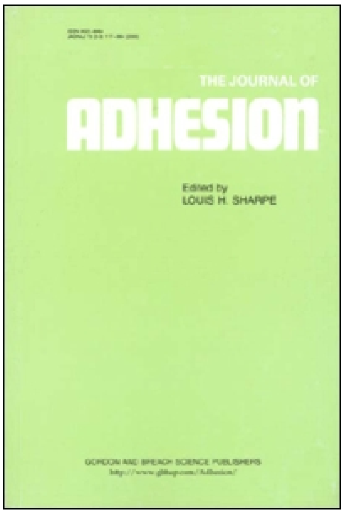

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Effect of the Secondary Transition on the Behaviour of Epoxy Adhesive Joints at High Rates of Loading*

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The shear yield behaviour of a modified epoxy joint has been investigated over a wide range of strain rates ($\dot{\gamma} = 10^{-2}\,s^{-1} - 10^{4}\,s^{-1}$) and at different temperatures (– 30°C, 24°C, 60°C, 80°C).

Assuming that high polymers exhibit pure viscous yield, the sharp increase of the yield stress in the strain rate sensitivity at high strain rates is explained in terms of a difference in relaxation times at low strain rates and high strain rates (α and β). The Bauwens's approach, which is a modification of the Ree-Eyring theory, gives an acceptable fit to the data. The yield behaviour of the modified epoxy joint, above a critical strain rate $\dot{\gamma}_\beta(T)$, may be described by the sum of the partial stresses τ_α and τ_β required to free the different kinds of molecular motions implied in the deformation process.

A good correlation between high impact resistance and the presence of the β mechanical loss peak in the range of the explored strain rates is established.

At very low temperature (– 30 °C), the data do not accurately fit the Ree-Eyring equation, meaning a heterogeneous deformation process characterized by the formation of local adiabatic shear bands and a permanent evolution of the molecular structure.

KEY WORDS: Epoxy; adhesive joints; high strain rates; temperature sensitivity; failure strength; secondary transition; non-linear behaviour.

INTRODUCTION

The impact behaviour of a new, lightweight bonded structure requires careful evaluation. Adhesives, being polymeric materials, have properties that are usually rate dependent. It is by no means certain that their performance under static conditions will be the same as under dynamic ones. There is, therefore, a need to give designers some confidence that, under impact conditions, bonded joints will maintain their structural integrity. Unfortunately, little work has been carried out to investigate properties of bonded joints at high strain rates. For this purpose, a new experimental set-up based on the inertia technique (the inertia wheel) has been used to characterise the impact resistance of structural adhesive joints ($\dot{\gamma} = 10^{3}\,s^{-1}$ to $10^{4}\,s^{-1}$) under shear loading. The first stage of this work was to confirm the accuracy of the device by comparing the

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behaviour of two different structural adhesives: a modified epoxy and an unmodified one. The difference of behaviour, slight but clear, allows us to confirm the accuracy of the inertia wheel technique and its measuring system to study carefully the behaviour of bonded joints at high strain rates. Then, a complete study of the modified epoxy joint was undertaken by means of static tests and tests at elevated temperatures. In addition, three thicknesses of joints have been considered (0.2, 0.5, 1 mm) in order to avoid the influence of the substrates and to reduce the dispersion of the yield strain. A critical strain rate $\dot{\gamma}_\beta(T)$, depending on the temperature, was noted. The joint becomes more resistant above this value. This change of behaviour, which affects not only the yield stress but also the energy, may be explained from molecular theories. The purpose of this paper is to show that the Bauwens approach[1-2] which consists of a modification of the Ree-Eyring[3] theory, linking the yield behaviour to the β mechanical loss peak, can be extended not only to thermoplastics but also to thermosets. It was indeed possible to calculate the activation energy associated with the β transition of our modified epoxy resin from this model; this activation energy is found to be in a good agreement with those given in the literature.

EXPERIMENTAL PROCEDURES

Materials

The two structural adhesives investigated were industrial one-part adhesives produced by CECA Adhesifs (France): An unmodified epoxy resin and a modified one. The two components of the unmodified resin are i) the epoxy resin (a blend of different DGEBA by-products) and ii) the curing agent (Dicyandiamide). The modified epoxy resin was fabricated by incorporating in the resin a block copolymer modifier (not revealed) and fillers (aluminium, amorphous silica, and calcium carbonate). The substrate was a galvanized steel sheet supplied by SOLLAC (France) (thickness: 1.5 mm). Before bonding, steel sheets were simply cleaned in an ethyl acetate bath.

Sample

The specimens are made of two galvanized steel sheets bonded by epoxy resin (Fig. 1). The two steel sheets are clamped together with PTFE spacers at each side of the

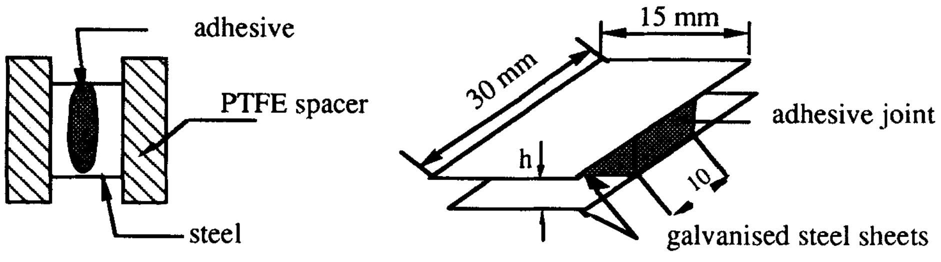

FIGURE 1 The adhesive joint specimen.

substrate to establish its desired thickness (0.2, 0.5, or 1 mm). The adhesive was cured by heating it in an oven, 30 minutes at 180 °C. To be loaded in the impact test system the sample was fixed onto rigid supports. Fixation was obtained by bonding with a cyanacrylate adhesive applied to the whole surface of the steel area, which is sufficient to attach it strongly to the support (Fig. 2).

High Strain Rate Tests

The high strain rate tests were carried out on a new experimental set up, the so-called "Inertia Wheel" (Fig. 3). This new device based on the inertia technique is very suitable; the tangential velocity of the wheel can be adjusted very accurately (from 1 m/s to 20 m/s). When the wheel reaches the nominal tangential velocity, the specimen rotates just before the hammer fixed on the wheel by means of a pendular mechanism activated by a pneumatic jack (Fig. 4).

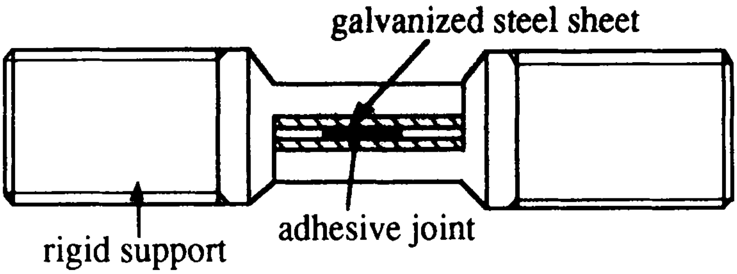

FIGURE 2 The joint fixed onto rigid supports.

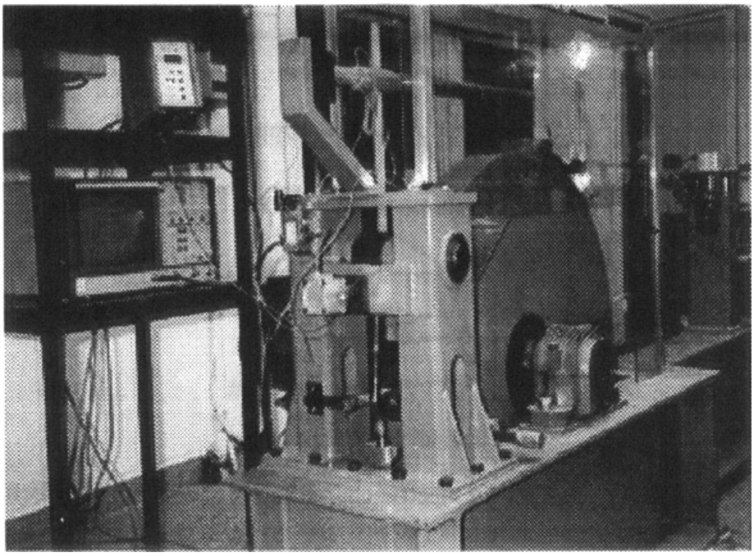

FIGURE 3 The inertia wheel.

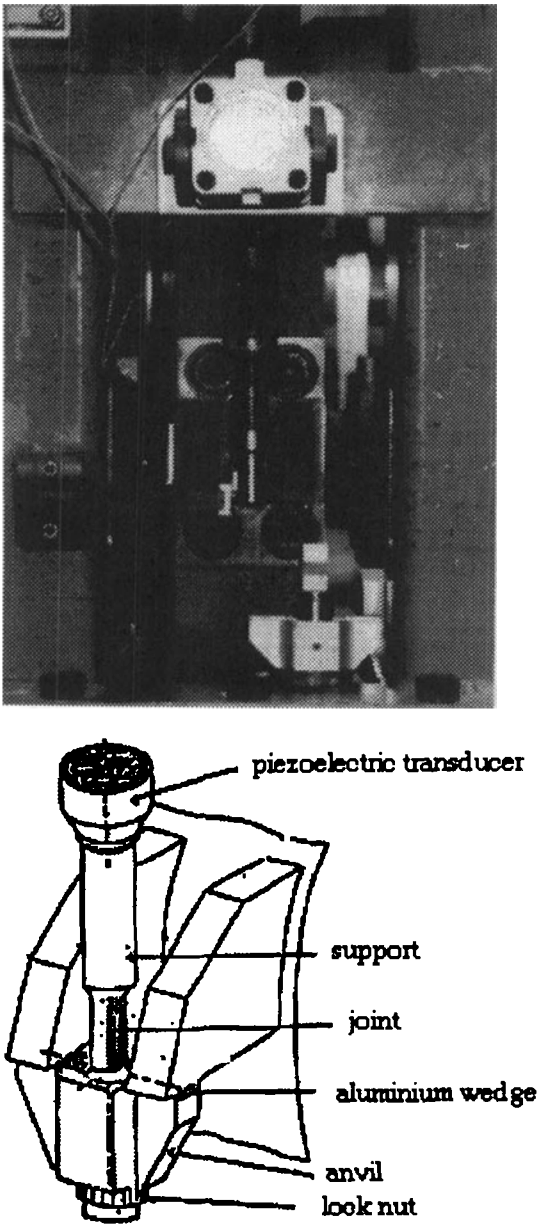

FIGURE 4 The loading system.

A charge amplifier converts the electric charge supplied by the piezoelectric transducer into a voltage signal which is proportional to the applied force. The signal is stored into a numerical oscilloscope. A Zimmer OHG extensometer (bandwidth: 200 kHz) is used to follow the relative displacement of the two substrates by means of two marks stuck on each support (Fig. 5). The high energy accumulated by the wheel compared with the energy required to break a joint allows us to get a strain rate, which is nearly constant throughout the test (Fig. 6). Since the inertia effects can be neglected, it is possible to affirm that the properties of the sample are not altered by the mounting accessories. The frequency response of the total test system remains the frequency response of the quartz washer which is about 40kHz. Since the smallest time to failure in any test was about 30 μs, this system is adequate.[4–5]

Since the displacements due to the rigid supports are not negligible, they must be taken into account. For this reason, further tests with the supports alone were carried out (Fig. 6).

We can see from Figure 6 that the polymer does not exhibit a purely linear behaviour. The maximum point on the curve is sufficiently remarkable to consider it as the yield point to account for the pre-plastic deformation of the epoxy, related to the multiplication of shear bands which self-accelerate.[6]

$$\gamma_m = \frac{V_{\mathrm{ham}}(t_f - t_S)}{h_a}. \qquad (1)$$

$$E_c = \frac{V_{\mathrm{ham}}}{A_{\mathrm{joint}}}\left[\int_0^{t_f} F_1(t)\,dt - \int_0^{ts} F_2(t)\,dt\right] \qquad (2)$$

$$\tau_y = \frac{F_{\mathrm{max}}}{A_{\mathrm{joint}}} \qquad (3)$$

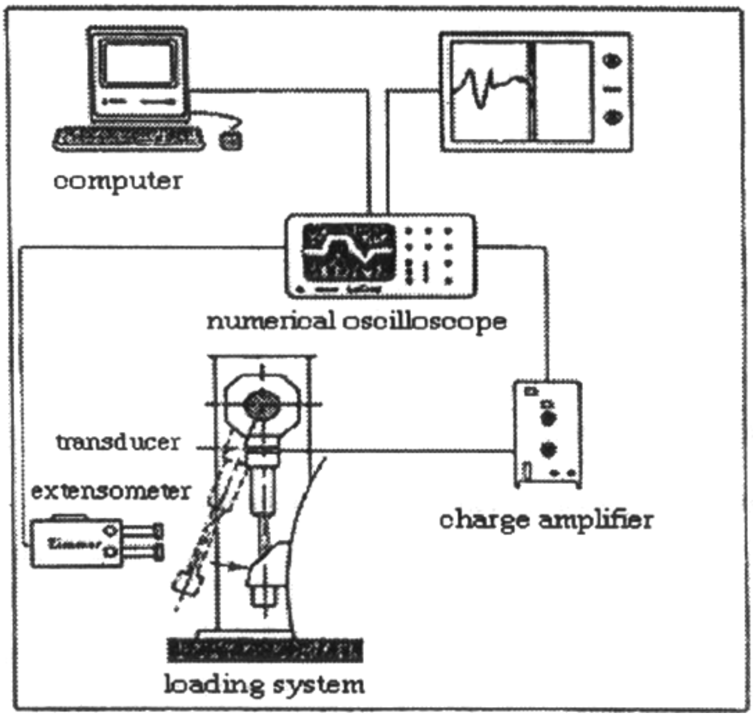

FIGURE 5 The measuring system.

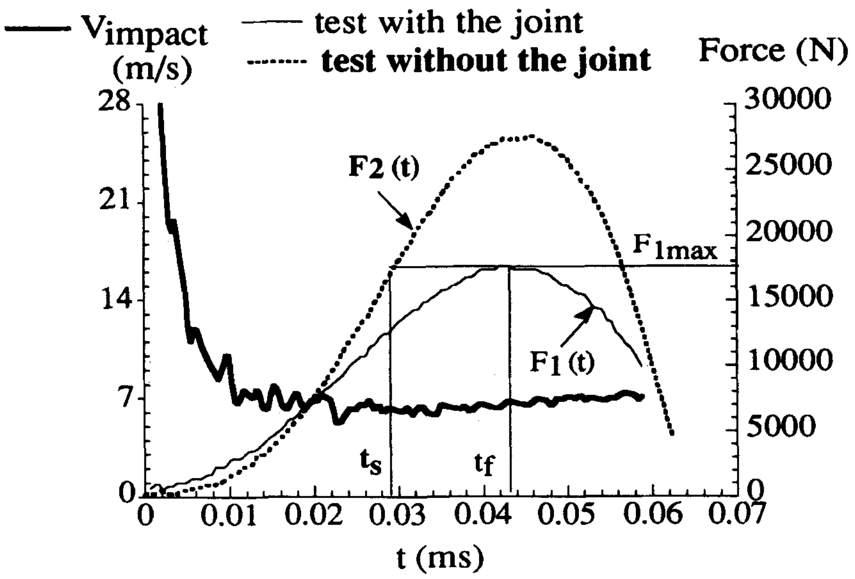

FIGURE 6 Force and displacement velocity *versus* time for a test on the unmodified epoxy resin at 7 m/s.

Where:

V_{Ham} : velocity of the hammer
$V_{\mathrm{Ham}} t_f$: displacement of the adhesive joint and the supports
$V_{\mathrm{Ham}} t_S$: displacement due only to the supports
A_{Joint} : area of the joint
h_a : thickness of the joint.

Tests at Lower Strain Rates

The shearing tests at lower speeds were carried out using an Instron test machine (10^{-2} s^{-1} – 10^{1} s^{-1}) and a hydraulic tensile machine (10^{2} – 10^{3} s^{-1}).

RESULTS AND DISCUSSION

Modified and Unmodified Joint Behaviour at High Strain Rates

Figures 7–9 show, respectively, the evolution of the yield stress, the ultimate strain and the critical energy *versus* the strain rate for both joints (0.2 mm thick joint) at room temperature.

As expected, the behaviour of the unmodified epoxy joint at high strain rate is much more brittle than the modified one. The evolution of the yield stress with the strain rate is nearly identical for both joints, but the yield strain, and so the critical energy, are always lower for the unmodified one.

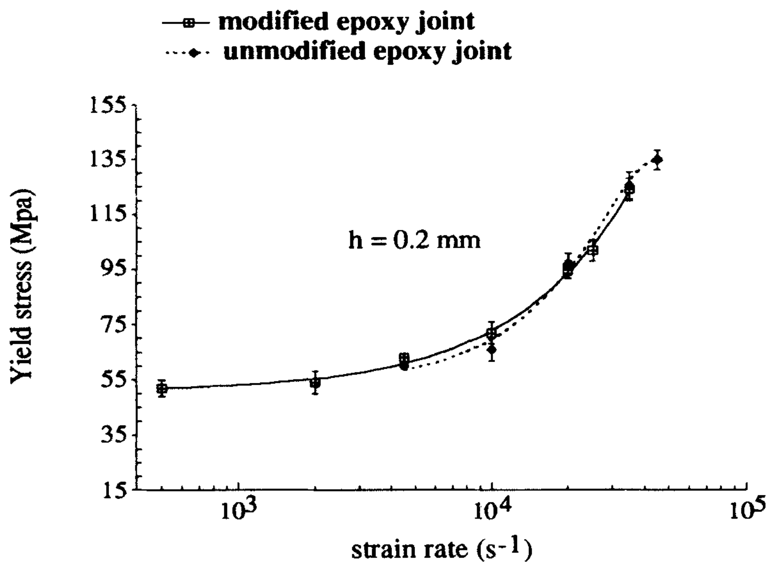

FIGURE 7 The yield stress *versus* the strain rate for the modified and the unmodified epoxy joint at room temperature.

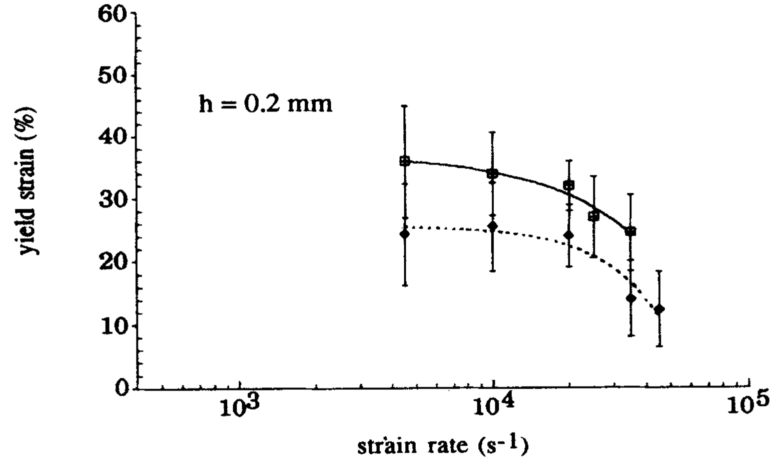

FIGURE 8 The yield stress *versus* the strain rate for the modified and the unmodified epoxy joint at room temperature.

This difference of behaviour, slight but clear, allows us to confirm the accuracy of the inertia wheel and its measuring system to study carefully the behaviour of bonded joints at high strain rates.

The extended study of the modified epoxy joint behaviour at intermediate strain rates (10^2 s^{-1}) shows the existence of a critical strain rate, noted $\dot{\gamma}_\beta$, at around 3.10^3 s^{-1}

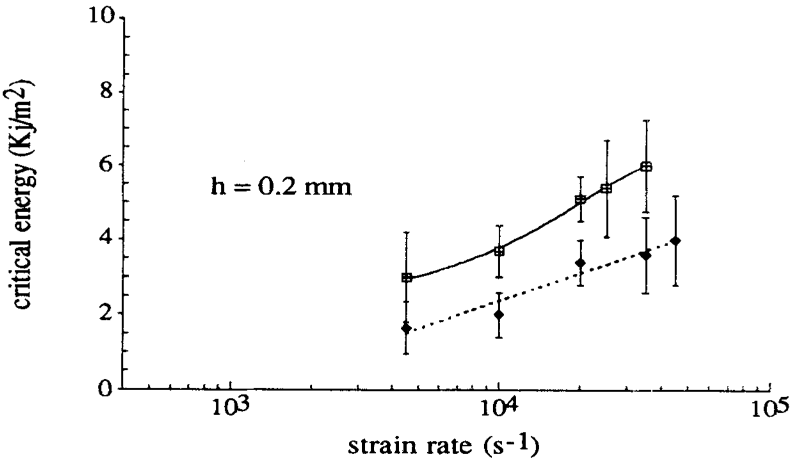

FIGURE 9 The critical energy *versus* the strain rate for the modified and the unmodified epoxy joint at room temperature.

with a sharp increase of the measured yield stress above this value, where the joint becomes more yield resistant (Figs. 6, 8). In order to explain this behaviour, an extensive study of the modified epoxy joint was done by means of static tests and tests at elevated temperatures. Furthermore, to avoid the influence of the substrates and to reduce the dispersion of the strain measurements, two other thicknesses of joint were tested (0.5 and 1 mm).

Extensive Study of the Modified Epoxy Joint

In the previous paragraph, a sharp increase of the measured yield stress at high strain rate was noted, but we will further observe that the change of behaviour above $\dot{\gamma}_\beta$ concerns not only the yield stress but also the yield strain and the critical energy. The evolution of the yield stress with the strain rate is first discussed, with the following discussions concerning the evolution of the critical energy and the yield strain.

Evolution of the yield stress with the strain rate

Eyring-Bauwens model

When the polymer is capable of exhibiting a secondary (β) transition, (associated with the local relaxation modes of the macromolecular structure or the relaxation of the side groups), Bauwens showed that, at high strain rates, the variation of the yield stress with the strain rate can be described by the generalized theory proposed by Ree-Eyring[3]:

$$\frac{\tau_y}{T} = A_\alpha\left[\mathrm{Ln}(2C_\alpha\dot{\gamma}) + \frac{Q_\alpha}{RT}\right] + A_\beta \sinh^{-1}\left[C_\beta\dot{\gamma}\exp\left(\frac{Q_\beta}{RT}\right)\right] \tag{4}$$

where T is the absolute temperature and R is the universal gas constant. The parameters A_α, C_α, A_β, C_β are characteristics of the material and Q_α, Q_β are the energy barriers of, respectively, the α relaxation and the β relaxation. These barrier energies have to be overcome so that a macromolecular segment can jump from one equilibrium position to another.

This model considers that below a critical strain rate, $\dot{\gamma}_\beta$ (T), only the activation of the main relaxation (α relaxation), associated with the relaxation of the crosslinked polymer network, requires mechanical energy. On the other hand, above $\dot{\gamma}_\beta(T)$, the jumping of the α and β barriers is required: the thermal fluctuations are not enough to activate, by themselves, the local motions such as rotations of side groups associated with the β relaxation. Because of the reduced motions of these polymer segments, the activation of the β mechanism requires the contribution of additional mechanical energy which causes an appreciable increase of the yield stress.

In epoxy systems, this β peak is related to motions of the ether linkage segments in the epoxy component of the resin.[7]

Comparison of model with experimental results

The Figure 10 shows the ratio of the yield stress to absolute temperature *versus* the logarithm of $\dot{\gamma}$ for different thicknesses at room temperature. The solid lines plotted on Figure 10 correspond to the theoretical variation using the following Eyring

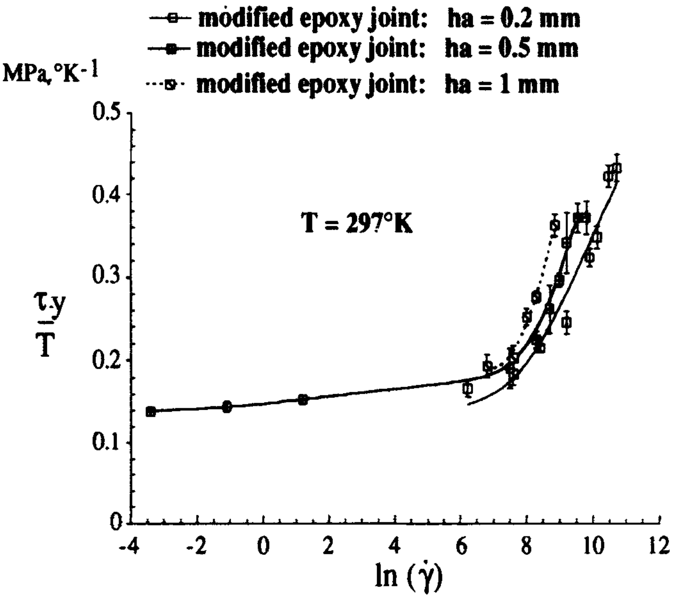

FIGURE 10 The ratio of the yield stress to the absolute temperature *versus* ln $\dot{\gamma}$ at room temperature for different joint thicknesses.

equation:

$$\frac{\tau_y}{T} = A_\alpha(\ln(\dot{\gamma}) + X_\alpha) + A_\beta \sinh^{-1}\left(\frac{1}{2\dot{\gamma}_\beta}\dot{\gamma}\right) \tag{5}$$

$$\text{with } X_\alpha = \ln(2C_\alpha) + \frac{Q_\alpha}{RT} \text{ and } \dot{\gamma}_\beta = \frac{1}{2C_\beta}\exp\left(\frac{-Q_\beta}{RT}\right)$$

The parameters fitted to Equation (5) for different joint thicknesses are given in Table I.

We note that the strain rate at which this sudden increase in strain rate sensitivity occurs is not influenced by the thickness of the joint and so by the specimen geometry (Fig. 10, Table I). The slight shift of the critical strain rate with the thickness ($1.3 \cdot 10^3 \leq \dot{\gamma}_\beta \leq 2.1 \cdot 10^3$) may be caused by a change in the polymerisation processes which are influenced by the thickness of the joint.[8]

Consequently, the sharp increase cannot be interpreted as a change in the way the structure evolves with strain. The inertial resistance to longitudinal and radial deformation cannot be responsible.[9-10] This critical strain rate would be a characteristic of the material which might be linked, according to the Bauwens model, to the activation of the β relaxation.

In order to check the accuracy of this interpretation, temperature tests were performed for a given joint thickness (0.5 mm). Figure 11 shows the ratio of the yield stress to absolute temperature *versus* the logarithm of $\dot{\gamma}$ at different temperatures, for a 0.5 mm thick joint. For each temperature, the parameters of Equation (5) are fitted to the experimental results, allowing us to determine Q_α, Q_β, C_α and C_β (Table II).

It is worth noting that the parameters are still constant whatever the temperature (except for $-30\,°C$). Furthermore, the activation energies are in good agreement with those given in the literature for amine-based DGEBA[11] (Table III). This means that, in the temperature range from 24 °C to 80 °C, the yield behaviour of the modified epoxy joint, above $\dot{\gamma}_\beta(T)$, may be described by the sum of the partial stresses, τ_α and τ_β, required to free the different molecular motions implied in the deformation process, in accord with the Bauwens treatment.

On the other hand, the significant diminution of A_β and C_β at $-30\,°C$ is likely to arise due to microstructural changes in the polymer: at high strain rate and low temperature, the deformation is confined in a reduced volume with important local internal heat generation which promotes a concentration of adiabatic shear bands and

TABLE I
Parameters adjusted to the results for different joint thicknesses

$T = 297\,°K$	0.2 mm	0.5 mm	1 mm
A_α	$9.10^{-4}\,MPa \cdot K^{-1}$	$9.5 \cdot 10^{-4}\,MPa \cdot K^{-1}$	$9.5 \cdot 10^{-4}\,MPa \cdot K^{-1}$
$X_\alpha = \ln(C_\alpha) + Q_\alpha/RT$	146	147	148
A_β	$0{,}09\,MPa \cdot K^{-1}$	$0{,}09\,MPa \cdot K^{-1}$	$0{,}1\,MPa \cdot K^{-1}$
$\dot{\gamma}_\beta$	$2.10^3\,s^{-1}$	$1.4 \cdot 10^3\,s^{-1}$	$1.3 \cdot 10^3\,s^{-1}$
Coef. of correlation	0.977	0.987	0.973

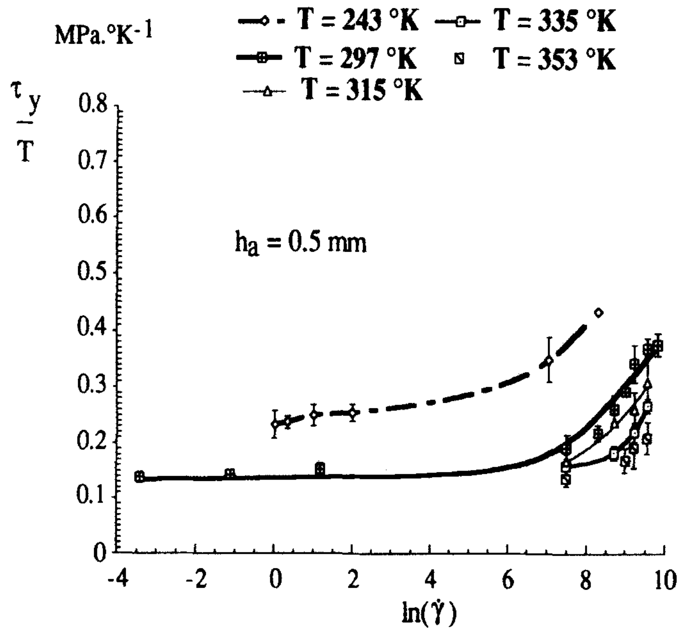

FIGURE 11 The ratio of the yield stress to the absolute temperature *versus* ln $\dot{\gamma}$ for a 0.5 mm thick joint at different temperatures.

TABLE II
Parameters adjusted to the results for different temperatures

$h_a = 0.5$ mm	$T = 243$ °K	$T = 298$ °K	$T = 315$ °K	$T = 335$ °K	$T = 353$ °K
A_α(MPa.K^{-1})	$12.5 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$	$10.5 \cdot 10^{-4}$	$11 \cdot 10^{-4}$
C_α(s)	$15 \cdot 10^{-20}$	$14 \cdot 10^{-20}$	$11 \cdot 10^{-20}$	$13.5 \cdot 10^{-20}$	$15 \cdot 10^{-20}$
Q_α(kJ/mole)	470 ± 10	470 ± 10	470 ± 10	470 ± 10	470 ± 10
A_β(MPa.K^{-1})	0.04	0.1	0.1	0.13	0.14
C_β(s)	$4 \cdot 10^{-11}$	$8 \cdot 10^{-11}$	$8.5 \cdot 10^{-11}$	$8.3 \cdot 10^{-11}$	$8.3 \cdot 10^{-11}$
Q_β(kJ/mole)	38 ± 1	38 ± 1	38 ± 1	38 ± 1	38 ± 1
$\dot{\gamma}_\beta$(s^{-1})	$7.3 \cdot 10^1$ s^{-1}	$1.4 \cdot 10^3$ s^{-1}	$3 \cdot 10^3$ s^{-1}	$7 \cdot 10^3$ s^{-1}	$14 \cdot 10^3$ s^{-1}
Correlation	0.988	0.987	0.99	0.975	0.99

TABLE III
Calculated activation energies compared with those given in literature

Activation energies	Values given in the literature[10]	Values from this work	Value from the Arrhenius relation
Q_α	400–800 kJ/mole	470 kJ/mole	
Q_β	42–60 kJ/mole	38 kJ/mole	37.5 kJ/mole

a decrease of the yield stress (characterized by a decrease of A_β). The deformation is no longer homogeneous (non-linear behaviour) and the parameter C_β (which contains a frequency factor), related to the relaxation time τ_β, becomes very sensitive to the temperature.[3, 6]

Dynamic mechanical analysis, conducted at 1 Hz, has pointed out the existence of the β transition for our modified epoxy adhesive at -60 °C. Let us note the fact that the secondary transition is well below room temperature does not mean that, above this temperature, the local molecular motions are free to occur. For instance, an impact stress pulse corresponds to a high-frequency measurement which, by the time-temperature superposition principle, has the effect of virtually raising the secondary transition to higher temperatures.

In that way, depending on the temperature and the strain rate, the molecular motions of the β relaxation may be frozen. The transition point is given by $\dot{\gamma}_\beta(\mathrm{T})$.

The relation between the test frequency and the temperature corresponding to the maximum of $\tan(\alpha, \beta)$ is given by the Arrhenius relation:

$$\mathrm{Ln}\, a_t(\alpha, \beta) = \mathrm{Ln}\left(\frac{\omega}{\omega_0}\right) = \frac{Q(\alpha, \beta)}{R}\left(\frac{1}{T_{m_0}} - \frac{1}{T_m}\right) \tag{6}$$

We have extended the study by performing a Fourier analysis to obtain the complete frequency spectrum of the impact pulse corresponding to $\dot{\gamma}_\beta(\mathrm{T})$ and related to the test temperatures, 24 °C, 40 °C, 63 °C, and 80 °C. Every $\dot{\gamma}_\beta(\mathrm{T})$ is linked to a frequency $f_c(\mathrm{T})$, defined as the frequency for which there arises a signal attenuation of 10% (Figs. 12–14). These values are used in the Arrehenius time-temperature conversion, Equation (6),

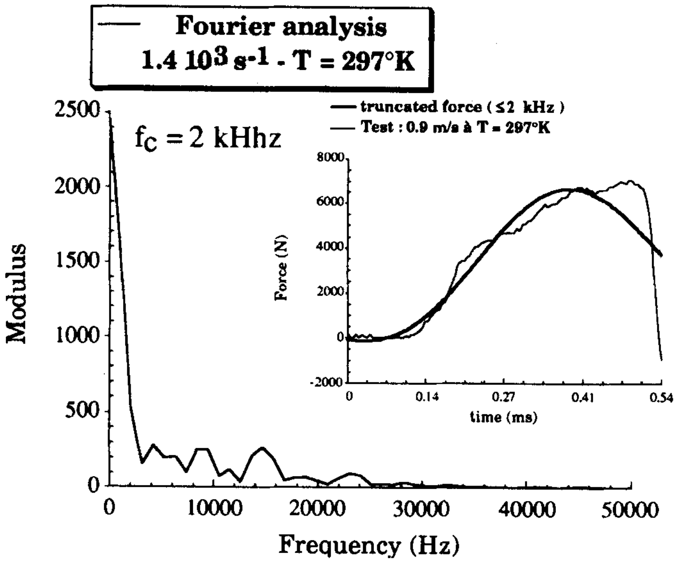

FIGURE 12 Fourier analysis of the impact pulse related to $\dot{\gamma}_\beta$ (24 °C).

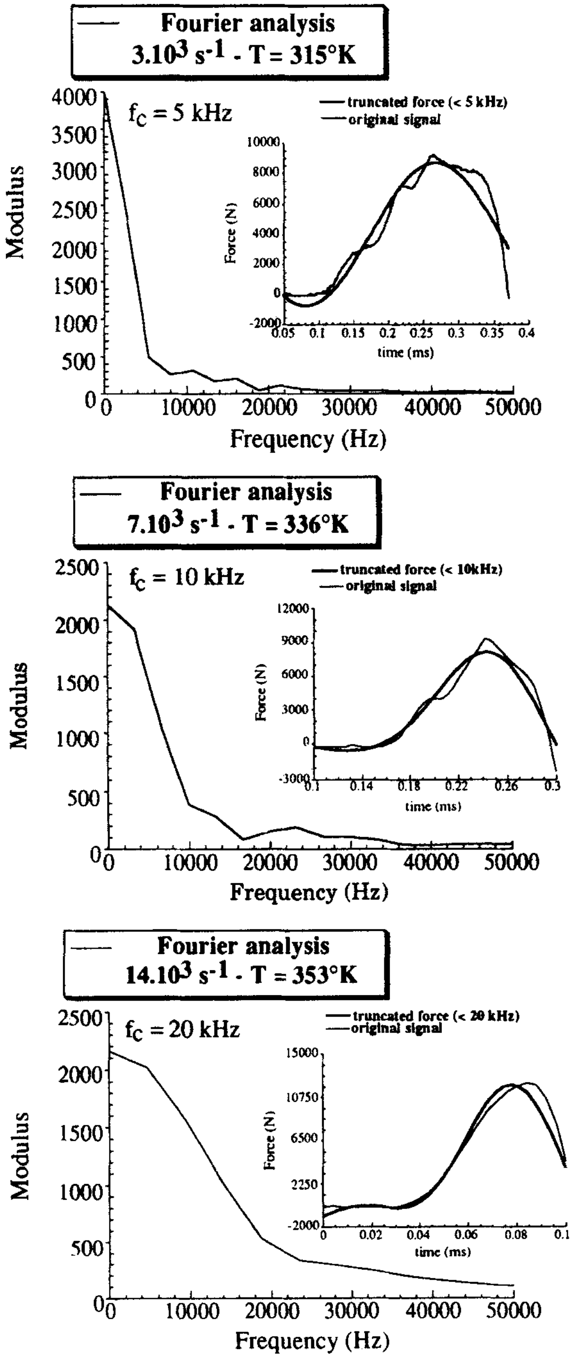

FIGURE 13 Fourier analysis of the signals for $\dot{\gamma}_\beta$ (42 °C), $\dot{\gamma}_{\beta'}$ (62 °C) and $\dot{\gamma}_\beta$ (80 °C).

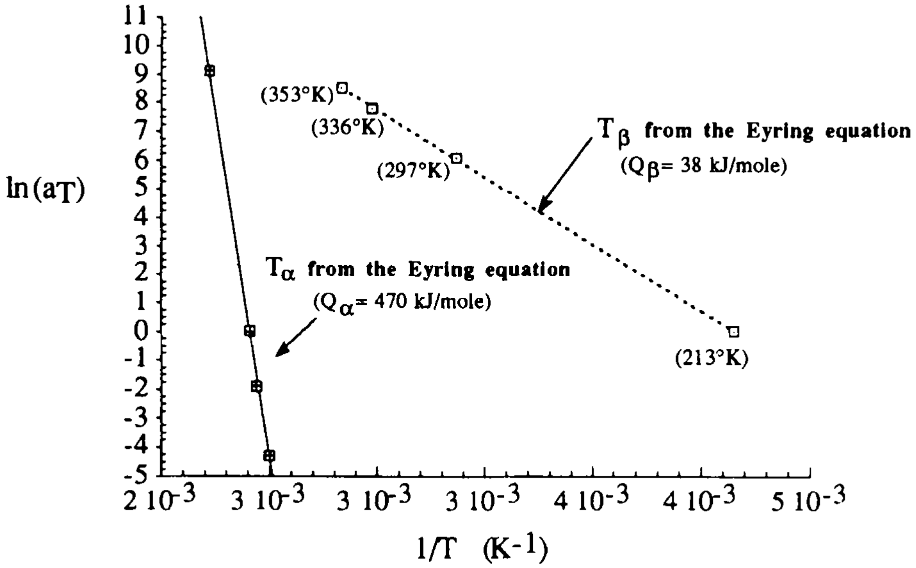

FIGURE 14 Shift factor of the α and β transitions *versus* the temperature.

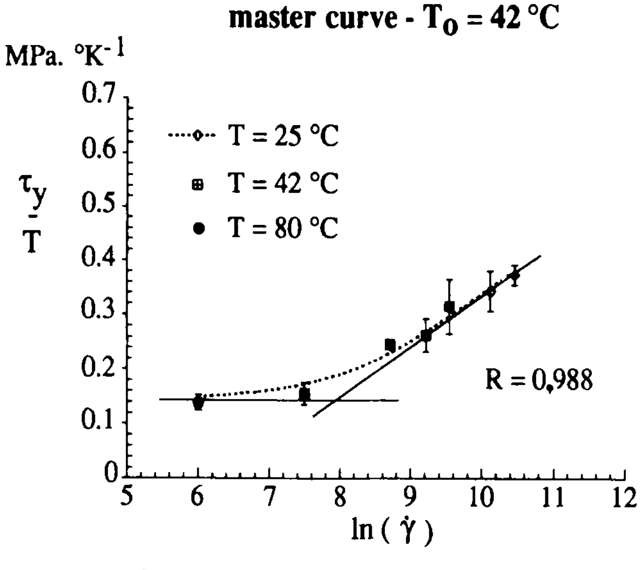

FIGURE 15 Master curve reduced to 42 °C.

and allow us to calculate an activation energy, Q_β, close to those found in the literature or calculated from the Eyring equation (Table III), reinforcing the Bauwens approach.

The shift factor a_{T_β} (or a_{T_α}) of the β (or α) relaxation peak can be assessed from the Arrhenius equation (Equation (6)). The evolution of a_T with the temperature is shown

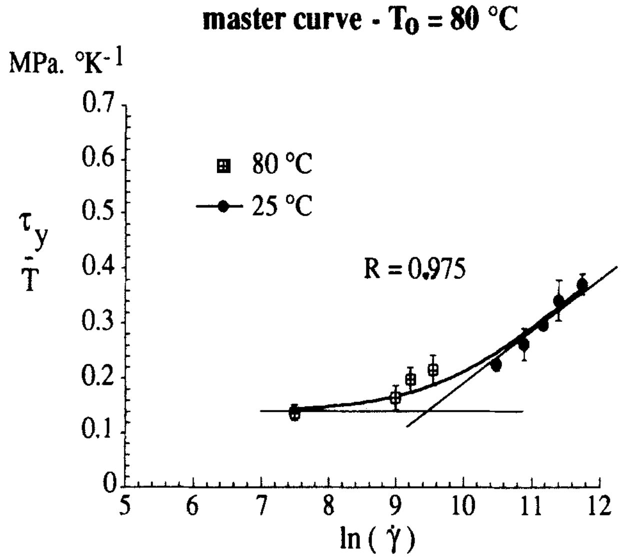

FIGURE 16 Master curve reduced to 80 °C.

in Figure 14. Using these shift factors, $a_{T\beta}$ and $a_{T\alpha}$, we have plotted the master curves reduced to the temperatures 42 °C and 80 °C (Figs. 15 and 16). The object is to extend the frequency scale and to evaluate accurately the critical strain rates for these temperatures. It is worth noting that the measured critical strain rates, $\dot{\gamma}_\beta(T)$, are in very good agreement with those calculated from the Ree-Eyring equation (Table II).

The fact that the time-temperature superposition principle is effective, even in the region where a change of deformation process arises ($\alpha \rightarrow \alpha + \beta$), implies that the transition point can be explained both in terms of critical strain rate and critical temperature. In order to check this property, we have deduced from the data the curve representing τ_y as a function of the temperature at a constant strain rate: $\dot{\gamma} = 1.4 \cdot 10^3$ s^{-1}. This latter curve is given in Figure 17, where it is seen that the temperature at which the transition behaviour occured is exactly the temperature expected (24 °C) according to the Bauwens approach.

Evolution of the critical energy with the strain rate

Figures 18a and 18b show the critical energy (energy at the yield point) *versus* the strain rate for, respectively, different thicknesses at room temperature (Fig. 18a) and different temperatures for a 0.5 mm thick joint (Fig. 18b). The sharp increase of the critical energy, which occurs for the same critical values of $\dot{\gamma}_c(T)$ computed previously, may be also linked to the presence of the β transition in the range of the explored strain rate. Moreover, the change in the behaviour is still independent of the geometry of the joint. The energy dissipated in the material by the local motions of the structure will be all the

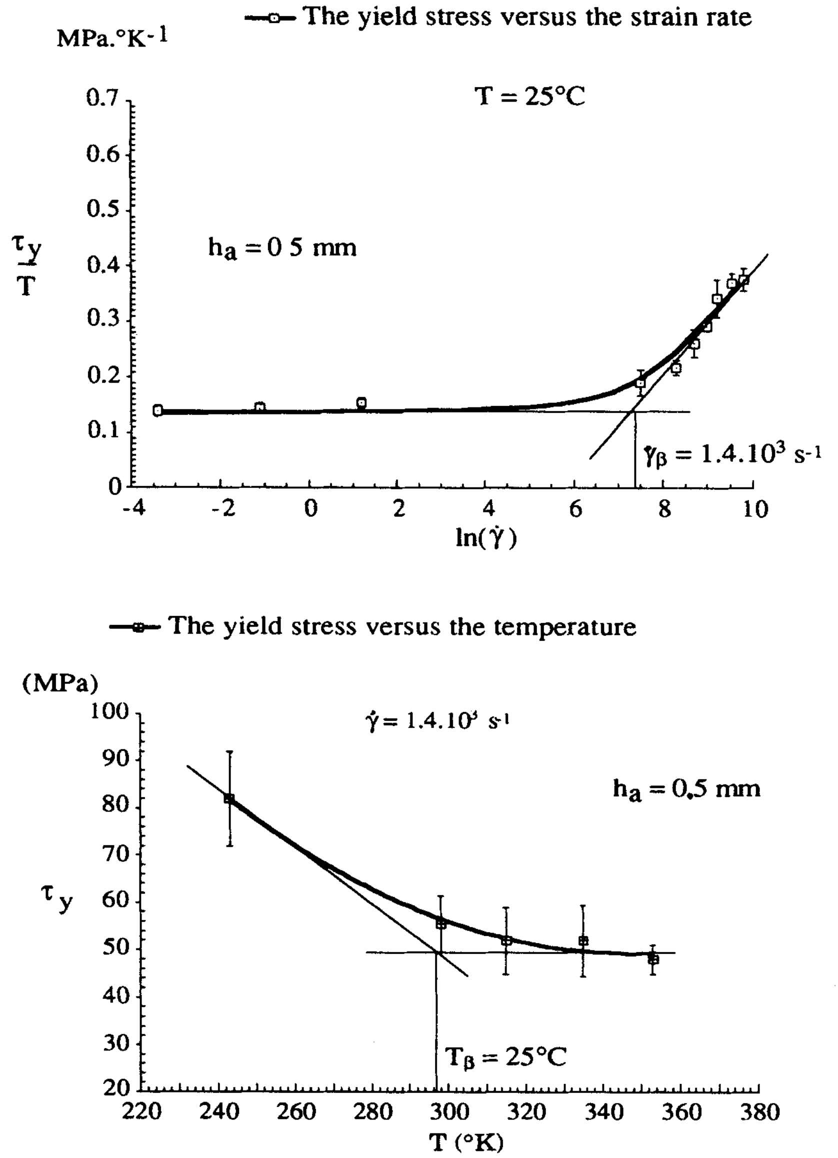

FIGURE 17 Expression of the transition point in the yield behaviour of the epoxy joint in terms of the critical strain rate or critical temperature.

more important as the macromolecular mobility is important. Since the dynamic mechanical loss factor is higher in the vicinity of the secondary transition, some of the impact energy can be absorbed in the form of heat, thus offering protection from fracture.[12]

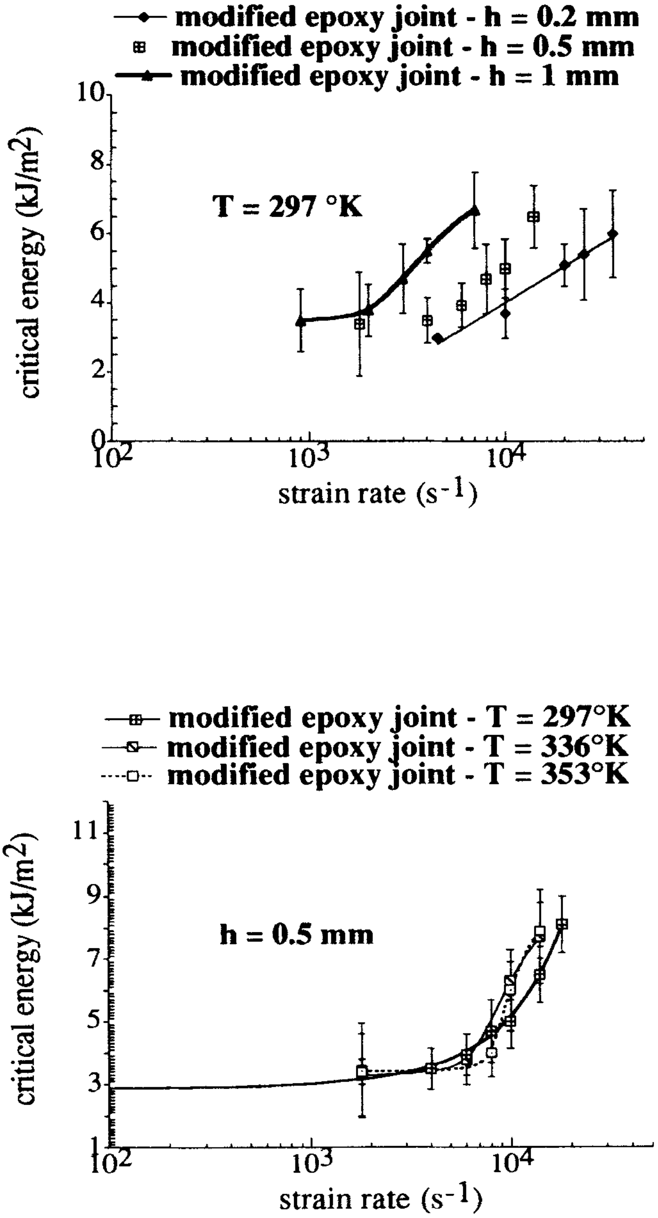

FIGURE 18 (a) The critical energy *versus* the strain rate for different thickness joints at room temperature (24 °C); (b) the critical energy *versus* the strain rate for a 0.5 mm thick joint at different temperatures.

CONCLUSION

The yield stress of the modified epoxy joint is greatly influenced by the strain rate and the temperature, but it is not the only mechanical parameter affected. The energy and the yield strain also show a change in their evolution above the same critical strain rate, $\dot{\gamma}_c$(T). This strain rate sensitivity led us to determine the nature of the elementary mechanism in action according to the molecular mobility present in the range of temperatures and strain rates explored. The Bauwens molecular approach, which is a modification of the Ree-Eyring theory, gives an acceptable explanation of the results. This model links the yield behaviour with the β mechanical loss peak and points out a critical strain rate which is the boundary between two modes of deformation (from the α mode to the α mode combined with the β local deformation modes). It is worth noting that the Bauwens approach can be extended not only to thermoplastics but also to thermosets.

But if the evolution of the yield stress is quite explainable in the temperature range from 24 °C to 80 °C, at low temperature (– 30 °C) the Bauwens treatment is no longer valid. The evolution of the micromolecular structure with the formation of adiabatic shear bands causes heterogeneous deformation which cannot be interpreted from this model.

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