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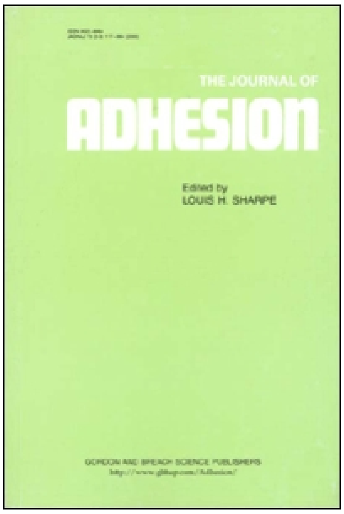

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Effect of a Gradient in Viscoelastic Properties on the Debonding Mechanisms of Soft Adhesives

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Effect of a Gradient in Viscoelastic Properties on the Debonding Mechanisms of Soft Adhesives

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The effect of a composition gradient along the thickness in soft adhesive films was investigated. The adhesion properties of bilayer films made from acrylic solutions, one layer being more cohesive and the other more dissipative, were studied by performing probe tack experiments. To understand the mechanisms that determine the bulk and the interfacial contributions to the debonding, tests on different surfaces were carried out. The results show that the presence of a composition gradient can enhance the adhesive properties, particularly on a low-energy surface such as polyethylene. On steel, the presence of the thin layer of a more elastic adhesive in contact with the adherent can influence significantly the debonding mechanism, transforming the fracture from cohesive to adhesive.

Keywords: Adhesion; Debonding; Pressure-sensitive adhesives; Tack

INTRODUCTION

Pressure-sensitive adhesives (PSAs) need to be "sticky" upon contact, and to have a high viscoelastic character to dissipate energy through deformation during the debonding [1]. This process for a typical commercial film is initiated by cavitation, followed by the formation of a fibrillar structure, which can extend several times the initial thickness

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of the film in the direction normal to the plane of the adhesive film. Good PSAs must also be able to strain-harden at high levels of strain and to fail adhesively, without leaving a residue on the surface. Finally, some adhesives, to be effective, are required to have a good resistance to shear, *i.e.*, to sustain a moderate level of stress for long periods of time [1,2].

Each of these requirements can be met by specific material properties, and often formulations used in commercial applications are the result of a compromise between them. For homogeneous PSA layers, these compromises have been extensively studied and do not allow much further optimization [3–5]. Molecular parameters such as molecular weight [6,7] and degree of branching or entanglement [3,8] can modify large-scale organization and rheological behavior and thus affect tackiness. Cross-linking has been widely used to tune the properties of PSAs. The results of previous studies can be briefly summarized as follows: uncross-linked polymers are not effective PSAs [6,9]. These materials can make a good contact with the surface because of their liquid behavior, but they are not suitable adhesives because they do not have enough cohesive strength to form stable fibrils or to resist shear stresses for extended periods of time without flowing. In a peel or a tack test, the fracture of the fibrils will lead to a cohesive failure, characterized by the transfer of part of the adhesive on the adherent surface. The presence of entanglements or branching points will prevent the polymers from flowing and will increase the fibrils' stability, leading to higher adhesion energies [8]. In this case, a transition from a cohesive to an adhesive failure with increasing degree of branching can be observed, with a complete detachment of the foot of the fibrils from the surface [10–12]. Additional cross-linking can lead to a significant strain-hardening, which occurs in extension and is responsible for a clean adhesive removal of the PSA from the surface. However, this strain-hardening will appear for an increasingly lower value of strain with increasing degree of cross-linking, causing an easier detachment of the adhesive at low levels of strain. Thus, in an optimized homogeneous tacky material, the degree of cross-linking of the polymer is optimized to have a balance between good adhesion during the contact and cohesion during the debonding step.

In this article, to go beyond this existing optimization, we investigate with a probe tack test the adhesive properties of PSA films with a gradient in composition along their thickness. To characterize the linear viscoelastic properties, rheology measurements have been combined with the adhesion tests.

To create a gradient in the viscoelastic properties of the adhesives, we prepared bilayer films, one layer being more elastic and the other one more dissipative. Our study focused on two acrylic PSAs characterized by different cross-linking densities [13]. We tested two different configurations: bilayers with the less cross-linked layer directly in contact with the adherent surface, and systems where the more dissipative layer was not in contact with the probe. The aims of our experiments were to explore a different strategy to control adhesion properties and to extend our understanding of the physics underlying the debonding. This strategy is now justified by some more detailed theoretical considerations.

THEORETICAL BACKGROUND

To justify the approach outlined previously, it is important to describe in more detail the rather complex microscopic deformation mechanisms observed experimentally: from simple interfacial failure, where a crack propagates at the interface, to cavitation or bulk fingering followed by fibrillation, where larger deformations of the adhesive are achieved [14]. In all these cases, the debonding process is determined by the coupling of bulk and interfacial properties of the material. If a linear elastic model is considered, the growth of a defect initially present at the interface is governed by the competition between two different simple mechanisms: the interfacial propagation of a crack, which is governed by the energy-release rate, G_c, and the bulk deformation, determined by the average stress within the layer, and thus essentially controlled by the elastic modulus of the adhesive, E. As a result, G_c/E represents a key parameter related to the displacement that can be applied to the adhesive before failure occurs [15,16]. For PSAs, the situation is more complex: because adhesives are viscoelastic and strained in the nonlinear elastic regime, $\mathrm{G_c}$ will depend also on the velocity [17]. However, the ratio G_c/E can still be used to predict the growth pattern of an initial defect [14,18].

For lower values of G_c/E, the critical stress at which an initial defect starts to expand is determined mainly by G_c and the defects will propagate at the interface so that an adhesive failure occurs before an extensive deformation of the materials is possible. It is useful to recall that G_c for viscoelastic materials can be written as [19,20]

$$G_c = G_0(1 + \varphi\ (a_T v)) \tag{1}$$

where G_0 is the limiting value of the energy-release rate at low rates and $\varphi(a_T v)$ is a multiplicative factor representing the viscoelastic dissipation. In this regime, therefore, increasing the interfacial interactions or increasing the dissipative properties of the adhesive results in an increase in the adhesion energy.

If G_c/E increases, cavities grow increasingly into the bulk, and a foam is formed as the walls between cavities are extended into fibrils. At larger strains corresponding to the fibrillation regime, the behavior of the adhesive is dominated by a competition between viscoelastic extension of the cavity walls and adhesive failure that causes the detachment from the substrate. In this case, the adhesion energy depends primarily on E and on the nonlinear elastic properties of the material [21], and it is less sensitive to G_c.

If this simplified model is applied to the bilayer systems studied, the value of G_c is mainly determined by the layer at the interface with the probe, whereas E is given by a combination of the elastic moduli of the two layers. Thus, we expect that the presence of a more dissipative layer in contact with the probe should increase G_c and therefore limit the propagation of internal cracks and favor the cavitation and the early stage of fibrillation, as schematically represented in Fig. 1.

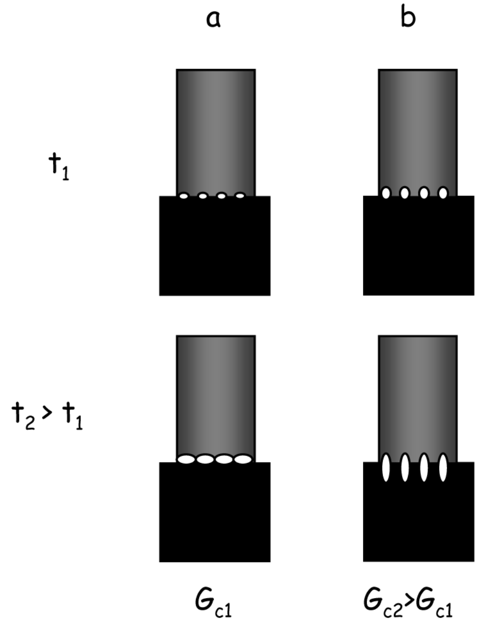

FIGURE 1 Schematic illustration of the failure mechanism at the early stage of the debonding for systems with different values of the critical energy-release rate G_c. For systems with low values of G_c (G_{c1}), growth of internal cracks, followed by an interfacial fracture, is observed. For adhesive-surface pairs with higher G_c (G_{c2}), the cavities expand into the bulk leading to fibrillation (b).

On the other hand, the elastic modulus will control the expansion of cavities into the bulk; thus, in a more compliant layer, less energy is required to deform the sample.

The failure mechanism of an adhesive is controlled by the viscoelastic properties of the PSA but also by the characteristics of the adherent [18], because the value of G_c is strongly dependent on the surface of the probe [22,23]. To elucidate the important role played by the probe surface, we tested the bilayer systems on two different surfaces, a high-energy surface (steel) and a less adherent surface (polyethylene).

EXPERIMENTAL SECTION

Materials

We performed our experiments focusing on a particular class of materials, PSAs prepared from acrylic solutions, synthesized by Cytec Surface Specialties (Drogenbos, Belgium). The adhesive formulation was a random copolymer based on the following monomer composition: 2-ethyl hexyl acrylate (54%), acrylic acid (5%), ethyl acrylate (31%), and iso-octyl acrylate (10%). The copolymers were dissolved in a solvent mixture of 54.6% of ethyl acetate, 35.7% of heptane, and 9.7% of isopropanol. Additionally, the solutions contained different amounts of temperature-activated cross-linking agent: the material denoted with the letter A had 0.15% of cross-linking agent whereas B had 0.35%. The glass-transition temperature of the materials was found to be -33°C, and it was not significantly affected by the amount of cross-linking agent.

Rheological Measurements

The viscoelastic properties of the two copolymers depend on the cross-linking density. To characterize the linear viscoelasticity of the two materials, we performed some rheological measurements. The viscoelastic properties of the adhesives were measured under torsional shear conditions, using a Rheometrics RDA II parallel plate rheometer (TA Instruments, New Castle, DE) Adhesive samples were made by deposition of a precise amount of solution in a mold. The solvents were evaporated at room temperature for 1 day. The films were then put in an oven at 130°C under a slight vacuum (800 mbar) to allow the cross-linking reaction to take place. With this drying procedure, because the solvents used are rather volatile, the evaporation is expected to occur before the cross-linking process. Therefore, we do not expect variations in the degree of cross-linking. The resulting films had a thickness of 500 μm. Disks with a diameter of 8 mm were then cut and placed between the two disk plates of the rheometer. Tests were carried out at a fixed temperature of 30°C and frequencies were varied between 0.01 and 50 Hz. Preliminary strain sweeps were performed to ensure that the materials were strained in their linear range. The strain level was then set to 20% between 0.01 Hz and 1 Hz and to 10% in the range 1–50 Hz. The results obtained are shown in Fig. 2, where the storage modulus, G′, the loss modulus, G″, and the tangent of the loss angle, tan δ, are displayed as a function of the frequency. As can be observed in the figure, the rheological behavior of the two adhesive films differs significantly for frequencies less than 1 Hz. Material A presents a lower G′ and a well-defined minimum in tan δ, whereas material B has a higher loss modulus and values of tan δ are considerably smaller at low frequencies. A similar behavior is obtained at room temperature. At $T = 20$°C, by considering a shift factor $a_T = 0.31$ for polymer A and $a_T = 0.35$ for polymer B [13], polymer A presents a considerable increase in tan δ for frequencies less than 0.3 Hz. Additional characterizations of these two materials in shear at large strains can be found elsewhere [13].

These observations make clear that at room temperature material A is more dissipative whereas material B shows a more elastic response.

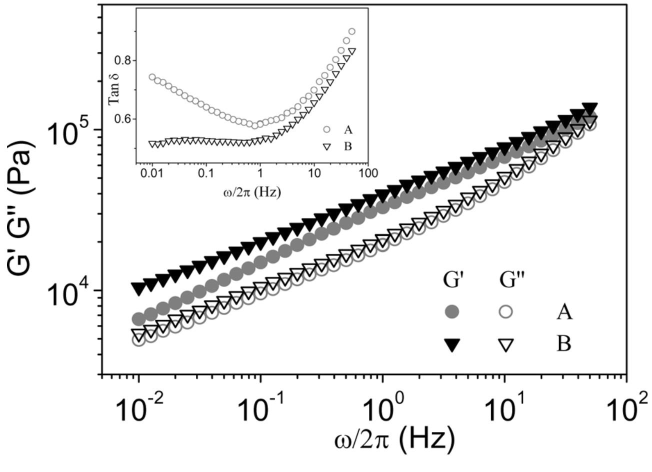

FIGURE 2 Frequency dependence of the storage modulus G′ (full symbols) and of the loss modulus G″ (empty symbols) for the adhesives A and B in oscillatory shear at 30°C. In the inset, the tangent of the loss angle tan δ is shown.

Tack Experiments

We performed probe test experiments on a custom-designed apparatus based on an MTS 810 hydraulic testing machine [10] (MTS, Minneapolis, MA). During the test, a flat cylindrical probe (diameter 10 mm) approaches the PSA film on a microscope glass slide at a constant velocity. When the contact compressive force of $-70\,\mathrm{N}$ is reached, corresponding to 1 MPa of pressure for a probe fully in contact, the probe stops for a contact time of 1 s and is then removed at a constant debonding velocity of 10 μm/s. All the tests were run at room temperature. To test different surfaces, a stainless steel probe and a probe coated with a polyethylene disc (glued with an undeformable epoxy adhesive) were used. During this test, a high-resolution camera allowed the observation of the debonding process.

Adhesive films were made by deposition of precise volumes of solution on a substrate kept on a perfectly horizontal support. After the preparation, the films were left to dry for few hours at room temperature and then put in a vacuum oven at 130°C to allow the cross-linking to occur. To verify that the reaction was completed, we performed some tests, leaving the samples at room temperature for up to 1 week before performing tack tests. No differences were observed in the adhesion properties in this case.

For bilayer systems, the first layer of adhesive was prepared on a glass slide, and the second layer was first prepared on a silicone release liner and, once dried and cross-linked, reversed and deposited onto the first layer. Because of the miscibility of the materials and the low degrees of cross-linking, the two layers interdiffuse, forming an interface. Although we expect the interfacial region not to be very broad [24], its strength is sufficient to avoid the detachment of the first layer during tack experiments and to allow the deformation of the whole bilayer system. Adhesion between the layers in general however, will, depend on miscibility so that fully immiscible layers cannot be easily combined.

In all the systems studied, the top layer, in direct contact with the probe, had a thickness of $\sim 35\,\mu\mathrm{m}$ while the backing layer was approximately 75 μm thick. The results obtained for the bilayers were then compared with those obtained from films of single layers of the materials A and B with a thickness of $\sim 110\,\mu\mathrm{m}$. The uncertainty estimated for the thickness of the layers was about 10%. Figure 3 illustrates schematically the geometry of the bilayers $\mathrm{A}+\mathrm{B}$ and $\mathrm{B}+\mathrm{A}$: in the first configuration, the A layer is deposited onto the glass substrate, whereas in the second case it is on top of layer B.

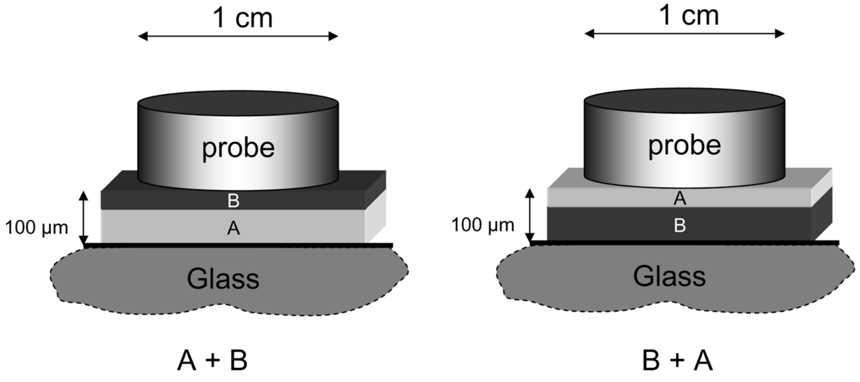

FIGURE 3 Schematic illustration of the geometry of the bilayer adhesive A + B and B + A during the tack test.

RESULTS AND DISCUSSION

To correctly understand the mechanical results, we analyzed the debonding mechanisms observed for both single layers and PSA bilayers. We first discuss the results obtained on a steel probe.

As an example, images taken during the debonding of the PSAs B, B (backing) + A (top), A (backing) + B (top), and A, at different times, are compared in Fig. 4. For the material B, the debonding was initiated by the appearance of cavities, followed by the formation of fibrils. An adhesive fracture then occurred by the detachment of the foot of the fibrils from the surface of the probe. For a single layer of A, due to the less cohesive character of the film, we observed instead a liquid-like behavior. The debonding was characterized by the formation of cavities and successively by air penetration and fibrillation and by the propagation of fingers from the edge of the contact zone into the material at a constant contact area. The failure was cohesive in this case, with the fracture of the fibrils themselves and the transfer of part of the adhesive on the probe. For bilayers where the less dissipative material is the majority component and the more dissipative material is in contact with the probe (B + A), our tests showed that the debonding mechanism was very similar to the one observed for the more elastic layers, with cavitation followed by fibrillation. However, more time was needed to detach the PSA bilayers from the probe, compared with a B single layer.

More interesting is the other configuration, where the more dissipative material is the majority component and the more elastic layer is directly in contact with the steel surface (A + B). In this case, we

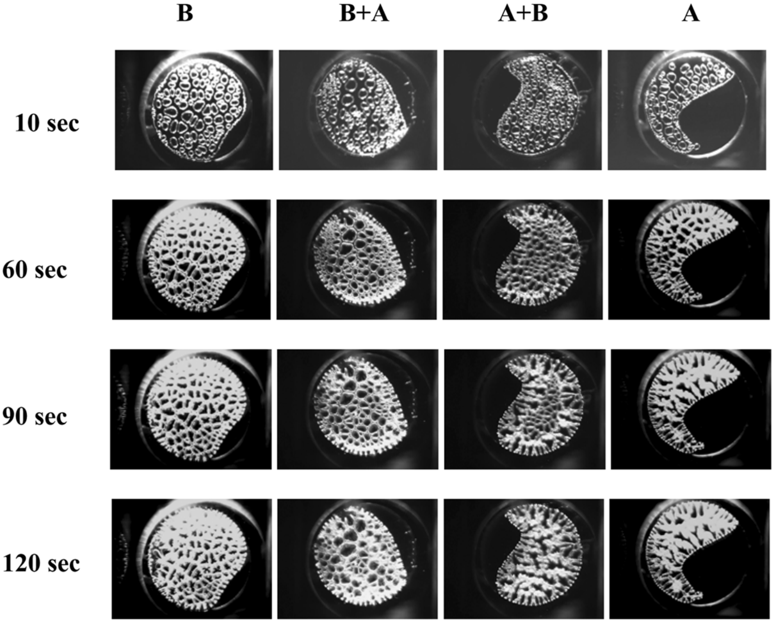

FIGURE 4 Sequence of images taken at different times during the debonding process for the PSAs B, B(backing) + A(top), A(backing) + B(top), and A. All the tack tests were made on a steel probe, and the debonding speed was 10 μm/s.

observed a liquid-like behavior with the formation of fibrils and fingers at the same time. However, the presence of the thin layer of a more elastic adhesive on top significantly influenced the failure, and we observed an adhesive fracture, with no residues of PSA left on the probe.

By considering the true contact area between the probe and the films, we obtained the *nominal stress vs.strain* curves for all the system studied. In Fig. 5 the results found for both single layers and bilayers are compared. The curves typically showed a peak in stress, $\sigma_{\max}$, corresponding to the beginning of cavitation, followed by a decrease of the stress to an almost constant value (plateau), due to the growth of fibrils. The adhesion energy is conventionally defined as the integral under the stress–strain curve. The values of adhesion energy, W_{adh}, $\sigma_{\max}$, and strain at which failure occurs, $\varepsilon_{\max}$, are reported in Table 1.

On steel, the material B presents a marked strain-hardening in the plateau region of the stress–strain curve, where the stress value increases again, before the detachment. The film A has instead a lower peak and a low value of stress in the plateau. Because this material is

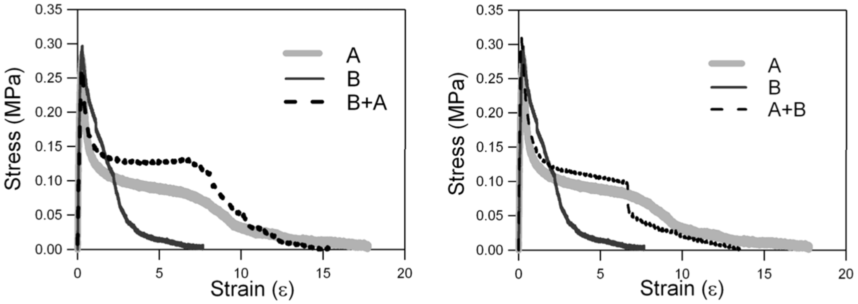

FIGURE 5 Nominal stress vs. strain curves obtained for the single layers of materials A and B and for the bilayers B + A (a) and A + B (b) on a steel probe. The debonding speed was 10 μm/s.

more viscous and less cross-linked, fibrils formed can stretch more before being finally fractured, and, thus, the extension of the plateau, ε_{max}, reaches high values of strain and failure is cohesive.

The bilayer B + A (Fig. 5a) shows a peak similar to B and a higher ε_{max} but no strain-hardening. Thus, no improvement in the adhesion is observed. The system A + B, if compared with A, shows an increase in σ_{max} and in the level of the plateau, as displayed in Fig. 5b. Moreover, it presents a very similar ε_{max}; thus, the adhesion energy is higher. This result implies that the configuration (more dissipative layer) + (more elastic layer) could be used to improve the adhesion on a high-energy surface such as steel while maintaining an adhesive release and no transfer of material.

It is important to note that the same adhesive can have different failure mechanisms on different adhering surfaces [18,25]. In practical

TABLE 1 Values of Adhesion Energy, W_{adh}, of the Maximum Stress, σ_{max}, and of Strain at which Failure Occurs, ε_{max}, Obtained from Tack Experiments Performed on a Steel Surface and on a PE-Coated Probe for the Single Layers of Materials A and B and for the Bilayers B + A and A + B

Surface	Material	W_{adh} (J/m^2)	σ_{max} (MPa)	ε_{max}
Steel	A	280	0.48	32.9
Steel	B	331	0.50	15.4
Steel	**A + B**	**380**	0.54	32.1
Steel	B + A	291	0.52	28.2
PE = coated probe	A	80	0.27	17.5
PE = coated probe	B	46	0.30	6.9
PE = coated probe	A + B	110	0.31	15.7
PE = coated probe	**B + A**	**138**	0.28	13.2

applications, two surfaces are particularly important: the silicone surfaces used as release coatings from which the adhesive must be easily detached and the polyolefin surfaces representative of many plastic surfaces on which self-adhesive labels or tapes are being used. As a model polyolefin surface, we used high-density polyethylene (PE) (obtained from Cytec) and repeated our experiments by gluing a PE disc on the steel probe. Different results were indeed found on polyethylene. In Fig. 6, the *stress vs. strain* curves obtained are displayed, and the values of W_{adh}, σ_{max}, and $\varepsilon_{\mathrm{max}}$, are reported in Table 1. The adhesion energy of A on PE is much higher than that of the B film, where no plateau is observed. The bilayer A + B, compared with single layers A and B, shows a higher peak and an increase in the plateau level, whereas the extension $\varepsilon_{\mathrm{max}}$ remains similar to the one found for A. The best tack results are obtained with the bilayer B + A (Fig. 6a), which combines a more dissipative layer near the interface with the probe with a more cohesive layer as backing: this film shows a higher plateau. It should also be pointed out that in this case a small strain-hardening is also observed before the detachment, due to the elasticity of the B layer on the backside of the PSA layer. The adhesion energy is substantially increased relative to either A or B alone.

From these results we can conclude that a bilayer configuration, where a more dissipative layer is on top of a more elastic one, could be used to improve adhesion on a low adhesion surface such as PE.

The different results obtained on the two different surfaces can be explained if the parameter G_c/E is considered, G_c being the energy-release rate and E the elastic modulus [14,16]. In elastic layers where dissipative mechanisms are limited to the interface, this

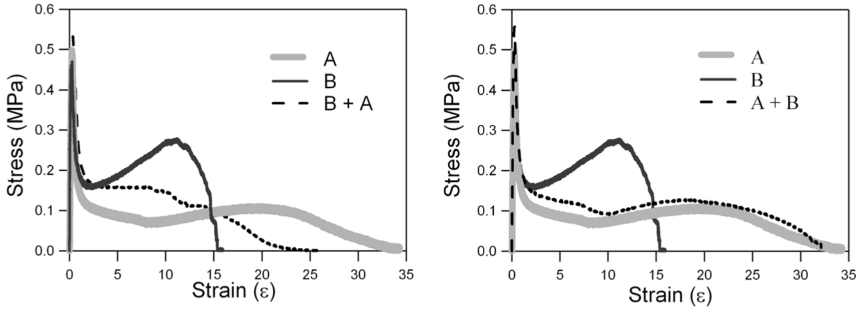

FIGURE 6 Nominal stress vs. strain curves obtained for the single layers of materials A and B and for the bilayers B + A (a) and A + B (b) on polyethylene. The debonding speed was 10 μm/s.

parameter is related to the displacement that can be applied to the adhesive before failure occurs [11,15]. More specifically, one can write [11]

$$\left(\frac{G_c}{Eh}\right)^{1/2} \approx \varepsilon_{\max} \tag{2}$$

where h is the layer thickness. For values of $G_c/E < h$, the peak stress is controlled by E and the energy of adhesion is determined mainly by G_c. The defects will propagate at the interface, and an adhesive failure occurs before an extensive deformation of the materials is possible. If G_c/E increases well beyond h, cavities propagate instead into the bulk, and a foam structure is formed as the walls between cavities are extended into fibrils. At larger strains, corresponding to the fibrillation regime, the behavior of the adhesive is dominated by a competition between viscoelastic extension and adhesive failure that causes the detachment of the feet of the walls between cavities from the substrate. In this case, the adhesion energy depends primarily on E and on the nonlinear elastic properties of the material, and it is much less sensitive to G_c.

To have a better understanding of the adhesive behavior, we try to estimate the quantity G_c/E for our systems. The elastic modulus E can be obtained from the rheology measurements. By using the simple relation between the frequency in a shear measurement, $\omega/2\pi$, and the strain rate, $\dot{\varepsilon}$, in a tack test, $\omega/2\pi = V_{\mathrm{deb}}/h_0(1+\varepsilon)$, where V_{deb} and h_0 are, respectively, the debonding speed and the initial thickness of the film, we find that the debonding velocity of $10\,\mu\mathrm{m/s}$ used in probe tests corresponds to shear frequencies between $\sim 0.1\,\mathrm{Hz}$ and $\sim 0.01\,\mathrm{Hz}$. From the values of the storage modulus, G′, at 0.1 Hz, we obtain $E = 0.04\,\mathrm{MPa}$ for the material A and $E = 0.06\,\mathrm{MPa}$ for B.

The determination of G_c is rather complex [11,22,26]. This parameter depends on the linear and nonlinear viscoelastic properties of the adhesive layer and on the frictional properties of the interface between the adhesive and the probe. However, to a first approximation, if an ideally elastic material is considered, its value is related to the thermodynamic work of adhesion, w, which describes the variation of free energy that occurs in the system when the probe–layer interface is replaced by two free surfaces. Thus, the surface energy of the probe plays an important role in defining G_c.

The surface energy of steel is rather high [27], $\gamma \sim 0.5\,\mathrm{J/m^2}$; thus we expect to be in a regime where the parameter G_c/E assumes larger values. When we introduce a gradient in the adhesive film by making a bilayer A + B where the majority component and backing layer A has a lower cross-linking density, we increase the adhesion energy by allowing a much higher extension of the fibrils, while we keep a higher peak stress due to the surface layer. Because we are not too sensitive to G_c, the decrease due to the more elastic B layer at the interface [see Eq. (1)] appears not to be detrimental, and the observed $\varepsilon_{\max}$ is the same for pure A and for A + B.

Instead, PE is a low-energy surface ($\gamma \sim 0.03\,\mathrm{J/m^2}$) [28], thus G_c/E is rather low, and the actual value of G_c becomes more important in determining the adhesion energy. In the bilayer B + A, the presence of a more dissipative layer in contact with the probe improves G_c and allows fibrillation to take place. The stress necessary for the extension of the fibrils is then mainly determined by the more cross-linked layer B and, as a result, the plateau stress is higher and the overall adhesion energy is higher than either pure adhesive.

It is interesting to note, however, that even though the measured values of $\varepsilon_{\max}$ are much higher than unity even on PE surfaces, the resistance to interfacial crack propagation, G_c, still plays a role in controlling the detachment of the fibrils on PE, but it does not on steel. This implies that the flow of elastic energy to the interface still has an influence on the propagation of fingers and cavities on PE surfaces.

Although this work demonstrates some interesting synergy effects, it leaves some open questions: Is there a minimal thickness of the top layer required to obtain this synergistic effect and in general, what is the effect of the relative thickness of the layers and of the absolute thickness? What is the role of the more or less dissipative layer during the fibril extension?

Several experiments are currently in progress to answer these questions and will be the object of a forthcoming publication. It is therefore difficult at this stage to speculate, but it is clear that a minimum thickness of the top layer is required to see an effect and that this minimum thickness depends on the difference in properties between the two layers. The effect of the overall thickness is complex, but generally speaking, thinner layers are less sensitive to interfacial fracture and more to bulk deformation because the driving force for crack propagation is the released elastic energy (proportional to thickness), whereas the dissipation resisting crack propagation is localized closer to the interface, as demonstrated by our experiments. This suggests that the optimum thickness ratio will depend on total thickness and on the properties of the individual layers.

CONCLUSIONS

To conclude, our results show that adhesive properties can be significantly modified by using bilayer systems and that the use of a gradient in composition is an interesting option to improve adhesion. The adhesion properties of the two layers are very important in determining the adhesion of the bilayer, and to enhance the adhesion, a very dissipative layer and a more elastic one are needed. The order of the layers plays an important role. On high-energy surfaces such as steel, the combination of dissipative (backing) + elastic (top) layer appears to increase the work of adhesion of the PSA: in this case, although we observe a liquid-like debonding, the mechanism is not cohesive, and the presence of the more elastic layer on the top avoids the transfer of the adhesive on the probe.

The opposite configuration, with the dissipative layer in contact with the adherent surface and the elastic one acting as a backing, gives better results on a low-energy surface such as PE, where the composition gradient in the film presumably increases G_c and allows the fibrillar structure to extend further, thereby improving considerably the adhesion.

On a more fundamental level, these results show that the dissipative part of the parameter G_c, which characterizes the resistance to crack propagation, extends well beyond the immediate vicinity of the interface for these highly viscoelastic layers.

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REFERENCES

[1] Creton, C., *MRS Bulletin* **28**, 434–439 (2003).

[2] Creton, C., Materials science of pressure-sensitive adhesives, in *Processing of Polymers*, H. E. H. Meijer (Ed.) (VCH, Weinheim, 1997), Vol. 18, pp. 707–741.

[3] Zosel, A., *Colloid Polym. Sci.* **263**, 541–553 (1985).

[4] Zosel, A., *Adv. Pressure Sensitive Adhes. Technol.* **1**, 92–127 (1992).

[5] Creton, C. and Fabre, P., Tack, in *The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius (Eds.) (Elsevier, Amsterdam, 2002), Vol. 1, pp. 535–576.

[6] Lakrout, H., Creton, C., Ahn, D., and Shull, K. R., *Macromolecules* **34**, 7448–7458 (2001).

[7] Krenceski, M. A., Johnson, J. F., and Temin, S. C., *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C26**, 143–182 (1986).

[8] Zosel, A., *Int. J. Adhes. Adh.* **18**, 265–271 (1998).

[9] Poivet, S., Nallet, F., Gay, C., Teisseire, J., and Fabre, P., *Eur. Phys. J. E* **15**, 97–116 (2004).

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

[11] Drzal, P. L. and Shull, K. R., *J. Adhes.* **81**, 397–415 (2005).

[12] Brown, K., Hooker, J. C., and Creton, C., *Macromol. Mat. Eng.* **287**, 163–179 (2002).

[13] Sosson, F., Chateauminois, A., and Creton, C., *J. Polym. Sci. B* **43**, 3316–3330 (2005).

[14] Shull, K. R. and Creton, C., *J. Polym. Sci. B* **42**, 4023–4043 (2004).

[15] Webber, R. E., Shull, K. R., Roos, A., and Creton, C., *Phys. Rev. E* **68**, 021805 (2003).

[16] Crosby, A. J., Shull, K. R., Lakrout, H., and Creton, C., *J. Appl. Phys.* **88**, 2956–2966 (2000).

[17] Josse, G., Sergot, P., Dorget, M., and Creton, C., *J. Adhes.* **80**, 87–118 (2004).

[18] Creton, C., Hooker, J. C., and Shull, K. R., *Langmuir* **17**, 4948–4954 (2001).

[19] Maugis, D. and Barquins, M., *J. Phys. D: Appl. Phys.* **11**, 1989–2023 (1978).

[20] Shull, K. R., Ahn, D., Chen, W. L., Mowery, C. L., and Crosby, A. J., *Macromol. Chem. Phys.* **199**, 489–511 (1998).

[21] Creton, C., Roos, A., and Chiche, A., Effect of the diblock content on the adhesive and deformation properties of PSAs based on styrenic block copolymers, in *Adhesion: Current Research and Applications*, W. G. Possart (Ed.) (Wiley-VCH, Weinheim, 2005), pp. 337–364.

[22] Léger, L. and Amouroux, N., *J. Adhes.* **81**, 1075–1099 (2005).

[23] Ahn, D. and Shull, K. R., *Langmuir* **14**, 3646–3654 (1998).

[24] Aradian, A., Raphael, E., and de Gennes, P. G., *Macromolecules* **35**, 4036–4043 (2002).

[25] Amouroux, N., Petit, J., and Léger, L., *Langmuir* **17**, 6510–6517 (2001).

[26] Zhang Newby, B. M. and Chaudhury, M. K., *Langmuir* **13**, 1805–1809 (1997).

[27] Israelachvili, J., *Intermolecular and Surface Forces* (Academic Press, London, 1992), p. 450.

[28] Fetters, L. J., Lohse, D. J., and Colby, R. H., Chain dimensions and entanglement spacings, in *Physical Properties of Polymers Handbook*, J. E. Mark (Ed.) (Americal Institute of Physics, New York, 1996), pp. 335–340.