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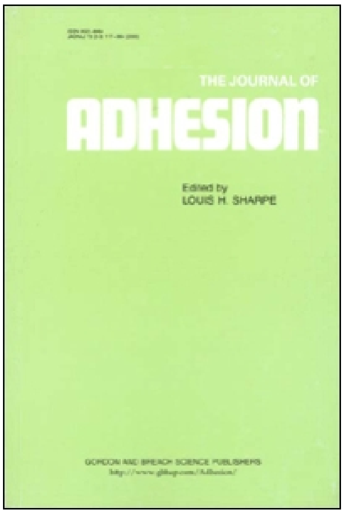

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Environmental Attack on Adhesive Joints Studied by Cleavage Fracture†

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The cleavage of a joint by a wedge gives its resistance to fracture, R. R is a function of the thermodynamic energy of adhesion W_a, the crack speed v, and a dissipative function ϕ

$$R = W_a(1 + \phi_{(T)}v^n), \qquad n \leq 1$$

Any change in the environment modifies W_a and thus causes the fracture to proceed towards a new equilibrium position. The results presented concern the changes introduced by the vapor or liquid of various solvents including water. When the fracture starts again it always proceeds along the interface independently of the initial locus of fracture.

The speed of propagation is slow and obeys a v^n law. The assistance of external agents to the fracture of ionic crystals, glasses and polymers has been already observed and attributed to a decrease in W_a. There is no simple relation between the fracture results obtained and the physical properties of the liquids or vapors and the possibility of strain-induced reactivity is suggested.

KEY WORDS Wedge test; fracture; environment; influence of liquids, vapors; water; joint strength.

PRINCIPLE OF THE WEDGE-TEST

Upon the introduction of a wedge into an adhesive joint, the substrate deforms and stores elastic energy.

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This elastic energy releases when the joint breaks. An equilibrium is reached when the elastic energy remaining in the substrate is equal to the resistance to fracture, R, of the adhesive. The resistance to fracture R, strain energy relase rate G and energy of adherence W_s are in that case equal to each other.

Provided that the substrate deformation is purely elastic and that no elastic energy is stored in the adhesive, we have:[1]

$$R = 3Eh^2e^3/16l_0^4 \tag{1}$$

where the parameters are defined in Figure 1. If the fracture proceeds in the adhesive, R is characteristic of the adhesive; if it proceeds along the interface, R is characteristic of the joint.

The deformation imposed by the wedge is equivalent to that of a double cantilever stressed by a constant force P_a (Figure 2). In the double cantilever, the force P and the displacement, h, of the wedge-test are related by:

$$P = Ee^3wh^2/8l_0^3 \tag{2}$$

That equation points out that the behaviour of the wedge-test is that

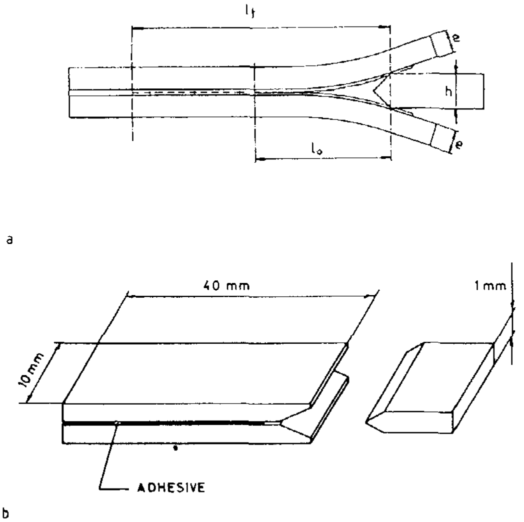

FIGURE 1 (a) Schematic description of the wedge test. (b) dimensions used.

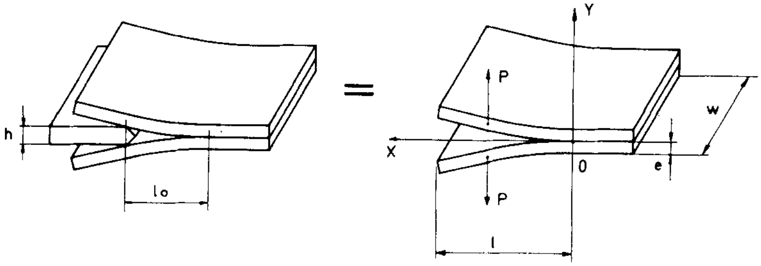

FIGURE 2 Wedge deformation is equivalent to that of a double cantilever.

of a stressed joint. In our experimental conditions a wedge of 1 mm typically corresponds to a force to 33*N*.

MAUGIS' ADHESION THEORY

Fracture of an Adhesive Joint

Maugis[2] describes the progression of a crack in an adhesive joint by the relation between the strain energy release rate G and the fracture speed v. He supposes that this function is the result of the superposition of a function of the viscoelastic losses (line AB in Figure 3) described by the equation:

$$G - W_a = \phi a_T^n v^n W_a \tag{3}$$

which superposes to the elastic response (line AC in Figure 3) of the system. Upon the introduction of a wedge in a joint, a high energy is suddently introduced which produces a crack progressing at a high speed (limited by the speed sound in the medium).

Then, v decreases as G decreases until the point B_1 is attained. At that point the speed suddenly changes to a low value v_2 and the crack apparently stops. Equation (4) has been experimentally verified by Barguins in the case of the adhesion of polyurethane to glass[3] or gold[4] as well as the form of Figure 3 in the case of an adhesive supported on Mylar®.[5]

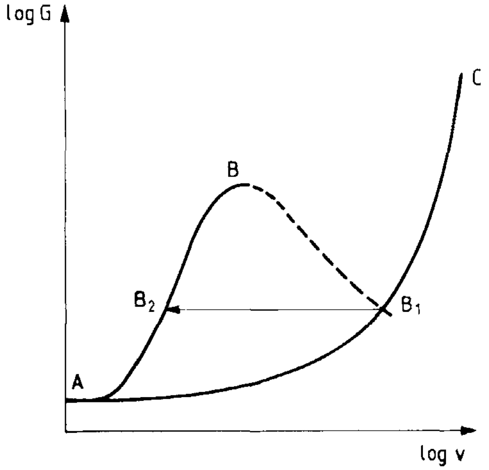

FIGURE 3 Theoretical variation of the strain energy release rate G with the fracture speed v.

Influence of the Environment on Adhesion

Eq. (3) relates viscoelastic losses to the difference $G - W_a$ between G and the thermodynamic energy of adhesion W_a. Let W_a^{12} denote the energy of adhesion of two bodies 1 and 2 of surface energy γ_1^i and γ_2^i; we have:

$$[W_a^{12}]^a = \gamma_1^a + \gamma_2^a - \gamma_{12}^a \tag{4}$$

where γ_{12} is the interfacial energy of the bound system and $\gamma_1^a + \gamma_2^a$ denotes the surface energy of bodies 1 and 2 in air. In the presence of the environment (e) the parameters of Eq. (4) change into:

$$[W_a^{12}]^e = \gamma_1^e + \gamma_2^e - \gamma_{12}^e \tag{5}$$

It is that change in W_a^{12} which explains the instability of a fracture in a humid environment. Let us consider the cleaved adhesive joint that was stable under the conditions of point B_2 in Figure 3 or 4. The decrease in W_a due to the presence of water displaces the dissipative function from AC to A′C′ (Figure 4). B_2 is not longer in a stable state and the fracture progression starts again with speed v_3 (point B_3 of Figure 4). The variation of W_a may be obtained from peel measurement[6] and amounts to some 0.1 J m^{-2}.

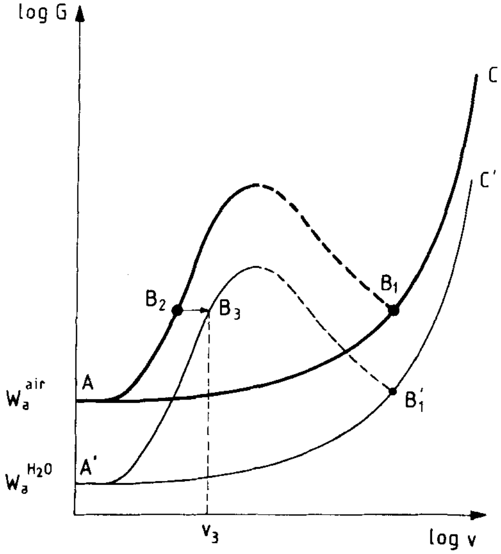

FIGURE 4 Influence of the environment upon the viscoelastic losses. As the adhesion energy W_a decreases the $G(v)$ curve translates down.

INFLUENCE OF THE ENVIRONMENT UPON THE INITIAL CRACK LENGTH FORMED UPON CLEAVAGE

We already have stated that the initial fracture upon cleavage in air[7] is stable, but progresses under tropical conditions.[8] We also have mentioned that methanol or methylene chloride vapors have an effect similar to water and that acid vapors are even more aggressive than water toward adhesive joints.

The cleavage of an adhesive joint shows that the environment has an influence both upon the initial length of fracture and upon the long-term resistance of the joint. Figure 5 shows the resistance to fracture R of an adhesive joint, cleaved by a wedge, as a function of time under normal (about 25°C 40% RH) and tropical (40°C 90% RH) conditions. Often, the initial fracture is cohesive while its progression occurs at the interface. In Maugis's description, this corresponds to two different modes of fracture at high and low speed. For that reason, we distinguish the initial fracture and its progression under a given environment.

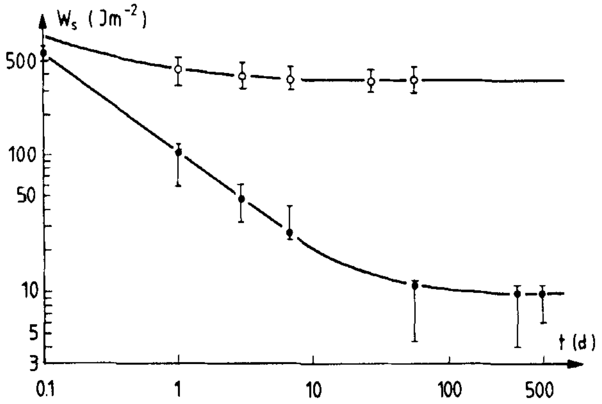

FIGURE 5 Development of the crack length under laboratory conditions, ○, and in tropical climate, ●, for two series of wedge tests made under ths same conditions.

Influence of a Liquid Environment

If instead of cleaving the adhesive joint in air it is cleaved in a liquid, we observe that:

1) the crack generally is longer than in air, except for some inactive non-polar liquids

2) the crack occurs along the interface from the very beginning, instead of progressing inside the adhesive as in air, and that is observed even with the inactive liquids although the resistance to fracture is the same in both cases. Actually, interfacial failure is found for 3 joints out of 5 for paraffin and silicone oil, for the same fracture length.

3) three categories of liquids may be distinguished: inactive, active and aqueous, the last having the strongest influence. The average initial length of fracture for one set out of 39 adhesive joints cleaved in various liquids (3 of each) are found in the first column of Table I. There, one sees that white spirit, silicone oil and Freon® have no influence upon the crack length compared to air. Polar liquids increase the crack length from 10 to 13 mm and aqueous solutions bring it from 14 to 18 mm. Table II shows the propagation speed together with an indication of quoting the permittivity.

TABLE I
Effect of various fluids on crack development in wedge test

Fluid	Crack length (mm)		
	l_0	$l_{24\ \mathrm{hr}}$	$l_{16\ \mathrm{days}}$
Air	8.5	9	9
White Spirit	8.5	9	9
Freon	8.5	9	9
Silicone oil 41 vl	8.5	9	9
Paraffin oil	8.5	9	9
Chloroform	10	11	11
Ethylene trichloride	10	11.5	13.8
Tetrahydrofuran	12	12	12
Methanol	13	13	13
Ethylene glycol	13.5	14.5	17.5
Water	14.5	17.5	17.5
Acetic acid, 10%	14	27	debond
Ammonia, 25%	14	17	17.5
Triton® X100	14	17	17.5

TABLE II
Effect of various fluids on speed of fracture compared with dielectric permittivity

Fluid	Speed of crack propagation 10^8 m s^{-1} (average over 24 hr)	ε
Air	0.1	1
Fluorocarbon	0.1	2
Paraffin oil	0.2	2.2
Silicone oil	0.2	3
White spirit	0.2	2
Chloroform	4.6	4.8
Methanol	3.5	32.7
Methylene chloride	4.2	8.9
Acetonitrile	5.8	37.5
Tetrahydrofuran	5.8	7.6
Acetone	5.8	20.7
Ethylene trichloride	5.8	3.4
Ethylene glycol	5.8	37.7
Dimethyl formamide	6	49
Water	8	78.5
Water + Triton® X100	8.5	78.5
Acetic acid, 10%	4.7	78.5
Ammonia, 25%	9–10	70.5

Effect of Acids and Bases Upon the Initial Fracture

Following Fowkes[10] and Bolger[11] much importance has been given to acid-base interactions in adhesive processes. Andrews[12] has shown that the presence of acid or base increased the kinetics of hydrolysis of epoxy adhesive joints to glass. For that reason, we observed the influence of diluted acetic acid (pH 4) and ammonia (pH 12) over both the initial fracture length and fracture progression in the case where the fracture was initiated in air, acid or base vapor and dilute solution of acid or base.

The results are found in Table I and show no difference between pure water, acetic acid or ammonia upon the initial length of fracture; it is only on the slow crack progression that later occurs that the very different values of pH show similar effects.

Influence of a Detergent

Beside these aggressive chemicals, detergents are also known[13] to lower the resistance of adhesive joints to fracture and we have observed this on peeling stainless steel epoxy joints in the presence of a solution of Triton® X100 (2%) in water. For that reason we have examined whether it has an influence on the initial fracture upon cleavage. We have observed that the initial length of fracture of an adhesive joint cleaved in a 2% solution of Triton X100 shows only a slight difference, if any, with its value in water. That is to say that the effect observed upon peeling is not seen on cleavage as in the case of acid or basic solutions. It seems that the fracture progresses so fast that the detergent does not follow up its advance. In the case of peel experiments the progression is necessarily much slower than the very fast progression in cleavage and the effect of a solution may then be observed. In cleavage, vapor only plays a role as long as it follows the fracture speed.[14] Thus liquid water as well as water vapor decrease the initial resistance of the joint and changes the locus of fracture. The decrease in adhesive strength, $510\,\mathrm{J\,m^{-2}}$, is due to that change. The addition of a non-ionic detergent produces no further change nor does the presence of acetic acid or 25% ammonia.

Influence of Vapor

The immersion of an adhesive joint in a liquid may change its properties. Although our experiments of cleavage are very rapid and the joint is not immersed for more than 5 minutes in the liquid before cleavage, a period which should not change the polymer properties, we have observed the cleavage of joints in a vapor of white spirit, methanol and water. In all three cases, the initial fracture lengths in the liquid or its vapor were equal, showing that the effect observed is due to the environment and not to a variation of the properties of the polymer.

INFLUENCE OF THE ENVIRONMENT ON THE PROGRESSION OF FRACTURE

The rupture of an adhesive joint under stress is a different process from the delamination in a given environment. The former occurs rapidly in a cohesive mode, while the latter progresses slowly along the interface. We have seen that the initial crack was longer in a liquid than in air and grew at the interface instead of in the adhesive. In both cases, when the crack seems to stop, its speed becomes vanishingly small. When the cleaved joint is exposed to certain aggressive chemicals, the crack propagation starts again, the shorter cracks having the faster progression. For that reason, the conditions of the initial fracture influence the behaviour of the joint only at the beginning of its progression, and soon both the joints which cracked in air and in liquid show the same evolution. This may be illustrated in the case of water.

Joints Cleaved in Air or in Liquid Water

We have shown above that, for a joint cleaved in air, $l_0 = 8.5 \pm 5$ mm and for a joint cleaved in water $l_0 = 14$ mm. That corresponds to a fracture energy $R = 750$ and $R = 140\,\mathrm{J\,m^2}$ respectively. When both joints are immersed in water, the fracture grows again at a speed equal to $12 \times 10^{-8}\,\mathrm{m\,s^{-1}}$ for the one cracked in air and $2.5 \times 10^{-8}\,\mathrm{m\,s^{-1}}$ for the other during the first two days, after which both joints have the same crack length which increases at the same speed. This behavior is represented on Figure 6. As the initial fracture in air is between 8 and 10 mm, we have taken the example of one joint with initial fracture $l_0 = 9$ mm. The initial fracture in water is between 12 and 18 mm; the crack development of an average joint having $l_0 = 14$ mm and of the extreme $l_0 = 18$ mm are

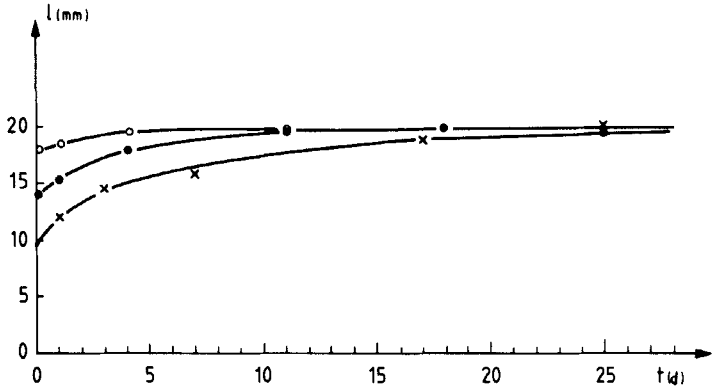

FIGURE 6 Development of the adhesive crack length under tropical conditions depending upon the initial fracture conditions: ○ cracked in water (maximum length); ● cracked in water (minimum); × cracked in water vapor.

plotted. What is evident from Figure 6 is that all joints tend toward the same limit whatever their initial fracture length. The cracks formed in air grow faster than those formed in water. After some 20 days, all joints have reached the same length of fracture, which grows at the same low speed under water vapour, in accordance with Maugis's expectations. We assume that this situation occurs for any chemicals; from now on, we consider the progression of the fractures that have been initiated in air.

The Influence of Various Liquids on the Progression of Fractures Created in Air

We have observed the progression of the fracture of adhesive joints cleaved in air and immersed in various liquids for 24 hours. Results are given in Table III as the average speed $l_{24} - l_0/t$ in meter per second for the various liquids in the order of increasing activity. At this stage, it is difficult to correlate our results with any physical properties, although they seem to follow the value of the solvent permittivity with a few exceptions such as tetrahydrofuran and chloroform, exceptions that could be due to some unfavourable experimental conditions.

During that stage of slow development, the effect of acids, bases

TABLE III
Strain energy release rate and crack speed

Water		Ethylene glycol		Paraffin oil	
G	v	G	v	G	v
$\mathrm{J\,m^{-2}}$	$\mathrm{m\,s^{-1}}$	$\mathrm{J\,m^{-2}}$	$\mathrm{m\,s^{-1}}$	$\mathrm{J\,m^{-2}}$	$\mathrm{m\,s^{-1}}$
960	2.5×10^{-8}	1100	7×10^{-8}	1000	2.4×10^{-9}
370	3.3×10^{-9}	120	4×10^{-9}	960	1.6×10^{-9}
190	1.6×10^{-9}	63	2×10^{-10}	850	1.25×10^{-9}
140	2.5×10^{-10}			450	10^{-10}

and detergents, which did not appear during the initial step, starts to show up.

Influence Upon the Variation of *G*(*v*) of the Immersion of a Cleaved Joint in Various Liquids

For practical reasons, these series of experiments have been done with a modification of the previous adhesive and silane treated surfaces. This does not seem to change the general trend. The development of fracture has been observed in paraffin and silicone oil, water and ethylene glycol. In that case, either because of the immersion or of the effectiveness of the silane treatment, ethylene glycol has a stronger effect upon the joint than water, but paraffin or silicone oil have almost no effect upon the fracture behavior compared to air. As we observed in the case of the cleavage in a liquid, the energy for cohesive or adhesive failure are nearly the same in oil. Among ten samples, one half presented a cohesive failure as in air and one half an adhesive failure progressing at a slightly higher speed. Plotting the length of fracture after various times, the crack speed at any value of l is obtained from the slope of the curve. Translating l into the energy release rate G *via* Eq. (1) allows us to obtain the values of Table III which leads to the parallel set of curves of Figure 7 in accordance with Maugis' theory. However, the magnitude of the translation is much higher than can be explained by a variation of W_a. This could be accounted for by the dissipation factor introduced by Schultz[15] giving W as: $W = G(M)W_a f(R)$, instead of the simpler expression of Maugis: $W = GW_a f(R)$, the dissipation factor taking into account the amplification of W_a due to dissipation of energy in the adhesive network.

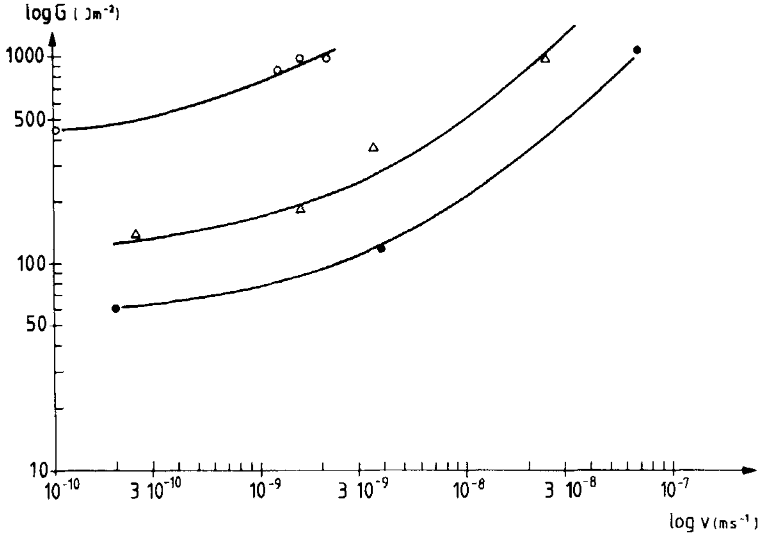

FIGURE 7 A liquid environment translates the G (O) curves parallel to each other. △ in paraffin oil; × in water; ● in ethylene glycol.

DISCUSSION

We have observed that many chemicals modify the resistance to fracture and the durability of adhesive joints. We have not found much difference between the action of the liquid or the vapor, neither on the initial crack nor on its further progression in aggressive environments.

We note that in all liquids, the fracture, which is initially cohesive changes to interfacial failure even for liquids that are inactive (Figure 8). The influence of solvents may be attributed to different parameters, but permittivity bears the closest relation to the observed results. One denotes three classes of liquids:

i) non polar liquids, such as alkanes and silicones, which do not affect the resistance to fracture, but only change the location of fracture in many instances;

ii) polar liquids, which accelerate the progression, lower the fracture resistance and change the location of fracture;

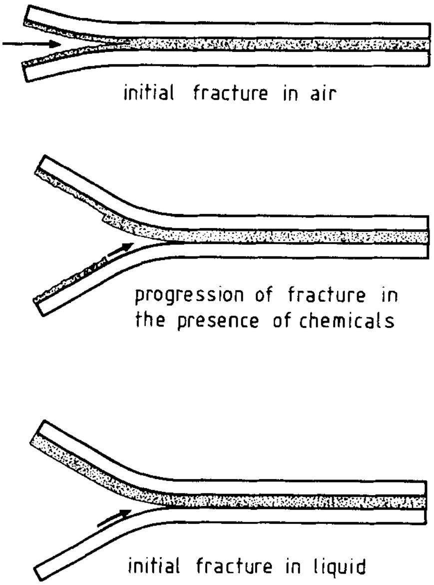

FIGURE 8 Variation of the location of fracture upon cleavage depending upon the environmental conditions.

iii) water, which has the highest effect upon the cleavage of that epoxy joint.

The change in location of the observed variations may be explained by Maugis' theory if one introduces an amplification factor g independent of the viscoelastic dissipation, which gives

$$G - W_a = gW_a(1 + \phi(\varepsilon, v, n))$$

g being of the order of 5×10^3 in the case of the adhesive considered here.

The influence of various chemicals having different acidic-basic character may be accounted for by a chemical reaction during which the initial acid-base bonds formed between the substrate and the adhesive are displaced by the environment. The rôle of stresses indicate that the reaction is easier with strained bonds, which has been shown to be the case in glasses.[16]

EXPERIMENTAL

Adhesive Carboxy terminated butadienerubber modified epoxy, polymerised at 140° for 45 minutes except where stated.

Substrate Adherends were two plates of flat stainless steel AISI 301. Details are given in Refs 1 and 8.

Cleaning (i) hot basic detergent under ultrasonic agitation; (ii) Deionised water rinse; (iii) no treatment with a silane except where indicated; (iv) isopropylalcohol rinse; (v) hot air drying.

Bonding adhesive applied with a brush on both sides. The plates were maintained in contact with two springs.

Adhesive thickness between 50–100 μm, typically 80 μm.

Fracture in a liquid or vapor the micrometric vise is provided with a tank made of Delrin® containing the solvent.

Tropical climate Oven maintained at 40°C 90% RH. (The adhesive is not affected by a temperature of 40°C).

Measurement of fracture speed Fracture length l is measured at various times. Then the plot $l(t)$ is drawn, from which the speed v is obtained for each time.

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