

Adhesion and tack of polymers: Influence of mechanical properties and surface tensions

A. Zosel

Kunststofflaboratorium, BASF Aktiengesellschaft, Ludwigshafen am Rhein, F.R.G.

Abstract: The adhesion of various polymers used as model adhesives, polyisobutylene, polyacrylates etc. has been investigated by means of an apparatus measuring the adhesive failure energy w in dependence on contact time, contact pressure, rate of separation, and temperature. The adhesive failure energy of adhesive joints formed with low contact pressure during a short contact time is called "tack". After a sufficiently long contact time and with a high bonding pressure an adhesive joint exhibits its maximum energy of separation w_m .

The viscoelastic properties of the model adhesives were characterized by creep experiments in dependence on time and temperature. The surface tension of the polymer adhesives and adherents could be determined by contact angle measurements. Adhesion measurements of polyisobutylene on a number of adherents were carried out in air and in various liquids in order to obtain information about the influence of surface tension on tack and maximum adhesive failure energy.

w_m can be written as the product of two terms: the thermodynamic work of adhesion W_A which is related to the surface and interfacial tensions of adhesive and adherent and a dimensionless function dependent on temperature and rate of separation which describes the viscoelastic properties of the adhesive and which obeys the rate-temperature superposition principle known from linear viscoelasticity. The tack is related to incomplete bond formation and cannot be described in the same manner. It is, however, strongly dependent on the viscoelastic properties of the adhesive showing a maximum at about 50 to 70 °C above the glass transition temperature. It is, moreover, influenced by the compliance in the plateau range above the glass transition which is determined by the entanglement network of the polymer. Wetting of the adherent by the adhesive is a further important condition for high tack values which is fulfilled if the adherent has a higher surface tension than the adhesive.

Key words: Adhesive failure energy, creep compliance, glass transition temperature, entanglements, contact angle.

1. Introduction

When an uncross-linked or lightly cross-linked polymer is brought into contact with the surface of another material at temperatures above its glass transition in most cases an adhesive bond of measurable strength is formed. This phenomenon of polymer adhesion is of great significance to the application of polymers in various fields, e. g. as adhesives, sealants, coatings etc.

The investigations described below were concerned with adhesion phenomena where bond formation and

bond separation occurred at the same temperature and where the polymers used as model adhesives underwent no modifications in the time interval between both events, e. g. by cross-linking or crystallization. Polymer adhesion in this restricted sense is connected with a two-stage process: with bonding and unbonding. During bond formation contact in molecular dimensions is achieved in isolated regions of the geometric contact area A , the number and size of which is increased with increasing contact time by deformation and flow processes as well as by wetting.

The strength of the adhesive joint thus formed can be characterized by the work of detachment per unit area of interface which is given by the equation

$$w = \frac{1}{A} \cdot \int F \cdot v dt, \quad (1)$$

where v is the rate of separation and F the tensile force during the unbonding process. This fracture energy per unit of interface or intrinsic "adhesive failure energy", as it has been defined by Andrews, Gent and Kinloch [1-3], is subsequently used as a measure for the adhesive bond strength. The separation of both materials comprises the deformation of the whole test-piece and the creation of two new surfaces under destruction of the interface. Accordingly, polymer adhesion as referred to bond formation as well as bond separation is intimately related to the mechanical or viscoelastic properties and to surface properties such as surface and interfacial tensions, surface roughness, adsorbed layers etc. This study was undertaken in order to obtain information how polymer adhesion is influenced by these two groups of parameters, whereby the correlation with surface properties is restricted to surface tension.

2. Measurements of adhesive joint strength

The apparatus developed for the measurement of the adhesive failure energy simulates the bonding and unbonding process just described. A simplified and schematic diagram of this device is given in figure 1. The polymer to be tested is applied as a solution or a latex to a flat rigid plate (2) of stainless steel, after drying forming a thin layer of definite thickness (3). By means of an electronically controlled motor (1) the surface of this polymer film is brought into contact with a probe (5) of metal or another material such as glass or a hard polymer. The contact force as well as the contact or dwell time can be adjusted in rather broad ranges. At the end of the contact period the motor is driven in the opposite direction thus separating the polymer film and the probe surface with a defined and in a wide range adjustable velocity. The probe is firmly connected to a piezoelectric force transducer (6) which determines the forces during bond formation and separation as a function of time. The sample and the probe are placed in a temperature chamber (4) permitting measurements between about -40 and $+200$ °C by means of a nitrogen thermostat. The whole instrument is interfaced to a mini-computer which enables an automatic measurement of the force vs. time curve during bond formation and separation. For most measurements described in this paper a cylindrical probe of stainless steel with a diameter of 1.75 mm was used. For studying the influence of surface tensions hemispherical probes of various polymers were chosen which are listed in the corresponding section of this paper. The main parameters determining bond formation and separation can be varied in the following ranges:

— The dwell time between about 10^{-2} s and arbitrarily long times.

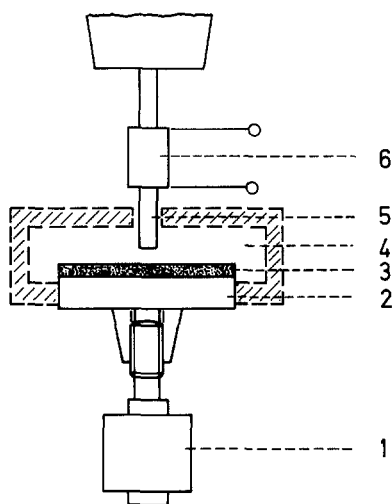


Fig. 1. Simplified diagram of the apparatus used for the determination of the adhesive failure energy. 1 electronically controlled motor; 2 sample holder; 3 sample; 4 temperature chamber; 5 probe; 6 piezoelectric force transducer

— The contact force between about $2 \cdot 10^{-2}$ N and 10^2 N corresponding to a contact pressure between $8 \cdot 10^{-3}$ and $4 \cdot 10^1$ N/mm² for the probe with a diameter of 1.75 mm.

— The rate of separation between 10^{-1} and $2 \cdot 10^1$ mm/s.

In figure 2 a schematic diagram is shown of the time dependence of the force F , the distance h between sample and probe, and the velocity v of the sample during the bonding and the unbonding process. In the moment where probe and sample surface come into contact a negative force is observed which quickly increases until the pre-chosen value F_1 is attained. Then the motor is stopped for a definite time interval. In this period the relaxation of the contact force can be compensated for by small additional motions of the sample so that a constant contact force is prevailing during the whole contact time. At the end of the contact time the probe and the polymer surface are separated with a velocity v_2 . In this period a positive (tensile) force is registered as function of time which normally shows a pronounced maximum and then decreases to zero in the moment where complete separation is achieved, whether it is by adhesive separation or by cohesive fracture within the polymer film. By integration over the force vs. time curve during the separation phase and dividing by the probe area the formerly defined adhesive failure energy w is obtained.

With the apparatus briefly described above the strength of adhesive bonds can be determined under variation of the most important parameters such as contact pressure, contact time, rate of separation and temperature. This is essential if relations between adhesion and viscoelastic properties are to be studied. If the contact pressure has a low value and if the contact time is very short the adhesive strength of the bond is called "tack" [4], a quantity which is decisive for the use of a polymer as a pressure-sensitive adhesive. Under the influence of a sufficiently high contact pressure and after a sufficiently long bonding time molecular contact over the total interface between probe and sample may be achieved. In this case the maximum energy of separation, w_m , is measured. Besides the adhesive failure energy a lot of information can be obtained from the shape of the force vs. time curve, which, however, is not the subject of this paper.

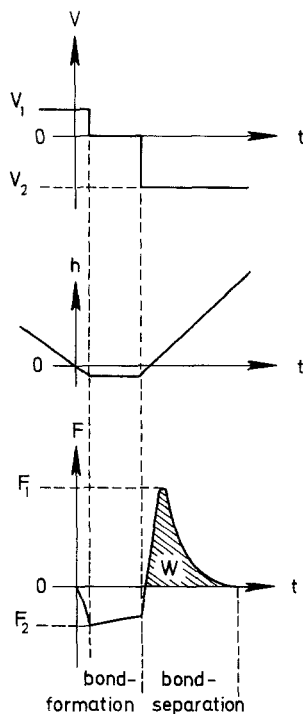


Fig. 2. Bonding and debonding process during an adhesion measurement (schematically). v = velocity of sample; h = distance between sample surface and probe surface; F = force acting on the probe

3. Samples and preparation of testpieces

In order to investigate the influence of viscoelasticity and surface energetics on adhesion polymers with very different properties were chosen as model adhesives which are listed in table 1. The glass transition temperatures in table 1 have been determined with the viscoelastic measurements described in the next section of this paper viz. the determination of the tensile compliance D as function of temperature. The inflection point of the reciprocal compliance D^{-1} plotted vs. temperature as shown in figure 5 is in this paper defined as the glass transition temperature. The T_g -values given in table 1 are obtained by determining D at a fixed time of 10 s.

Table 1. Polymers used as model adhesives

Polymer	Abbreviation	T_g [°C]	\bar{M}_w [g mole ⁻¹]
polyisobutylene I	PIB I	- 60	$3.8 \cdot 10^5$
polyisobutylene II	PIB II	- 60	$1.3 \cdot 10^6$
polyethylhexylacrylate I	PEHA I	- 62	
polyethylhexylacrylate II	PEHA II	- 62	
polyethylacrylate	PEA	- 14	$3.5 \cdot 10^5$
polystyrene	PS	100	$3.5 \cdot 10^5$
polybutadiene	PBu	- 97	

Polyethylhexylacrylate II is an emulsion polymer with a high but unknown molecular weight and presumably a certain percentage of lightly cross-linked material as it is typical of polyacrylates obtained by emulsion polymerization.

From viscosity measurements on dilute solutions and the bulk polymer it can be assumed that the molecular weight of PEHA I should be comparable to that of PIB I, PEA and PS. The same is true for the polybutadiene sample. The polymers used as model adhesives can, thus, roughly be divided in two groups: two polymers with high molecular weights and nearly equal glass transition temperatures, viz. PIB II and PEHA II, and a series of polymers with comparable molecular weights in a medium range covering a very extended T_g -range between about -100 and $+100$ °C.

For the adhesion measurements the polymers were applied as solutions or — in the case of the high molecular PEHA — as emulsion to flat plates of stainless steel. After drying they formed films with thicknesses between 50 and 60 μm . The compliance D was determined with free films having thicknesses between 50 and about 200 μm .

4. Adhesion and mechanical behaviour

4.1 Determination of viscoelastic properties

Polymers are viscoelastic materials, which means that, especially in certain temperature ranges such as the glass transition zone, the mechanical properties are not only dependent on temperature but also on the time scale or the frequency of the experiment. For a complete characterization of the viscoelastic behaviour a material function such as a modulus or a compliance has to be determined with dependence on temperature and time or frequency. In this work the viscoelastic behaviour of polymers is investigated by creep measurements in the linear-viscoelastic regime. In a creep experiment a constant stress σ_0 is imposed on a sample and the resulting strain ϵ is measured as a function of time. From stress and strain the compliance $D(t)$ of the sample can be calculated:

$$D(t) = \frac{\epsilon(t)}{\sigma_0}. \quad (2)$$

The compliance of the polymers used as model adhesives is measured with an instrument described in detail elsewhere [5]. A constant tensile stress is applied to the sample to be studied and the resulting elongation is continuously recorded dependent upon time between about 0.3 s and $1 \cdot 10^3$ s. The creep experiments can be carried out at different temperatures between about -100 and $+250$ °C. Materials with not too high molecular weights begin to flow considerably above the glass transition range. In this case the tensile creep experiments were supplemented by creep measurements in shear using a rheometer with parallel plates and by dividing the shear compliance $J(t)$ by 3 in order

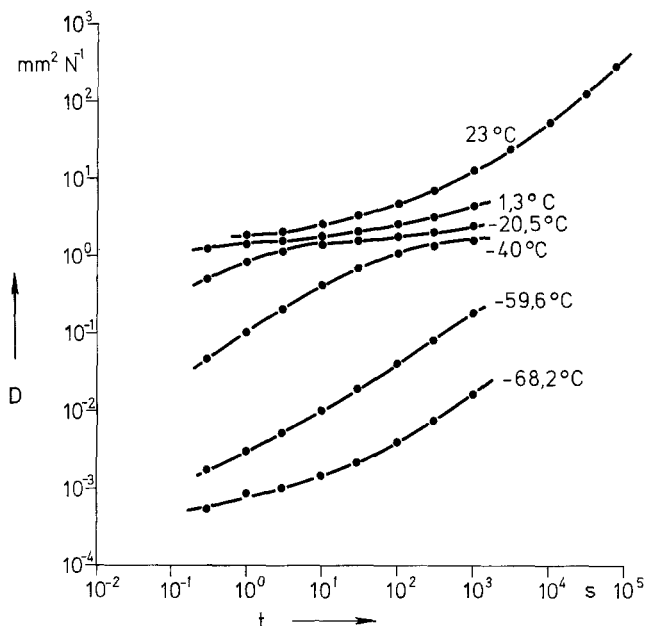


Fig. 3. Creep compliance D of polyisobutylene I with $\bar{M}_w = 3.8 \cdot 10^5 \text{ g mole}^{-1}$ plotted logarithmically versus time at various temperatures

to obtain the tensile compliance, a procedure which is possible above the glass transition because the samples can be regarded as incompressible.

With both these methods the compliance vs. time curves at various temperatures can be determined. An example is given in figure 3 showing a double logarithmic plot of D against t for polyisobutylene I. The measurements comprise the mechanical behaviour from the glassy state at the lowest temperature up to viscous flow at 23 °C and long times. From the curves in figure 3 a master-curve at a certain reference temperature can be obtained by applying the well-known principle of time-temperature superposition [6]. The compliance $D(t)$ measured at a temperature T is multiplied by a factor T/T_0 ¹⁾. Then each curve is shifted on the logarithmic time scale until optimum overlap with the curve determined at the reference temperature T_0 has been achieved.

The resulting master-curve at the reference temperature $T_0 = 23 \text{ °C}$ for the polyisobutylene sample is shown in figure 4 a, the shift factor a_T is plotted versus the reciprocal temperature in figure 4 b. The master-

¹⁾ To be exact $D(t)$ has to be multiplied by $\rho(T) \cdot T/\rho(T_0) \cdot T_0$, ρ being the density. The density ratio is, however, not far from unity and the loss of accuracy by neglecting it is not serious for these investigations.

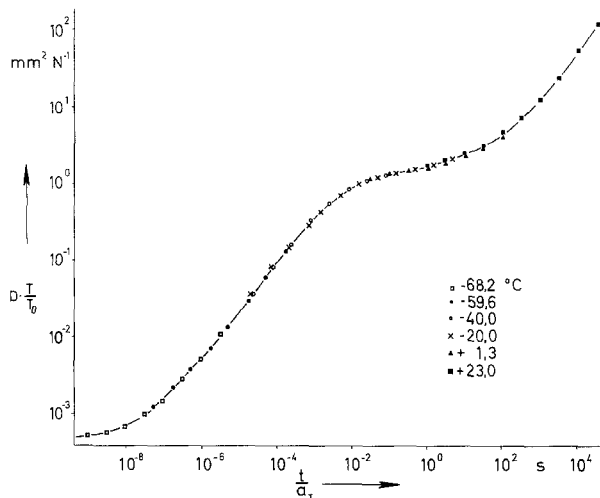


Fig. 4 a. Master-curve of polyisobutylene I, obtained from the data of figure 4. Reference temperature $T_0 = 23 \text{ °C}$

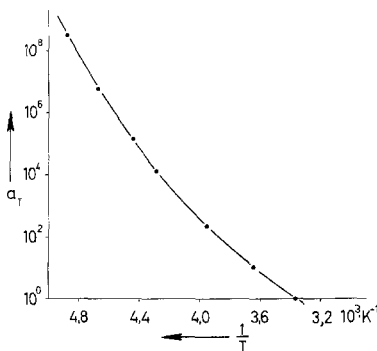


Fig. 4 b. Shift factor a_T of polyisobutylene I in dependence on reciprocal temperature

curve in figure 4 a shows various time ranges with different viscoelastic behaviour: glass-like behaviour with a compliance between 10^{-4} and $10^{-3} \text{ mm}^2/\text{N}$ at short times, an increase in D corresponding to the glass transition between about $t/a_T = 10^{-8}$ and 10^{-2} s , a time interval with minor time dependence of D , the so-called plateau zone, influenced by the entanglement network of the polymer (between about 10^{-2} and 10^2 s), and an increase at long times reflecting the beginning of viscous flow. At sufficiently long times $D(t)$ increases linearly with t . The shift factor a_T follows the well-known WLF-equation at temperatures between about T_g and $T_g + 100 \text{ °C}$ [6] and an Arrhenius equation at higher temperatures. The figures 4 a and b completely characterize the linear viscoelastic behaviour of a polymer in an extended temperature range in which the principle of time-temperature equivalence is valid.

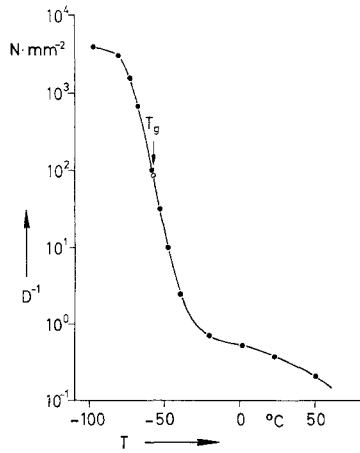


Fig. 5. Temperature dependence of the reciprocal compliance of polyisobutylene I at a fixed time of 10 s

A simpler way to obtain some restricted information on the mechanical behaviour is a plot of the compliance D determined at one fixed time against temperature. In figure 5 the reciprocal value of D at $t = 10$ s, which conforms to Young's modulus of the polyisobutylene determined in a creep experiment, is plotted versus T^2). This modulus vs. temperature curve also shows the transition of the polyisobutylene from glass-like to melt-elastic behaviour. The glass transition temperature T_g which is defined as the inflection point is marked on the curve.

The other polymers studied in this paper have been characterized in the same way. Some of the results are shown in the following section.

4.2 Maximum adhesive strength and tack

In the adhesion measurements discussed in this paper unbonding occurred exclusively by adhesive separation. Cohesive fracture which was only observed in some cases at higher temperatures will be excluded. It has been pointed out in the introduction that the adhesive failure energy w should increase with increasing contact time due to a growth of the number and the size of the contacted areas. In figure 6 w for polyethylhexylacrylat I is shown as a function of the contact time t . The contact pressure was 0.2 N/mm^2 , the temperature $23 \text{ }^\circ\text{C}$. w increases with increasing contact time until a constant value is obtained at about 300 s.

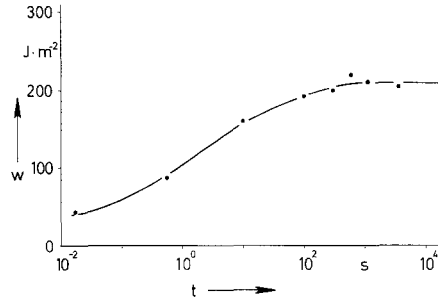


Fig. 6. Adhesive failure energy w of polyethylhexylacrylate I in dependence on the contact time t at $23 \text{ }^\circ\text{C}$

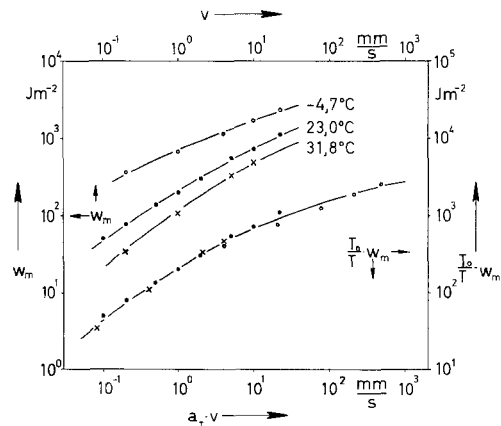


Fig. 7. Maximum adhesive failure energy w_m of polyethylhexylacrylate I plotted logarithmically against rate of separation v at three different temperatures as indicated and master-curve of w_m at $T_0 = 23 \text{ }^\circ\text{C}$, using the shift factor a_T from the compliance measurements

This constant value is independent of the contact pressure, it is, thus, the maximum energy of adhesion w_m for the adhesive joint of the PEHA sample and stainless steel at $23 \text{ }^\circ\text{C}$.

In figure 7 w_m is plotted versus the rate of separation v for the same polymer at three different temperatures. Using the shift factor a_T from the compliance measurements a master curve of $(T_0/T) \cdot w_m$ versus $a_T \cdot v$ can be constructed which is shown in figure 7, too. The time-temperature or, in this case, the rate-temperature superposition principle is thus valid for adhesion measurements with the same shift factor as for linear viscoelasticity indicating that segmental mobility is governing both in the same way. This fact completely confirms with results known from literature. Several authors found that the peel strength [7–11] and the adhesive strength determined with tensile tests [1, 12] follow the rate-temperature superposition principle.

The maximum adhesive failure energy w_m additionally depends on the type of the experiment and on

²⁾ The reciprocal compliance is plotted vs. temperature in this paper in order to obtain diagrams similar to the well-known modulus vs. temperature curves.

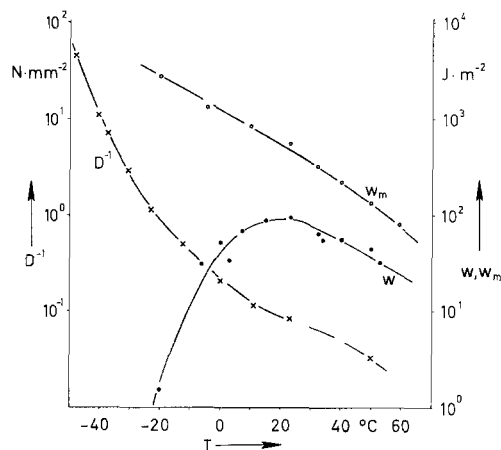


Fig. 8. Tack w , maximum adhesive failure energy w_m , and reciprocal compliance D^{-1} of polyethylhexylacrylate I as a function of temperature

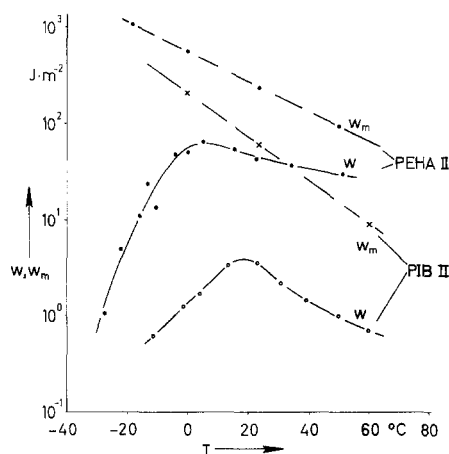


Fig. 9. Tack w and maximum adhesive failure energy w_m of the polyisobutylene and the polyethylhexylacrylate with high molecular weights (PIB II and PEHA II)

geometric factors such as probe diameter etc. Similar to the compliance the quantity w_m can be calculated for a given temperature T and separation rate v in a certain range of both variables if the functions $w_m(a_T \cdot v)$ and $a_T(T)$ are known. This principle is invalid if a change in the type of separation, e. g. from adhesive to cohesive fracture, occurs. In this paper "tack" is defined as the adhesive failure energy of bonds formed under low contact pressure and with a short dwell time. It is obvious that the tack is strongly dependent on the conditions of bond formation. In figure 8 the adhesive failure energy w under low pressure/short time conditions ($8 \cdot 10^{-3} \text{ Nmm}^{-2}$, $1.6 \cdot 10^{-2} \text{ s}$) is plotted versus temperature for the PEHA with the lower molecular weight. The rate of separation v was 5 mm/s. In figure 8 are additionally shown the maximum energy of separation at the same rate v and the reciprocal value of the creep compliance, D^{-1} , corresponding to the dwell time, i. e. to a time of $1.6 \cdot 10^{-2} \text{ s}$. D and w_m have been calculated from the $D(t/a_T)$ - and $w(v \cdot a_T)$ -plots by means of the time(rate)-temperature superposition principle. From the D^{-1} vs. temperature plot a glass transition temperature of -47°C corresponding to the time of $1.6 \cdot 10^{-2} \text{ s}$ can be deduced.

The tack w shows a pronounced maximum at about 70°C above T_g whilst w_{max} monotonically decreases with increasing temperature. This maximum indicates that w is influenced by bond formation and the maximum energy of separation as well. It can be assumed that the decrease of w at low temperatures is caused by imperfect bond formation and that the decrease at high temperatures reflects the decrease of w_m . Before dis-

cussing these effects in more detail the tack of the other polymer samples determined under the same conditions will be regarded.

In figure 9 the tack w and the maximum adhesive failure energy w_m for polyisobutylene II and polyethylhexylacrylate II, the samples with high molecular weights, are shown as functions of temperature. w_m is about a factor of 3 to 6 higher for PEHA than for PIB depending on the temperature. On the other hand, the tack of PEHA is about 30 to 50 times that of the PIB sample. That means that there are two reasons for the different tack of both polymers, differences in the maximum adhesive joint strength and differences in the ability to form an adhesive bond whereby the latter point is responsible for the major part of the tack difference. One reason for this different ability for adhesive bond formation is illustrated in figure 10 showing the master-curves of the compliance D at 23°C for both polymers. The PEHA sample has a higher compliance than PIB over the whole range of reduced time. Especially in the time range between about 10^{-2} and 10^4 s where, as already mentioned, the viscoelastic behaviour is primarily influenced by non-permanent entanglements there is a difference of more than one order of magnitude between both compliances. There are several approaches to approximately determine the entanglement spacing, i. e. the mean molecular weight M_e between entanglements from viscoelastic measurements which have been summarized by Ferry [13]. By transforming the creep compliance D to the imaginary part D'' of the dynamic compliance by means of a standard approximation [14] M_e could be calculated from

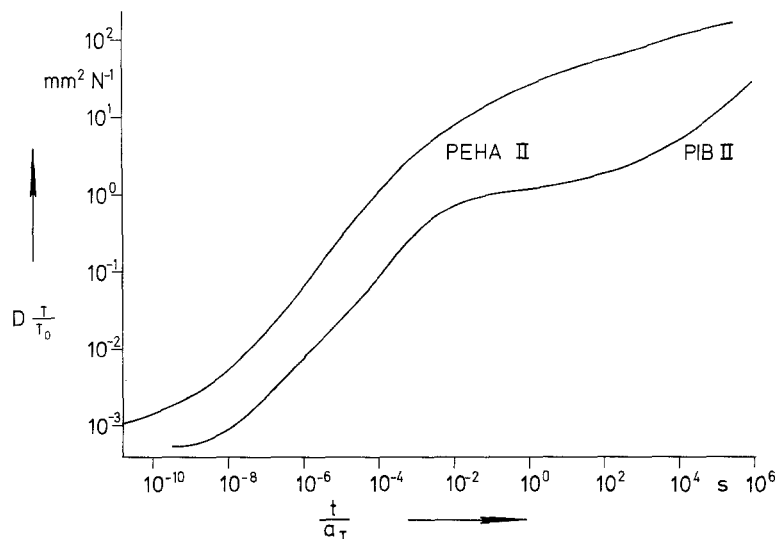


Fig. 10. Master-curves for the creep compliance of the high molecular weight polyisobutylene II and polyethylhexylacrylate II at $T_0 = 23^\circ\text{C}$

the maximum of D'' following a procedure of Marvin and Oser [15]. One obtains

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

in accordance with the literature [13] and a very high value of

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

Thus, PEHA has an entanglement network with much longer network strands compared with PIB. This fact is the main reason for the higher compliance in the time range determined by entanglements.

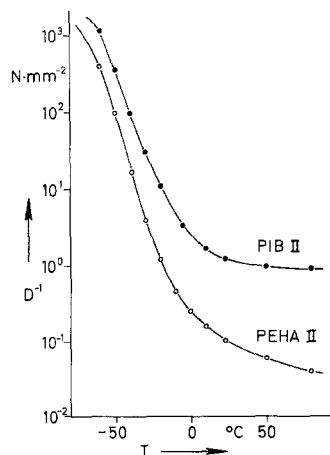


Fig. 11. Reciprocal compliance D^{-1} of PIB II and PEHA II vs. temperature at a fixed time of $1.6 \cdot 10^{-2}$ s

The differences between both polymers are also evident from figure 11 presenting the reciprocal compliances of both polymers as a function of temperature at a time of $1.6 \cdot 10^{-2}$ s corresponding to the dwell time. The glass transition temperatures are -47°C for PEHA and -40°C for PIB respectively at this short time. The maxima of w are thus found about $50\text{--}60^\circ\text{C}$ above the glass transition temperatures.

The tack for the PIB I and PEHA I samples with the lower molecular weights and of the polybutadiene have been determined under the same conditions as mentioned before. Here, too, very remarkable differences for w are found (fig. 12). The tack of the polybutadiene is not much more than 1% of that of the polyethylhexylacrylate, between PIB and PEHA, again, a difference of about one order of magnitude can be recognized. From figure 13 showing the corresponding

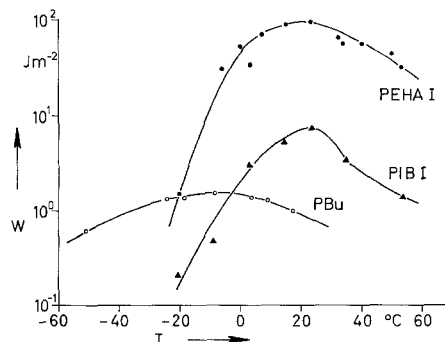


Fig. 12. Tack w of polyisobutylene I, polyethylhexylacrylate I, and polybutadiene in dependence on temperature

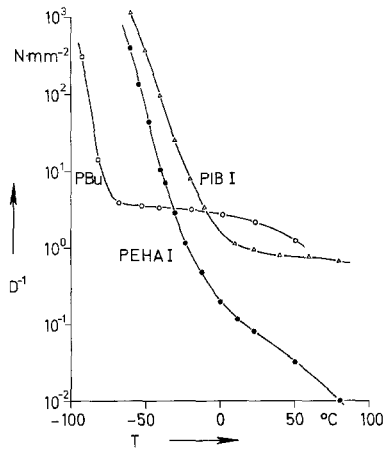


Fig. 13. Reciprocal creep compliance of the three samples shown in figure 12 in dependence on temperature, $t = 1.6 \cdot 10^{-2}$ s

temperature curves of reciprocal compliance it can be concluded that the tack maxima are again found about 60 to 75 °C above the respective glass transition temperatures and that the tack is apparently influenced by the compliance just above the glass transition range which, as already pointed out, is interrelated with the entanglement network of the polymers. The lowest value for M_e is found for polybutadien with $2.5 \cdot 10^3$ g mole⁻¹. Viscous flow is of no essential influence in the temperature range regarded here and during the low contact time of $1.6 \cdot 10^{-2}$ s. In all cases adhesive separation was observed, as already stated.

In figure 14 the tack w and the corresponding reciprocal compliance D^{-1} is shown for three polymers of very

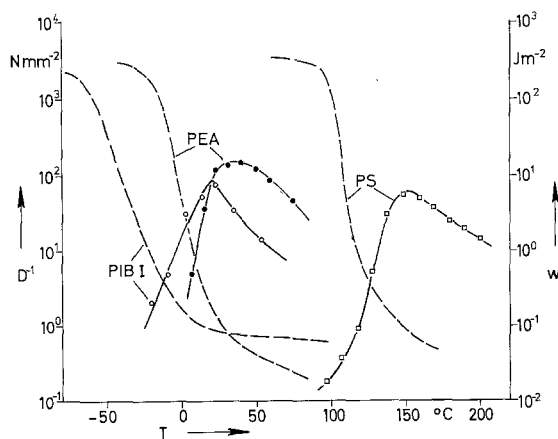


Fig. 14. Tack w (full curves) and corresponding reciprocal compliance D^{-1} (dashed curves) for polyisobutylene I, polyethylacrylate, and polystyrene

different T_g and nearly equal molecular weights: polyisobutylene I, polyethylacrylate and polystyrene. Here, too, a rather strong correlation between the tack and the glass transition range of the polymers is observed. In all three cases w has a pronounced maximum about 40 to 60 °C above the glass transition temperatures which are -40 °C for PIB, -4 °C for PEA and +107 °C for PS for $t = 1.6 \cdot 10^{-2}$ s.

It has been stated in the introduction that bond formation comprises the achievement of intimate molecular contact in isolated regions of the total contact area by deformation, flow and wetting. The first and second processes are determined by the compliance which, as is defined in this paper, includes both elastic and viscous deformations. A high compliance means a high ability to deform and flow under the influence of external forces.

A second assumption is that the increase in the tack w with rising temperatures until the tack maximum is reached is primarily influenced by the increasing ability to deform and to flow. Consequently, at least a qualitative relation between w and the corresponding value of D , i. e. determined at the same temperature and a time equal to the dwell time of $1.6 \cdot 10^{-2}$ s, should be expected. In figure 15 the tack w is plotted versus the corresponding values of D for all samples investigated in this work. There is of course no strong and exact relationship between w and D , this cannot be expected for these very different polymers. But there exists,

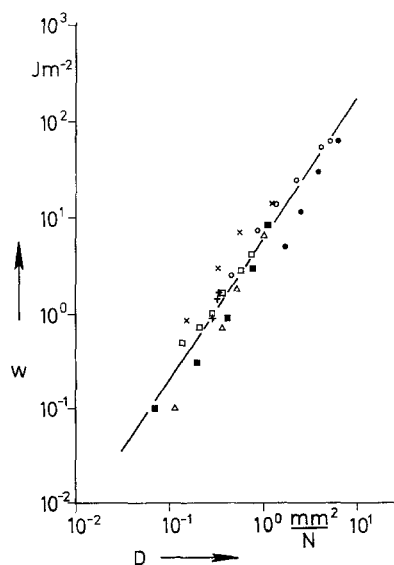


Fig. 15. Tack w at temperatures below the maximum plotted vs. the corresponding values of the creep compliance D . (■ PIB I; □ PIB II; ● PEHA I; ○ PEHA II; × PEA; △ PS; + PBu)

nevertheless, a very pronounced influence of D on the tack w which seems to be more or less independent of the particular polymer.

Several efforts are known from literature to correlate the tack and the mechanical behaviour of adhesives. Dahlquist seems to be the first to stress the association between tack and elasticity as well as viscosity [16, 17]. He found “excellent correlation between the tensile modulus of pressure-sensitive adhesives and the force generated when the probe was separated from the adhesive” [16] and that a serious loss of tack results when the one-second creep compliance for the adhesive falls below $10^{\circ} \text{ mm}^2 \text{ N}^{-1}$ – sometimes called the Dahlquist criterion. If the second statement of Dahlquist is not understood in the sense that zero-tack is found below $10^{\circ} \text{ mm}^2 \text{ N}^{-1}$ and measurable tack at compliances above this value figure 15 can be regarded as an extension and an exacter version of the Dahlquist criterion establishing a strong correlation between tack and the viscoelastic behaviour during bond formation.

Various authors [18–21] have found that one effect of a tackifier in pressure-sensitive adhesives of natural rubber, polyacrylates and styrene-diene blockcopolymer is the reduction of the modulus in the plateau zone. This is achieved by an increase in the entanglement spacing in full agreement with the results presented here. Before discussing the influence of viscoelasticity on tack and maximum adhesive strength in more detail some interrelations between both quantities and the surface energetics of adhesive and adherent will be regarded.

5. Adhesion and surface and interfacial tension

5.1 Evaluation of surface tensions

Measurements of the surface tension of solids are normally based on interactions with other media, especially liquids carrying out contact angle measurements and calculating the so-called wetting tension $\gamma_{SV} - \gamma_{SL}$ by means of Young’s equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos \theta, \quad (3)$$

where γ_{SV} and γ_{LV} are the surface tensions of the solid and the test liquid in equilibrium with the saturated vapour of the liquid. γ_{SL} is the solid-liquid interfacial tension and θ the measured contact angle. Neither γ_{SL} nor γ_{SV} can be determined independently, however. This is one reason for the difficulties in determining the surface tension of solids. The discussion of these problems which have caused very interesting and fruitful

investigations is by far beyond the scope of this paper [22–24].

If the influence of the vapour on the solid surface tension is neglected or the so-called film pressure $\pi = \gamma_S - \gamma_{SV}$ is assumed to be zero, γ_{SV} can be set equal to γ_S , the surface tension of the solid against its own saturated vapour, and if γ_{LV} is written as γ_L one obtains

$$\gamma_S - \gamma_{SL} = \gamma_L \cdot \cos \theta. \quad (4)$$

An unambiguous determination of γ_S and γ_{SL} requires a second equation, an equation-of-state of the system solid-liquid-saturated vapour which does not exist in general form. This fact resulted in numerous theoretical efforts during the last decades.

Here the work of Good [25] and Fowkes [26] who correlated the surface and interfacial tensions with the intermolecular interactions turned out to be most powerful, leading to a splitting up of the surface tension in components according to the various molecular forces:

$$\gamma_S = \gamma_S^d + \gamma_S^p \text{ and } \gamma_L = \gamma_L^d + \gamma_L^p \quad (5)$$

γ_S^d and γ_L^d are the contributions of the nonpolar (London) forces to γ_S and γ_L respectively. All other forces, i. e. the “polar” forces based on permanent and induced dipoles, hydrogen bonds etc. are comprised in γ_S^p and γ_L^p . A relatively simple relation for the interfacial tension can be deduced for the case of nonpolar liquids on nonpolar solids,

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S \cdot \gamma_L)^{1/2}, \quad (6)$$

which is indeed a second equation-of-state for this special case [24].

Tamai [27], Dann [28], Owens and Wendt [29] and Kaelble [30] tried to transfer this procedure to the general case including polar interactions:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} - 2(\gamma_S^p \cdot \gamma_L^p)^{1/2}. \quad (7)$$

A similar approach using the harmonic instead of the geometric means was developed by Wu [31]. It has, however, to be emphasized that these methods found in numerous studies in literature may possibly lead to satisfactory results for “weakly polar” polymers but give rather unsatisfactory results with broad scatter for the case of strong polar interactions and forces such as H-bonds. Here the novel concept of acid-base interactions applied to surface tensions by Fowkes is expected to give better results [32].

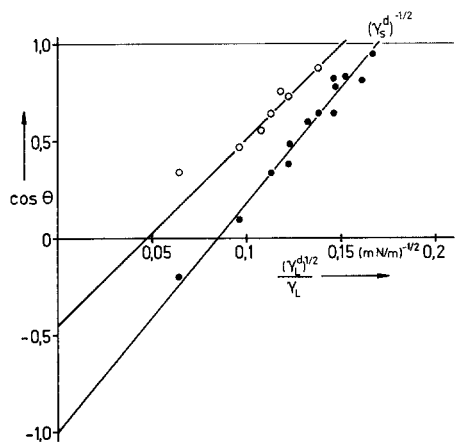


Fig. 16. Cosine of the contact angle, $\cos \theta$, plotted against $(\gamma_s^d)^{1/2} / \gamma_L$ according to equation (8) for polyethylene (●) and 6.6-polyamide (○)

The surface tensions of the polymers used as adhesives and adherents in this paper were determined via contact angle measurements by the well-known Wilhelmy balance method [33] and the sessile drop method [34] using a series of test liquids. For nonpolar polymers $\cos \theta$ is plotted against $(\gamma_s^d)^{1/2} / \gamma_L$ which according to equation (6) and Young's equation (4) gives a straight line going through $\cos \theta = -1$ for $(\gamma_s^d)^{1/2} / \gamma_L = 0$:

$$\cos \theta = -1 + 2 (\gamma_s^d)^{1/2} \cdot \frac{(\gamma_L^d)^{1/2}}{\gamma_L} \tag{8}$$

It follows from figure 16 that equation (8) is very well fulfilled by the results for polyethylene showing that this polymer is predominantly nonpolar. From the slope of the straight line or from its intercept with the line $\cos \theta = 1$ the quantity γ_s^d can be calculated which, in this case, is equal to γ_s . For a polar material, 6.6-polyamide with strong contributions of H-bonds to γ_s , the origin of the straight line in figure 16 is not at $\cos \theta = -1$. For polar polymers γ_s^d is also calculated from the extrapolation to $\cos \theta = 1$. As the test liquids which give values of $\cos \theta$ near 1 have only small polar components it is assumed that the interactions between the polymer and these liquids are predominately nonpolar [35]. The polar component is calculated with equation (7) and equation (4) using the value for γ_s^d determined in this way. It is obvious from the fore-going remarks that this procedure is only an approximation, especially for samples with strong polar interactions.

In order to investigate the influence of surface and interfacial tensions on the adhesive failure energy w

one of the model adhesives, polyisobutylene I, was bonded to various other polymers and adhesion measurements were carried out. For these experiments polymers were chosen as adherents which have compliances considerably lower than that of the adhesive, i. e. which are much stiffer than PIB. In this case, the deformation of the adherent can be neglected, and differences in the adhesive failure energy can be attributed to the surface and interfacial tensions.

The polymers used as adherents are listed in table 2, together with the surface tension γ_s and the nonpolar and polar components. The running index in the last column of table 2 refers to figure 17 where it is used to identify the various adherents.

Table 2. Surface tension of polymers

Polymer	γ_s	γ_s^d [mNm ⁻¹]	γ_s^p	Index
Adherents				
polytetrafluoroethylene	19.5	19.5	0	1
polysiloxane	22	22	0	2
polyvinylidene fluoride	25	25	0	3
polypropylene	29	29	0	4
polyethylene	34.5	34.5	0	5
polyvinyl chloride	41	39.5	1.5	6
polymethyl methacrylate	41	40	1	7
polystyrene	42	42	0	8
polyethylene terephthalate	42.5	40.5	2	9
6-polyamide	43	38	5	10
6.6-polyamide	44	39	5	11
Adhesive				
polyisobutylene	33	33	0	

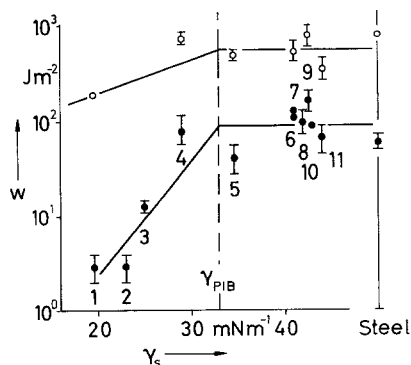


Fig. 17. Adhesive failure energy w for two different contact periods, plotted against the surface tension of the polymers used as adherents. $T = 23^\circ\text{C}$; ● $t = 1.5 \cdot 10^{-2}$ s; ○ $t = 1 \cdot 10^{-2}$ s. The numbers conform to the running index in the last column of table 2. They identify the various adherents

From γ_S and γ_L the thermodynamic work of adhesion, W_A , can be calculated for the corresponding solid and liquid using the well-known Young-Dupr -equation

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \tag{9}$$

5.2 Influence of surface tensions on adhesion and tack

The experimental results discussed in this section were obtained under slightly different conditions. Instead of the cylindrical probe a probe ending in a hemisphere with a radius of 5 mm was used. Thus, the absolute values of w are not comparable with that of section 4. The hemispheres of the various polymers listed in the foregoing table were made either by compression molding at higher temperatures or by drawing a thin polymer film over a hemisphere of stainless steel. In all cases it was tried to obtain probe surface as smooth as possible. Probes prepared in this way were forced against the PIB surface for two different contact times of $1.6 \cdot 10^{-2}$ and $1 \cdot 10^2$ s, and the adhesive failure energy was determined. All measurements were carried out at 23 °C.

In figure 17 w is plotted logarithmically against the surface tension γ_S of the adherents for the two contact times. The surface tension of the model adhesive PIB, γ_{PIB} , is shown as a dotted line. Furthermore, the adhesive failure energy against a steel surface is also shown, however outside the γ_S -scale.

It follows from figure 17 that for $\gamma_S < \gamma_{PIB}$ the apparent energy of adhesion decreases with decreasing surface tension of the adherent. This decrease is much more pronounced for the short contact time than for the longer time of 10^2 s. For $\gamma_S > \gamma_{PIB}$ no clear influence of γ_S on w is observed, w seems to be approximately independent of γ_S . The mean value of w for all polymers in this γ_S -range is also found for stainless steel. The behaviour illustrated in figure 17 can be rather easily understood. The adhesive, polyisobutylene, is the liquid which has to wet the various adherents. Complete wetting can occur only if the solid surface tension γ_S is higher than that of the liquid, γ_{PIB} . At lower γ_S incomplete wetting occurs and w decreases with decreasing γ_S . Apparently there are other effects superimposing the influence of surface tensions, e.g. polyethylene has a considerably lower value for w compared with polypropylene which is in contradiction to the surface tensions of both polymers. A possible explanation is a weak boundary layer which is supposed to be one reason for the poor adhesion on polyethylene [36].

In the literature only very few and fairly contradictory results are found concerning the relation between surface tension and tack. In contradiction to the results in this work Toyama [37, 38] found a tack maximum for γ_S -values which are equal to the surface tension of the adhesive. Sherriff [18] and Counsell [39] found an increase of the tack with increasing γ_S . Their findings, however, are based on measurements with rather few, only 4 to 5 adherents.

A proportionality between w and the thermodynamic work of adhesion W_A as will be shown for the maximum adhesive failure energy w_m can neither be proved nor excluded for $\gamma_S > \gamma_{PIB}$ due to the large scatter of the results. For low γ_S the adhesive failure energy, however, is much more strongly dependent on γ_S . Here the contact time which is the time for wetting the adherent has pronounced influence.

The influence of the surface tensions on the maximum adhesive failure energy w_m can be studied by a procedure reported for the first time by Gent and Schultz [9, 35] and which is illustrated in figure 18. The separation of two materials in air requires the thermodynamic work of adhesion

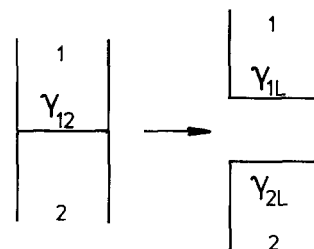
$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{10}$$

the same separation carried out in a liquid, however, requires

$$W'_A = \gamma_{1L} + \gamma_{2L} - \gamma_{12} \tag{11}$$

where γ_{1L} and γ_{2L} are the interfacial tension between both materials, respectively and the liquid. From equations (10) and (11) and Young's equation it can easily be deduced that

$$W'_A = W_A - \gamma_L (\cos \theta_1 + \cos \theta_2) \tag{12}$$



$$W'_A = \gamma_{1L} + \gamma_{2L} - \gamma_{12}$$

Fig. 18. Separation of the surfaces of two materials in a surrounding liquid. γ_{12} = interfacial tension between both materials; γ_{1L} , γ_{2L} = interfacial tension between the liquid and material 1 respectively 2; W'_A = thermodynamic work of adhesion

θ_1 and θ_2 are the contact angles of the liquid on both materials, respectively. If W_A is, at least, approximately calculated by equation (7) and (9) and if $\cos \theta_1$ and $\cos \theta_2$ are determined experimentally W'_A is known.

Adhesive joints of polyisobutylene and hemispherical probes of some of the polymer adherents already known were formed in air with sufficiently long contact times in order to obtain the maximum energy of separation. These joints were separated in air and in various liquids (methanol, butandiol and water) under the same conditions as in air. The adhesive failure energy in air is w_m , in the liquid w'_m . The three liquids used had no influence on the bulk properties of adhesive and adherents, e. g. by swelling. If the friction in the surrounding liquid during separation can be neglected the deformation energy associated with the unbonding process should be independent of the surrounding medium (air or liquid) and differences in the adhesive failure energies, w_m and w'_m , should exclusively originate from the surface and interfacial tensions. In figure 19 the ratio w'_m/w_m is plotted versus the ratio of the corresponding thermodynamic energies of adhesion W'_A/W_A . The median drawn in figure 19 means that w_m is proportional to W_A :

$$w_m = C \cdot W_A \quad (13)$$

In spite of some experimental scatter which has to be expected for measurements of this kind it can nevertheless be concluded that the experimental results, at least approximately, obey this proportionality. Thus, the adhesive failure energy which can be some orders of magnitude larger than W_A is proportional to the thermodynamic work of adhesion. This result which

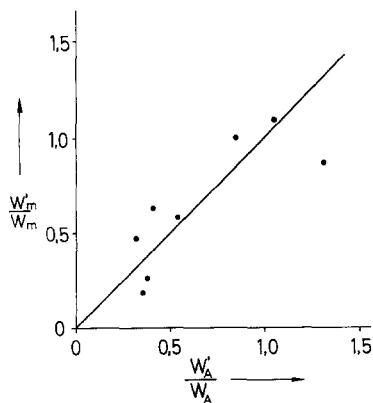


Fig. 19. Ratio of the adhesive failure energies for separation in a liquid and in air versus the corresponding ratio of the thermodynamic works of adhesion

is in agreement with the literature will be discussed in more detail in the final section.

6 Conclusion

Investigations of the maximum adhesive strength and the tack of polymers, both characterized by the adhesive failure energy, are the subject of this paper. The maximum value of this energy, w_m , which is related with optimum or fully developed interfacial contact between adhesive and adherent is a viscoelastic quantity of the adhesive insofar as it fulfils the temperature-rate superposition principle like a linear viscoelastic function such as a modulus. Moreover, it is proportional to the thermodynamic work of adhesion W_A as has been shown in the foregoing section. These results are in full agreement with peeling experiments carried out by Gent and Schultz [9], adhesion measurements of Andrews and Kinloch [2, 3] and the thermodynamic approach of Maugis [40] which result in the following equation for w_m :

$$w_m = W_A (1 + \Phi(a_T v, T)) \quad (14)$$

In the case of a relatively soft adhesive and a comparatively hard adherent the function $\Phi(a_T v, T)$ characterizes the viscoelastic behaviour of the adhesive because deformations of the adherent can be neglected. W_A on the other hand is determined by both components, the adhesive and the adherent. At low rates of separation the viscoelastic losses in the adhesives become smaller i. e. in the limit of $v \rightarrow 0$ the quantity w_m is equal to the thermodynamic work of adhesion W_A . In spite of the fact that the adhesive failure energy is orders of magnitude larger than W_A the latter thus plays an important role in determining adhesion.

The reason formulated by Andrews and Kinloch [2] is that viscoelastic deformations can only arise if the interface itself is capable of withstanding stresses. w_m is thus a characteristic parameter of the system adhesive – adherent which is, however, beyond that dependent on the type of experiment and on geometric parameters such as probe diameter and shape.

For the second quantity regarded in this paper, the tack, this statement is not correct, however. The adhesive failure energy, determined after a short contact time with low contact pressure, to a great extent reflects the incomplete molecular contact in the interface between adhesive and adherent and is, therefore, strongly dependent on the bonding process. This is the reason why no effort was made to establish a T, v -superposition for the tack which is not a material

parameter or function as it is w_m . The tack of a polymer is, nevertheless, strongly influenced by the viscoelastic properties of the material and the surface and interfacial tensions of adhesive and adherent as it has been demonstrated in this paper. Tack is connected with the glass transition of the adhesive, it is related to the corresponding compliance just above the glass transition range which itself is determined by the entanglement network of the polymer. A second factor influencing tack is the wetting of the adherent by the adhesive. Both viscoelasticity and wetting behaviour are of particular importance during the bond formation as has been shown in the preceding sections. A third parameter which is important during the unbonding process is of course the maximum energy of adhesion w_m . A polymer with a low w_m cannot be expected to have a high tack. Tack is not a fundamental material property with mathematical exact correlations to other quantities. By carrying out experiments of the type described here, however, the very pronounced influence of other properties such as viscoelasticity and surface energetics can clearly be realized.

Acknowledgements

Thanks are due to my colleagues Dr. Hoene and Dr. Penzel for some of the model adhesives and Dr. Mächtle for determining the molecular weights of PEA and PS.

References

- Gent AN, Kinloch AJ (1971) *J Polym Sci A-2* 9:659
- Andrews EH, Kinloch AJ (1973) *Proc Roy Soc A* 332:385
- Andrews EH, King NE (eds) (1978) Clark DT, Feast WJ, *Polymer Surfaces*, John Wiley and Sons, Chichester, p 47
- ASTM D (1978) – 61 T
- Zosel A (1980) *Prog Organic Coat* 8:47
- Ferry JD (1980) *Viscoelastic Properties of Polymers* 3 ed, John Wiley and Sons, New York, p 264
- Gent AN, Petrich RP (1969) *Proc Roy Soc A* 310:433
- Kaelble DH (1969) *J Adhesion* 1:102
- Gent AN, Schultz J (1972) *J Adhesion* 3:281
- Hamed GR, Shieh CH (1983) *J Polym Sci, Polym Phys Ed* 21:1415
- Aubery DW (ed) (1977) Wake WC, *Developments in Adhesives*, Vol 1, Applied Science Publ, London, p 127
- Gent AN (1971) *J Polym Sci A-2* 9:283
- Ferry JD, reference 6, p 366
- Schwarzl F (1970) *Pure Appl Chem* 23:219
- Oser H, Marvin RS (1963) *J Res Nat Bur Standards* 67B:87
- Dahlquist CA (ed) (1969) Patrick RL, *Treatise on Adhesion and Adhesives*, Vol 2, Marcel Dekker, New York, p 219
- Dahlquist CA (ed) (1970) *The Ministry of Technology, Adhesion: Fundamentals and Practice*, Elsevier Publishing Co, Amsterdam, p 143
- Sheriff M, Knibbs RW, Langley PG (1973) *J Appl Polym Sci* 17:3423
- Colpaert MN et al (1975) *Lecture at 13th Annual Conference on Adhesion and Adhesives*, London
- Kraus G et al (1977) *J Adhesion* 8:235
- Kraus G et al (1979) *J Adhesion* 10:221
- Good RJ (eds) (1979) Good RJ, Stromberg R, *Surface and Colloid Science*, Vol 11, Plenum Press, New York, p 1
- Good RJ (1977) *J Coll Interf Sci* 59:398
- Fowkes FM (ed) (1967) Patrick RL, *Treatise on Adhesion and Adhesives*, Vol 1, Marcel Dekker, New York, p 325
- Good RJ, Girifalco LA (1960) *J Phys Chem* 64:561
- Fowkes FM (1962) *J Phys Chem* 66:382
- Tamai Y et al (1967) *J Phys Chem* 71:4176
- Dann JR (1970) *J Coll Interf Sci* 32:302, 321
- Owens DK, Wendt RC (1969) *J Appl Polym Sci* 13:1741
- Kaelble DH (1970) *J Adhesion* 2:50
- Wu S (1971) *J Polym Sci C* 34:19
- Fowkes FM, Mostafa MA (1978) *Ind Engng Chem Prod Dev* 17:3
- Wilhelmy L (1863) *Ann Physik* 119:177
- Fox HW, Zisman WA (1950) *J Coll Sci* 5:514
- Schultz J, Gent AN (1973) *J Chim Phys* 70:708
- Wu S (1982) *Polymer Interface and Adhesion*, Marcel Dekker, New York, p 449
- Toyama M et al (1970) *J Appl Polym Sci* 14:2039
- Toyama M, Ito T (1973) *Polym Plast Technol Engng* 2:161
- Counsell PJC, Whitehouse RS (ed) (1977) Wake WC, *Developments in Adhesives*, Vol 1, Applied Science Publ, London, p 99
- Maugis D, Barquin M (ed) (1980) Lee LH, *Adhesion and Adsorption of Polymers (Polymer Sci Technol, Vol 12 A)*, Plenum Press, New York, p 203

Received September 18, 1984;
accepted December 18, 1984

Author's address:

Dr. A. Zosel
BASF Aktiengesellschaft
Kunststofflaboratorium, G 201
D-6700 Ludwigshafen, F.R.G.