MOLECULAR STRUCTURE, MECHANICAL BEHAVIOUR AND ADHESION PERFORMANCE OF PRESSURE SENSITIVE ADHESIVES

Albrecht Zosel
BASF AG
Ludwigshafen, Germany

INTRODUCTION

The adhesion performance of a pressure sensitive adhesive is determined by three properties: tack, peel strength and shear resistance. The shear resistance which characterizes the behaviour of an adhesive under static, long lasting stresses will not be discussed in this paper. The work presented here is focussed on the tack; but tack and peel strength are similar in several aspects, so that some conclusions from our studies are also valid for the peel strength.

Tack is a dominant property of pressure-sensitive adhesives which is defined as the ability of an adhesive to form a bond of measurable strength to another material under conditions of low contact pressure and short contact time. Tack is, thus, not a fundamental material property but depends on the test methods and the conditions of measurement.

The procedure for measuring tack is a two-stage process of bond formation and bond separation. During bond formation, contact in molecular dimensions between the adhesive and the adherend is established by deformation and flow as well as by wetting. The second step, the bond separation with a certain rate, is connected with deformation and crack propagation in the adhesive joint. Adhesion and tack are accordingly related to surface properties and to the mechanical behaviour. The latter correlation is the topic of this paper.

EXPERIMENTAL PART

In order to study the effect of the mechanical properties and the deformation behaviour on adhesion, an instrument of the probe tack type has been developed in our laboratory a number of years ago [1-3], by means of which the force is measured with time during the whole process of bond formation and separation. The most important parameters during bonding and debonding such as contact time, contact pressure, rate of separation, and temperature can be adjusted and measured in sufficiently wide ranges.

The primary result of a measurement is a force versus time curve, as shown in Fig. 1. The contact force is plotted as positive values and the debonding force as negative values. A stress strain diagram of the debonding process can be calculated from this force vs. time plot. The strength of the adhesive joint is given by the energy of separation or failure energy per unit of the geometric interface, $G_a$, which is determined by the integration of the force versus time curve over the separation phase. According to the definition, given above, the tack is thus defined as the failure energy under conditions of short contact time and low contact force.
The viscoelastic behaviour of the polymers is determined by dynamic mechanical measurements (DMA) with an instrument with parallel plates. With this method the two components of the complex dynamic shear modulus, the storage modulus $G'$ and the loss modulus $G''$, are determined as a function of temperature and angular frequency.

Fig. 1: Force versus time plot of a tack measurement

Fig. 2: Storage modulus $G'$, loss modulus $G''$ and adhesive failure energy (tack) $G_a$ in dependence on temperature for polyethylhexylacrylate
It is well-known that the temperature strongly influences the viscoelastic properties of polymers, and the same is true for the adhesion performance. In Fig. 2, the components of the dynamic shear modulus and the adhesive failure energy $G_a$ are plotted versus temperature for an emulsion polymer of ethylhexylacrylate (PEHA). The dynamic measurements cover the glassy state at low temperatures, the glass transition range with a strong decrease of both moduli, and a temperature range where both moduli decrease with rising temperature more gradually. Just above the glass transition range the viscoelastic behaviour is governed by entanglements [4]. The gradual decrease over a broad temperature range is typical for a polymer with a certain gel content and a very broad molecular mass distribution, which are often found in polyacrylates from aqueous latices.

The adhesive failure energy, determined after a contact time of 1 s, shows a maximum in the temperature interval above the glass transition range. The pronounced increase of $G_a$ is caused by the fact, that the material is more easily deformed with increasing temperature and can develop contact during the short contact time. The decrease of $G_a$ at higher temperatures is connected with the debonding process. It correlates with the general observation that the ability of a polymer to dissipate deformation energy has a maximum in the glass transition range and decreases at higher temperatures.

The position of the tack maximum is of course related to the glass transition temperature [5]. There are however other parameter influencing this position, e. g. molecular mass, crosslinking etc., so that different samples of the same polymer can show a tack maximum at slightly different temperatures.

![Fig. 3: Storage modulus $G'$ and tack $G_a$ in dependence on temperature for polyethylacrylate (closed symbols) and polyisobutylene (open symbols)](image)
Concerning the height of the tack maximum or, more generally, the tack level, interesting conclusions can be drawn from Fig. 3 which shows the storage modulus $G'$ and the adhesive failure energy $G_a$ for PEHA and a high molecular weight polyisobutylene (PIB). Both polymers are similar in various aspects ($T_g$, molecular mass) but have an adhesive failure energy which is different by more than one order of magnitude. The reason is the large difference in the storage moduli of both polymers in the plateau range which is due to a different molecular mass between entanglements (entanglement length $M_e$) in both polymers. $M_e$ can be calculated from the storage modulus in the plateau range [6] and is found to be 8.700 g/mole for PIB and about 60.000 for PEHA.

MICROMECHANICS OF BOND SEPARATION

Fig. 3 could mislead to the conclusion that there is only a gradual difference between PEHA and PIB, due to the different entanglement networks. Investigations of the deformation behaviour during debonding, however, demonstrate that this is not the case.

![Stress strain diagrams of the debonding process for a polymer with low tack (a) and high tack (b)](image)

Fig. 4: Stress strain diagrams of the debonding process for a polymer with low tack (a) and high tack (b)

Two types of stress versus strain curves have been observed in our investigations of a large number of polymers which are presented in Fig. 4 [3]. The curve in Fig 4a shows a sharp stress maximum and adhesive debonding at comparatively low strains. It has a similar shape, however different ultimate elongation, as the stress strain plots of brittle polymeric materials in the usual tensile tests. This type of diagram is observed for polymers with low tack, e. g. PIB.

The stress strain plot shown in Fig 4b with a stress maximum and a pronounced plateau, leading to a large area under the curve, and a high strain at break is
observed for polymers with high tack. It has some similarity with the stress strain characteristics of tough polymers which show yielding or plastic deformation. A number of years ago, we found by high speed photography that the adhesive deforms by the formation and growth of fibrils \[2,3\].

In order to get a deeper insight into this micromechanics, we have equipped our tack instrument with a video-optical device which allows the real time observation of the debonding process. As shown in Fig. 5, the contact area is observed from underneath through a transparent substrate, e. g. a microscope slide, and the also transparent adhesive layer. By focussing on the interface between adhesive and probe we can follow the nucleation and growth of cavities during debonding and relate the single pictures to the stress strain curve. The debonding process can also be monitored from the side, looking into the increasing gap between probe and substrate. Very interesting pictures are obtained by looking from above under a certain angle through a transparent probe. In this case we get a three dimensional picture of the deformation process.

![Diagram showing the components of the tack instrument](image)

**Fig. 5: Video optic observation of cavitation and fibrilation**

Fig. 6 shows the deformation during debonding in an acrylic pressure sensitive adhesive. The diameter of the probe surface is 6 mm. The Figure gives an overall impression of the deformation behaviour. The debonding starts with the formation of cavities in the polymer probe interface, presumably at preexisting nuclei. It is caused by the high dilatant stresses at the beginning of the deformation process. We have found cavitation to occur in all polymers, studied so far, wether they debond by fibril
formation or not. In the case of the deformation behaviour of polymers with low tack, illustrated in Fig. 4a, the cavities remain small after nucleation; and the tensile stress increases rapidly until failure occurs in the interface. In polymers with low plateau modulus, i.e. high entanglement length, the cavities grow very rapidly after nucleation until they form some kind of foam-like structure. Video optic observation with a higher magnification shows the formation and growth of cavities, which are at last separated by thin walls or lamellae. That means that this process which is often called "fibrillation", is in reality the formation of a system of connecting lamellae, which should be better named "lamellation".

Fig. 6: Video images at different stages of the debonding process, observed from underneath through a transparent substrate

Fibrillation is also observed in peel measurements where it has been published for the first time by Kaelble [7] and subsequently studied very extensively by several authors [8,9]. Creton and coworkers have recently developed a similar method as described here in order to study cavitation and fibrillation in probe tack measurements [10].

The micromechanics of bond separation is strongly affected by temperature and rate of separation [11]. The influence of temperature is illustrated in Fig. 7, where we have plotted the adhesive failure energy \( G_a \) versus temperature for the polyethylhexylacrylate, already shown in Fig. 2. One observes a very moderate increase of \( G_a \) between -30 and -10 °C, followed by a steep increase by nearly one
order of magnitude at higher temperatures. It follows from the stress vs. strain curves in the lower part of the Figure, that this jump in the tack is connected with a sharp transition from deformation without fibril formation below -12 °C to fibrillation above -10 °C, i.e. in a very narrow temperature interval. This demonstrates clearly, that fibrilation is essential for the high tack of PSA's.

The influence of the rate of separation or the strain rate is very pronounced, too. A sharp transition from fibrilation at low rates to the brittle type of deformation at higher rates can be observed.

Fig 7: Adhesive fracture energy in dependence on temperature for polyethylhexylacrylate (PEHA), and stress vs. strain plots of PEHA at various temperatures, as indicated.
INFLUENCE OF MOLECULAR STRUCTURE

It follows from the preceding sections of this paper that the adhesion of soft polymers is governed by their entanglement network. The molecular mass between two entanglements, \( M_e \), can be calculated from the so-called plateau modulus \( G^{\infty}_e \) which is inversely proportional to \( M_e \). Ferry summarizes various approaches to evaluate \( G^{\infty}_e \) [6]. A high entanglement length is favourable to contact formation as well as bond separation. High values of \( M_e \) lead to a low plateau modulus, and that means that the adhesive can more easily be deformed and develop a good contact to the substrate. According to a model of Gent et al, the critical stress for the expansion of pre-existing cavities is also proportional to the modulus [12].

The main effect of the entanglement length, however, is its effect on fibrillation or lamellation. Table 1 shows the correlation between fibrillation and the entanglement length \( M_e \) for some polymers. It follows that polymers with an entanglement length above about 1 to \( 1.5 \cdot 10^4 \) g/mole show fibrillation whilst materials with an entanglement length below this limit debond by homogeneous deformation.

Table 1  Influence of entanglements on the debonding behaviour

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_e ) [g/mole]</th>
<th>Fibril formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene [3]</td>
<td>2.5 ( \cdot ) 10^3</td>
<td>no</td>
</tr>
<tr>
<td>Natural rubber (NR) [5]</td>
<td>7.0 ( \cdot ) 10^3</td>
<td>no</td>
</tr>
<tr>
<td>PIB</td>
<td>8.7 ( \cdot ) 10^3</td>
<td>no</td>
</tr>
<tr>
<td>PEA</td>
<td>1.6 ( \cdot ) 10^4</td>
<td>yes</td>
</tr>
<tr>
<td>PBA</td>
<td>2.4 ( \cdot ) 10^4</td>
<td>yes</td>
</tr>
<tr>
<td>PEHA</td>
<td>6.0 ( \cdot ) 10^4</td>
<td>yes</td>
</tr>
<tr>
<td>NR/Tackifier 1:1 [5]</td>
<td>3.3 ( \cdot ) 10^4</td>
<td>yes</td>
</tr>
</tbody>
</table>

The data in Table 1 help to understand the well-known Dahlquist criterion [13]. Dahlquist found a "definite deterioration of tack" when the modulus exceeds a certain value which is \( 3 \cdot 10^5 \) Pa for the shear modulus. From this modulus a molecular mass between entanglements of about \( 1 \cdot 10^4 \) g/mole can be calculated. That means that the Dahlquist criterion is related to the transition from homogeneous to fibrilar deformation.

The effect of a tackifier on the tack of natural rubber based PSA's can also be explained within the framework of this deformation model. Natural rubber is a highly entangled polymer and consequently shows a stress strain behaviour as in Fig. 4a. Blending with a tackifying resin increases \( M_e \), as shown in Table 1 for a blend with 50% resin. Accordingly, this blend shows fibril formation and high tack.

In spite of the fact that entanglements are crucial for high tack and peel strength, a high entanglement length is not a sufficient condition for good adhesion performance. Other molecular parameters have to be taken into account. One of the most important ones are crosslinks, owing to their strong influence on the visco-
elastic properties of polymers. An appropriate way to test if a polymer is crosslinked or not is to measure the complex shear modulus above the glass transition range. If \( G' \) is larger than \( G'' \), the sample is crosslinked; if \( G' < G'' \), it is not. \( G' = G'' \) indicates the so-called gel point [14].

An example for the effect of crosslinking on the adhesive failure energy is given in Fig. 8, showing \( G' \), \( G'' \) and the tack of an UV crosslinked acrylic PSA, plotted versus the line speed during irradiation, which is inversely proportional to the UV dose [15]. A tack maximum is found near the gel point, a result which has been observed by investigations of other polymers, too. In the vicinity of the gel point, a polymer consists of a very loose and imperfect network structure and a high percentage of uncrosslinked material, which is supposed to have a broad molecular mass distribution and a high degree of long chain branching. This structure, which is extremely difficult to characterize, apparently gives a good balance between high cohesive strength and high energy dissipation. This morphology is found in acrylic emulsion polymers, too, and surely is one reason, why polyacrylates from aqueous latices are good PSA's.

Fig. 8: Storage and loss modulus (\( G', G'' \)), peel strength and tack versus line speed (UV dose) for a UV crosslinkable polyacrylate, \( T = 23 \, ^\circ \text{C} \)

A very interesting question, which seems not yet to have found much attention with exception of SIS and similar block copolymers, are two or multiphase structures in polymers and their influence on adhesion. A two phase morphology is often found in emulsion copolymers of comonomers with different polarity, which consists of the main polymer within the original latex particles and a honeycomb like phase with a

\[ \text{adhesive fracture} \quad \text{cohesive fracture} \]

\[ \frac{F}{b} \]

\[ G', G'' \]

\[ 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad \text{m/min} \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 10^3 \text{ Pa} \]

\[ \text{Nmm}^{-1} \]

\[ \text{Jm}^{-2} \]
high $T_g$ in the interphase and the wedges between the particles. This film structure should influence the mechanics of bond formation and separation.

Fig. 9 shows the tack in dependence on the contact force $F_c$ for four copolymers of ethylhexylacrylate with 0 and 5% acrylic acid (AA), two solution and two emulsion polymers. The two solution polymers have nearly the same tack which only slightly increases with $F_c$ to a saturation value at high forces. The emulsion homopolymer of EHA has a high tack already at low contact forces. The tack of the emulsion copolymer with AA, however, is much lower at low contact forces and depends on $F_c$ more strongly. This reflects the higher stiffness of the copolymer due to its two phase structure.

![Graph showing adhesive fracture energy vs. contact force for copolymers of ethylhexylacrylate (EHA) and acrylic acid (AA)].

**Fig. 9:** Adhesive fracture energy of copolymers of ethylhexylacrylate (EHA) and acrylic acid (AA) in dependence on the contact force $F_c$, contact time = 1 s, $T = 23°C$

**CONCLUSIONS**

The investigations summarized in this paper demonstrate that measurements of the adhesive failure energy under well defined conditions of bond formation and separation lead to a better understanding of the tack of pressure sensitive adhesives. A special deformation mechanism is crucial for a high tack and a high peel strength. Important macromolecular parameters and structures governing adhesion are entanglements, crosslinks, the "gel point structure", and two phase structures.
REFERENCES

6. Reference 4, Ch. 13