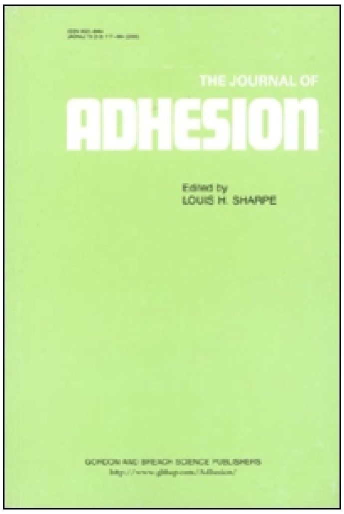

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FRACTURE OF METAL/POLYMER/METAL ASSEMBLIES: VISCOELASTIC EFFECTS

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The purpose of this work is to link the polymer viscoelastic properties (especially its relaxation time) and the adhesive behaviour of steel/polymer/steel assemblies. A wedge test device developed in the laboratory allows one to introduce the wedge into the assembly at a controlled speed and to follow the crack propagation with a camera-equipped microscope. The adherence energy (calculated from the equilibrium crack length) and the crack propagation rate are measured for different wedge introduction rates. Polymer equivalent relaxation time is determined for each introduction rate according to the time-temperature superposition principle. Relations between adherence energy, crack propagation rate, and calculated equivalent relaxation time values are proposed. These quantitative relations confirm the major influence of polymer viscoelastic properties on the rate sensitivity of adhesive behaviour.

Keywords: Adhesion; Fracture; Viscoelastic properties; Metal/polymer assemblies; Wedge test; Relaxation time

INTRODUCTION

Adherence measurements generally consist of a mechanical separation of an assembly. The energy required to separate the adhesive and

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the substrate is a function of the adhesion level (interfacial interactions), but it also depends on the mechanical and viscoelastic properties of the materials. A part of the adherence energy is actually used up in dissipation phenomena, induced by chain movements. Numerous works have studied the influence of dissipation phenomena on adherence energy [1–5]. In this study, the adherence level of a metal/polymer/metal assembly is quantified by using a wedge test. The purpose of this work is to link the polymer viscoelastic properties (especially its relaxation time) and the adhesive behaviour of polymer/steel/polymer assemblies. The wedge test device used in this study allows one to introduce the wedge at a controlled speed and to follow the crack propagation with a camera-equipped microscope. The adherence energy and the crack propagation rate are measured for several wedge introduction rates. Polymer relaxation time is determined for each introduction rate according to the time-temperature superposition principle and the WLF equation. Quantitative relations between adherence energy, crack propagation rate, and calculated relaxation time values are proposed.

EXPERIMENTAL

Materials

Metal/polymer/metal assemblies were composed of two steel plates (0.40 mm thick) and one thin polymer layer (45 μm thick) inserted between the metal plates. The substrate was a mild steel (Usinor France) with a chromate surface treatment.

An epoxy resin (DGEBA type) crosslinked with an anhydride was used. The crosslinked epoxy exhibits two glass transition temperatures, determined by dynamic mechanical measurements and equal to 36 and 70°C at 5 Hz.

Steel/polymer/steel assemblies were obtained by resin coating, solvent evaporation, and hot-lamination of the three-layer system.

Techniques

Polymer/steel adherence was quantified by using a wedge test. The assemblies (10 mm width and 50 mm length) were submitted to a deformation in mode I by introducing a wedge at 20°C, in air. Due to the sensitivity of the polymer to temperature variation, the wedge tests were performed in an air-conditioned laboratory with precise temperature regulation. The influence of temperature was not investigated. A temperature increase can indeed induce various phenomena that can modify the assembly behaviour, such as a differential dilatation of the steel substrates and the polymer layer (interfacial stress), or migration of low molecular weight species inside the polymer layer (additives, catalyst, trapped solvent molecules) with the possibility of interfacial contamination or chemical reaction. The device developed in the laboratory allows one to introduce the wedge into the assembly at a controlled introduction speed (from 0.8 to 75 mm/min) and to follow the crack propagation with a camera-equipped microscope (Figure 1). The wedge is introduced at a given speed and then stopped. The crack propagation is then followed until equilibrium. The crack length versus time evolution and the final equilibrium crack length are obtained by analysing the video images.

If the deformation of the steel substrate is purely elastic, and if no energy is stored in the polymer layer, the equilibrium is reached when the rate of loss of elastic energy by the steel substrates is equal to the failure energy of the assembly (per unit area).

Kanninen has introduced a model derived from the analysis of a finite length beam which is partly free and partly supported by an elastic foundation [7]. In 1993, Penado included the adhesive contribution in Kanninen's model [8]. For the DCB specimen with an

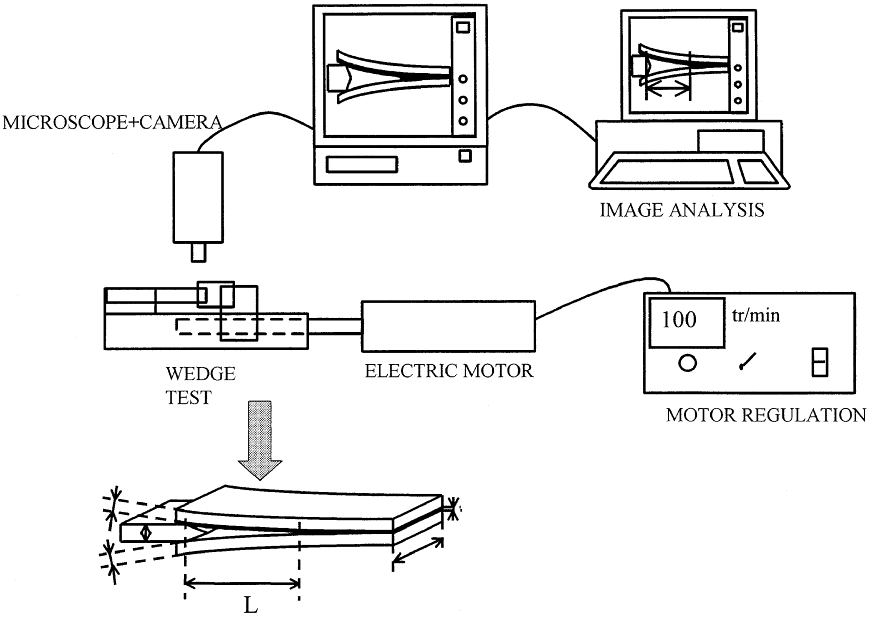

FIGURE 1 Schema of the wedge test device.

adhesive layer, it will be assumed that the adhesive and adherend act as springs in series.

The failure or adherence energy, G, can then be calculated from the crack length using the following equations [6]:

$$G = \frac{3Eh^3\delta^2}{16L^4}\frac{1}{\left(1+\frac{\lambda_0}{\lambda}0.64\frac{h}{L}\right)^4},$$

with $\lambda = \left(\frac{3k}{Ebh^3}\right)^{1/4}$ and $\lambda_0 = \left(\frac{3k_0}{Ebh^3}\right)^{1/4}$, and

$$k = \frac{1}{\frac{1}{k_0}+\frac{1}{k_a}},$$

with $k_0 = \frac{2Eb}{h}$, and $k_a = \frac{bE_a}{h_a}$, where E is the Young's modulus of the steel substrate (2.1×10^{11} Pa), h is the substrate thickness (0.4 mm), δ the wedge height (0.4 mm), and L the crack length.

$E_a = 3.03 \times 10^8$ Pa and $h_a = 4.5 \times 10^{-5}$ m are, respectively, the modulus and thickness of the adhesive layer, and b is the width of the assembly.

This equation, derived from the Penado and Kanninen approaches, presents the advantage of taking into account the polymer's mechanical properties, even if the analysis is purely elastic and consequently not perfectly appropriate to the viscoelastic behaviour of polymer materials.

Creep tests (imposed stress and strain measurement as a function of time) were also carried out on polymer films at a loading rate equal to 10 mm/min (rate at which the constant stress is applied).

RESULTS AND DISCUSSION

Figure 2 shows the evolution of adherence energy, G, as a function of wedge introduction speed, S_{intro}. The energy, G, is globally increased, and a transition is detected around 30 mm/min, attributed to the first glass relaxation of the polymer. Very high values of G are obtained, explained both by the rubbery nature of the epoxy-based polymer and by the special formulation of the adhesive (strong chemical bonds between the resin and the steel). It is also important to determine that the deformation of the steel is purely elastic. The measurement of the substrate curvature during the wedge test has indeed shown that the plastic yield of the metal is not reached. Moreover, the low wedge height (0.4 mm) avoids large deformation of the steel plates.

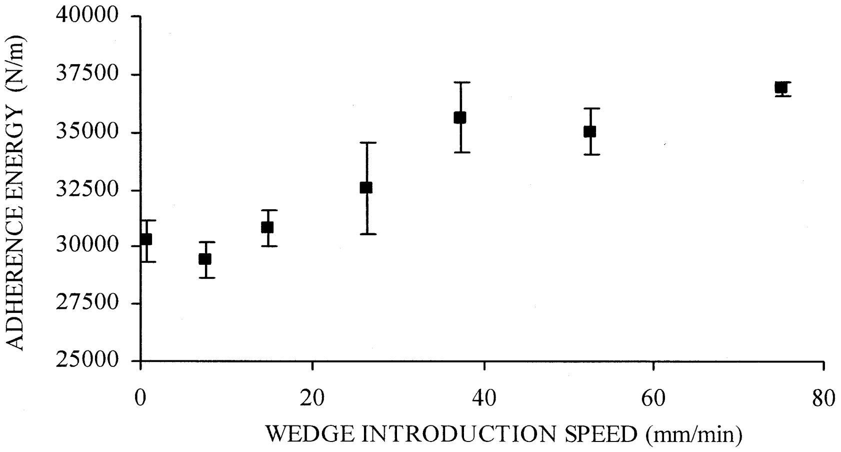

FIGURE 2 Adherence energy versus wedge introduction speed.

Figure 3 presents the evolution of the Young's modulus, E, of the polymer as a function of the tensile speed. A similar evolution is observed, i.e., an increase of the modulus and the presence of a transition due to the glass relaxation. The comparison of the G and E versus speed curves and the presence, in both cases, of a transition related to the glass relaxation, indicates that the rate dependence of the adherence energy is apparently governed by the rate dependence of the Young's modulus of the adhesive. Figure 4, which illustrates the evolution of G as a function of E, confirms this hypothesis.

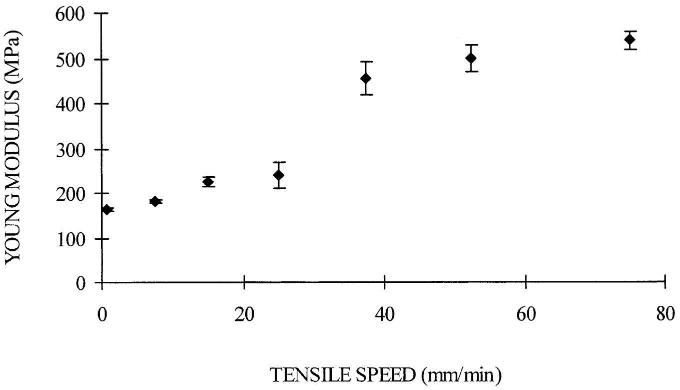

FIGURE 3 Young's modulus of the polymer versus tensile speed.

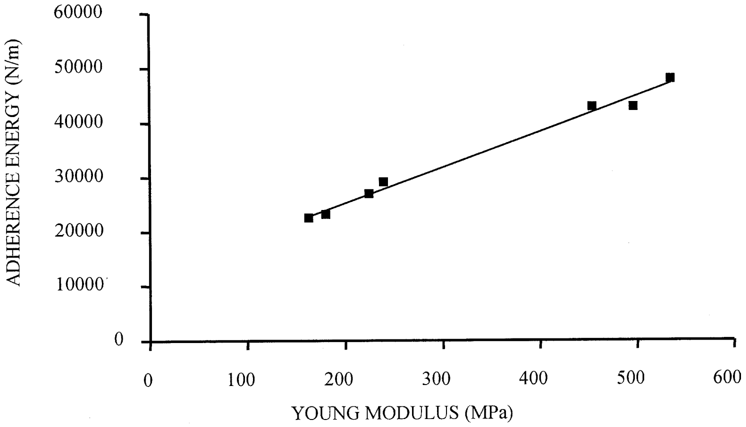

FIGURE 4 Adherence energy as a function of Young's modulus of the polymer.

A linear evolution is observed, leading to the following relation between G and E:

$$G_{(\mathrm{v})} \propto E^{\mathrm{n}}_{(\mathrm{v})},$$

with $\mathrm{n} \approx 1$ for the tested polymer.

This equation proves that the intrinsic mechanical and viscoelastic properties of the polymer directly determine the rate sensitivity of adherence [9].

The developed wedge test also allows one to follow the kinetics of the crack propagation for each wedge introduction rate. The shape of a propagation curve is presented in Figure 5. Two propagation rates can be distinguished: an initial quick propagation followed by a slower propagation step. The slope of the second part of the curve (slow propagation step) is determined for each introduction rate, as illustrated in Figure 5.

In Table 1, the crack propagation speed and the adherence energy values for each wedge introduction rate are reported. A higher introduction rate induces a slower propagation, corresponding to a viscoelastic "braking" mechanism. The objective is now to correlate both experimental results, i.e., adherence energy and crack propagation speed, with an intrinsic polymer viscoelastic characteristic, the relaxation time. Creep experiments have been carried out on bulk polymer film (constant stress $\sigma = 4$ MPa, applied at a loading speed equal to 10 mm/min at 20°C). Figure 6 shows the creep curve, which

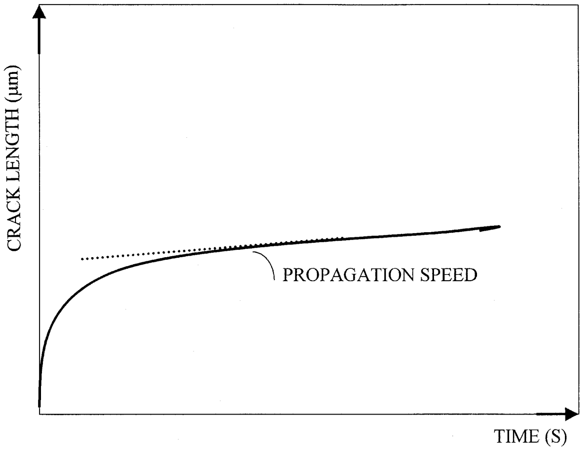

FIGURE 5 Shape of the evolution of the crack length as a function of time.

TABLE 1 Adherence Energy, G, and Crack Propagation Speed, S_{prop}, for Different Wedge Introduction Speeds, S_{intro}

S_{intro} [mm/min]	0.8	7.5	15	37.5	75
G [N/m]	30263	29408	30825	35607	36864
S_{prop} [μm/s]	0.0653	0.0655	0.0575	0.0467	0.0308

can be described, to a first approximation, by a Maxwell model (spring and dashpot in series, as illustrated on Figure 6). The relaxation time of the Maxwell element is equal to the ratio between the viscosity, η, of the dashpot and the elastic modulus, E, of the spring. The viscosity is deduced from the slope of the curve ($\eta = \text{slope}/\sigma$) and the extrapolation of the line, at zero time, is equal to σ/E, as indicated on Figure 6.

The relaxation time, τ, determined from the creep experiment, is equal to 2×10^3 s for a initial tensile speed equal to 10 mm/min.

By analogy, this calculated relaxation time is attributed to the wedge test experiment performed at 7.5 mm/min, which is the closest speed compared with the loading speed used in the tensile creep test. This rate is, therefore, taken as the reference speed, the ambient temperature (20°C) being the reference temperature. The other introduction speeds are then converted into equivalent temperatures, according to the time-temperature superposition principle. The following equations are used to calculate firstly the equivalent

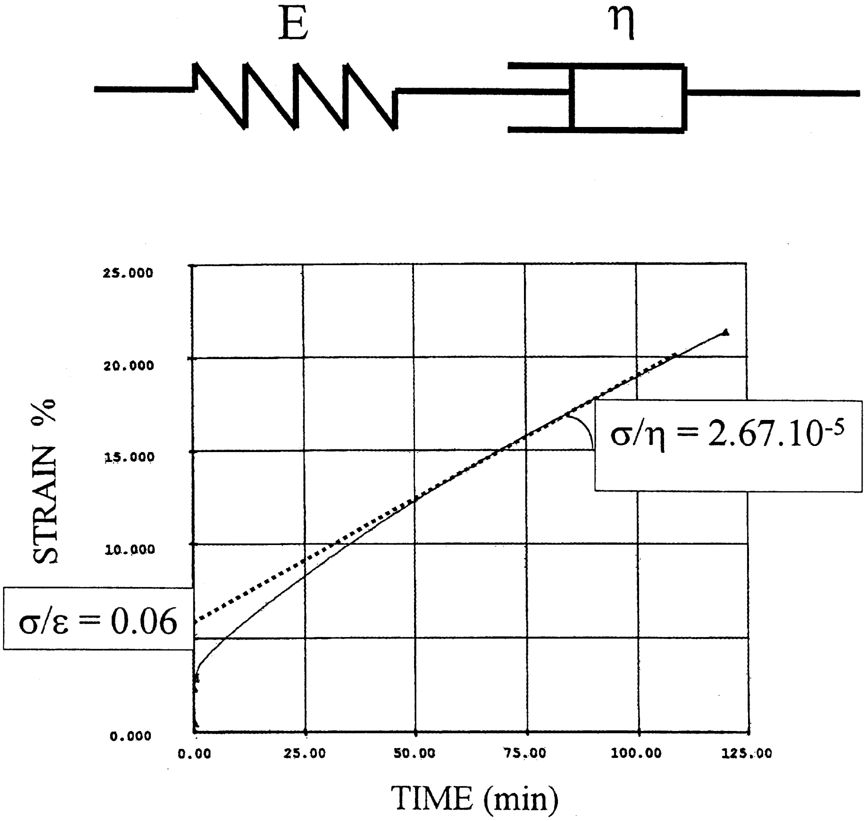

FIGURE 6 Maxwell model and creep curve of the polymer.

temperature and then the corresponding relaxation time related to each temperature:

$$\log(a_{T,Tg}) = \frac{-C_1 \times (T - Tg)}{C_2 + (T - Tg)} \quad \text{(WLF equation)},$$

$$a_{T,Tg} = \frac{\tau(Tg)}{\tau(T)},$$

$$a_T = \frac{V}{V_{\text{ref}}}.$$

The results, reported in Table 2, indicate that a higher speed corresponds to a slower temperature and a higher relaxation time. Direct

TABLE 2 Equivalent Temperature, Relaxation Time, τ, and Relationship between τ, Adherence Energy, G, and Crack Propagation Speed, S_{prop}, for Different Wedge Introduction Speeds, S_{intro}

S_{intro} [mm/min]	0.8	7.5 = ref	15	37.5	75
Equiv. T [°C]	23.1	20	19.1	18	17.1
Relax. Time [s]	63	2×10^3	5.9×10^3	2.5×10^4	7.82×10^4
S_{prop} [μm/s]	0.0653	0.0655	0.0575	0.0467	0.0308
$S_{\text{prop}} \log \tau$	0.117	**0.216**	**0.217**	**0.201**	0.15
G/log τ	16824	**8908**	**8164**	**8075**	7533

relations, presented in Table 2, have been established between adherence behaviour (energy, G, and crack propagation speed, S_{prop}) and relaxation time.

The propagation speed is inversely proportional to the logarithm of the relaxation time:

$$S_{\text{prop}} = k \cdot (\log \tau)^{-1},$$

with $k = 21 \times 10^{-2}$. The adherence energy, G, is directly proportional to the logarithm of the relaxation time:

$$G = k' \cdot \log \tau,$$

with $k' = 8 \times 10^3$. These quantitative relations highlight the major role of intrinsic polymer properties in the rate sensitivity of adherence, which is governed by adhesive viscoelastic behaviour, especially relaxation time, characterising the mobility of the chains responsible for the energy dissipation.

CONCLUSION

A wedge test device is used to determine the adherence energy and the crack propagation kinetics as a function of the wedge introduction speed. A Maxwell model is able to describe the polymer's viscoelastic behaviour. The chosen methodology, based on the time-temperature superposition principle, allows one to determine, for each speed, a corresponding relaxation time.

Quantitative relations between, first, crack propagation rate and relaxation time and, second, adherence energy and relaxation time are proposed. The established equations prove that the fracture behaviour of the assemblies and the associated energy dissipation phenomena are directly controlled by the viscoelastic properties of the adhesive.

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