

## How does tack depend on contact time and contact pressure ?

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*The tack of polymer melts on rigid substrates under conditions of short contact times and low pressures is examined. The substrate is modeled as a random rough surface with a distribution of asperities heights. The true contact area between the model adhesive and the substrate is calculated for a given contact time and total load assuming a time-dependent elastic modulus  $E$ . For relatively high pressures, the tack is predicted to scale with  $1/E$ . Consequently, for short contact times,  $t_c$ , the tack is predicted to scale with  $(t_c/\tau_e)^{1/2}$  where  $\tau_e$  is the entanglement time. For lower pressures, this simple scaling law is no longer valid and we predict a complex variation of tack with contact time and molecular parameters.*

### Introduction

From a qualitative standpoint, the tackiness of a surface is a well-known property: When one touches the surface of a pressure-sensitive-adhesive (PSA), even if the time of contact is very short, one feels the stickiness of the surface and a certain force is necessary to remove the finger. A more quantitative evaluation of this property however, requires a measure of the work necessary to separate the two surfaces. We will consider here a model situation of the adhesion between a high molecular weight polymer melt and a rigid non-reactive substrate. The work of adhesion in the case of a short contact time and a low pressure will be our definition of tack.

If the time of contact is long or the applied pressure is high, the measured work of adhesion is experimentally independent of both of these parameters. However this is no longer the case when the time of contact becomes very

short or the applied pressure very low. It is this experimental situation that we have examined in more detail<sup>1</sup>. In those conditions the measured tack decreases with decreasing contact time and applied pressure. This loss of adhesion has long been qualitatively explained in the literature with an argument of incomplete contact between the adhesive and the probe<sup>2-4</sup>, i.e. a short contact time or a low pressure did not allow the adhesive to wet properly the substrate. However a comprehensive and quantitative framework to account for this effect had not been previously published.

We describe here the bonding process within an elastic contact mechanics framework with two important assumptions:

- The adhesive is viscoelastic and has therefore a time-dependent elastic modulus

- The solid surface of the probe is a model random rough surface with a Gaussian distribution of asperities heights (see<sup>5</sup>).

We also assume that, in the regime where the adhesion is contact-limited, the measured tack is proportional to the maximum area of contact obtained during the bonding phase provided the debonding conditions (rate, temperature) are kept the same. This assumption is not trivial and its justification lies in the highly hysteretic nature of the deformation in PSA's<sup>1,6</sup>.

We consider two experimental situations:

1) The simpler case where Van der Waals forces are negligible compared to the external applied pressure and the contacts between asperities are Hertzian.

2) The case of smaller pressures where VdW forces become of the order of the externally applied forces and the JKR<sup>7</sup> approximation must be used to describe the contact of the asperities.

### High applied pressures

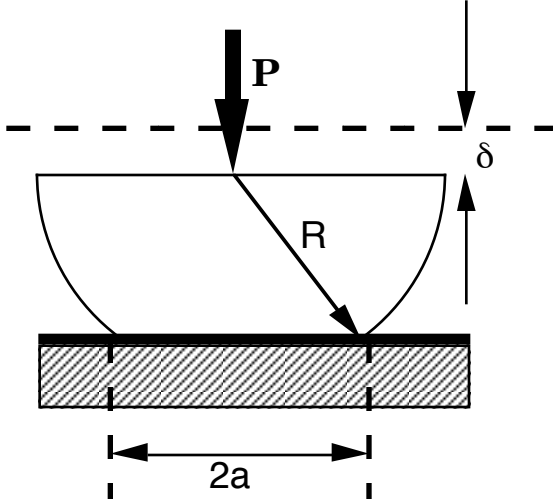
In this case, the contact radius  $a$  and the force  $P$  of a hemispherical model asperity of radius  $R$  on an elastic plane with an elastic modulus  $E$  are given by the Hertzian relationships.

$$a \approx (R\delta)^{1/2} \quad (1)$$

and

$$P \approx ER^{1/2}\delta^{3/2} \quad (2)$$

where  $a$ ,  $\delta$  and  $P$  are defined in figure 1.



**Figure 1:** Schematics of the elastic contact between a spherical cap and a plane.

The random rough surface is modeled, following Greenwood's approach<sup>5</sup>, with asperities that all have the same radius but have a distribution of heights,  $\varphi(z)$  relative to a reference plane. If the elastic plane is brought at a distance  $d$  from the reference plane of the rough surface, all asperities higher than  $d$  will be in contact with it. The total contact area and the total force can then be calculated for a given distribution of asperities  $\varphi(z)$ .

$$\varphi(z) = \frac{1}{\sigma} e^{-z/\sigma} \quad (3)$$

(For the Hertzian case we take an exponential distribution which does not change the essential results but has the advantage to be analytically tractable)

and one obtains Greenwood's classical result:

$$A_{tot} \approx P_{tot} \left( \frac{R}{\sigma} \right)^{1/2} \frac{1}{E} \quad (4)$$

where  $\sigma$  has the physical meaning of an average asperity height.

This result can be interpreted in molecular terms. For the case of a monodisperse high molecular weight polymer, the elastic modulus as a function of the time of contact ( $t_c$ ) shows three distinct regimes due to the progressive relaxation of the polymer chains. At short times, the relaxation is due to Rouse motions of the chains inside their tubes and the elastic modulus will decrease as:

$$E(t_c) \approx E_N^{(0)} \left( \frac{\tau_e}{t_c} \right)^{1/2} \quad (5)$$

where  $\tau_e$  is the entanglement time and  $t_c$  the contact time between the viscoelastic plane and the rough surface. For intermediate times, the modulus remains practically constant and only for times greater than the disentanglement time  $\tau_d$ , will the adhesive flow. Combining eq. 4 and 5, we postulate that for contact times shorter than  $\tau_e$ , the measured tack will vary as  $t_c^{1/2}$  to become independent of  $t_c$  for contact times  $t_c > \tau_e$ . Therefore the loss of adhesion for short contact times is controlled by the value of  $\tau_e$ , and should be independent of the molecular weight of the polymer.

### Small pressures

When the applied pressure is reduced and the average force on each asperity becomes of the order of the VdW forces, Hertzian mechanics does no longer describe the contact and one must use the JKR approximation. The incorporation of surface forces in the physical description implies that even under zero applied load, there is a finite area of contact between the asperity and the plane.

Using this approximation to describe the contact of one asperity and following the seminal work of Fuller and Tabor<sup>8</sup>, one can numerically calculate the total area of contact and the resulting pressure for a given separation  $d$  between the elastic plane and the reference plane of the rough surface.

The introduction of VdW forces gives the following main results:

1) If the elastic modulus of the plane falls below a critical value  $E^*$ , there will be a "complete"

contact (total area of contact  $A^*$ ) between the plane and the rough surface even under a vanishing external load. This critical modulus is given by:

$$E^* \approx W \left( \frac{R^{1/2}}{\sigma^{3/2}} \right) \quad (6)$$

It is worthwhile to point out that for numerical values of  $W = 50 \text{ mJ/m}^2$ ,  $R = 100 \text{ }\mu\text{m}$  and  $\sigma = 2 \text{ }\mu\text{m}$ , typical of a probe surface of a probe tack experiment and of a polymeric adhesive,  $E^*$  is approximately 0.2 MPa, a value very close to the empirical Dahlquist's criterion above which an important loss in tack is observed. The physical significance of this critical modulus is that of a lower limit below which there is always a good contact.

2) The total area of contact as a function of the applied force (at a given elastic modulus or equivalently, contact time) depends on the value of the elastic modulus relative to  $E^*$ . It is proportional to  $P$  for  $E \gg E^*$  and independent of  $P$  for  $E \leq E^*$ . Between these two limiting cases, the behavior is described on figure 2.

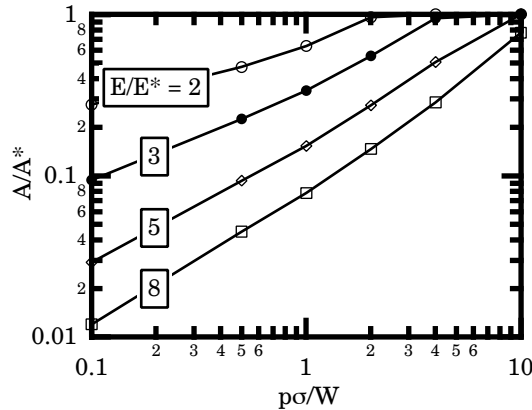


Figure 2: Normalized area of contact  $A/A^*$  as a function of the normalized pressure  $p\sigma/W$ .

3) The total area of contact as a function of the elastic modulus (at a given pressure  $p$ ) also shows two limiting cases. For  $p=0$ , the area decreases exponentially with the modulus when  $E > E^*$ . This result implies that if the modulus of the adhesive is above  $E^*$ , one might be able to obtain short term adhesion, but after the

pressure is released, the area of contact will eventually be strongly reduced. For  $p \gg \sigma/W$ , the area scales linearly with  $1/E$  and the maximum modulus for complete contact increases approximately linearly with  $p$  as illustrated in figure 3.

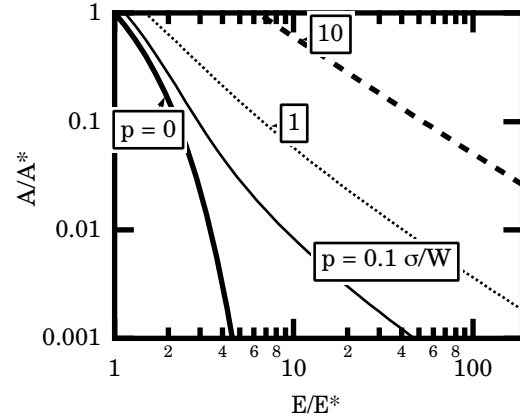
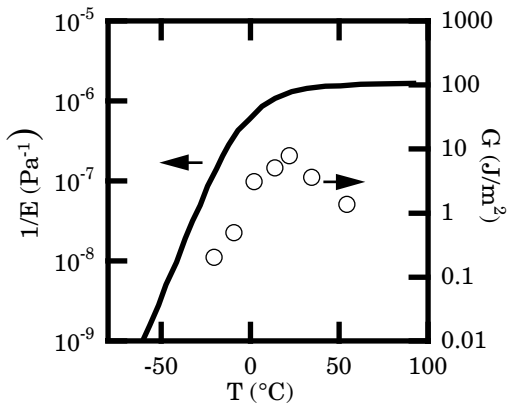


Figure 3: Normalized area of contact  $A/A^*$  as a function of the normalized modulus  $E/E^*$

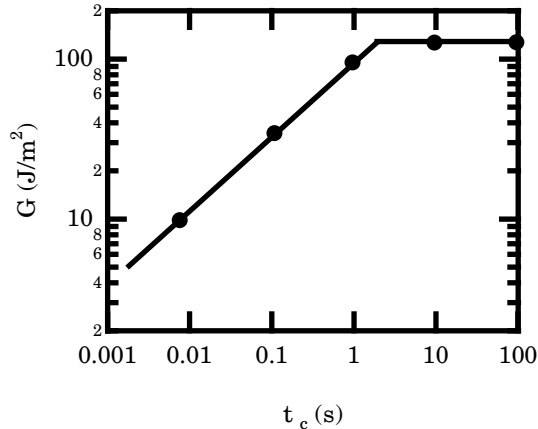
#### Comparison with experimental results

The available experimental results are mainly due to the work of Zosel<sup>4, 9</sup>. They agree with our theoretical predictions on two important points; firstly, the time of contact at which the measured tack saturates is comparable with  $\tau_e$ , the entanglement time and not  $\tau_d$ , the terminal relaxation time. This is further illustrated by a measure of the work of adhesion as a function of temperature for a sample of high-molecular weight Polyisobutylene. At low temperatures the tack decreases because of the loss of contact and it is interesting to plot on the same graph, the work of adhesion and the elastic compliance (measured for a relaxation time equal to the contact time between the probe end the adhesive). In the results shown on figure 4, one can clearly see that the maximum in the tack energy occurs at the same temperature where the compliance undergoes a transition from the plateau region to the transition region close to the  $T_g$ .



**Figure 4:** Inverse of the elastic modulus (compliance) and tack energy of Polyisobutylene on stainless steel as a function of temperature. data from <sup>4</sup>

Secondly, at short contact times, Zosel's probe tack experiments on a sample of high molecular weight poly(ethyl-hexyl acrylate) on stainless steel show that the adhesion energy increases as  $t_c^{1/2}$  consistent with the predictions of our model.



**Figure 5:** Work of adhesion  $G$  as a function of the time of contact for a poly(ethyl-hexyl acrylate) on stainless steel. Data from <sup>9</sup>

**Conclusions:**

Our model is in very good agreement with the available experimental results. In particular, the scaling laws successfully predict all the trends of the influence of the pressure and of the time of contact in regimes where adhesion is contact

limited. Roughness effects seem to be qualitatively well accounted for in our picture as well. The more quantitative comparisons based on molecular arguments would require simultaneous measurements of stress relaxation and tack on well characterized substrates and adhesives. In particular it will be interesting to study how does the temperature affect the pressure and time dependence of tack.

Clearly the physical picture presented here is only relevant in the regime where tack is contact limited. Furthermore it assumes that debonding conditions are kept constant. The interested reader is referred to a more thorough discussion of some of these issues in reference <sup>1</sup>.

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