After the components were thoroughly mixed and the bubbles escaped, the adhesive was cured between aluminum plates and the joint was kept in dry conditions until being tested. More details about the curing procedure were reported earlier.[3]

2.2. Investigation Techniques

2.2.1. Mechanical Testing was performed by applying a tensile load on the SLJ. This led to formation of shear stresses in the adhesive layer, due to the special configuration of the specimen. Therefore, the tests yield the shear strength of the SLJ in tension. More details regarding the test configuration and parameters were provided in previous publications.[3]

2.2.2. Thermal Testing. **DSC** was carried out by use of a Mettler TA 3000 instrument on samples of about 10 mg, while the heating rate was 10°C/min. The method of interpretation of the DSC thermograms was as shown in Figure 2; the difference between T_2 and T_1 (considered to be T_g) was defined as "transition zone width" (TZW).[9]

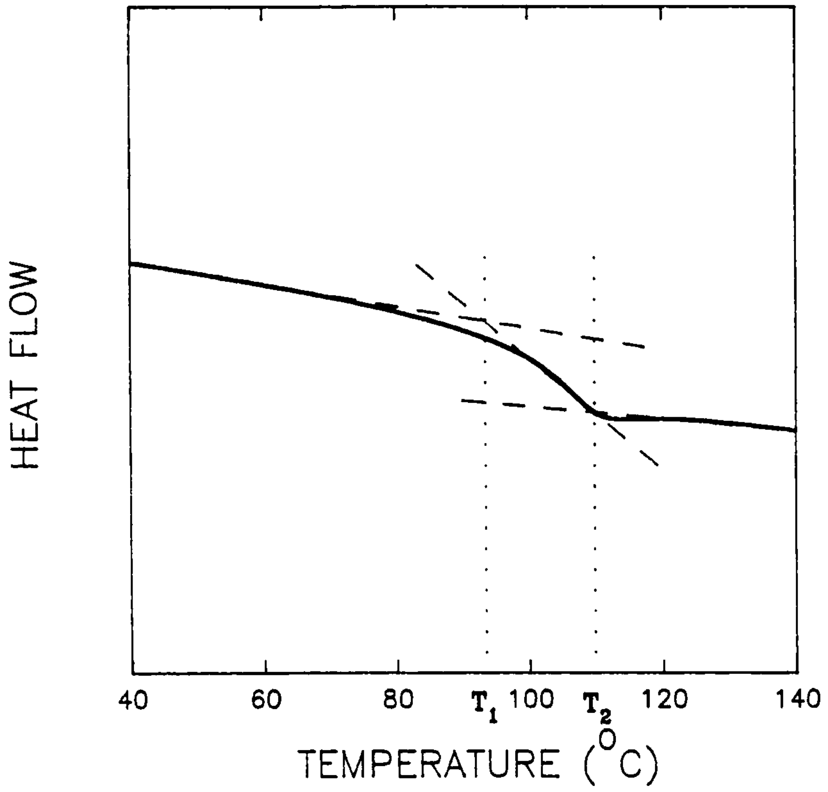

FIGURE 2 Typical DSC thermogram showing the calculation of T_g and TZW.

The experimental error in determination of the above characteristic temperatures was ±0.6°C (based on measurements performed on five samples). By superposing the first and the second run thermograms of the same specimen, the physical aging process which took place in the specimen before the first run may be estimated.[8,9] A more detailed description and discussion of the procedure will be given in the following section.

Thermo-mechanical Testing. The Gehman analysis (ASTM D1053-85), which yields curves of torsion modulus (G_{10}) *vs.* temperature, was used (the strain was measured 10 sec after application of torsional momentum). Specimens of adhesives used for this test were cast into RTV silicone rubber molds and cured under the same conditions as the joints. Silicone oil MS 200/200 of BDH was used as heating agent in the Gehman experiments and the uniformity of temperature in the oil bath was maintained by use of a mechanical stirrer. Cooling of the oil to temperatures lower than ambient was done by direct introduction of liquid nitrogen. The heating rate was about 1°C/min and the transition between the glassy and rubbery regions, occurring in these measurements, is close to the T_g of the polymer. The Gehman second and third runs caused systematic changes in the modulus-temperature curves, a fact which will be further analyzed.

3. RESULTS AND DISCUSSION

3.1. Mechanical Testing

Earlier results obtained in the above experiments were published previously.[1-3] The present paper shows some additional data (Fig. 3 and 4) represented as shear strength (in MPa) of joints *vs.* frequency (in Hz) of torsional oscillations acting simultaneously with shear creep stresses before testing. The computation of the error bars is based on the standard deviation shown by all the samples subjected to the same frequency of torsional oscillations.

In experiments performed in the glassy region of the adhesive (Fig. 3), the superposition of dynamic stresses on the static shear creep led to an increase of the shear strength of the joints.

The points representing the average shear strength of joints, subjected before testing to different combinations of dynamic and static stresses, are located above the dotted line; this line defines the average shear strength of reference specimens,

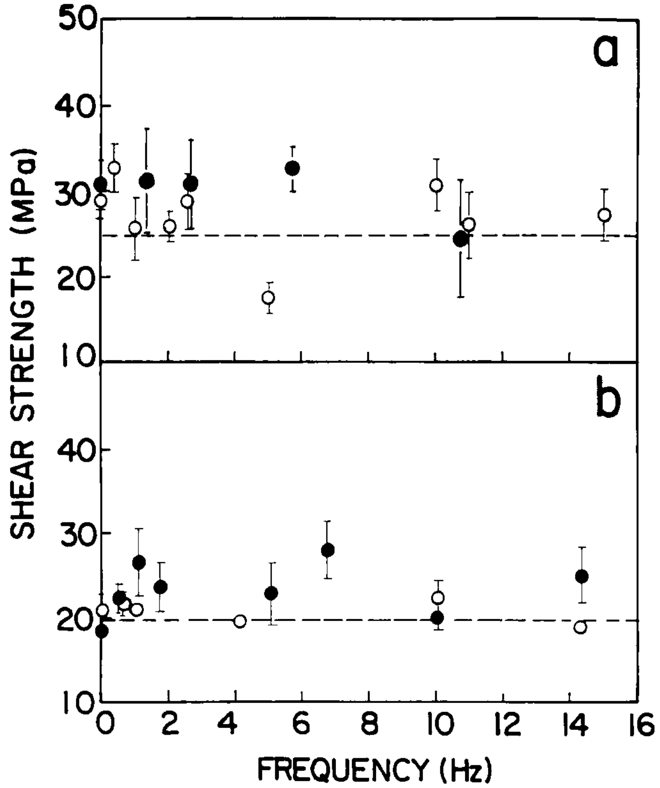

FIGURE 3 Shear strength of a) EV-2 specimens and b) E specimens, subjected before mechanical testing to superimposed dynamic and static stresses at temperatures lower than T_g. Creep load: 0.4% of load at break (open symbols) and 3.2% of load at break (filled symbols).

TABLE II
Summary of "Student-t" calculations

	EV-2		E	
	0.4% of σ_{break}	3.2% of σ_{break}	0.4% of σ_{break}	3.2% of σ_{break}
No. of tested specimens (n)	68	19	29	40
Average (μ)	27.08	30.07	20.86	23.73
Standard deviation (σ)	3.91	4.67	3.31	6.751
$t_{0.05}$	2.10		2.02	
t	3.36		2.69	

i.e. joints not subjected to any stresses during the period between their preparation and testing. In absolute values, the shear strength of joints made with adhesive E was smaller than that of joints made with adhesive EV-2 (Table II), a fact which is presumably due to the higher brittleness of resin E. The relative increase of the shear strength was more pronounced for joints made with adhesive E (Fig. 3b) than with adhesive EV-2 (Fig. 3a).

It seems that application of a higher creep load led to higher shear strength of the joints: the points representing the average shear strength of joints subjected before testing to the high creep load are located above points which show the mean shear strength of joints subjected before test to the low creep load. Due to the effect of variations within each set of specimens, this observation was verified by use of the Student-t test of hypothesis.[10] By means of this test it was checked whether the average strength of all the joints subjected before test to the high creep load is significantly different from the average strength of all the joints subjected before test to the low creep load. The results of the test, with regard to the adhesives EV-2 and E, for experiments performed at temperatures lower than T_g of the adhesive ($T_g-30°C$ and $T_g-80°C$, respectively), are shown in Table II. Calculation of the "t" parameter for the sample was based on the following formula:[10]

$$t=\frac{(\mu-\mu_o)}{s_p(1/n_1+1/n_2)^{1/2}} \tag{1}$$

where μ and μ_o represent the means of compared samples of data, n_1 and n_2 the number of data within each one of the samples and s_p, the pooled variance estimate. In both cases, the calculated value of t was higher than the critical value $t_{0.05}$ (as obtained from tables[10] for a two-tailed test at a confidence of 95% and for the suitable degrees of freedom). Therefore, the application of the higher creep load led, with 95% confidence, to a more pronounced strengthening of the joints, when compared with joints subjected to the smaller creep load.

After experiments performed at about T_g, in which combinations of dynamic and static stresses were applied, the shear strength of the joints decreased, as compared with the shear strength of reference joints kept at T_g for the same period of time but not subjected to any stress at all (solid lines in Fig. 4).

Nevertheless, when the same data were compared with the shear strength of reference joints kept at room temperature (dashed lines in Fig. 4), it is clear that subjecting specimens to superimposed stresses, even at T_g, led to an increase in their strength.

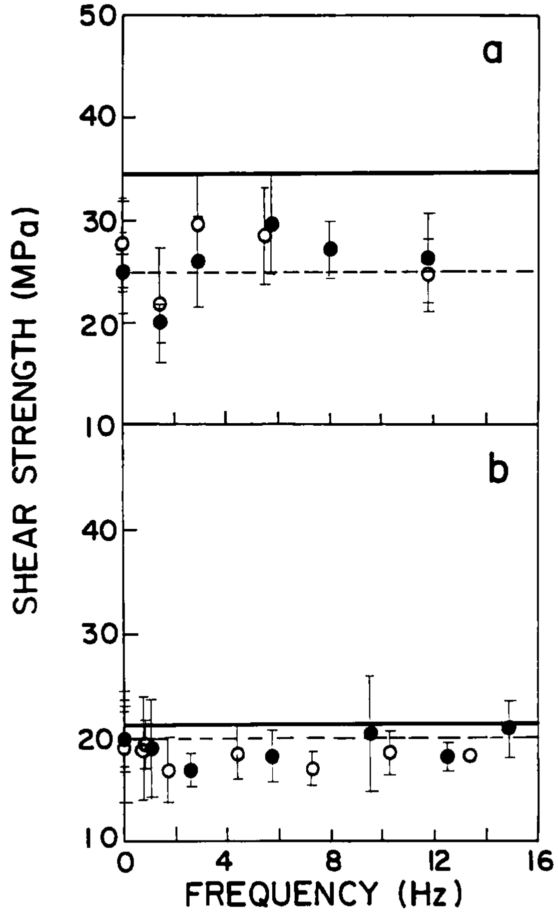

FIGURE 4 Shear strength of a) EV-2 specimens and b) E specimens, subjected before mechanical testing to superimposed dynamic and static stresses at temperatures close to T_g of the adhesive. Creep load: 0.4% of load at break (open symbols) and 3.2% of load at break (filled symbols).

On the other hand, keeping both adhesives (EV-2 and E) for 24 hours at T_g, without application of any stresses, led also to a significant increase of the shear strength (compare solid lines in Fig. 4 with dotted lines). This phenomenon is much more pronounced for the EV-2 than for the E composition. When corroborated with results shown in Figure 3, this behavior suggests that at least one of the mechanisms responsible for the increase of shear strength, when superimposed stresses were applied at temperatures lower than T_g, may be the heat-induced continuation of the crosslinking reaction. The energy dissipated as heat in the cyclic loading may have the same effect as keeping the joints at a higher temperature.

Two other mechanisms which seem to us more plausible are the following ones:

1. while keeping the samples at T_g, a relatively free movement of larger chain segments is allowed, thus enhancing the redistribution of free volume "holes"

and resulting in a more dense network, with a higher shear strength (physical aging);

2. preserving the specimens at T_g may result in annealing of some of the residual stresses which were induced into the specimens during curing. The decrease of the shear strength of joints subjected to cyclic and static stresses at that higher temperature may be, therefore, explained by assuming that the damage accumulating during cyclic loading has a larger impact on joint properties than either the increase of crosslink density, the network densification and/or the release of internal stresses.

It appears that the first assumption (heat-induced continuation of crosslinking) is rather doubtful because of the following reasons:

1. when subjected to different combinations of stresses and temperatures, the adhesives were already postcured at temperatures well above their T_g;[1-3]
2. the DSC thermograms of specimens before and after experiments did not show any exothermal peak which would indicate an incompleteness of the crosslinking reactions;[7,8]
3. it is well known that the maximum in damping capacity is usually recorded at T_g; if indeed the strengthening of the joints is a result of a heat-induced crosslinking continuation, then it should be expected that some strengthening should be recorded for experiments performed at T_g. The fact that it is not so suggests that either:
   - —the heat-induced crosslinking continuation does not play any significant role in the observed strengthening of joints, or
   - —there is some other mechanism(s) which competes with the supposed cyclic-loading-induced increase of crosslink density;
4. the applied stresses were very small (see Appendix 1). Consequently, the energy dissipated in the cyclic loading should be relatively small as well:[11]

$$dE/dt = \pi f J''(f,T)\sigma^2 \qquad (2)$$

where:

dE/dt = the rate of energy dissipation;
f = frequency;
$J''(f,T)$ = loss compliance of the specimens as a function of frequency and temperature T;
σ = maximum applied stress.

It is difficult to find in the literature data entirely relevant for our materials and experimental conditions but some useful comparisons could be found. For instance, Crawford and Benham[14] recorded, by means of infrared thermometry, an increase of only 7°C for specimens made of an acetal copolymer when subjected to a stress of maximum 15 MPa at a frequency of 5 Hz. At about 10^6 cycles the temperature of the specimens stabilized at some level due to a balance between the energy input and the heat dissipated to the surroundings. Sauer and Chen[13] measured, also by means of infrared thermometry, a temperature rise of about 50°C in PMMA specimens subjected to cyclic loading at a frequency of 2 Hz but this happened at stresses almost two orders of magnitude higher than those applied in our experiments (55.2 MPa in Ref. 13 as compared with 0.84 MPa in our work—see Appendix 1). It is worthwhile mentioning that the 50°C temperature rise was recorded by Sauer and Chen toward the end of the fatigue experiment, close to the failure of the specimen. At this final stage of the fatigue loading, the loss compliance of the specimens increases dramatically, while it remains almost constant during the first stages of cyclic loading.[11] In our work, most of the specimens did not fail during the application of combined dynamic and static stresses. Therefore, we expect that the loss compliance of our specimens would be rather constant during the experiments. Since the applied stresses were very small (Appendix 1), it is hard to expect a large temperature rise of the specimens in our experimental conditions. In Appendix 2 we compute the expected temperature rise of the adhesive in our study. The above assumption of loss compliance constancy is checked there using data of Herman *et al.*[11] and it is found to be valid.

It seems that in analyzing the possible heating effects in the present work, the following should also be taken into consideration:

—the damping capacity of polymers in the glassy region is relatively small; even if one assumes a temperature increase of 50°C, the glass transition temperature of the resin E will not be exceeded in joints subjected to superimposed stresses at room temperature ($T_g - 80°C$);

—the layer of adhesive has a very small thickness (200 μm); consequently, even if a heat build-up exists, it will easily be dissipated due to the closeness of the aluminum substrates. It also should be mentioned that the maximum stresses develop at the surface of the adhesive layer,[16] thus assisting even more a rapid and effective dissipation of the generated heat.

3.2. Thermal Testing

An additional observation which contradicts the possibility that crosslinking reactions took place during superimposed stressing, is the fact that a decrease of T_g was registered in the second DSC run when compared with the first run performed on the same specimen (Fig. 5).

Data are shown as the ratio between the glass transition temperatures in the first and second DSC scan *vs.* frequency of torsional oscillations. The dashed lines, obtained by linear regression, seem to indicate that with increasing frequency, the T_g in the first-run scans decreases toward the T_g in the second DSC scan. Usually, as a result of crosslinking continuation, the glass transition temperature may increase during the first DSC run and consequently a higher T_g would be revealed in the second one. The reduction of the T_g in the second run may suggest that the high value of T_g in the first run indicates only a physical effect.

Thus we believe that, although the idea of continuation of crosslinking reactions cannot be discarded, the main explanation for the observed phenomena can be found in some physical processes such as those leading to the densification of the resin. It is worthwhile mentioning that other authors, while working with thermoplastics, recorded during the first stages of fatigue experiments an increase in the

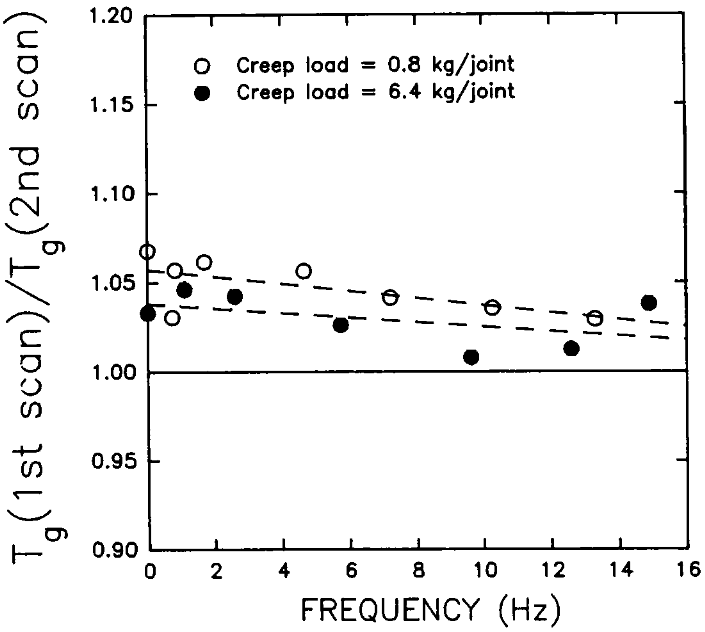

FIGURE 5 Ratios between glass transition temperatures in the first and second DSC scans of E adhesive from joints subjected before test to superimposed stresses at 105°C; filled symbols—6.4 kg creep load; open symbols—0.8 kg creep load.

storage modulus[18,39] and of the density of the sample.[19,39] Their findings seem similar in nature to the presently-observed increase in shear strength of joints subjected before the tensile test to combinations of dynamic and static superimposed stresses. On the grounds of the similarity between the phenomena recorded with thermosets in our work and with thermoplastics in the cited papers, we may reach a conclusion that the crosslinking continuation is not the only mechanism responsible for the densification of a polymer during fatigue loading. It is, therefore, suggested that the mechanism which governs the strengthening of the joints subsequent to application of superimposed dynamic and static stresses, is based on "physical" crosslinking processes, due either to short-range orientation of network chains and interaction between them, or to stress-enhanced physical aging. A similar hypothesis regarding the intensification of intermolecular secondary forces due to reorientation was made by one of the authors[21,34,38] when aging of epoxy resins subjected to large strains was investigated. In the following, further support for this hypothesis will be provided by analyzing the data obtained by DSC of the adhesives.

The effect of combined dynamic and static stresses on T_g of the adhesives are, to some extent, similar to changes occurring in the shear strength of the joint. For instance, when the experiments were performed at temperatures close to the glass transition temperature of blank specimens, the decrease of the joint shear strength (filled symbols—Fig. 6) was consistently accompanied, over the whole investigated range of frequencies, by a decrease of the T_g of the adhesives (hollow symbols—Fig. 6).

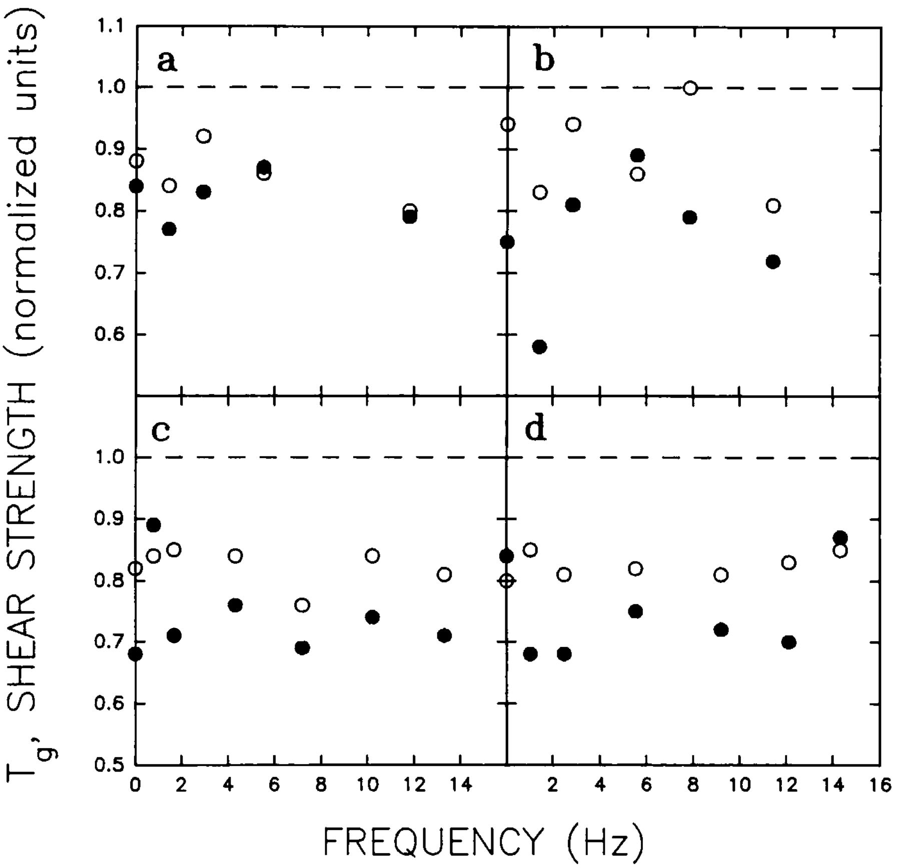

FIGURE 6 Normalized average shear strength (filled circles) and glass transition temperature (open circles) of joints subjected prior to test to superimposed stresses: a, b)—specimens made with EV-2 adhesive and c, d)—specimens made with E adhesive. The creep loads applied were: 0.8 kg per joint—a, c; 6.4 kg per joint—b, d. The superimposed stresses were applied at temperatures close to T_g of the adhesive: 52°C—a, b and 105°C—c, d.

The data are again shown in normalized units by reference to specimens unsubjected to any stress at all between their preparation and testing. Thus, the dashed line at 1 represents the shear strength and the glass transition temperature of the blank specimens. The behavior portrayed in Figure 6 agrees with observations made by Brett[7] and Cassidy *et al.*[22] regarding the apparent linear relationship between the lap joint strength and the glass transition temperature of the adhesive. In the cited papers, the change of the T_g was achieved by different curing and postcuring conditions[7] or by additions of different amounts and types of plasticizers.[22] It should be emphasized that, in the present work, modification of the glass transition temperature was attained without changing the composition of the adhesives, but by varying only the thermo-mechanical history of the joints.

The shear strength of the Single Lap Joints is plotted *vs.* the glass transition temperature of the adhesive in Figure 7.

The data are displayed as normalized values relative to reference specimens. The

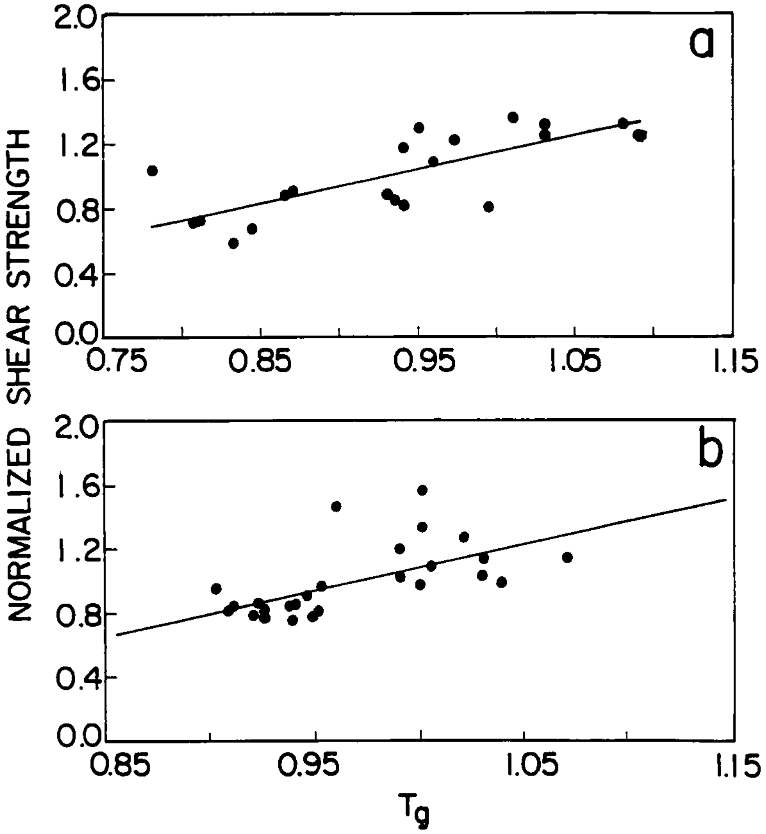

FIGURE 7 Normalized average shear strength of EV-2 specimens (a) and E specimens (b) as a function of the normalized glass transition temperature of the adhesive. Joints were subjected before mechanical testing to superimposed stresses at different frequencies and temperatures.

shear strength values were determined after superimposed stressing experiments performed at various temperatures (both below and above T_g). By comparing the location of data on the T_g scale with the glass transition temperature of blank specimens (Figs. 6 and 7), it appears that the glass transition temperatures of the adhesives changed considerably as a result of subjecting specimens to superimposed dynamic and static stresses. Moreover, a linear relationship between the two variables can be clearly seen in Figure 7, in spite of the quite large scatter of the data. The best fit lines are represented by the equations:

$$\text{E: } \sigma_n = -1.8 + 2.89T_{gn};\ R^2 = 0.37$$

$$\text{EV-2: } \sigma_n = -0.85 + 1.98T_{gn};\ R^2 = 0.53$$

where:

σ_n is the normalized shear strength;
T_{gn} is the normalized glass transition temperature;
R^2 is the correlation coefficient of regression.

The effect of experimental conditions on the width of the glassy-rubbery transition zone (TZW) of the adhesive, as it was calculated from the first DSC run, is summarized in Figure 8.

TZW is expressed in normalized units, *i.e.* TZW for each experimental condition is divided by the value obtained when blank specimens were analyzed by DSC (TZW_0). While the variation of TZW with the experimental conditions was quite large, it can be clearly seen that there was a general increase as a result of stressing the joint before DSC testing (most of the values are larger than unity). This tendency was clear even in cases in which the single applied stress was tensile creep (the values on the ordinate). The increase of TZW occurred not only in the glassy state, but also when the experiments were performed at, or above, T_g. A similar observation regarding the broadening of the transition zone was made recently by Ellis[25] who investigated amorphous polyamides and attributed it to increased mobility of the network chains due to the plasticization process by absorbed moisture. Contrary to this explanation, quite a large number of other authors showed by various techniques (DMA,[4,26,37] DSC,[9,45] TMA,[20] Gehman analysis[34] and stress relaxation[45]) that a broader transition zone is, in fact, an expression of an enhanced rigidity of the polymer chains. Based on these results, we may speculate that the

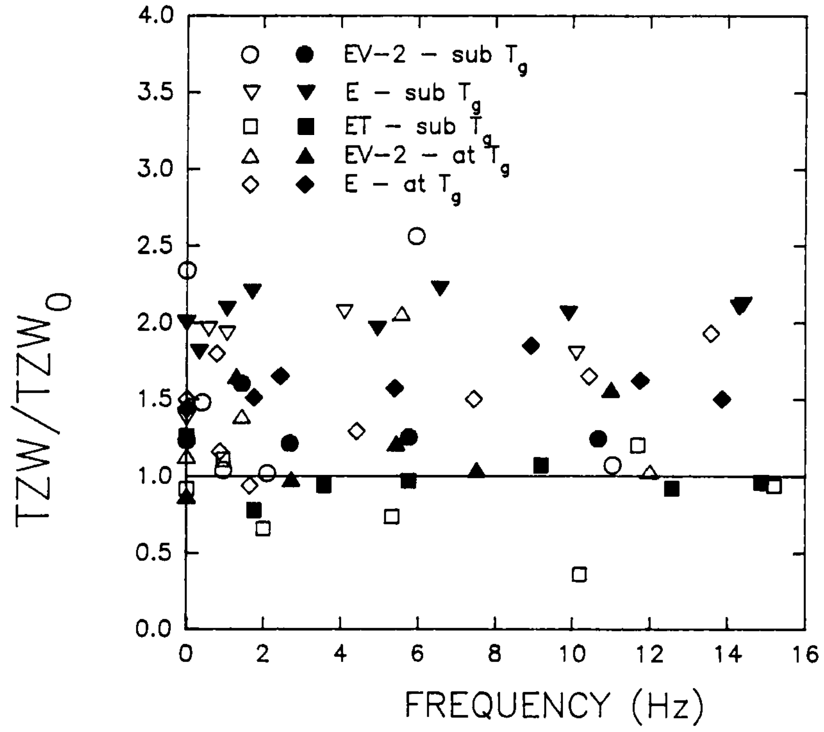

FIGURE 8 The effect of experimental conditions and resin composition on the normalized width of the glassy-rubbery transition range. The creep loads were: 0.8 kg/joint (open symbols) and 6.4 kg/joint (filled symbols).

increase in TZW observed in our work indicates an increase in the rigidity of the network as a consequence of subjecting the adhesive joints to combined dynamic and static stresses. It is worthwhile mentioning that this conclusion, based on TZW calculation from DSC tests, is in agreement with the observed increase in mechanical strength of the same joints, after superimposed dynamic and static stressing at temperatures lower than T_g (Fig. 3). However, an apparent conflict exists between the increase in TZW (*i.e.* the supposed increase in network stiffness) and the decrease observed in mechanical strength of joints after experiments performed at temperatures higher than T_g. We suggest that a reasonable explanation for this conflict is provided by the supposed creation of large thermal stresses in the joint when the specimens were removed from the hot oven at the end of the experiment. Microcracks generated due to these thermal stresses could negatively affect the mechanical strength of the specimens. In experiments performed at lower temperatures, the thermal shock was much more attenuated or it did not exist at all, so that the increased rigidity of the network expressed itself in an increase of the mechanical strength of the joints.

The glass transition temperature of adhesives containing Versamid 140® is more sensitive to the frequency of torsional oscillations than that of the amine cured epoxy (Fig. 6). This behavior can be explained by the higher moisture affinity of Versamid-containing systems.[29,36,39] The reduction of the glass transition temperature by as much as 10–12°C may be caused by absorption of only 0.5–1% of water.[29] The data existing in the literature about the weight gain of epoxies in moist environments are quite controversial, but an intake of about 1% in our experimental conditions seems possible. For example, Brewis *et al.*[41] reported that an epoxy resin cured with a polyamide gained about 2.9% within 3 days while exposed to 65% RH at room temperature, and Kwei[42,43] reported that films of amine-cured Epon 828® reached equilibrium with water vapor within 1 day at 100% RH. Although we did not perform water absorption measurements, it seems to us that a similar effect of ambient moisture was found when Gehman tests were performed on bulk specimens made with the same adhesive compositions as those used in joints. As shown in Figure 9, repeated runs performed on the same specimen based on Epon 828® cured with Versamid 140® led to a systematic shift of the transition region of the relaxation modulus temperature curve toward lower temperatures.

It is suggested that this behavior is due to the plasticizing effect of water penetrating into the resin during the experiment. The water originates from the surrounding atmosphere and enters the system due to condensation during repeated cooling with liquid nitrogen. Throughout the Gehman test, the mechanical stirrer disperses this condensed water in the bulk of the silicone oil from which it diffuses into the specimen. No such effect was observed when an Epon 828®-TETA specimen was tested in similar conditions: curves representing the first and the second run coincided with each other.[17] Confirmation of this hypothesis by drying the EV-2 specimens is very difficult, because the absorbed water does not leave the polyamide-cured resin even after several hours in vacuo[17,26,38] and we were not interested in heating the system.

Concluding, we assume that while performing the superimposed stressing in regular laboratory conditions in air with a relative humidity of 60%, the more hydro-

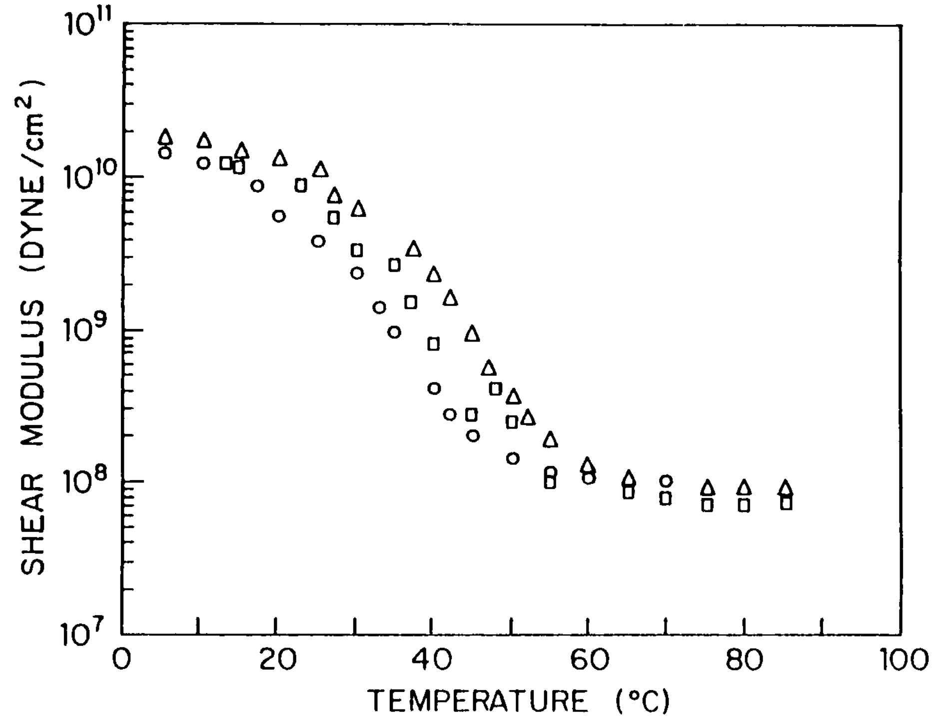

FIGURE 9 Torsional relaxation modulus (at 10 sec) *vs*. temperature: three consecutive Gehman scans of the same EV-2 specimens: △—first run, □—second run, ○—third run.

philic systems may absorb a higher amount of atmospheric moisture when subjected to torsional oscillations with increasing frequency. This stronger moisture absorption is probably due to the increase of the chain mobility caused by torsional oscillations and exposure of new absorption sites. It is known that a statically-stressed specimen is able to absorb a larger amount of moisture than a relaxed one.[30-32] This effect of stresses is attributed by the cited authors to formation of very fine microcracks which contribute to multiplication of the moisture absorbing sites; in other words, the applied stress may enhance the Langmuir mode of gas transport.[33,34] We suggest that the Langmuir mode of absorption is even more enhanced when cyclic loading is applied. Indeed, Krause *et al.*[40] found that immersion in water before monotonic testing has no effect on epoxy-bonded SLJ but, when applied before a fatigue test, the water immersion led to a significant deterioration in the fatigue life of the same bonds. More than that, they found that the combined effect of humidity and stressing (fatigue tests in a wet environment) is much more destructive for the fatigue life of the joints than the effect of either stress or humidity, considered separately.

While the decrease of the glass transition temperature of the adhesives may be tentatively explained by the effect of combined action of moisture, temperature and stress, the increase of T_g observed in some cases (Fig. 7) is much more difficult to explain. As mentioned before, a simple explanation may be related to a continuation of the crosslinking reactions during the experiments but, although this hypothesis cannot be dismissed, we have serious reservations about it, as mentioned in section 3.1. It seems to us that the increase of T_g is rather connected with the densification of the resin during superimposed stressing experiments. This hypothesis is supported by data in the literature[18,19,39] as discussed earlier. There is a large amount of literature data which confirms that there is no need for chemical reactions in order to incur a change in the T_g of a resin. For example, application of pressure leads, as anticipated, to an increase of the glass transition temperature due to the densification of the polymer and, in the same way, densification due to the physical aging process has a similar result. A support for the hypothesis that physical aging is one of the main processes taking place during superimposed dynamic and static stressing of adhesive joints, in our work, can be found by analyzing the shape of DSC thermograms obtained in two consecutive runs performed on the same specimen. It is well known that physical aging leads to the occurrence of an endothermic peak in the vicinity of T_g in the first DSC run of an aged specimen.[35,46] This is a result of the fact that, during aging, the polymer loses entropy and internal energy; when an aged specimen is heated through T_g, it absorbs the heat it lost during aging.[35] As well documented in the literature,[35,46] there seems to be a direct proportionality between the efficiency of the physical aging process and the area of the endothermal peak, as revealed in the first DSC scan. The correct method to evaluate the enthalpy recovery is by calculating the area enclosed between the two superposed first and second scan curves[46] as shown in Figure 10.

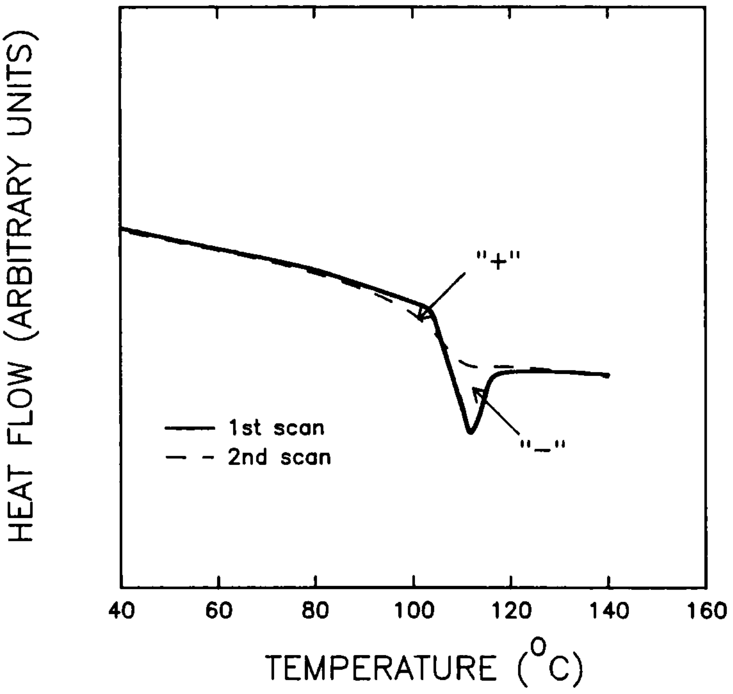

FIGURE 10 Typical DSC scans of epoxy resin E from an adhesive joint after a superposed dynamic and static stressing experiment. Traces for the first scan (solid line) and the second scan (dashed line) are superposed.

The evaluation of endothermal peak areas was performed by graphical superposition of the two consecutive thermograms, followed by cutting out the area of interest and weighing the paper pieces on a Ohaus electronic analytical balance with a precision of 0.01 mg. In those cases when two types of areas were enclosed by the superposed curves (Fig. 10), the enthalpy recovery was assumed to be represented by the difference between the "true" endothermic " – " peak area and the "apparent" exothermic " + " peak area. The method has an inherent error of approximately 1%, found by weighing paper pieces cut to a standard size. The measure of the enthalpy recovery was obtained then by normalizing the weight of the cut peak area to 1 mg of polymer; the results emerging out of this procedure will be called in the following discussion "physical aging peak area." One of the major factors affecting the physical aging process is the temperature; the closer the annealing temperature is to T_g, the higher is the efficiency of the physical aging process. This can be readily seen in Figure 11: the size of the physical aging endothermal peak is the largest when the experiments were performed at 105°C, very close to the glass transition temperature of the adhesive.

Also, it is worth mentioning that the extent of the physical aging process, as it can be estimated from the shape of the DSC thermogram, is quite low at room temperature (almost no endothermal peak) and it is not affected too much by the increase in temperature to 64°C (which is, also, within the glassy range of the resin).

The relationship between the area of physical aging peaks, calculated as above,

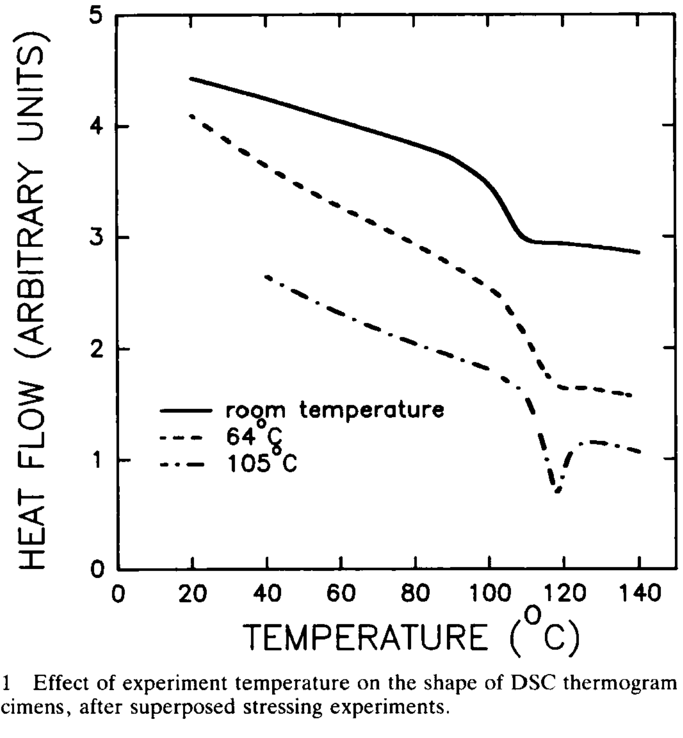

FIGURE 11 Effect of experiment temperature on the shape of DSC thermogram in the first scan of resin E specimens, after superposed stressing experiments.

and the experimental conditions (frequency, temperature, creep load) is shown in Figure 12.

It is evident that the physical aging process is not only temperature dependent, but it is also affected (in a complex way) by frequency and creep load. The extent of the physical aging process taking place in experiments performed at room temperature ($T_g - 80°C$) is the lowest among all experiments (all the points belonging to these experiments are located below the dashed line in Fig. 12, arbitrarily located at $y = 1.5$, while most of the points are above that line). The points on the y-axis (frequency $f = 0$) represent physical aging peak areas of specimens subjected only to creep before the DSC test. It appears that superimposing dynamic stresses on a statically-loaded specimen leads to an increase in the physical aging efficiency: almost all the physical aging peaks in experiments performed under superimposed dynamic and static stresses ($f > 0$) are larger than physical aging peaks in experiments performed in creep only.

One of the main points of this paper is that the experimental conditions used did not change the chemical structure of the investigated resins. We believe that the processes behind the recorded changes in T_g and TZW of the adhesives and mechanical strength of the joints are physical in nature, namely, a competition between physical aging and moisture plasticization, both dependent, in a complex way, on experimental conditions. Figure 13 provides support for this hypothesis.

For experiments performed at temperatures below T_g (all represented by hollow symbols), a linear dependence between the shear strength of the joints and the

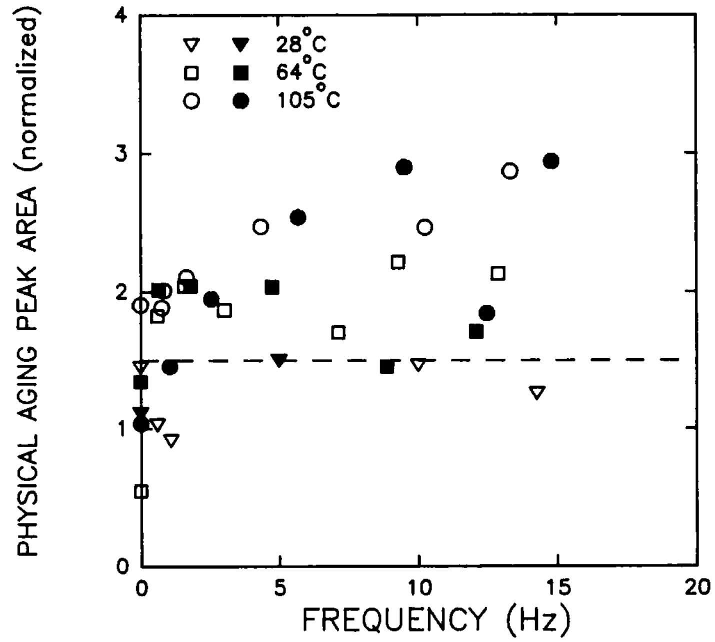

FIGURE 12 Effect of torsional oscillations frequency on the normalized area of the endothermal peak in the first DSC scan of E specimens, after superposed stressing at various temperatures. The applied creep loads were: 0.8 kg/joint (open symbols) and 6.4 kg/joint (filled symbols).

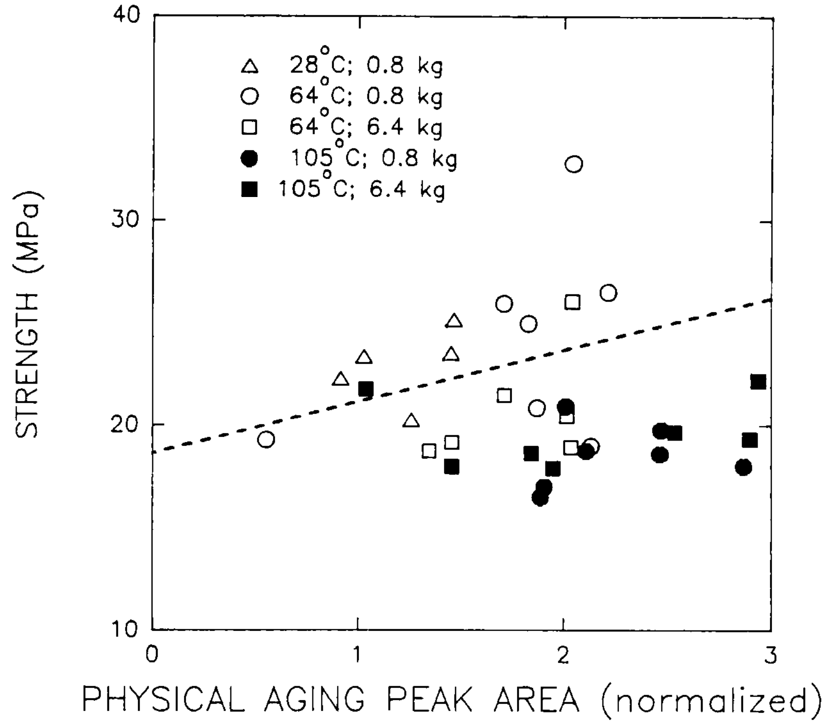

FIGURE 13 Relationship between the shear strength of resin E joints, after superimposed stressing experiments, and the extent of physical aging estimated by the area of the endothermal peak revealed in the first DSC scan of the adhesive.

physical aging peak area is obtained. In spite of the quite large scatter of data we think, based on all the considerations brought throughout this paper, and also on additional data which will be shortly published,[45] that the trend of increase of the mechanical strength with the physical aging in our experiments is real. Obviously, the factors affecting the mechanical strength of the SL joints are multiple and complex; for example, from Figure 13 it appears that specimens subjected to superimposed dynamic and static stresses at temperatures close to T_g (filled symbols), while exhibiting the largest physical aging peak areas, have the lowest mechanical strength among all the tested specimens. One explanation for this effect is connected, as mentioned earlier, with the large thermal stresses supposed to be induced in the specimen while cooling them rapidly in air at the end of each high temperature experiment.

CONCLUSIONS

1. The application of superimposed dynamic and static stresses at temperatures close to T_g of the adhesive led to a decrease in its glass transition temperature when compared with T_g of the same resin in unstressed joints and kept for the same length of time at the same temperature.
2. Experimental evidence shows that superposition of torsional oscillations, on

specimens subjected for the same time to shear creep below T_g of the adhesive, led to an additional increase of the joint strength and of the T_g of the adhesive. Based on the above observation and on some existing literature information, it was suggested that the strengthening of the joint, as well as the increase of T_g, is due mainly to short-range orientation of network chains and to an increase in intermolecular interactions between highly polar sites of the network. The possibility of changes in chemical crosslinking cannot be discarded.

3. In most of the investigated cases, the application of superimposed stresses led to significant changes in the glass transition temperature and in the width of the rubbery transition region. The broadening of the glassy-rubbery transition was tentatively attributed (based on literature data) to an increase of the network stiffness as a result of subjecting the adhesives to combined dynamic and static stresses.

4. It was found that a linear relationship exists between the shear strength of the joints and the T_g of the investigated adhesives in the experimental conditions used in this work.

5. The increase in strength was found to be correlated with the extent of physical aging as it was estimated by measuring the area of the endothermal peaks occurring in first DSC scans.

6. It seems that some additional processes, which may have adverse effects to those leading to a densification of the resin, take place during superimposed stressing. An example of such a process could be plasticization of the adhesive due to diffusion of atmospheric moisture into the resin. The approach of Struik,[35] Adamson[23] and Gupta[24] was adopted: the increase of free volume of the resin occurring upon stressing allows higher mobility of the network chains in their glassy state, accelerates physical aging of the resin and favors the moisture diffusion process.

APPENDIX 1

Computation of Stresses Within the Adhesive Layer

1. Shear stresses due to creep. The overlap area is 9×9 mm^2 (Fig. 2 of Ref. 3). The average shear stresses which developed during creep are (dividing the load by the overlap area) 0.086 MPa for a creep load of 0.8 kg and 0.69 MPa for a creep load of 6.4 kg.

2. Shear stresses due to torsion. The analysis of such stresses developed in noncircular cross sections of bars subjected to torsion is very complex.[12] The cross section of the adhesive layer is rectangular with the following dimensions:

—width $a = 0.009$ m;

—height $b = 0.0002$ m (the thickness of the layer). The stresses are not uniform across the cross section; the maximum shear stress is encountered at the middle of the wide side, while at the corners there are no shearing stresses at all.

The maximum shear stress formula is:[12]

$$\tau_{max} = \frac{(3a + 1.8b)\Omega}{a^2b^2} \tag{A.1.1}$$

where:
Ω = twisting moment (N.m);

$$\Omega = \frac{\theta K G}{L} \tag{A.1.2}$$

θ = angle of twist (radians);
L = length (m);
K = a function of the cross section geometry (m^4);
G = elastic modulus (N/m^2).

The maximum angle at which the joints were twisted in the experiments was 11.3°, *i.e.* 0.2 rad.[17] The total free length of the specimens was (Fig. 2 of Ref. 3)

$$L = 2 \times 0.038 - 0.009 - 2 \times 0.010 = 0.047 \text{ m}$$

considering that 10 mm on each side were within the grips. The formula for computation of K is:[12]

$$K = \frac{ab^3}{16}\left[\frac{16}{3} - 3.36\frac{b}{a}\left(1 - \frac{b^4}{12a^4}\right)\right] \tag{A.1.3}$$

Substituting the above values in (A.1.3) one obtains:

$$K = 2.37 \times 10^{-14} \text{ m}^4.$$

The modulus of rigidity of the epoxy resins used in this work, as measured by means of the Gehman's test (Fig. 10), was about 10^{10} dyne/cm^2 in the glassy region:

$$G = 1 \text{ GPa}.$$

Therefore the torque, Ω, upon substituting all of the above values in (A.1.2), is:

$$\Omega = \frac{0.2 \times 2.37 \times 10^{-14} \times 1 \times 10^9}{0.047} = 1.0 \times 10^{-4} \text{ N.m}$$

and the maximum stress at the middle of the wide side is:

$$\tau_{max} = \frac{(3 \times 0.009 + 1.8 \times 0.0002) \times 1.0 \times 10^{-4}}{(0.009)^2 \times (0.0002)^2} = 0.84 \text{ MPa}$$

APPENDIX 2

Computation of Temperature Rise Within the Adhesive Layer

Due to their viscoelastic behavior, the polymeric materials show a temperature rise while under cyclic stress. The loss compliance (which is a measure of the energy dissipated as heat per cycle, eq. (2)) is defined as the ratio:[15]

$$J'' = \frac{\text{strain } 90° \text{ out of phase with the applied stress}}{\text{applied stress}} \tag{A.2.1}$$

The temperature change per unit time is:[15]

$$d\Delta T/dt = \pi.f.J''(f,T).\sigma^2/\rho.c_p. \qquad (A.2.2)$$

where ρ is the density (g/cm^3) and
c_p is the specific heat (cal.g^{-1}.°C^{-1}).

The remaining notations were explained in connection with eq. (2). In the following calculations the stress is in dyne/cm^2. The following approximations will be made:

1. The specific gravity of cured, unfilled epoxies is usually in the range 1.2–1.3.[9] We will use a value of 1.25 g/cm^3 for the density of our resins.

2. The values of the specific heat for different epoxies obtained by curing DGEBA with various amine curing agents are about within the range 0.25–0.35 cal.g^{-1}.°C^{-1} at room temperature.[29] We will use the value of 0.3 cal.g^{-1}.°C^{-1} in the following computations.

3. For the loss compliance J″ at room temperature we will use the value of 10^{-11} cm^2/dyne.[15]

4. We will consider the density and the specific heat to be constant. This assumption should not introduce any serious error.[15]

For a frequency of 16 Hz and a maximum cyclic stress of 84000 dyne/cm^2 (Appendix 1), the predicted rate of temperature rise will be:

$$d\Delta T/dt = \frac{\pi \times 16 \times 10^{-11} \times 84000^2}{1.25 \times 0.3 \times 4.184 \times 10^7} = 1.4 \times 10^{-8}\ °C/sec$$

For 24-hr experiments (86400 sec), the expected temperature rise should then be only 0.0012°C. In order for the temperature rise to have a significant effect on the crosslink continuation, it should be at least 3 to 4 orders of magnitude larger than the above figure. Therefore the approximations made before, even if coarse, have only a little impact on the validity of the conclusion: the temperature rise of the specimens in our experimental conditions is very small and cannot affect the crosslink density of the adhesives.

The calculations were based on the assumption that the loss compliance does not change significantly during the experiments.

We may check the validity of the above formula against data in the literature. Herman *et al.*[11] studied the temperature rise of Delrin® specimens by means of an infrared microscope. They used a quite large range of stresses and a frequency of 50 Hz. At a stress of 54 MPa, the specimens did not break and the temperature rise recorded after 10^4 sec was about 34°C.

Therefore, we suppose that for these specimens there was no significant increase of the loss compliance during the experiment.[11,13]

The predicted rate of temperature rise for their specimens is, by substituting the pertinent data in the eq. (A.2.2):

$$d\Delta T/dt = \frac{\pi \times 50 \times 10^{-11} \times 54000002}{1.25 \times 0.3 \times 4.184 \times 10^7} = 2.92 \times 10^{-3}\ °C/sec$$

For 10^4 sec, one may then expect a temperature rise of about 29.2°C, which is in good agreement with the reported data. This suggests that the assumption regarding the constancy of the loss compliance for these specimens was correct.

References

1. S. Bron and D. Katz, *Israel J. Tech.* **24,** 661 (1988).
2. S. Bron and D. Katz, *Makromol. Chem., Macromol. Symp.* **23,** 381 (1989).
3. D. Katz and S. Bron, *J. Mater. Sci.* **26,** 4733 (1991).
4. T. L. Smith, *J. Polym. Sci., Symp.* **46,** 97 (1974).
5. A. J. Kinloch, *J. Mater. Sci.* **17,** 617 (1982).
6. H. Miyari and H. Fukuda, *Polymer Science and Technology,* Vol. 12A (Plenum Press, New York, 1980).
7. C. L. Brett, *J. Appl. Polym. Sci.* **20,** 1431 (1976).
8. E. S. W. Kong, *ACS Symp. Ser.* **243,** 125 (1984).
9. J. R. Fried, F. E. Karasz and W. J. MacKnight, *Macromolecules* **11,** 150 (1978).
10. R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook* (McGraw-Hill Book Co., New York, 1985), pp. 2-82.
11. W. A. Herman *et al., J. Mater. Sci.* **25,** 434 (1990).
12. C. Carmichael, Kent's Mechanical Engineer's Handbook (Wiley Engineering Handbook Series, John Wiley & Sons, Inc., New York, 1956), chap. 8, p. 29.
13. J. A. Sauer and C. C. Chen, in *Scattering, Deformation and Fracture in Polymers,* G. D. Wignall *et al.,* Eds. (MRS, Pittsburgh, 1987), p. 371.
14. R. J. Crawford and P. P. Benham, *J. Mater. Sci.* **9,** 18 (1974).
15. M. N. Riddell *et al., Polym. Eng. Sci.* **6,** 363 (1966).
16. E. P. Popov, *Mechanics of Materials* (Prentice/Hall International Inc., New Jersey, 1978), p. 77.
17. S. Bron, Master of Science Research Thesis, Technion, Israel (1988).
18. M. Schrager, *J. Polym. Sci., Part A-2* **8,** 1999 (1970).
19. S. Rabinowitz and P. Beardmore, *J. Mater. Sci.* **8,** 11 (1973).
20. C. A. Bero and D. J. Plazek, *J. Polym. Sci., Part B: Polym. Phys.* **29,** 39 (1991).
21. A. Buchman and D. Katz, *Polym. Eng. Sci.* **19,** 923 (1979).
22. P. E. Cassidy, J. M. Johnson and C. E. Locke, *J. Adhesion* **4,** 183 (1972).
23. M. J. Adamson, *J. Mater. Sci.* **15,** 1736 (1980).
24. V. B. Gupta, L. T. Drzal, C. Y.-C. Lee and M. J. Rich, *Polym. Eng. Sci.* **25,** 812 (1985).
25. T. S. Ellis, *J. Appl. Polym. Sci.* **36,** 451 (1988).
26. T. K. Kwei, *J. Polym. Sci., Part A-2* **4,** 943 (1966).
27. R. W. Hertzberg and J. A. Manson, *Polymer* **19,** 358 (1978).
28. J. H. Petropoulos, *J. Polym. Sci., Part B: Polym. Phys.* **26,** 1009 (1988).
29. H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw-Hill Book Co., New York, 1967), pp. 6–47.
30. R. J. Morgan and J. E. O'Neal, *J. Mater. Sci.* **15,** 751 (1980).
31. A. J. Kinloch, *J. Adhesion* **10,** 193 (1979).
32. B. W. Cherry and K. W. Thomson, *J. Mater. Sci.* **16,** 1925 (1981).
33. V. T. Stanett and W. J. Koros, *Adv. Polym. Sci.* **32,** 71 (1977).
34. D. Katz and I. G. Zewi, *J. Polym. Sci., Symp.* **46,** 139 (1974).
35. L. C. E. Struik in *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).
36. A. Apicella and L. Nicolais, *Advances in Polymer Science* **72,** 75 (1985).
37. T. Murayama and J. P. Bell, *J. Polym. Sci., Part A-2* **8,** 137 (1970).
38. D. Katz, in *Polymer NDE,* K. H. G. Ashbee, Ed. (Technomic Publishing Co. Inc., Lancaster, PA, USA, 1986), p. 19.
39. V. Bouda *et al., J. Polym. Sci., Polym. Phys. Ed.* **14,** 2313 (1976).
40. A. R. Krause, J. W. Holubka and W. Chun, *Adv. Comp., The Latest Developments* (ASM, Metals Park, OH, USA, 1986), p. 193.
41. D. M. Brewis, J. Comyn and R. J. A. Shalash, *Int. J. Adhesion and Adhesives* **1,** 215 (1982).
42. T. K. Kwei, *J. Polym. Sci., Part A-2* **3,** 3239 (1965).
43. T. K. Kwei, *J. Appl. Polym. Sci.* **10,** 1647 (1966).
44. C. A. A. Rayner, Synthetic organic adhesives, in *Adhesion and Adhesives,* Vol. 1, R. Houwink and G. Salomon, Eds. (Elsevier Publ. Co., Amsterdam, 1965).
45. S. Bron and D. Katz, *J. Adhesion,* submitted.
46. S. E. B. Petrie, *J. Polym. Sci., Part A-2* **10,** 1255 (1972).