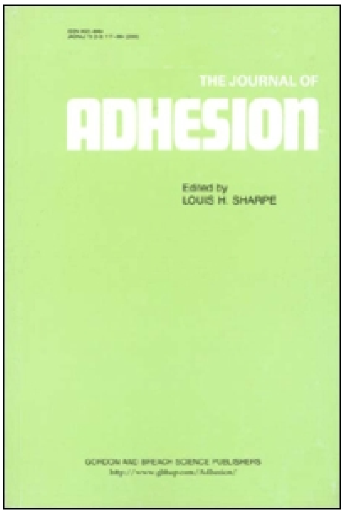

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Stress Relaxation During Bond Formation and Adhesion of Pressure-Sensitive Adhesives

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To cite this Article Novikov, Mikhail B. , Gdalin, Boris E. , Anosova, Julia V. and Feldstein, Mikhail M.(2008) 'Stress Relaxation During Bond Formation and Adhesion of Pressure-Sensitive Adhesives', The Journal of Adhesion, 84: 2, 164 — 190

To link to this Article: DOI: 10.1080/00218460801952841

URL: http://dx.doi.org/10.1080/00218460801952841

The Journal of Adhesion, 84:164–190, 2008
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ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460801952841

Stress Relaxation During Bond Formation and Adhesion of Pressure-Sensitive Adhesives

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Relaxation properties and adhesion of pressure-sensitive adhesives (PSAs) have been studied with the Probe Tack method under the conditions corresponding to the adhesive bond formation. Typical representatives of various PSA classes are examined: adhesives based on the styrene-isoprene-styrene (SIS) block copolymer, polyisobutylene of two molecular weights, acrylic and silicone PSAs. By comparison of the adhesive and relaxation behaviors of different PSAs it has been established that the PSA relaxation contributes appreciably to the strength of the adhesive bond and underlies the impact of contact time on adhesion. Direct correlation has been established between the compressive stress relaxation in the course of bond formation and the mechanism of debonding. All the examined PSAs can be classified into two groups: 1) the fluid-like PSAs that are capable of relaxing fully under compression (PIB, silicone adhesives) and 2) the PSAs, which reveal a residual unrelaxed stress. Physically crosslinked SIS and chemically crosslinked acrylic adhesives exemplify the PSAs of the second group. The occurrence of two peaks on the debonding stress–strain curves is typical of the PSAs of the second group. High adhesive strength requires the contribution of the longer relaxation times that vary for different PSAs in the range from 150 to 800 s. Minimum values of the longer relaxation times are featured for fluid adhesives, whereas the maximum values are found for crosslinked, network, and entangled adhesives. The adhesive strength achieves its maximum when the slow relaxation processes become dominating. Relative contributions of viscous and elastic deformations to relaxation properties of PSAs are assessed in terms of the Deborah number.

Keywords: Bonding pressure; Compressive stress relaxation; Effect of contact time on adhesion; Pressure sensitive adhesives; Probe Tack; Relaxation moduli; Relaxation times

This research was sponsored in part by Corium International, Inc., USA, under grant RUC 1-1658-MO-06 of the U.S. Civilian Research & Development Foundation. We wish to thank Prof. Costantino Creton, Prof. Anatoly E. Chalykh, Dr. Gary W. Cleary, and Dr. Parminder Singh for stimulating discussion.

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INTRODUCTION

Adhesive and mechanical (rheological) properties of viscoelastic polymer materials are time dependent [1]. These properties come into play when the material is subjected to flow under a compressive force [2] in the course of adhesive bond formation, or deformed under a detaching force. Both these stages require an input of energy. Under an applied force, a part of the energy imparted is irrecoverably dissipated through a mechanism of viscous flow, while another part is stored and can be released elastically upon the removal of the bonding or detaching force [3–5]. The dissipation never takes place instantaneously [6]. As a result, the response of an adhesive material lags behind the application of a stress. For this reason, adhesive properties are time dependent and this dependence cannot be ignored when dealing with such materials. Although the mechanical properties of the pressure sensitive adhesives (PSAs) are the subject of extensive study and reviewed in relevant books [7,8], nevertheless, the significance of relaxation properties for pressure sensitive adhesion still is not adequately understood [9].

While, in principle, all mechanical and adhesion properties are time dependent, they can, nevertheless, often be treated as if they had a purely elastic or purely viscous nature. Whether they can, or cannot, depends on the characteristic ratio of times, called the Deborah number n_D:

$$n_D = \frac{\tau_{mat}}{\tau_{\exp}}, \tag{1}$$

which is the ratio of the time scale of the material rearrangements, τ_{mat}, to the time scale of experimental observation, $\tau_{\exp}$ [10]. When the Deborah number approaches zero, the material may appear to the observer as purely viscous; when it approaches infinity, as purely solid (elastic). Real materials fall in between and are viscoelastic. In particular, polymeric materials have Deborah numbers around unity and are the viscoelastic materials *par excellence*.

Time-dependent mechanical properties are traditionally characterized in terms of so-called response times, in fact, almost always by a distribution of such times [1]. If the material is strained to a fixed value which is then held constant, the stress relaxes and the response times are called relaxation times. Each response time is associated with a corresponding spectral strength that may be a modulus, G_i, or a compliance, J_i. The time dependence of a material is, thus, revealed in a finite, discrete set of response times and their associated spectral strengths. When a shear strain is fixed and a stress relaxation occurs, this set is $\{G_i, \tau_i\}$ [3,11]:

$$G_t = G_{eq} + \sum_{i=1}^{i=n} G_i \exp(-t/\tau_i), \tag{2}$$

where G_{eq} is the equilibrium relaxation modulus, τ is the relaxation time, (s), and G_i is the relaxation modulus associated with τ.

Most well known examples of time dependence in pressure sensitive adhesion are the effects of contact bonding time [12–15] and debonding velocity [16,17] on the strength of adhesive joints. For adhesive joints between PSAs and polymer substrates, the former effect may sometimes be explained by the molecular diffusion of the PSA into the substrate [18,19]. However, as has been recently shown [20,21], both the diffusion coefficient of the PSA material, D, and τ contribute to the work of viscoelastic deformation of the adhesive film and failure of the adhesive bond, that control the 180° peel force by the following equation:

$$P = b \cdot l \cdot \frac{a \cdot D \cdot \tau}{3kT} \cdot \sigma_b^2, \tag{3}$$

where b and l are the width and the thickness of the adhesive layer, a represents the size of PSA polymer chain segment, σ_b is the ultimate tensile stress of the adhesive film under uniaxial drawing, k is the Boltzmann constant, and T is temperature. Equation (3) has been derived from the analysis of the correlation between peel adhesion and the work of viscoelastic deformation and break of adhesive films, under their uniaxial extension in a tensile test, without resorting to the so-called diffusion theory of the adhesion [20,21]. A range of crude approximations has been made in the derivation of this equation, including ignoring the spectrum of relaxation times. For this reason, Eq. (3) is inappropriate for quantitative calculations of peel force, but it is qualitatively illustrative and predicts the significance of the molecular mobility and cohesive strength of a polymer material (expressed in terms of σ_b) in adhesion.

In the following discussion we focus on the contribution of the relaxation process in adhesion. According to Eq. (3), for proper adhesion a high D should be coupled with a long τ. Both these factors are measures of molecular mobility; nevertheless, they vary in opposite directions under the transition from glasses to liquids. The D increases, while τ declines with the rise of molecular mobility. To make their product and, consequently, peel adhesion large enough, the D and τ values must fall in a specified range of magnitude. Our research described in this paper is intended to elicit the values of relaxation times which provide high adhesion.

Adhesion is traditionally defined as the phenomenon in which surfaces of contacting materials are held together by interfacial forces [22]. In this way, this definition relates only to adhesive bond formation. In fact, pressure sensitive adhesion represents the response of an adhesive material to applied mechanical stress, which is a pressure during bonding and extension in the course of debonding. More recently, the phenomenon of adhesion was revised by treating the adhesion as a three-stage continuous process that involves adhesive bonding as a first stage, followed by the stages of material relaxation upon the withdrawal of bonding pressure and adhesive joint failure under a detaching force [20,21]. Adhesive polymer relaxation accompanies all three stages of the process of adhesion. Taking into account dramatic distinctions between the deformation mechanisms of the PSA polymers in the course of adhesive bonding and debonding, we believe that the relaxation properties of adhesives can also be different in various stages of the process of pressure sensitive adhesion. In our recent paper [23], we considered the retardation times of PSAs upon the removal of compressive force in the final stage of adhesive bond formation. The relaxation properties under compressive bonding force represent the focus of our present paper, while the relaxation in the course of debonding will be a subject of a following publication.

MATERIALS AND METHODS

Five kinds of commercial PSAs were used as received: silicone adhesive BIO-PSA® 7-4302 (Dow Corning Corporation, Midland, MI, USA), acrylic adhesive Gelva® Multipolymer emulsions 737 and 3011 (Cytec Surface Specialties Inc., Smyrna, GA, USA), Styrene-Isoprene-Styrene (SIS)-based adhesive DURO-TAK® 34-4230 (National Starch & Chemical company, Bridgewater, NJ, USA) and two kinds of polyisobutylene (PIB) of different molecular weights—Oppanol B12 $M_w = 51{,}000\,g/mol$ and Oppanol B15 $M_w = 88{,}000\,g/mol$ (BASF Company, Ludwigshafen, Germany). The adhesive films, except DURO-TAK 34-4230 hot melt adhesive, were prepared by casting solutions of the PSA onto a glass slide previously cleaned with ethyl alcohol. The films of required thickness were prepared by drying at room temperature until constant weight was achieved. As a rule, the thickness of the films was 0.5–0.6 mm unless otherwise specified. The adhesive films of thermoplastic SIS elastomer DURO-TAK 34-4230 (0.5 mm in thickness) were prepared by pressing the polymer between two sheets of the release liner in a mold formed by two parallel, flat stainless plates at 70°C for 20 min, followed by cooling the samples in the mold to ambient temperature and relaxation for 24 h.

To evaluate the adhesive and relaxation properties of the adhesives we performed the Probe Tack test using TAXT2 (texture analyzer) (Stable Micro Systems, Godalming, Surrey, UK). The Probe Tack test is intended to mimic and evaluate quantitatively the touching of the adhesive film's surface and sensing the force required to break the bond [24]. The Probe Tack experiment allows the performing of the tests under two different conditions. First, when the compression force remains constant during contact time (Fig. 1A), and second when the deformation of the adhesive layer is kept constant

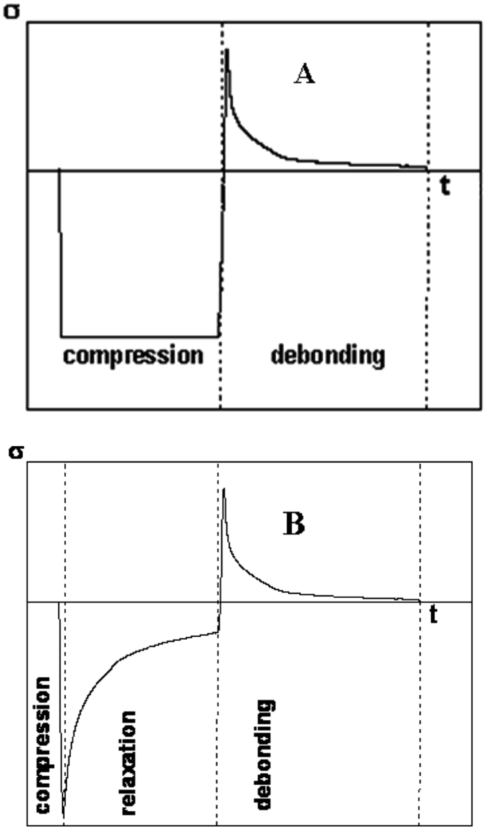


FIGURE 1 Nominal stress *vs.* time (displacement) curves of a typical probe test. A: The compressive stress remains constant during the contact time. B: The strain of the adhesive layer is kept constant during the contact time and the adhesive is allowed to relax in the course of bond formation.

during the contact time and the material is able to relax in the course of bond formation (Fig. 1B).

If the compressive stress remains constant during the contact time (Fig. 1A), the stage of relaxation is missed. The sample comes into contact with a flat cylindrical probe of the tester (4 mm in diameter), approaches the adhesive layer at a constant velocity (0.2 mm/s), and continues to move with a velocity of 0.1 mm/s until the predetermined contact force (1,000 g) is attained. Then the motor maintains a constant contact force during the specified bond formation time. Under the constant value of compressive stress, σ continuously decreases for fluid PSAs. For physically or chemically crosslinked PSAs possessing yield stress, under the tester probe may never achieve a zero value. In this case, a steady-state limiting value of σ under the probe depends on the ratio between an applied compressive stress and yield stress. At the end of the contact time, the probe is separated from the adhesive with a constant velocity (0.1 mm/s) and a tensile force is recorded as a function of time (displacement) [13]. When, on the other hand, the deformation of the adhesive layer is kept constant, the probe test can be divided into three successive stages (Fig. 1B). The first stage is compression, when the flat cylindrical probe approaches the adhesive layer with a constant velocity of 0.2 mm/sec and penetrates by 0.1 mm into its depth and then stops. The averaged thickness of tested samples was 0.5 ± 0.1 mm and more, thus, the deformation of the adhesive layer never exceeds 20%. The second is the stage of relaxation, when the adhesive material under the probe relaxes during the predetermined contact time (we varied contact times from 1 s to 1000 s). And, finally, the third stage is debonding, when the probe is removed with a constant debonding rate of 0.1 mm/s.

The probe used in this test was a standard, cylindrical, polished stainless steel probe (Stable Micro Systems). The probe was cleaned with acetone after each test. Such a cleaning procedure was adequate to obtain meaningful and reproducible results. Force *vs.* time and displacement *vs.* time curves were, thus, directly obtained from this test.

Nominal stress (σ) and strain (ε) curves are obtained using the values of the initial film thickness (h_o) and the initial contact area (A): $\sigma = F(t)/A$ and $\varepsilon = (h(t) - h_o)/h_o$. All the nominal values that were obtained in the course of the Probe Tack test were recalculated according to the compliance of a test machine, 4 µm/N. This compliance has been measured using a blank test, as has been reported by Josse *et al.* [25]

For each experimental condition, we carried out three to five probe tests. The specific stress-strain curves shown in this paper are representative of one of these individual tests while the mechanical parameters such as the maximum stress, $\sigma_{\max}$, and the maximum extension, $\varepsilon_{\max}$, are average values. Adhesive films were tested at room temperature (20–22°C).

The relaxation properties of the adhesives were evaluated by fitting the relaxation curves with the sum of exponents using Eq. (2). The best fit was obtained when we used three exponents in Eq. (2); the application of more than three exponents did not result in improvement of fitting. The found value of the regression coefficient, R^2, was always between 0.98 and 0.99. The relaxation properties for PSAs were estimated within the range of contact time, varied from 1 to 1000 s.

An apparatus of test machine and elastic layer of adhesive sample can be considered as two springs in series. Inertia of the test machine can appreciably affect the measured values of the relaxation characteristics of the adhesive material under study. Figure 2 shows a compressive stress and probe displacement as a function of time for the motor of our test machine under direct contact of movable probe to immovable rigid supportive steel plate in the absence of any adhesive film deposited between them. As is seen from Fig. 2A, if the probe is put into contact with the rigid plate under a predetermined pressure of 0.4 MPa, the designated value of stress is achieved practically immediately, while the probe oscillates at first during 5–7 seconds and then begins a steady movement, achieving a limiting value of nominal displacement of 0.13 mm in 117 s. A difference between the nominal probe displacement and true displacement (zero) characterizes the compliance of our instrument. If the nominal probe displacement has been kept constant (0.1 mm, Fig. 2B), the predetermined value of nominal deformation is achieved over 1.3 s, while the stress grows continuously and is unable to relax.

The implication of the presented data for the examination of relaxation properties of viscoelastic adhesives under bonding pressure is that the Probe Tack tester does not provide an accurate characterization of comparatively fast relaxation processes, described by the relaxation times of 1–10 s. For this purpose, classical rheological techniques seem to be much more appropriate. Nevertheless, a final objective of our research is to draw a parallel between the relaxation behavior of PSAs under bonding pressure and mechanisms of their debonding, and with this point of view the setup of the Probe Tack test is very illustrative and attractive. Moreover, according to Eq. (3), the longer relaxation time is the most important factor contributing to high adhesion strength. For this reason, we decided eventually to give our preference to the Probe Tack setup that allows us to study both

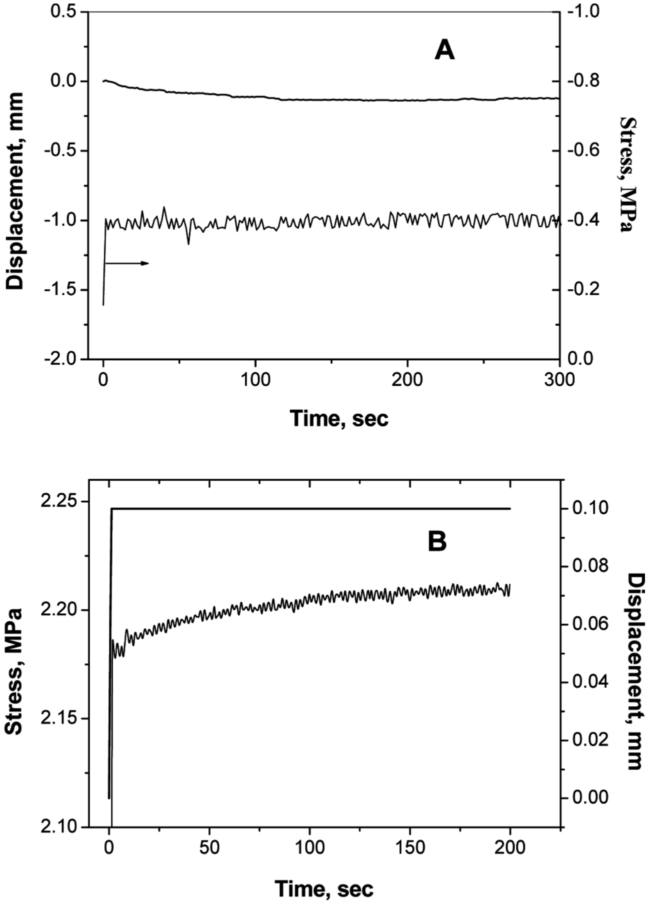


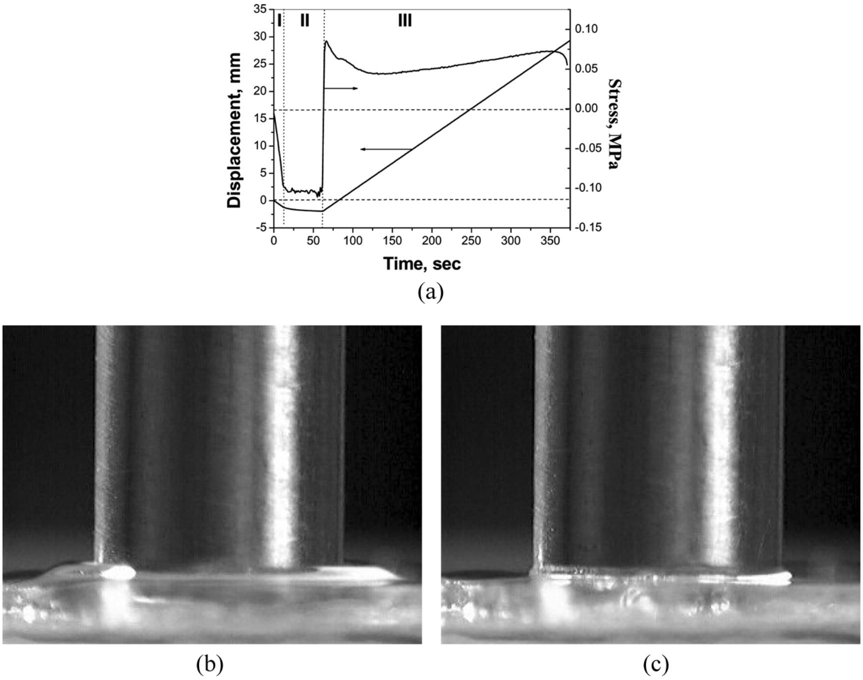
FIGURE 2 Motor displacement and stress as a function of time during compression stage of a probe test. **A**: The stress is kept constant (0.4 MPa). **B**: Probe displacement is constant (0.1 mm).

the relaxation and adhesion with the same sample in the course of a single experiment.

RESULTS AND DISCUSSION

1. Adhesion in the Absence of Compressive Stress Relaxation

As is obvious from the data shown in Fig. 2, the relaxation test under a fixed value of probe penetration into a depth of adhesive layer (displacement) is less sensitive to instrument compliance than the test performed under a fixed compressive force. To make a firm decision between these two test variants, let us consider first how a contact time affects the stress and probe displacement if a film of elastic adhesive separates the probe and rigid immovable plate. Figure 3 illustrates the behavior of Gelva 3011 crosslinked acrylic PSA in the course of probe testing under a fixed compressive stress of 0.1 MPa and a contact time of 1 s. In the Stage I (compression) at the probe movement velocity of 0.1 mm/s the predetermined value of compressive stress is achieved over 14 s. In the course of this stage the probe penetrates into the depth of adhesive layer by 1.31 mm (initial thickness of the film is 2.52 mm). As is seen from the bottom (left) picture presented in Fig. 3, where the behavior of Gelva 737 crosslinked acrylic adhesive is illustrated, this process leads to partial squeezing



(a)

(b) (c)

FIGURE 3 Top: Nominal stress and probe displacement as a function of time during Probe Tack test of Gelva 3011 PSA under fixed compressive stress (0.1 MPa). The probe velocity is 0.1 mm/s, initial thickness of adhesive layer is 2.52 mm. I: Compression; II: Contact period (50 s); III: Detachment. Bottom: The pictures of PSA adhesive joint between the probe and Gelva 737 adhesive layer at the end of contact time period (left) and at the moment corresponding to the peak stress on Probe Tack curve (right).

of adhesive material from under the flat end of the probe. As the result, the thickness of the adhesive layer under the probe's end decreases, while the squeezed adhesive gathers around the cylindrical probe, increasing the area of probe contact with the adhesive. The squeezed adhesive surrounding the walls of the cylindrical probe is allowed to relax. Over the contact time of 50 s (Stage II) the probe penetrates further into the adhesive layer, achieving a value of 1.94 mm. Finally, under probe detachment with the same velocity of 0.1 mm/s (Stage III), the probe displacement increases linearly with time, whereas, the value of debonding stress goes through a maximum and pronounced plateau. The peak on the stress-time (strain) curve corresponds to the formation of cavities (bubbles) in the adhesive layer under end of the probe, which are visible in the bottom (right) picture shown in Fig. 3. Further probe detachment results in PSA fibrillation (not shown in Fig. 3). Obviously, the friction force between the walls of the cylindrical probe and the adhesive squeezed from under the probe creates an additional increment in the maximum value of debonding stress.

Figure 4 demonstrates the curves of stress and nominal displacement as a function of time for Gelva 3011 crosslinked acrylic PSA. As the adhesive film is subjected to the action of bonding pressure until the predetermined value of probe penetration depth of 0.1 mm is achieved, the compressive stress attains the value of 0.96 MPa over 1 s and then relaxes to 0.29 MPa during a contact period of 50 s. After

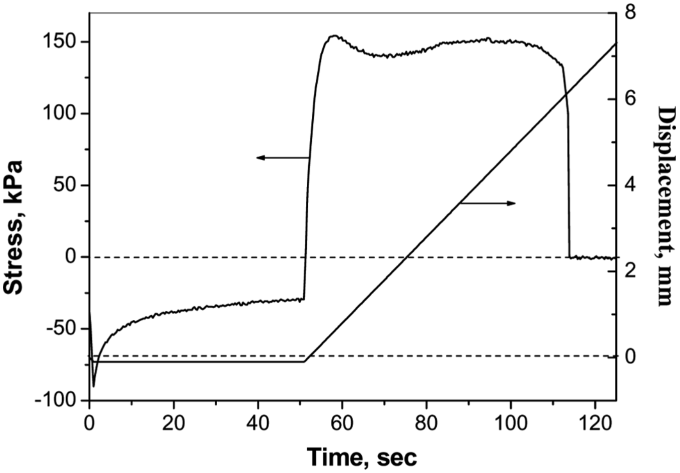


FIGURE 4 Nominal stress and probe displacement as a function of time during Probe Tack test of Gelva 3011 PSA under a fixed value of probe penetration depth into adhesive layer (0.1 mm). The probe velocity is 0.1 mm/s.

this time, the probe is separated with a detachment velocity of 0.1 mm/s and the stress shows a smooth peak followed by an extended plateau.

As is seen from Fig. 5, if the adhesive is not allowed to relax during or after the process of bond formation, the value of contact time has a significant effect on the mechanism of adhesive deformation in the course of the debonding process. At comparatively short contact times (1–20 s) and correspondingly small values of probe penetration depth (1.05–1.67 mm), the Probe Tack stress-strain curves show a pronounced plateau without a peak in the area of low relative extension. The increase of contact time and probe penetration depth above this limit results in the appearance of the peak at $\varepsilon \approx 0.2$. The height of the stress peak increases with the contact time and probe penetration. The most plausible explanation for the observed rise of peak stress is the improvement of probe contact with the adhesive layer. At the microscopic level this means that the average size of the contact defects (microbubbles) decreases with contact time [20]. Another possible reason behind the increase in maximum stress is that the thickness of the adhesive layer under the probe decreases with contact time. As has been recently shown [26], the peak stress grows as the thickness of adhesive layer reduces. The area under the Probe Tack

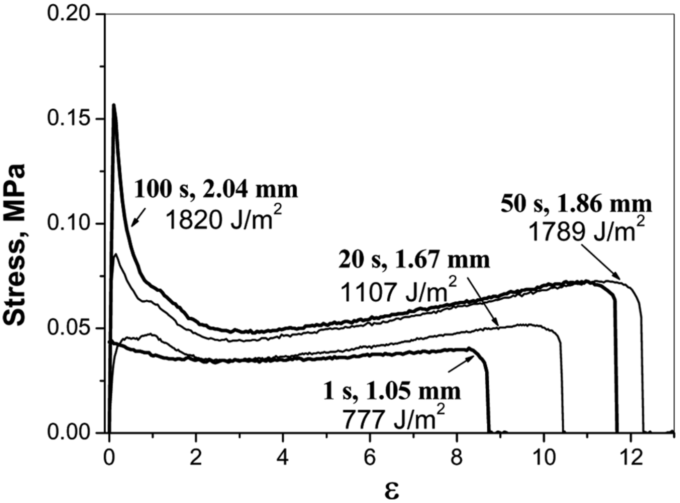


FIGURE 5 Effect of contact time, probe penetration depth, and W on the curves of probe separation for the acrylic adhesive Gelva 3011. Bonding pressure is constant (0.1 MPa), debonding velocity is 0.1 mm/s, and initial thickness of adhesive film is 2.52 mm.

curves that refer to the practical work of adhesion increases with both contact time and probe penetration depth.

2. Relaxation and Adhesion of Typical PSAs

An alternative procedure for the Probe Tack test includes the relaxation of compressive stress during contact formation, while the probe position (and material deformation) remains fixed with the contact time (Fig. 1B). This procedure has the advantage of keeping the layer thickness independent of contact time and, therefore, to avoid any dependence of the debonding stress on the layer thickness. Also, if the depth of probe penetration into the adhesive layer is constant, the increment of additional contact area of the adhesive with the walls of cylindrical probe (Fig. 3 bottom left) is uniform for all the samples and allows comparison of their debonding curves. The relaxation curves for PIB (Oppanol B15), silicone (BIO-PSA 7-4302) and SIS-based DURO-TAK 34-4230 PSAs are shown in Fig. 6 [27]. By fitting the exponential relaxation curves in Figure 6 with the sum of exponents [Eq. (2)] it has been established that three populations of relaxation times and corresponding moduli can approximate the curves of stress relaxation in Fig. 6. All found values are presented in Table 1. For all the adhesives examined, the following ranges of relaxation times and moduli have been established: $G_{eq} = 0\text{–}0.6\,\text{MPa}$,

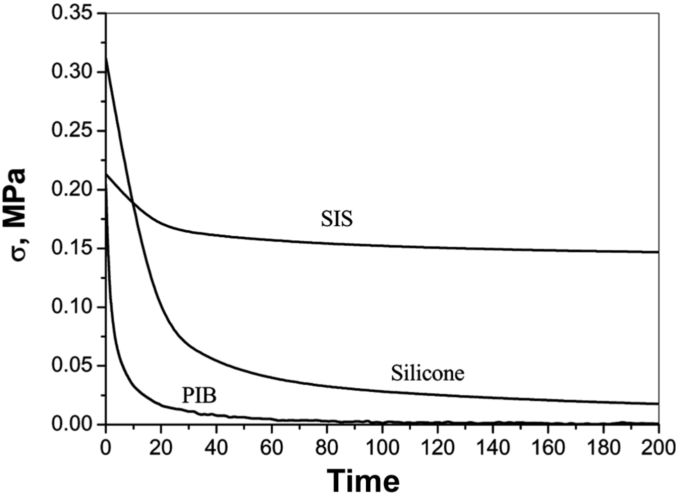


FIGURE 6 Compressive stress relaxation curves for PIB (Oppanol B15), silicone (BIO-PSA 7-4302), and SIS-based (DURO-TAK 34-4230) adhesives.

TABLE 1 Relaxation Times and Corresponding Moduli for Acrylic (Gelva 3011), PIB (Oppanol), Silicone (BIO-PSA 7-4302), and SIS-Based (DURO-TAK 34-4230) Adhesives Obtained by Fitting the Compressive Stress Relaxation Curves with Eq. (2)

Adhesive type	G_{eq} (MPa)	G_1 (MPa)	τ_1 (s)	G_2 (MPa)	τ_2 (s)	G_3 (MPa)	τ_3 (s)
BIO-PSA 7-4302	0.025 ± 0.0007	0.8 ± 0.02	3.3 ± 0.1	0.5 ± 0.02	21.4 ± 0.8	0.2 ± 0.005	150 ± 5.4
Oppanol B15	0	0.57 ± 0.01	$1{,}2 \pm 0.03$	0.4 ± 0.01	7.2 ± 0.2	0.07 ± 0.003	48 ± 1.8
Oppanol B12	0	0.2 ± 0.01	1.8 ± 0.04	0.17 ± 0.01	5 ± 0.4	0.02 ± 0.005	35 ± 3.4
DURO-TAK 34-4230	0.6 ± 0.005	0.2 ± 0.006	5.3 ± 0.3	0.1 ± 0.004	44.5 ± 2.9	0.2 ± 0.004	770.7 ± 56.1
Gelva 3011	0.035 ± 0.0006	0.08 ± 0.003	5.1 ± 0.3	0.06 ± 0.002	43.4 ± 3.04	0.05 ± 0.001	355.7 ± 20.3

$G_1 = 0.08–0.8\,\text{MPa}$, $\tau_1 = 1–6\,\text{s}$, $G_2 = 0.06–0.5\,\text{MPa}$, $\tau_2 = 5–50\,\text{s}$, $G_3 = 0.02–0.2\,\text{MPa}$, $\tau_3 = 30–800\,\text{s}$.

Figures 7–10 illustrate the effects of contact bonding time on the tack behavior for a variety of PSAs. All employed adhesives can be classified into two groups: 1. fully relaxing PIB adhesives (Oppanol B15, Oppanol B12, Fig. 5). 2. adhesives which are able to store energy in the course of deformation and exhibit a residual (unrelaxed) stress during the contact time. SIS-based (DURO-TAK-34-4230, Fig. 9), and to a somewhat less extent the acrylic Gelva 3011 PSA, (Fig. 10). Silicone adhesive BIO-PSA 7-4302 (Fig. 7) takes an intermediate position.

G_{eq} is a direct measure of the stored energy in a polymer material. As a rule, the appearance of the second maximum on the Probe Tack curve results from a network structure of the adhesive material. For instance, in the SIS-based DURO-TAK-34-4230 adhesive, the network structure is provided by the glassy domains of polystyrene blocks. Polymer networks frequently reveal an apparent yield stress that is defined as a minimum pressure at which the material ceases to flow under an applied stress [28]. Such behaviors are typical for SIS-based DURO-TAK 34-4230 (Fig. 9) and to a less pronounced extent for acrylic Gelva 3011 (Fig. 10) adhesives. As follows from the data in Table 1, the relaxation times of SIS DURO-TAK 34-4230 and acrylic Gelva 3011 PSAs are appreciably higher than those for PIB Oppanol

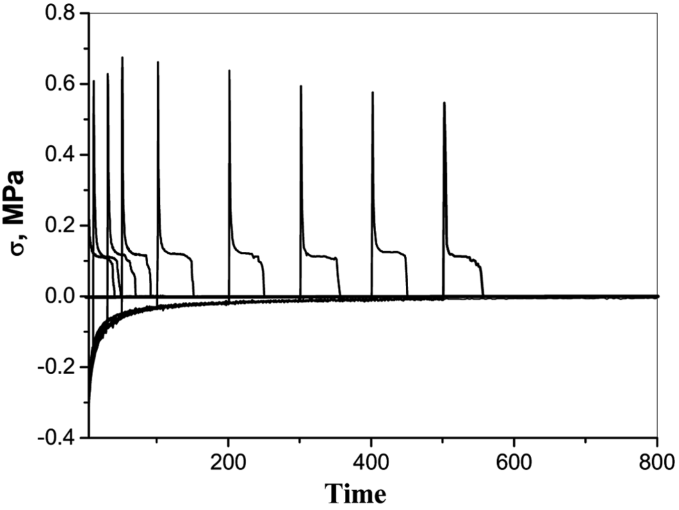
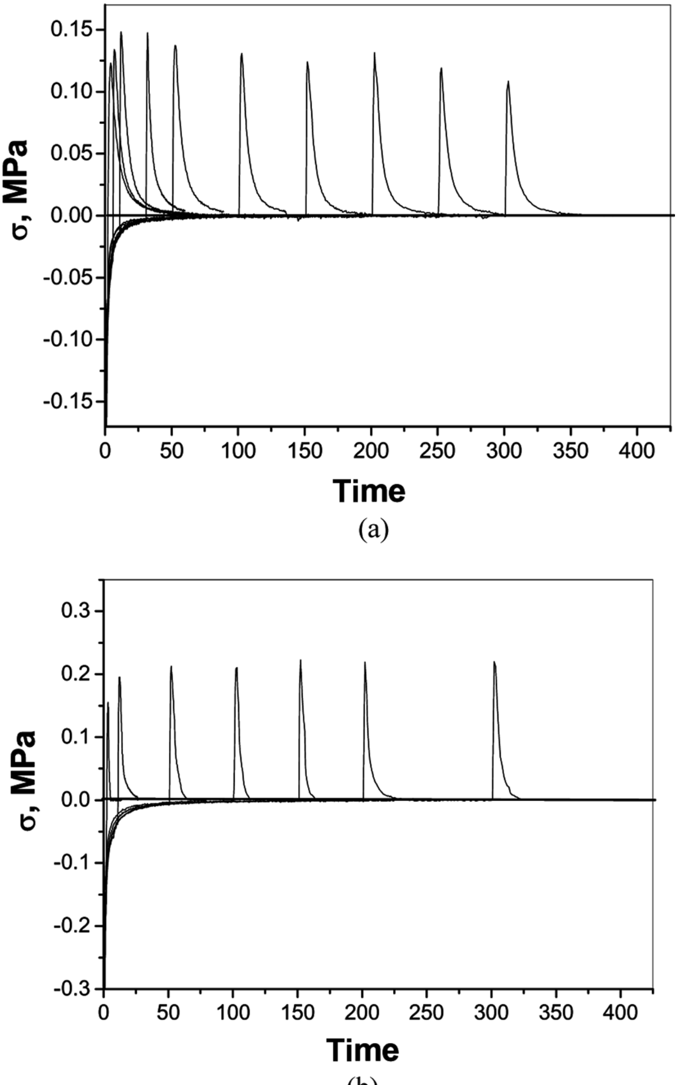


FIGURE 7 Effect of contact time on Probe Tack curves of silicone adhesive BIO-PSA 7-4302. The depth of probe penetration into adhesive layer is 0.1 mm and the velocity of probe separation is 0.1 mm/s.



(a)

(b)

FIGURE 8 Kinetics of nominal compressive stress relaxation during adhesive bond formation, followed by the debonding process for PIB Oppanol B12 (top) and for Oppanol B15 (bottom).

B12, Oppanol B15, and silicone BIO-PSA 7-4302. Thus, the longer relaxation processes are mostly associated with the appearance of a pronounced plateau on the debonding curves (silicone BIO-PSA

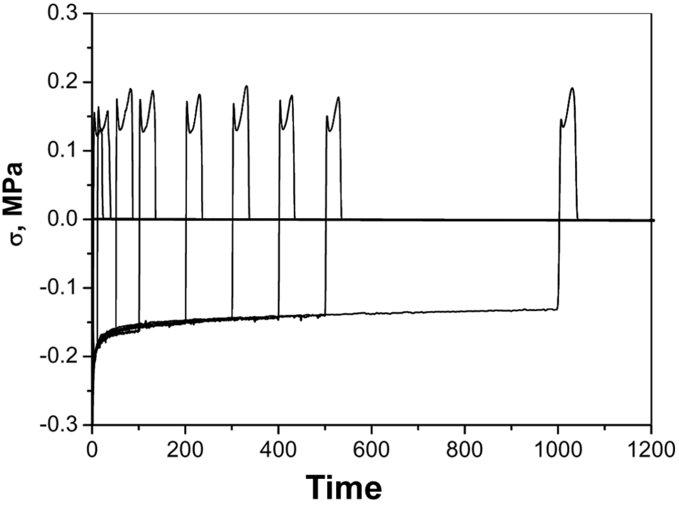


FIGURE 9 Probe tack curves of DURO-TAK 34-4230 obtained under different contact times.

7-4302, Fig. 7) or even a second maximum (SIS DURO-TAK 34-4230, Fig. 9, and acrylic Gelva 3011 PSA, Fig. 10). Fully relaxing, soft viscous adhesives such as Oppanol B12 or B15 have low relaxation

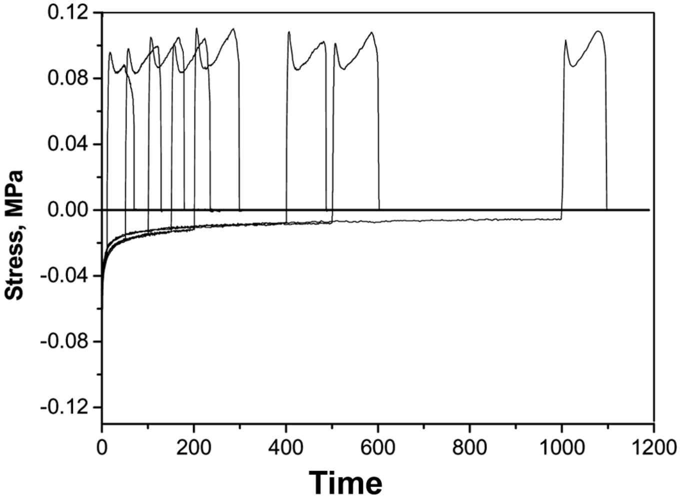


FIGURE 10 Effect of contact time on Probe Tack of acrylic adhesive Gelva 3011.

times and a liquid-like debonding mechanism typical of fluid adhesives (Fig. 8). The values of characteristic modulus associated with shortest relaxation times, G_1, are generally higher than G_2 and G_3. G_{eq} is a direct measure of the stored elastic energy in a polymer material. Fluid PIB adhesives (Oppanol B12 and Oppanol B15) do not reveal any apparent yield stress (Fig. 8) and, consequently, no equilibrium modulus (Table 1).

The complex geometry of the Probe Tack test does not allow us to present the straightforward physical meaning of the two shorter τ values, because, in addition to the viscoelastic response of the adhesive material and small-scale recovery of the material structure, these values also account for the formation of adhesive contact and instrument compliance. However, let us take into consideration that, as Eq. (3) predicts, the longer τ contributes to high adhesive strength.

3. Correlation between Contact Time, τ, and Adhesion

As is obvious from the data presented in Figs. 7–10, the contact time does not appreciably affect the mechanism of the debonding process. The peak stress grows with increasing contact time during the first 20 s and achieves its limiting value after 50 s for PIB and in 100 s for all other examined PSAs.

Figures 5 and 10 compare the behavior of Gelva 3011 acrylic PSA under two bonding conditions: at fixed compressive stress (Fig. 5) and at constant value of relative deformation of compression, defined as a ratio of probe penetration depth to initial thickness of the adhesive layer ($\varepsilon = 0.2$, Fig. 10). The adhesive films are thick enough in the former case (2.52 mm, Fig. 5) and comparatively thin in the latter (0.5 mm, Fig. 10). As is seen from Fig. 5, the contact time, the depth of probe penetration, and the thickness of adhesive film under the probe appreciably affect the mechanism of debonding and the shape of the Probe Tack curve. In contrast, the debonding mechanism is independent of contact time if the relative depth of probe penetration is kept constant. The implication of this important observation is that the ratio between the depth of probe penetration and the initial thickness of the adhesive layer is the major factor governing the mechanism of adhesive bond failure in the course of the Probe Tack test, not the absolute values of adhesive film thickness, probe penetration depth, and contact time. This finding needs further special research.

The value of the practical work of adhesion, W, is shown in Figs. 11–14 along with the maximum debonding stress as a function of contact time. The work of debonding is an increasing function of contact (relaxation) time. It is noteworthy that the maximum practical

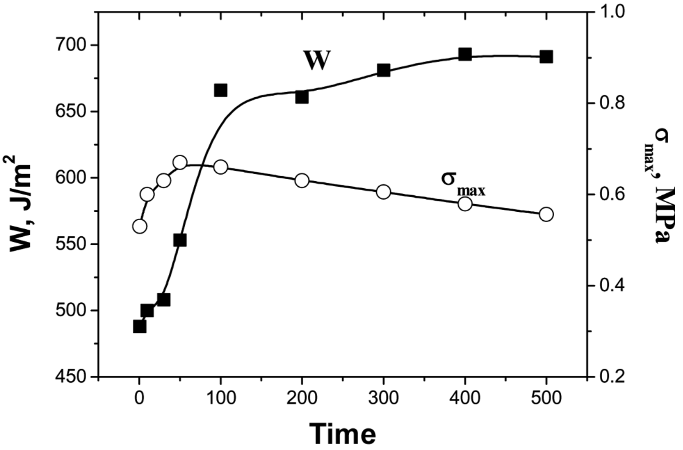


FIGURE 11 Debonding energy (W) and maximum stress values ($\sigma_{\max}$) *versus* the contact time for silicone adhesive BIO-PSA 7-4302.

work of adhesion is achieved if the adhesive material is allowed to relax for 200 s and longer. For fluid adhesives (PIB Oppanol B12 and B15) the time to achieve a steady state regime of W values is

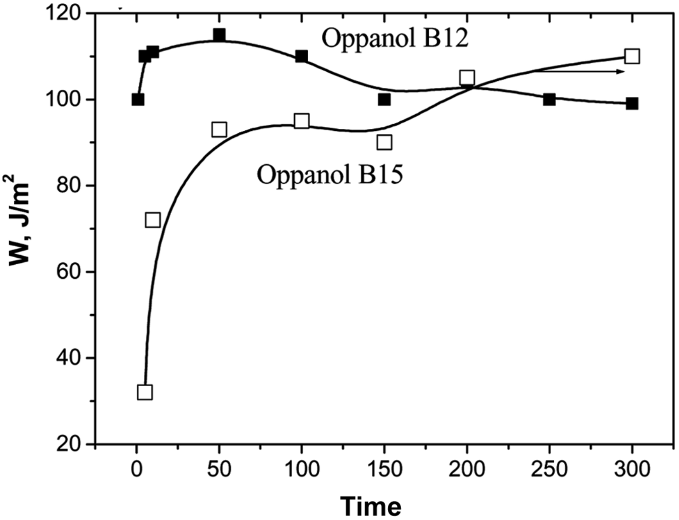


FIGURE 12 W *versus* the contact time for PIB Oppanol B12 and Oppanol B15 adhesives.

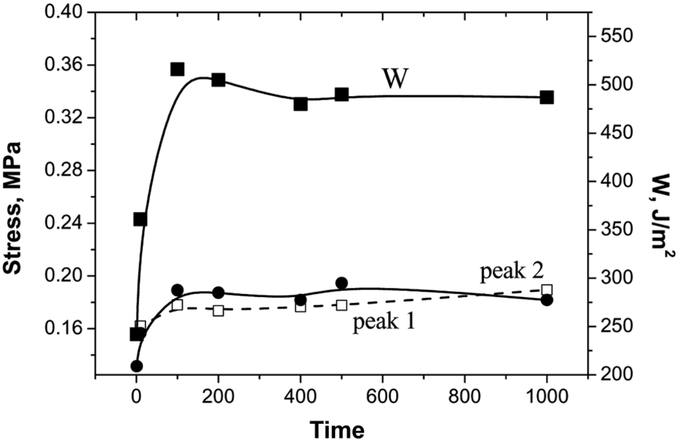


FIGURE 13 Effect of contact time on the work of debonding and the values of two stress peaks for SIS-based DURO-TAK 34-4230 PSA.

shorter: 25 and 50 s, respectively (Fig. 12). This fact suggests that for maximum adhesive strength the contact time of PSAs should be comparable with the longer τ.

Of course, many PSAs have very long relaxation times because they are very solid-like and the contact time dependence reflects more the

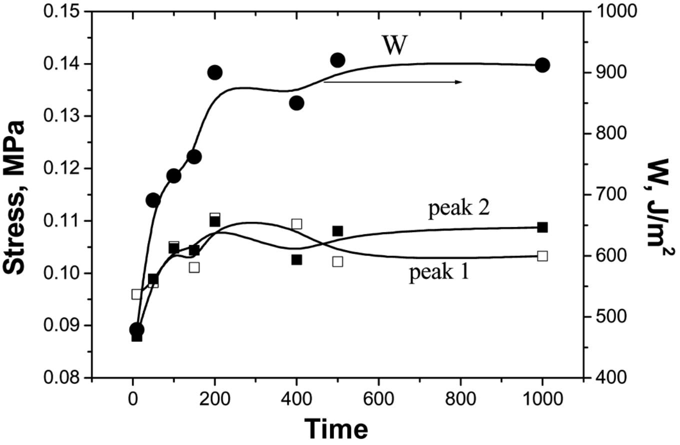


FIGURE 14 The contact time dependence of the work of debonding and the values of two stress peaks on Probe Tack curve for acrylic Gelva 3011 adhesive.

annealing of surface defects than a true relaxation of the material *per se*, although the relaxation process contributes to the driving force for such an annealing. At best, this example is illustrative of the fact that, in general, it is not wise to ignore the effect of the bonding stage when analyzing the debonding stage. This is particularly true when the PSA is very fluid-like with a very important viscous component.

4. Impact of the Relaxation of Entangled and Network Structures on Adhesion

While it is difficult to attribute unequivocally the shorter and intermediate values of the τ to the relaxation of polymer segments and macromolecules, due to the complex geometry of the Probe Tack Test, the longer relaxation times of the order of 50 s and higher relate most likely to the effects of a complex polymer supramolecular structure and chain entanglements [29]. Figure 12 illustrates the comparison of relaxation and debonding curves for two PIB adhesives of different molecular weights (M_w). Oppanol B12 is reported to have $M_w = 51{,}000$ g/mol and Oppanol B15 has $M_w = 88{,}000$ g/mol. The entanglement M_w of PIB is reported to be 8,700 g/mol [30]. As is evident from Fig. 12, for lower M_w PIB W achieves its steady state values of 100–110 J/m^2 almost instantaneously, whereas, for the higher M_w fraction this process takes appreciable time that is comparable with the value of longer τ for this polymer (50 s). Fluid, low M_w adhesives, relax faster then elastic PSAs of higher M_w, however, the observed difference in the behaviors of these two PIB adhesives can be hardly explained only by the difference in their M_w. Aggressive tack of highly soft low Mw PIB promotes the formation of good adhesive contact and less time is required to achieve the maximum value of W.

The correlation between relaxation and adhesion is presented in Figs. 15 and 16 for silicone BIO-PSA 7-4302 and for SIS-based physically crosslinked DURO-TAK 34-4230 adhesives. The former (Fig. 15) represents the behavior of fluid, fully relaxing adhesives with very low values of G_{eq}, whereas, the latter stores mechanical energy under bonding pressure, demonstrating a high value of G_{eq} (see Table 1) and appreciable unrelaxed residual stress (Fig. 16). As is seen from the stress-relaxation curves, the initial period of fast relaxation (20–35 s) is followed by an intermediate period and, finally, the process of slow relaxation (since 125–150 s). It is clear that shorter relaxation times dominate within the period of fast relaxation, while the longer relaxation times govern the steady-state (equilibrium) adhesion of both types of the PSAs. In both cases, the

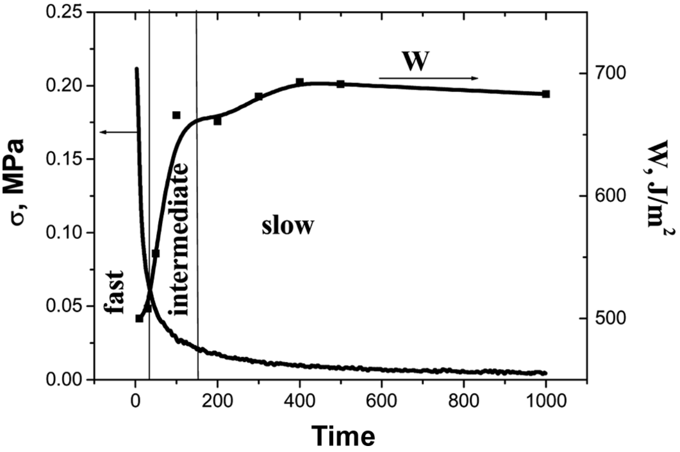


FIGURE 15 Effect of contact time on W as compared with bonding stress relaxation curve for silicone BIO-PSA 7-4302 adhesive.

achieving of maximum adhesion falls on the end of the intermediate relaxation period and the onset of slow relaxation.

Thus, in full agreement with Eq. (3), high adhesion is associated with the longer relaxation times. The relaxation mechanism provides a connection between all the stages of the process of pressure sensitive adhesion.

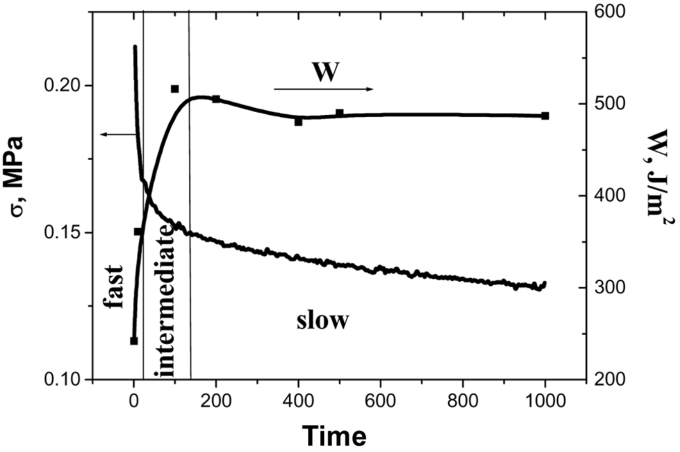


FIGURE 16 Comparison of bonding stress relaxation curve with the change in *W* as a function of contact time for SIS-based DURO-TAK 34-4230 PSA.

5. Optimum Range of Longer Relaxation Times Providing Strong Adhesion

As is shown in a series of our earlier publications [20,21,31], for high adhesion a compromise has to be reached between the values of the cohesion energy, diffusion coefficient, and relaxation times of PSAs. Figure 17 establishes the correlation between W and the values of longer relaxation times measured for the examined adhesives. Adhesion appears with the rise of longer relaxation times exceeding 50 s and increases passing through a maximum (acrylic Gelva 3011 PSA) at $\tau_3 = 330–380$ s. A further increase of the longer relaxation times results in a gradual decline in the adhesion. The best adhesion is assured as the longer τ varies in the range from 150 to 800 s.

6. Deborah Numbers of PSAs

Viscoelastic polymers have well-defined relaxation times such as a reptation time, Rouse time, or entanglement time. Such relaxation times do not depend on the observation time but only on the chemical structure of polymer, its M_w, and T. As follows from Eq. (1), the n_D (for a given material) is a function of the observation time. On the other hand, PSAs have very complex relaxation spectra and the

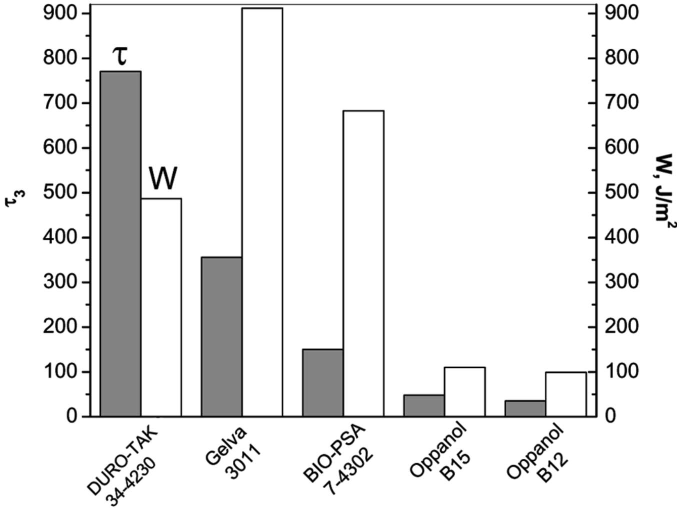


FIGURE 17 Longer relaxation times and *W* for SIS-based DURO-TAK 34-4230, acrylic Gelva 3011, silicone BIO-PSA 7-4302, and two grades of PIB adhesives (Oppanol B12 and B15).

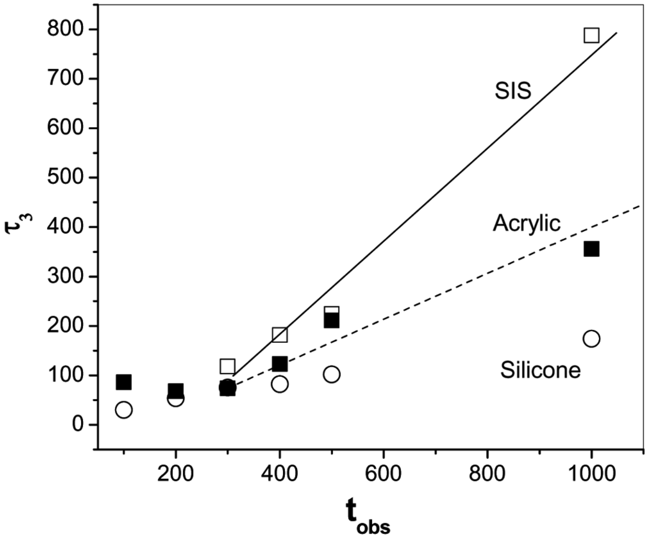


FIGURE 18 Effect of observation time on the values of longer relaxation time, τ_3, for SIS-based DURO-TAK 34-4230, acrylic Gelva 3011, and silicone BIO-PSA 7-4302 adhesives.

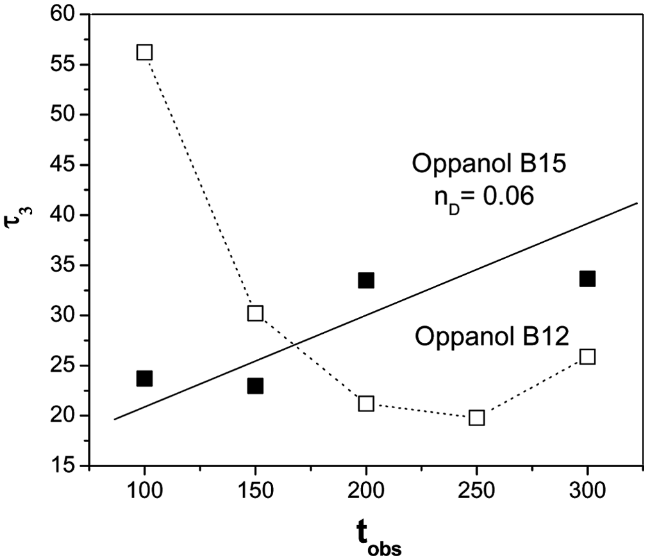


FIGURE 19 Effect of observation time on the values of longer relaxation time, τ_3, for PIB Oppanol B12 and B15 adhesives.

approximate results obtained from the fit of Eq. (2) to experimental data depend markedly on the experimental window used. Figures 18 and 19 illustrate the effect of the observation window, t_{obs}, on the values of the fitted value of the longer relaxation time, τ_3, for SIS-based DURO-TAK 34-4230, acrylic Gelva 3011, silicone BIO-PSA 7-4302, and PIB Oppanol B12 and B15 adhesives. As is obvious from Figures 18 and 19, for all the PSAs examined, except the most fluid low M_w PIB (Oppanol B12), the fitted longer τ is an increasing linear function of the observation window, although the points for the smaller observation window tend to deviate from the linear relationship for the most elastic, crosslinked SIS DURO-TAK 34-4230 and acrylic Gelva 3011 adhesives. Interestingly, however, the slopes of the linear parts of the curves presented in Figs. 18 and 19 are constant and, therefore, can be related to the n_D of the PSAs. The found values of the n_D are listed in Table 2 along with parameters of R^2.

All PSAs are viscoelastic materials that couple the properties of solids and liquids. The values of the n_D are informative on the liquid-like and solid-like contributions. As $n_D = 1$, a material is 50% solid and 50% liquid. This is the case of physically crosslinked SIS-based adhesive characterized by the magnitude of the n_D that approaches unity (Table 2). For all other adhesives considered, the liquid-like viscous contribution dominates the solid-like elastic one. While the elastic contribution is appreciable for the chemically crosslinked acrylic Gelva 3011 adhesive ($n_D = 0.388$), silicone BIO-PSA 7-4302 and PIB adhesives are typical viscous liquids. For most liquid-like, lower M_W PIB fraction (Oppanol B12), the fitting of stress relaxation curves with Eq. (2) at observation times less than 200 s does not yield plausible values of relaxation times (Fig. 19). Crosslinked adhesives (SIS-based and acrylic) as well as silicone PSAs, which exhibit best adhesion, demonstrate n_D values between 0.15 and 1.

TABLE 2 The Values of n_Ds Determined for SIS-Based (DURO-TAK 34-4230), Acrylic (Gelva 3011), Silicone (BIO-PSA 7-4302), and PIB (Oppanol B15) Adhesives by Treating the Relationships Between the Longer Relaxation Times and the Observation Times

PSA	n_D	R^2	Notes
SIS (DURO-TAK 34-4230)	0.857 ± 0.090	0.9788	Complete data set
	0.989 ± 0.089	0.9921	Taking 4 last points only
Acrylic (Gelva 3011)	0.388 ± 0.061	0.9765	Taking 4 last points only
Silicone (BIO-PSA 7-4302)	0.155 ± 0.008	0.9952	Complete data set
PIB (Oppanol B15)	0.058 ± 0.027	0.8378	Complete data set

The values of n_D values described in this section are only approximate and are calculated with the longer τ. They are only used to give an idea of the type of behavior (liquid or solid) of the PSA examined. In reality, the spectrum of the relaxation times in the linear viscoelastic region is a well-defined material property that does not depend on observation time. However, measured values of such viscoelastic properties as moduli G' and G'' depend on both the τ and the observation time.

CONCLUSIONS

At the conditions corresponding to the process of adhesive bond formation under compressive force, for which the mode of deformation is typically in shear, PSAs reveal three relaxation times, which in their magnitudes are about one decade apart. Only the longer relaxation times (150–800 s) are significant for high adhesion of various PSAs and they relate mainly to the energy-dissipating processes and chain entanglements which, in turn, are associated with translational movement (self-diffusion) of polymer segments and entire macromolecules in the course of large-scale structural rearrangements. The minimum values of longer τ are typical of fluid adhesives. Chemically or physically crosslinked, network adhesives have much greater values of the longer relaxation times. Compressive stress relaxation in the course of adhesive bonding governs the mechanism of adhesive joint failure during debonding under the detaching force. The adhesives exhibiting complete stress relaxation debond mainly as fluids with or without pronounced plateau on the Probe Tack stress-strain curves. In contrast, network adhesives, such as SIS and covalently crosslinked acrylic PSAs, are capable of storing mechanical energy under bonding pressure. They show occurrence of residual, unrelaxed stress and typically have two peaks in the debonding stress-strain curves. For all the PSAs, the practical work of adhesion achieves its maximum value as the contact time becomes comparable with the longer relaxation time, or more precisely, as the mechanism of slow relaxation is rendered dominating. If the stress during adhesive bonding is not allowed to relax, the mechanism and the energy of debonding are independent of the contact time. However, if the bonding stress can relax, the contribution of the contact time to the work of adhesive debonding is appreciable. Correlation between the adhesion and τ for all the PSAs examined can be described fairly reasonably with Eq. (3) that relates peel adhesion to the τ and translational mobility of adhesive polymer.

PSAs are viscoelastic materials, which combine the properties of solids and liquids. Relative contributions of viscous and elastic behaviors can be estimated in terms of so-called Deborah numbers that relate the time scale of structural rearrangement in the material to the time of experimental observation. The n_D values for the examined adhesives range between 0.06 (low molecular weight PIB fractions) and unity (physically crosslinked SIS-based PSA). Crosslinked adhesives (SIS-based and acrylic) as well as silicone PSA, which exhibit best adhesion, demonstrate Deborah numbers between 0.15 and 1 if the longer τ is chosen as the characteristic τ of the adhesive.

REFERENCES

[1] Tshoegl, N. W., *Mechan. Time-Depend. Materials* **1**, 3–31 (1997).

[2] Moonan, W. K. and Tschoegl, N. W., *J. Polym. Sci., Polym. Phys. Ed.* **23**, 623–651 (1985).

[3] Ferry, J. D., *Viscoelastic properties of polymers* (Wiley and Sons, New York, 1980), 3rd ed.

[4] Aklonis, J. J. and MacKnight, W. J., *Introduction to Polymer Viscoelasticity*, 2nd ed., (Wiley and Sons, New York, 1980).

[5] Christensen, R. M., *Theory of Viscoelasticity*, 2nd ed. (Academic Press, New York, 1982).

[6] Matsuoka, S., *Relaxation Phenomena in Polymers* (Oxford University Press, New York and Carl Hauser Verlag, Munich, 1992).

[7] Satas, D., (Ed.), *Handbook of Pressure-Sensitive Adhesive Technology*, 3rd ed. (Satas & Associates, Warwick, Rhode Island, 1999).

[8] Dillard, D. A. and Pocius, A. V., (Ed.), *The Mechanics of Adhesion* (Elsevier Science, New York, 2002).

[9] Zosel, A., *J. Adhesion Sci. Technol.* **11**, 1447–1457 (1997).

[10] Tschoegl, N. W., *The Phenomenological Theory of Linear Elastic Behavior* (Springer-Verlag, Heidelberg, 1989), p. 126.

[11] Schramm, G., *A Practical Approach to Rheology and Rheometry* (Haake Rheometers, Karlsruhe, 1994), p. 104.

[12] Hammond, F. H., *ASTM Spec. Techn. Publ.* **360**, 123–134 (1964).

[13] Zosel, A., Fracture energy and tack of pressure sensitive adhesives, in *Advances in Pressure Sensitive Adhesive Technology*, D. Satas (Ed.) (Satas and Associates, Warwick, RI, 1992), Vol. 1, Ch. 4.

[14] Creton, C. and Leibler L., *J. Polym. Sci.: Part B: Polym. Phys* **34**, 545–554 (1996).

[15] Zosel, A., *J. Adhesion Sci. Technol.* **11**(11), 265–271 (1997).

[16] Lakrout, H., Sergot, P. and Creton, C., *J. Adhesion* **69**, 307–359 (1999).

[17] Creton, C. and Fabre, P., Tack in *Adhesion Science and Engineering*, D. A. Dillard and A. V. Pocius (Eds.) (Mechanics of Adhesion, Elsevier, Amsterdam-Boston-London, 2002), Vol. I, Ch. 14.

[18] Wool, R. P., *Rubber Chem. Tech.* **57**, 307–319 (1984).

[19] Voyutskii, S. S., *Autohesion and Adhesion of High Polymers* (Wiley Interscience, New York, 1963).

[20] Feldstein, M. M. and Creton, C., Pressure-sensitive adhesion as a material property and as a process, in *Pressure-Sensitive Design, Theoretical Aspects*, I. Benedek (Ed.) (VSP, Leiden, Boston, 2006), Vol. 1, Ch. 2.

[21] Feldstein, M. M., Molecular fundamentals of pressure-sensitive adhesion, in *Developments in Pressure-Sensitive Products*, I. Benedek (Ed.) (CRC-Taylor & Francis, New York-London, 2006), 2nd ed., Ch. 4.

[22] Zisman, W. A., Adhesion and bonding, in *Encyclopedia of Polymer Science and Technology, Interscience Publishers*, H. F. Mark, N. G. Gaylord, and N. M. Bikales (Eds.) (J. Wiley & Sons, N.Y.-London, 1964), p. 445–477.

[23] Novikov, M. B., Borodulina, T. A., Kotomin, S. V., Kulichikhin, V. G., and Feldstein, M. M., *J. Adhesion* **81**(1), 77–107 (2005).

[24] Satas, D., Tack, in *Handbook of Pressure Sensitive Adhesive Technology*, D. Satas (Ed.) (Satas & Associates, Warwick, Rhode Island, 1999), 3rd ed., Ch. 4.

[25] Josse, G., Sergot, P., Dorget, M., and Creton, C., *Journal of Adhesion*, **80**(1–2), 87–118 (2004).

[26] Chiche, A., Dollhofer, J., and Creton, C., *European Physical Journal E*, **17**, 389–401 (2005).

[27] Novikov, M. B., Anosova, J. V., and Feldstein, M. M., *Proceed. 29th Annual Meeting Adhesion Soc.*, (2006) p. 315.

[28] Feldstein, M. M., Kulichikhin, V. G., Kotomin, S. V., Borodulina, T. A., Novikov, M. B., Roos, A., and Creton, C., *J. Appl. Polym. Sci.* **100**, 522–537 (2006).

[29] Bartenev, G. M. and Barteneva, A. G., *Relaxation Properties of Polymers* (Chemistry Publishers, Moscow, 1992), p. 384.

[30] O'Connor, A. E. and Willenbacher, N., *Int. J. Adhes. Adhes.* **24**, 335–346 (2004).

[31] Feldstein, M. M., *Polym. Sci., Ser. A.* **46**(11), 1165–1191 (2004).