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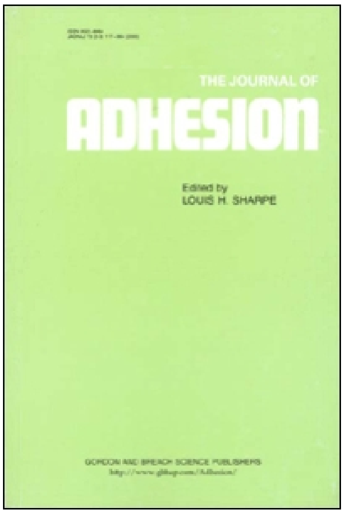

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Adhesive Failure and Deformation Behaviour of Polymers

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Adhesive Failure and Deformation Behaviour of Polymers

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An instrument has been developed to determine the adhesive fracture energy as a function of the most important parameters such as temperature, contact time etc. and to study the stress–strain behaviour during bond separation. Additionally, the deformation processes during debonding were observed by high speed photography. Investigations of two high molecular weight polymers, polyisobutylene (PIB) and polyethylhexylacrylate (PEHA), showed two different types of bond separation: "brittle" behaviour with low adhesive failure energy for PIB and the formation and deformation of fibrillar structures for PEHA leading to much higher strains at break and adhesive failure energies. It follows from mechanical measurements that both polymers differ mainly by their entanglement networks. The much longer entanglement spacing for PEHA leads to the formation of fibrillar structures which, in accordance with a theory of Good, seem to be the reason for strong adhesion.

KEY WORDS Polymer adhesion; adhesive fracture energy; stress–strain behaviour during bond separation; fibrillar structure; creep compliance; entanglement network.

1 INTRODUCTION

The adhesion of a polymer to a solid substrate is influenced by the viscoelastic behaviour of the polymer and the surface and interfacial tensions of polymer and substrate. The influence of viscoelasticity on the formation of an adhesive joint has been demonstrated by various papers showing a correlation between adhesive strength and a viscoelastic material function of the polymer such as the creep compliance.[1–4]

Strong correlations are also operative in the process of bond separation. Mathematically this has been expressed by the factorisation of the energy of separation w into two terms,

$$w = W_a \cdot (\phi + 1)$$

where W_a is the thermodynamic work of adhesion and ϕ a viscoelastic function of temperature and rate of separation describing the energy dissipation in the polymer during debonding.[5–8] In contrast to this well established relation, however, there exists only a rather poor understanding of the deformation processes occurring during bond separation and their dependence on the molecular structure of the polymer. One exception is the detection of fibrillar structures in the peeling of pressure-sensitive adhesives.[9,10] On the basis of these findings and the crazing of hard polymers Good developed an isothermal theory which describes the separation of polymers from solid substrates.[11,12] The model used is based on the drawing of filaments between the bulk polymer and the solid. The theory correlates strong adhesion to the formation and deformation of fibrillar structures.

This work has two objectives: Firstly, to obtain information about the deformation behaviour of an adhesive joint during bond separation by measuring the stress–strain characteristics and, secondly, to make visible the deformation of the polymer during the separation process by means of high speed photography. The investigations described in this paper deal with polymers above their glass transition temperatures which undergo no physical or chemical modifications between bond formation and separation, *e.g.* crystallization, cross-linking. Stainless steel is used as the adherend, exclusively. It can be regarded as infinitely rigid in comparison with the polymer adhesive. Thus, only the deformation of the polymer has to be taken into account.

2 EXPERIMENTAL

2.1 Measurement of adhesive strength and tack

In order to realize the aforementioned intentions, an apparatus is required so that the most important parameters during the bonding and unbonding processes such as contact time, contact pressure, rate of separation and temperature, can be adjusted in sufficiently wide ranges, and which determines stress and strain during bond separation as a function of time. In Figure 1 a schematic and simplified diagram of this instrument is given which already has been described in greater detail in a preceding publication.[4]

The polymer to be tested is applied as a solution or a latex to a flat rigid plate of stainless steel (2), forming a layer of definite thickness (3) after drying. By means of an electronically controlled motor (1) the surface of the sample is brought into contact with a cylindrical probe (5). This probe is firmly connected to a piezoelectric force transducer (6) which determines the force during bond formation and separation as a function of time. The motor is stopped when a certain preselected contact force in the range between about 2×10^{-2} and 1×10^{2} N is reached. This contact force or the corresponding contact stress can be held constant during an also preselected time interval between about 1×10^{-2} s and arbitrarily long times. At the end of the contact period the motor is driven in the opposite direction separating the sample and the probe surfaces with a definite velocity which varies between 1×10^{-1} and 2×10^{1} mm s^{-1}. The sample and the probe are placed in a temperature chamber (4) which can be

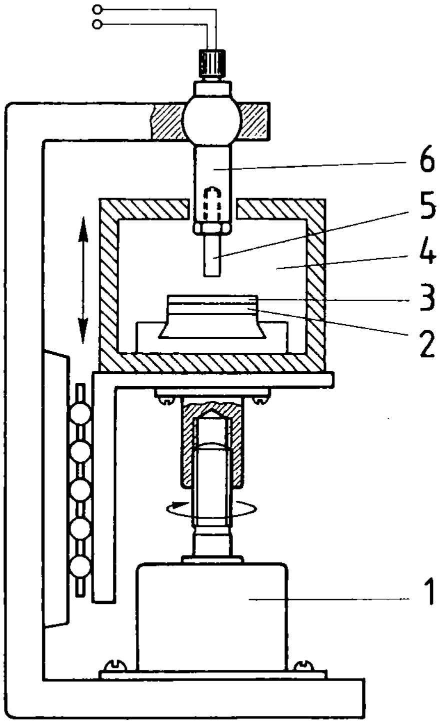

FIGURE 1 Apparatus for measuring the adhesive failure energy and the stress–strain behaviour during bonding and debonding (simplified). 1 Motor, 2 Sample holder, 3 Sample, 4 Temperature chamber, 5 Probe, 6 Force transducer.

thermostated to temperatures between about −50 and +200°C with a nitrogen thermostat. The instrument is interfaced to a laboratory computer which enables an automatic measurement of the force *vs.* time curve during the whole bonding and debonding process.

The measurements described in this paper were carried out with a probe of stainless steel having a diameter of 1.75 mm. The contact stress was $2 \times 10^{-1}\,\mathrm{Nmm}^{-2}$, the contact time 1 s, and the rate of separation $5\,\mathrm{mm\,s}^{-1}$.

In Figure 2 a typical force *versus* time plot is shown, in this case, however, with a contact time of about 40 ms. The force during the contact period is plotted as a negative force, the tensile force during bond separation appears positive. During the separation phase the force normally shows a maximum and falls off to zero when complete separation is achieved. The force *vs.* time plot can easily be transformed into a common stress–strain curve, because the probe cross-section A, the sample thickness d and the separation velocity v are known. In the remaining part of this paper, the tensile stress $\sigma = F/A$ is plotted *vs.* the tensile strain $\varepsilon = v \cdot t/d$ whereby the contact period is suppressed.

An appropriate measure of adhesive bond strength is not the maximum tensile

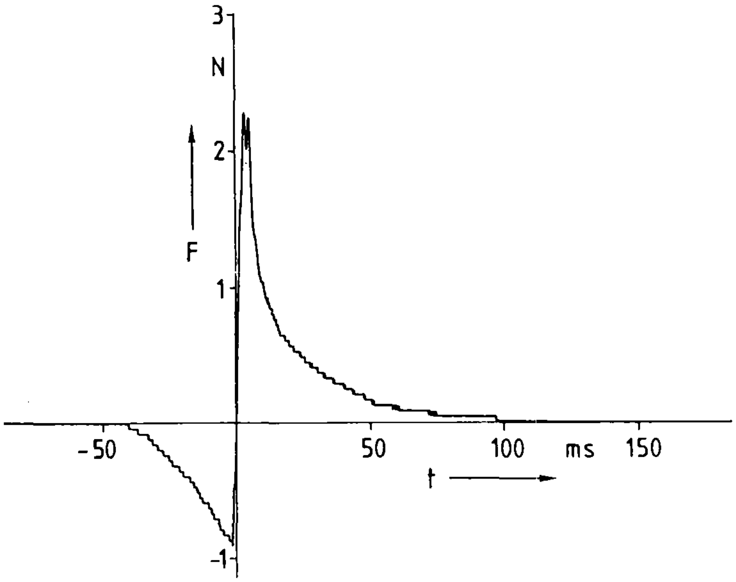

FIGURE 2 Example of a force *vs*. time plot during bond formation and bond separation.

stress but the energy of separation per unit area of interface, w, which can be calculated by integration of the stress–strain curve over the separation period.

$$w = \frac{1}{A} \cdot \int F \cdot v \cdot dt = d \cdot \int \sigma \cdot d\varepsilon$$

w has been introduced by Andrews, Gent, Schultz and Kinloch.[5,6,13,14] For short contact times and low contact pressures it is a measure of the tack of the polymer.

The deformation of the polymer during the separation phase could be made visible by high speed photography with a picture sequence of $500\,s^{-1}$.

2.2 Mechanical measurements

The mechanical properties of the polymers were investigated using two methods. The first determines the creep compliance D in the linear-viscoelastic regime as a function of time and temperature. These measurements, which have been described in greater detail elsewhere,[4,15] were carried out by applying a constant tensional stress to a free film of the material to be tested and determining the resulting elongational strain as a function of time.

The mechanical behaviour at large deformations and the ultimate mechanical properties were studied by stress–strain measurements under uniaxial tension by means of a commercial tensile tester.

2.3 Samples

Two linear, amorphous polymers were chosen for this study which reveal a very different stress–strain behaviour as will be shown:

- Polyisobutylene (PIB) with a glass transition temperature $Tg = -53°C$, determined by creep measurements with a time of 1 s, and a mean molecular mass of $\overline{M_w} = 1.3 \times 10^6$ g/mole.
- Polyethylhexylacrylate (PEHA), obtained by emulsion polymerization in an aqueous phase, with $Tg = -59°C$ and an unknown molecular mass which, however, is likely to be very high as is common for emulsion polymers.

For the adhesion measurements, films with a thickness between 35 and 40 μm were formed from solutions in hexane in the case of the PIB sample and from the original aqueous latex for PEHA. The mechanical measurements were carried out with free films with a thickness of about 200 μm.

3 STRESS–STRAIN CHARACTERISTICS OF THE DEBONDING PROCESS

Generally three types of stress–strain curves have been obtained from investigations of a large number of different polymers. The first type, which shall not be discussed here, is observed for polymers of comparatively low viscosity. In this case the tensile stress rapidly reaches a maximum and, then, falls off to zero gradually. The adhesive joint breaks by cohesive fracture within the polymer film; the debonding process is governed by viscous flow.

3.1 "Brittle" fracture

The high molecular weight polyisobutylene investigated in this study exhibits a very different stress–strain behaviour as compared to the aforementioned "liquid-like" type of separation. For this second type, exemplified in Figure 3, a sharp maximum is reached at rather low strains. At a strain of about 0.5 the probe separates from the polymer by purely adhesive debonding.

According to the small area under the stress–strain curve the energy of separation is low. This type of deformation behaviour will be called "brittle" in the following sections of this paper. This specification, of course, may not be confused with the normal brittle fracture which occurs in polymers below their glass transition temperature and has typical elongations at break in the range of 10^{-2} to 10^{-1}. The bond separation exemplified in Figure 3 takes place well above Tg, and "brittle" in this case only means low strain and energy of separation compared with "liquid-like" debonding and the type of stress–strain characteristic described in the next section.

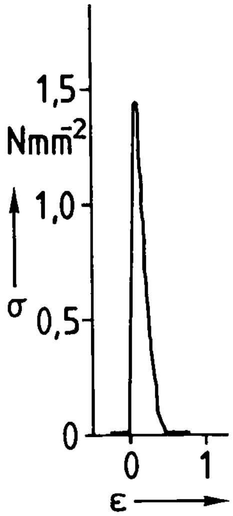

FIGURE 3 Stress-strain curve for polyisobutylene (PIB) at 23°C during the separation phase.

3.3 Fibrillar behaviour

The most interesting mode of separation is revealed by polyethylhexylacrylate. The stress *vs.* strain plot for this polymer shown in Figure 4 is characterized by a maximum of the stress similar to that in Figure 3 and, adjacent to this, a very pronounced "shoulder" which leads to a high strain at break of about 9. As this shoulder gives rise to a large area under the curve, a high energy of separation is calculated for PEHA.

The deformation of the polymer film during the separation phase could be made visible by high-speed photography. In order to obtain better spatial resolution a stainless steel probe with a diameter of 4 mm was used. The thickness of the polymer film was about 100 μm, the rate of separation was 2 mm s^{-1}. These altered experimental conditions, however, have no influence on the deformation

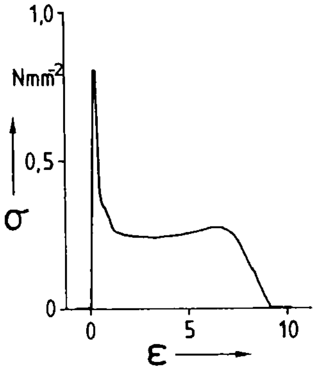

FIGURE 4 Stress-strain curve for polyethylhexlacrylate (PEHA) at 20°C during bond separation.

behaviour of the sample during bond separation. In Figure 5 four different stages of the separation process are shown corresponding to the time intervals after starting the downward motion of the sample indicated in the caption. It can be clearly seen that the material is split into separate filaments or fibrils which are anchored on both the substrate and the probe surfaces. These fibrils are increasingly stretched causing the storage and dissipation of energy. In photo 5c, the fibrils already begin to separate from the probe surface by purely interfacial failure. This rupture starts at the rim of the probe where the inhomogeneous distribution of tensile stress has a maximum. After complete debonding the deformed material recovers and finally restores the original film surface. The

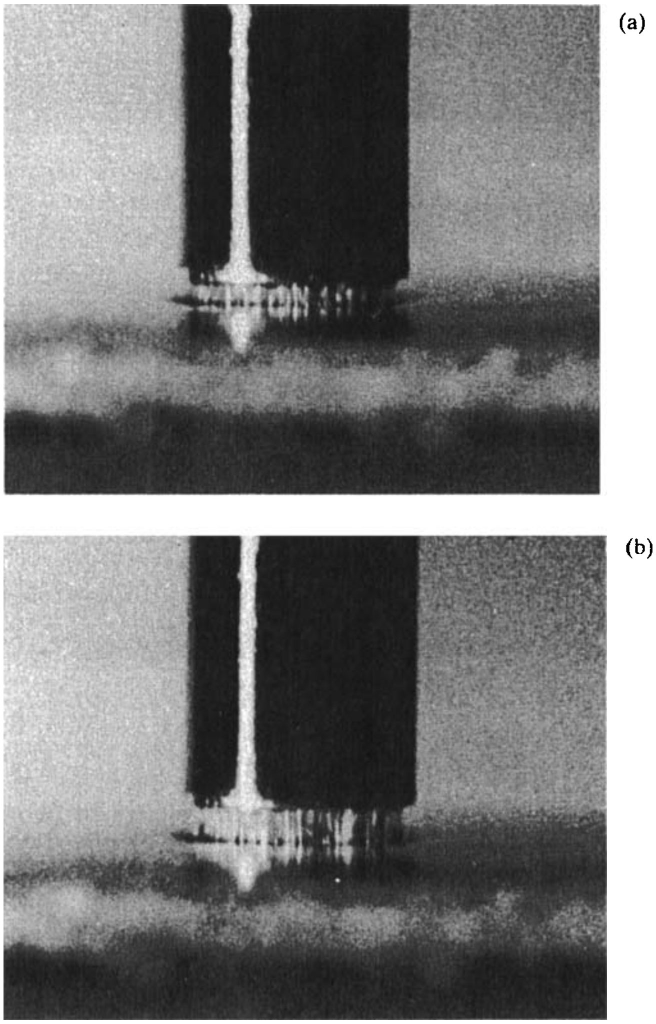

FIGURE 5 Photographs of the debonding process of PEHA. Probe diameter = 4 mm. a $t = 200$ ms, b $t = 300$ ms, c $t = 380$ ms, d $t = 510$ ms.

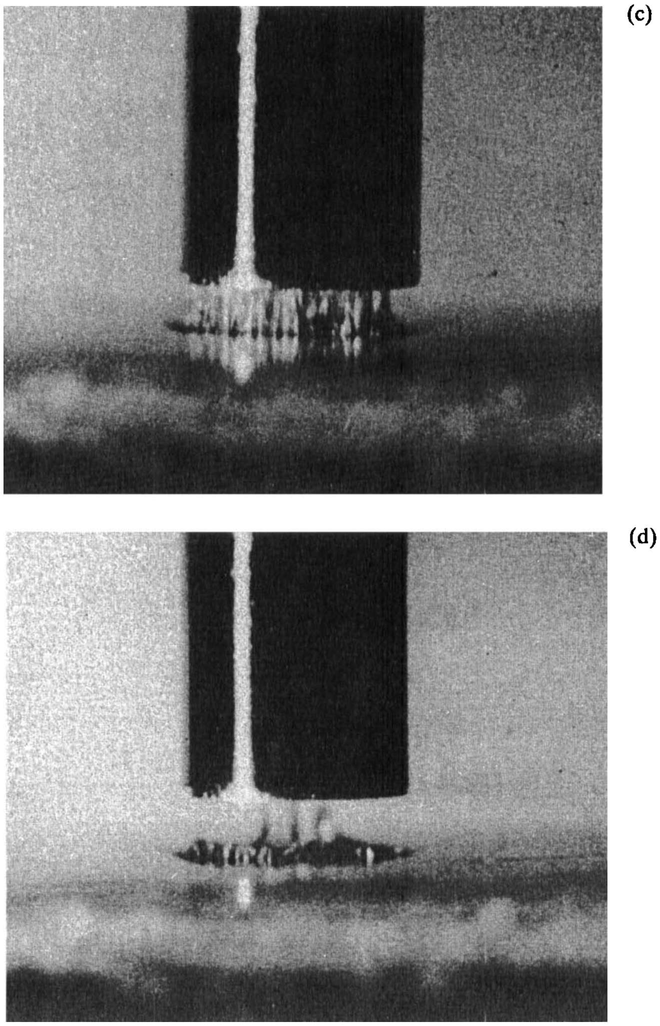

FIGURE 5 (*continued*)

deformation of the brittle polymer could not be made visible as clearly as for PEHA, because fracture occurs at very low elongations of about 50 μm for a 100 μm thick film. The photographs, which, for that reason, shall not be shown here, do not give any indication of filaments.

4 TEMPERATURE DEPENDENCE OF ADHESIVE FAILURE ENERGY

In order to understand better the deformation behaviour of "brittle" and "fibrillar" polymers, the influence of temperature on the adhesive fracture energy

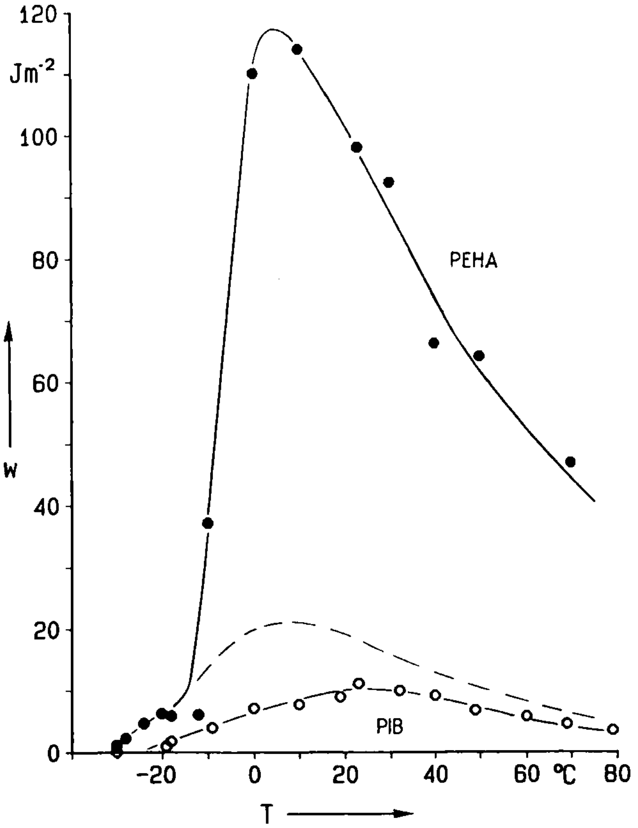

FIGURE 6 Adhesive fracture energy, *w*, as a function of temperature for PEHA (●) and PIB (○). Broken curve *vide* text.

and on the stress–strain characteristics has been studied. In Figure 6, *w* is plotted *versus* temperature for both polymers. As already described in a previous paper[4] *w* shows a maximum about 50 to 70°C above the glass transition temperature. The large difference between both polymers becomes again quite evident: the maximum energy of separation for PEHA is more than one power of ten higher than that for PIB. That indicates that according to the equation $w = W_A \cdot (\phi + 1)$ PEHA has a much higher viscoelastic dissipation factor ϕ than PIB,[5–8] because W_A is very similar for both polymers.

In Figure 7, the stress–strain curves for the PIB sample are shown at various temperatures, as indicated. There is no change in the type of these curves from low temperatures to the highest temperatures measured, *i.e.* brittle fracture behaviour is observed throughout the whole temperature range. At still higher temperatures and low separation rates PIB approaches a more or less liquid-like behaviour. There is, however, no transition to fibrillar debonding. As a result, PIB remains on a comparatively low level of adhesion.

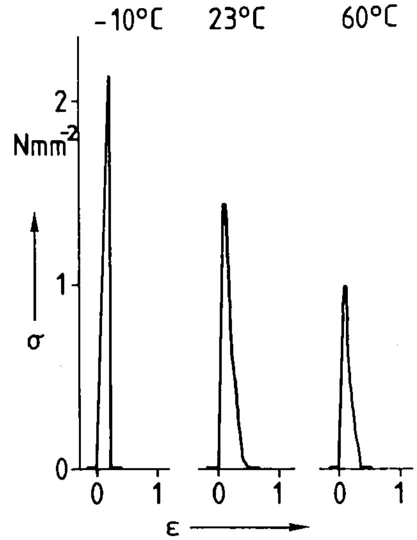

FIGURE 7 Stress–strain curves for PIB during bond separation at various temperatures as indicated.

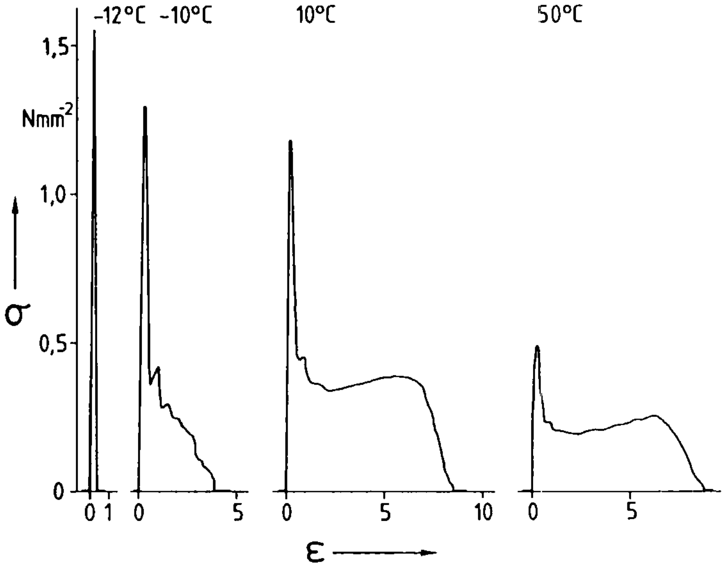

FIGURE 8 Stress–strain curves for PEHA during bond separation at various temperatures as indicated.

Such a transition is found for PEHA (Figure 8) for which brittle fracture is observed at temperatures below about −12°C, connected with low fracture energies. Between −12 and −10°C the mode of debonding rather abruptly changes to fibrillar behaviour leading to a steep increase in *w*, as shown in Figure 6. At higher temperatures no further change in the debonding behaviour is found. It follows, thus, from Figures 6 and 8 that the formation and extension of fibrils is the reason why PEHA has a much higher level of adhesion than PIB. This is confirmed by the broken curve in Figure 6 which was obtained for PEHA by integrating the stress–strain curves only in the region of the first stress peak. In this case only a gradual difference exists between PIB and PEHA. The transition from brittle to fibrillar behaviour is shifted to lower temperatures with decreasing rate of separation, as it is generally observed for viscoelastic phenomena.

5 CORRELATIONS TO MOLECULAR STRUCTURE

In Figure 9 the reciprocal creep compliance $E = 1/D$, which corresponds to Young's modulus determined by a creep experiment, is plotted *versus*

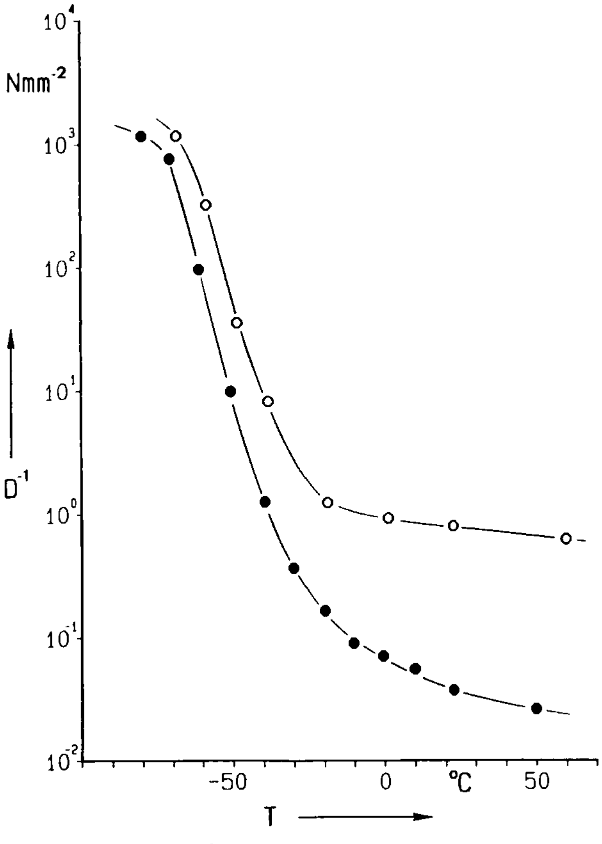

FIGURE 9 Reciprocal compliance D^{-1} of PEHA (●) and PIB (○) *vs.* temperature, determined at a time of 1 s.

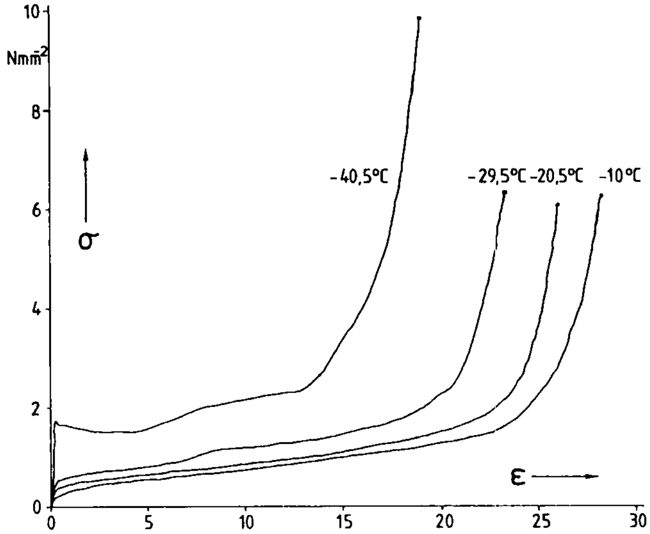

FIGURE 10 Stress-strain curves in uniaxial elongation for free films of PIB at various temperatures.

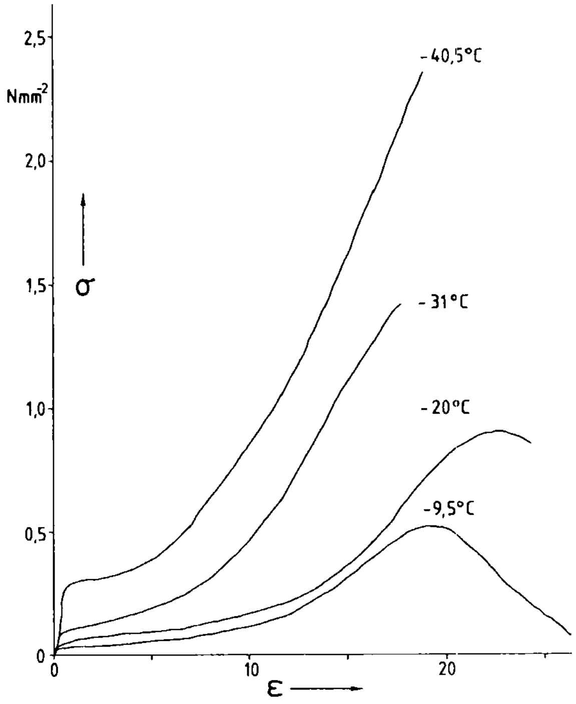

FIGURE 11 Stress-strain curves in uniaxial elongation for free films of PEHA at various temperatures.

temperature for both polymers at a fixed time of 1 s which corresponds to the contact or dwell time in the adhesion measurements. There are rather small differences in the position of the glass transition ranges of both samples according to the similar glass transition temperatures of −53°C for PIB and −59°C for PEHA, determined as the point of inflection of the modulus decay. Very large differences, however, are observed at temperatures above about −30°C where both polymers begin to form adhesive bonds with measurable strength. PIB has a modulus which is more than one power of ten higher than PEHA. It has been shown before that this difference is one reason for the very different adhesive failure energies of both polymers.[4]

It is well known that the viscoelastic behaviour of polymers at temperatures just above the glass transition range is determined by their entanglement network and that it is possible to evaluate the mean molecular mass between two entanglements, M_e, from the compliance *versus* time curves.[16] Using the approximation of Marvin and Oser[17] one obtains

$$M_e = 8.7 \times 10^3 \text{ g mole}^{-1} \text{ for PIB}$$

and

$$M_e = 1.3 \times 10^5 \text{ g mole}^{-1} \text{ for PEHA.}$$

Thus, a significant difference between both polymers investigated in this work is that they consist of entanglement networks with very different network spacings.

Stress–strain measurements of free films under uniaxial elongation were performed with a constant strain rate of $1.7\,\text{s}^{-1}$ which is about the same as the lowest rate of separation in the measurements of adhesive failure energy in order to have comparable conditions for both types of experiments. Figures 10 and 11 show the stress–strain diagrams for both polymers at temperatures between −40 and −10°C. Tensile strength σ_B, elongation at break ε_B and fracture energy w_B per unit area of cross-section of the sample are summarized in Table I. PIB and PEHA have comparable ultimate elongations ε_B; the fracture energies differ by a factor of 2 to 4. The main differences are found with respect to the tensile strength which is markedly higher for PIB. For both polymers a nearly constant

TABLE I
Ultimate properties of PIB and PEHA

T [°C]	σ_B or $\sigma_{\max}$ resp. [Nmm^{-2}]	ε_B	W_B [Jm^{-2}]
	PIB		
−40.5	9.8	19	3.7×10^5
−29.5	6.3	23	2.6×10^5
−20.5	6.1	26	2.4×10^5
−10.0	6.2	28	2.5×10^5
	PEHA		
−40.5	2.5	20	1.9×10^5
−31.0	1.1	20	1.2×10^5
−20.0	0.9	24	0.9×10^5
−9.5	0.5	26	0.6×10^5

stress level is reached at low strains which is nearly a power of ten higher for PIB than for PEHA. At high strains, σ again increases sharply with increasing ε. Between −20 and −10°C, *i.e.* in the temperature range where the transition from brittle to fibrillar debonding occurs, the stress–strain curves for PEHA change their shape showing a maximum tensile stress and a decrease of σ at higher strains. It seems, however, questionable if this more gradual change has something to do with the distinct transition from brittle to fibrillar adhesive failure which occurs in the same temperature interval. The main differences between both polymers are obviously the different stresses during elongation which are caused by the different entanglement networks.

6 CONCLUSIONS

Measurements of the adhesive fracture energy, w, of two high molecular weight polymers, polyisobutylene and polyethylhexlacrylate, to stainless steel showed remarkable differences in the deformation behaviour during debonding: "brittle" adhesive separation with low fracture energy for PIB and formation of fibrils with large strains at break and high values of w in the case of PEHA which, however, also debonded by purely adhesive failure. Both polymers differ mainly by their entanglement densities which result in very different moduli and different stress levels in tensile experiments. Besides these differences, there is no evidence of a completely different deformation behaviour of both samples in uniaxial extension.

Since PIB and PEHA are nonpolar polymers with rather similar surface tensions of 33 and 28 $\mathrm{mNm^{-1}}$, respectively, they are supposed to have comparable interfacial forces to steel. During the separation phase, however, PIB exerts a tensile stress on this interface which is about a factor of ten higher than for PEHA and which apparently exceeds the interfacial strength at rather small deformations. Except at low temperatures, this tensile stress is lower than the interfacial strength in the case of PEHA resulting in the formation of fibrils and in high adhesive failure energies.

The experimental work described in this paper, thus, seems to be a further verification of the model proposed by Good, besides the similar phenomena observed in peel measurements. We have observed fibrillar deformation behaviour during debonding also for other polymers with high adhesive fracture energies such as blends of natural rubber and resins which are used as pressure-sensitive adhesives. That leads, in accordance with the work of Good, to the conclusion that strong adhesion is intimately connected with the formation of fibrils.

Acknowledgement

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