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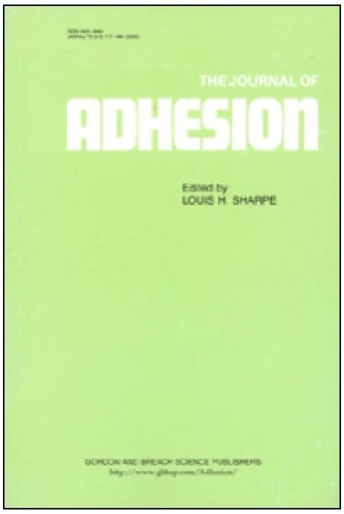

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Peeling of PSAs on Viscoelastic Substrates: A Failure Criterion

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Peeling of PSAs on Viscoelastic Substrates: A Failure Criterion

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This work deals with the study of the viscoelastic and adherence properties of pressure-sensitive adhesive (PSA) formulations dedicated to medical applications. We have developed a specific viscoelastic substrate to measure the adherence properties of PSAs that mimics adhesion on human skin. In the present article, we describe several experiments dedicated to a better understanding of adhesion on viscoelastic substrates without discussing specifically the case of human skin. In this way, we have studied different model adhesive formulations based on real medical formulations, and we have related the rheological behavior to the adherence properties obtained on different substrates to study the various specific effects due to the viscoelasticity of soft substrates. We propose from this study a failure criterion that allows one to derive a reasonable estimate of the peeling transition rate from cohesive to interfacial or stick–slip failure.

Keywords: Interfacial failure; Medical formulations; Peeling properties; Peeling transition; Pressure-sensitive adhesive; Rheological properties; Skin; Stick–slip; Viscoelastic substrate

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) have become familiar household and industrial adhesives. More precisely, hot-melt pressure-sensitive adhesives (HMPSAs), which exhibit variable adhesive strength from removable to permanent bonds obtained with double-side presentation, are widely used for label and tape applications [1]. It is well established, since the pioneering work of Gent and Petrich [2] and Kaelble [3] as well as more recent studies [4–6], that rheological behavior plays a major role in the adherence properties of systems using these types of adhesives. To establish a fundamental relationship between rheological properties and adherence properties, it seems important to select model polymers (*i.e.*, with a polydispersity index close to 1). In this case, the main relaxation domains are well separated, and it is possible to correlate viscoelastic properties with peeling data [4,7,8]. As the structure/rheological properties relationships are now well defined, it is possible to play with physicochemical parameters to improve the design of formulations as Marin and Derail have shown for model block copolymers [9–11]. We have shown how the pioneering vision of the diffusion and relaxation processes of flexible macromolecular chains initiated by de Gennes [12] has lead to very effective and predictive models of viscoelasticity of polymer melts [13], allowing one, as a consequence, to design new blends leading to better adherence properties [14]. However, it is important to state that such a direct correlation is relevant for high-energy surfaces and rigid elastic substrates as demonstrated in [8]. Indeed, the rheology/adherence relationship is more complex when dealing with viscoelastic substrates [15,16] because it depends on the substrate mechanical properties as well as the adhesive properties as shown, for instance, by Chivers, who compares the peel force measured with different backing materials [17]. Few references [18, for instance] deal specifically with this case, whereas it is particularly important for medical applications such as peeling on human skin, which is a viscoelastic substrate with highly variable properties depending on several parameters (gender, age, and site) that make comparisons difficult.

In this article, we present original peeling results obtained on a viscoelastic substrate (named synthetic substrate) exhibiting a rheological behavior close to the rheological behavior of the adhesive itself. It is important to notice that this synthetic substrate has been designed to mimic the adherence behavior on human skin (*in vivo* test on the forearm of different subjects). In subsequent papers, we will compare more specifically the adherence behavior obtained with medical formulations deposited on this synthetic film and/or on real skin. We have used, in the present work, adhesive formulations based on medical formulations containing a high content of hydrocolloid filler. This filler promotes the absorption of wound secretions as well as sweat, in order to maintain good adhesion of the dressing. Without these hydrocolloid fillers, a film of sweat will appear between the adhesive and the skin, rapidly producing poor adhesion.

We describe experimental results obtained on different substrates with various formulations and, as a consequence, derive a criterion regarding failure location. We conclude by proposing a failure transition diagram, which estimates the type of failure as a function of peeling rate (from cohesive failure to interfacial failure). We demonstrate, in particular, that the filler content within the adhesive formulation plays a major role.

MATERIALS AND METHOD

Adhesives

We have used model formulations based on polyIsobutylene blends with different molecular weights. For confidential reasons, we do not give the exact composition of the polymer base used. We particularly focus in this article on different formulations with a variable amount of hydrocolloid filler, an important component of medical PSAs. We demonstrate that these fillers play the same role as a regular filler component for the rheological behavior of filled polymers. We have reported in Table 1 the data describing the various formulations presented here. In this table, we indicate the polymer and filler contents. Notice that there are some more additives (named “other components”: plasticizer, oil, tackifying resin) that allow one to fine-tune the processing behavior and adhesion properties of the industrial adhesive.

TABLE 1 Data on Formulations

Sample	Polyisobutylene content (%) ($10^5 < M_w < 10^4$)	Filler content (%)	Other components (%)
I1	35	55	10
M1	90	0	10
M2	77	15	8
M3	63	30	6
M4	54	40	6
M5	45	50	5

Substrate

We have prepared a synthetic film based on a natural protein with appropriate ingredients to obtain a rheological behavior of the substrate close to the behavior of the adhesives themselves. This synthetic film could mimic the role of human skin. We focus on the rheological behavior of the synthetic film given in Figure 1. For the same reasons as for adhesive formulations, we do not detail the additives used for the preparation of this film. In the present article, however, we consider this synthetic film mainly as a model viscoelastic substrate that creates competition between the rheological behaviors of the adhesive and the substrate, and we focus on this competition. The substrate is a 1-mm-thick film, to stay close to the mechanical properties of human skin. Surface topography of real skin was mimicked by molding the film on an aluminum surface modified by chemical abrasion. Modifications in the formulation of the synthetic film (concentration of the matrix, quantity of plasticizers) allow one to obtain a very broad range of values for Young's modulus, which are close to the values reported in the literature for human skin [19]. If we assume a strong elongational deformation of the substrate during a peeling test, the reference value that we take into account will be Young's modulus, and we have reported the relevant data for skin and for the synthetic film used in Table 2.

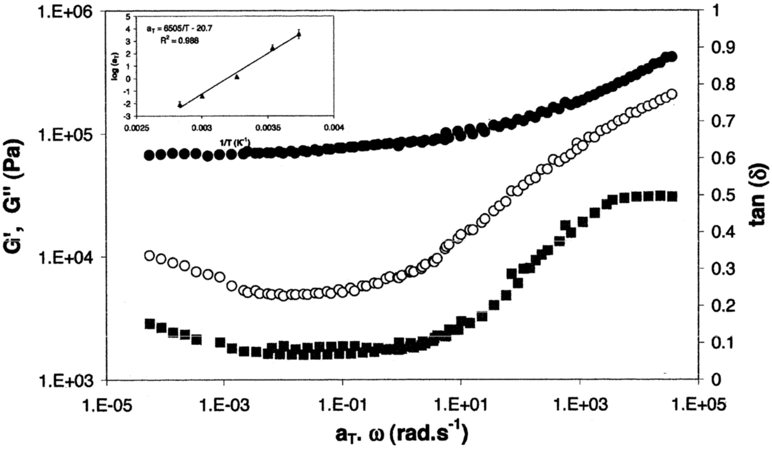

FIGURE 1 G′ (●), G″ (○), and tan δ (■) *versus* frequency for synthetic film ($T_{ref} = 33°C$) on a log–log scale. Insert graph exhibits a_T obtained to build the master curve versus 1/T.

TABLE 2 Young's Modulus and Interfacial Energy of the Synthetic Film Compared to Values Found in the Literature for Human Skin [19,20]

Substrate	Young modulus (Pa)	γ_s (mN.m^{-1})
Human skin prepared	2.10^4 to 1.10^8	25.3
Synthetic film	$\sim 3.10^5$	29

Peeling Experiments

The peel sample is based on an adhesive formulation applied to a film backing layer (flexible aluminum). Each strip is 1.5 cm wide, with a thickness of 1.5 mm. We have performed peeling experiments on the synthetic film to evaluate the adherence properties: the adhesive strip is stuck on the synthetic film and left in a ventilated oven at 33°C for 24 h. The sample is then attached to a peeling fixture under the following testing conditions: fixed peeling angle (180° or 90°), different peeling rates (ranging from 1 mm/min to 1000 mm/min) and various temperatures (ranging from -5°C to 33°C). We have also performed the usual peeling experiments using a floating roller test. The peeling angle is close to 90° in this case [4].

All peeling experiments were performed using an Alliance 50 N tensile machine (MTS, Paris, France).

Rheological Measurements

The rheological characterization of the adhesives and synthetic film has been carried out made by measuring the complex shear modulus as a function of frequency, ω, at various temperatures and in the linear domain. These mechanical spectroscopy experiments have been performed in the frequency range (10^{-2}–100 rad.s^{-1}) using a Rheometric RDA II or ARES rotational rheometer in a parallel-plate geometry (Rheometrics, New Castle, Delaware, USA). The time–temperature superposition principle can be used to plot a master curve leading to the relevant relaxation domains. The master curves are reported at a reference temperature $T_{ref} = 33$°C.

EXPERIMENTAL RESULTS

Rheological Behavior of the Synthetic Film and Adhesives

We have reported in Figure 1 the rheological master curve obtained for the synthetic film. The sample exhibits a viscoelastic solid behavior with a modulus of about 1×10^5 Pa at 10 rad.s^{-1}. Elasticity remains constant, as a first approximation, for about 5 decades of frequencies, whereas the loss angle, tan (δ), varies between 0.1 and 0.2 in the same frequency domain (from 10^{-4} to 10 rad.s^{-1}). The value of the elastic modulus of the substrate is close to the elastic moduli of the adhesives in the experimental frequency range. We have reported in Figure 2 the rheological behavior of these model formulations. For more clarity, we have focused on the variation of the storage modulus and plotted the whole data (G′ and G″) only for the blend with the higher filler content (M5). The formulations exhibit a viscoelastic liquid behavior even at high filler content (see M5, for instance), which explains the cohesive failure behavior observed at the lowest peeling rates as described in the next part.

The elastic modulus of the Mi formulations increases with filler content as shown in Figure 3. We have reported in this figure the variations of the elastic modulus of the formulations normalized with respect to the elastic modulus of the filler-free formulation, at a fixed frequency (10 rad.s^{-1}). The evolution can be described by a quadratic extension of Einstein's law at high filler contents [21,22].

Evolution of Peeling Properties as a Function of Peeling Rate for Mi Formulations

We recall that the extension of a debonding crack within an adhesively bonded assembly can usually be either cohesive (*i.e.*, within the bulk of

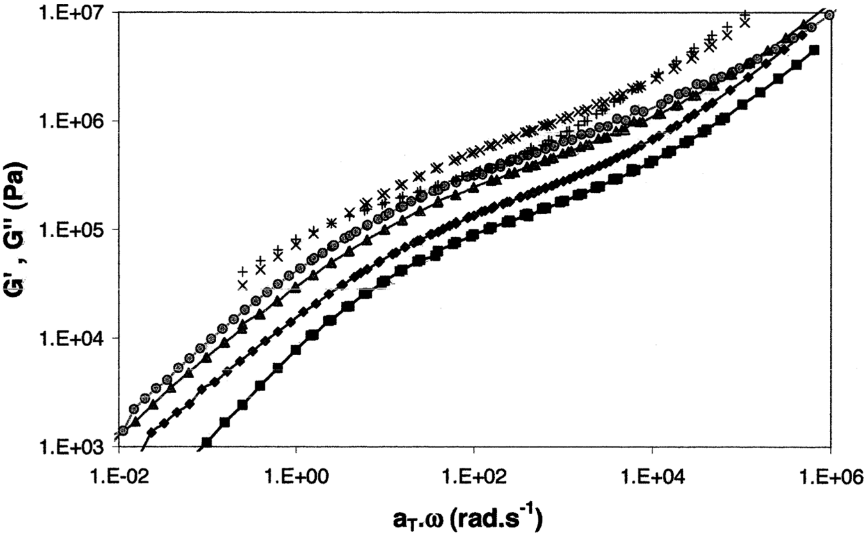

FIGURE 2 G′ (M1: ■; M2: ◆; M3: ▲; M4: ⊛; M5: ×) and G″ (M5: +) *versus* frequency ($T_{ref} = 33°C$) for model formulations on a log–log scale.

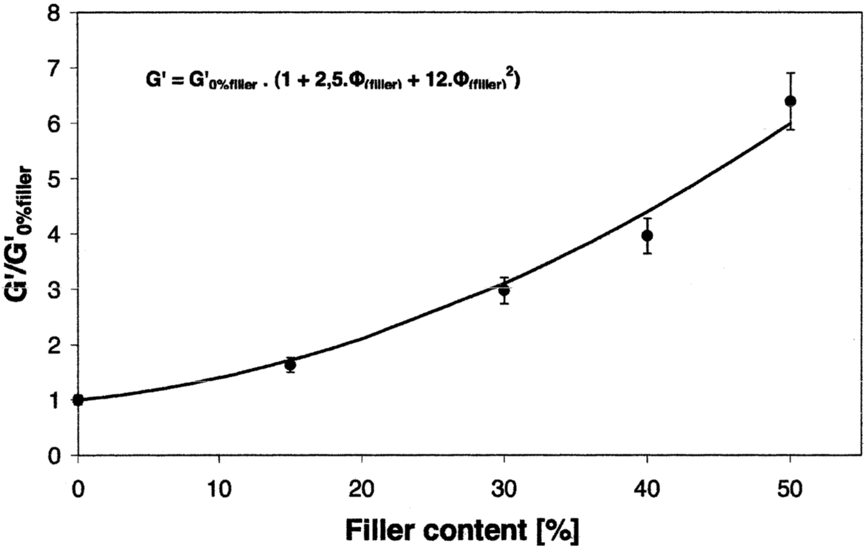

FIGURE 3 Evolution of the ratio between G′ of the different blends and G′ for the blend without filler, at a fixed frequency (10 rad.s^{-1}). The line is the result of Einstein's law.

the adhesive layer) or adhesive (interfacial, *i.e.*, along one of the two adhesive–substrate interfaces), or may present an unstable crack propagation called stick–slip; in that case, the peeling of the tape becomes jerky, with the emission of a characteristic noise [4]. On a usual representation of the peeling force *versus* removal rate for a PSA deposited on a rigid substrate, one can observe these three domains clearly. At low peeling rates, the force increases with increasing rate and generally may be fitted as a power law of the crack-propagation rate. In that case, the extension of the crack is cohesive. As the removal rate increases, changes occur in the debonding mode, and adhesive cracking appears: in the case of a rigid substrate, the adhesive generally follows the flexible support and the crack propagates at the adhesive–rigid substrate interface. At higher peeling rates, a complex and unstable phenomenon occurs, which is called stick–slip, where some adhesive residues are periodically left on one of the substrates. Finally, a brittle interfacial extension of the crack appears at the highest rates. In that case, however, the crack generally propagates at the flexible substrate–adhesive interface [2,4,6,7].

We have reported in Figure 4 the peeling experiment data for the Mi formulations deposited on the synthetic film. The same shift factor as for the rheological data presented in Figure 2 has been used for the peeling

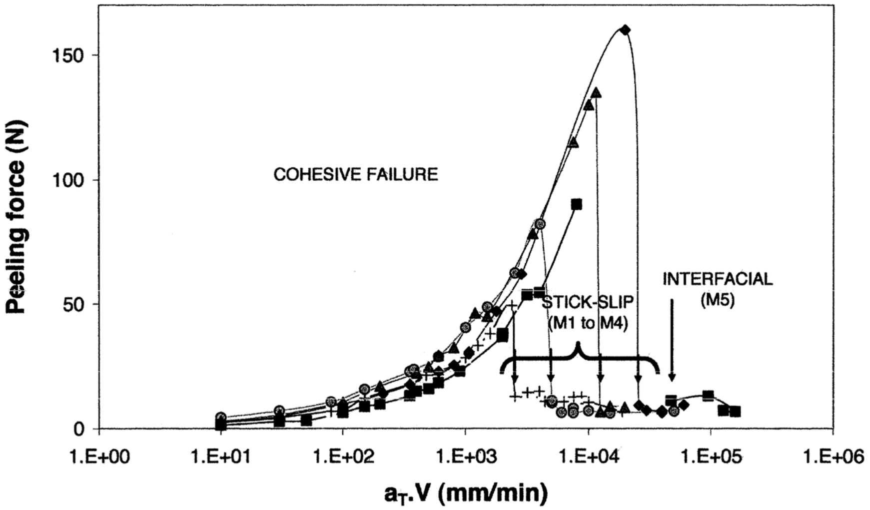

FIGURE 4 Peeling force *versus* peeling rate on a semilogarithm scale ($T_{ref} = 33°C$) for model formulations at a fixed peeling angle of 180°. M1: ■; M2: ◆; M3: ▲ M4: ⊛; M5: +.

master curve. One can notice that we indeed obtain master curves similar to those obtained for rigid substrates [4]. For the lowest peeling rates, one obtains also cohesive failure. At intermediate frequencies, one can observe for all formulations a transition to another type of failure, which may be different depending on the filler content. For the formulation with the highest filler content, we get a transition from cohesive failure to interfacial failure. For the other formulations, we have observed a transition from cohesive failure to stick–slip (*i.e.*, there is no interfacial domain). We have reported in the stick–slip case the average force between the F_{max} and F_{min} as presented before [4]. We have reported the variation of the peeling rate at the transition (from cohesive to interfacial or stick–slip domain) as a function of filler content in Figure 5. One can notice that when the hydrocolloid filler content increases (from 0% to 50%), the rate at the transition from cohesive to interfacial fracture or stick–slip decreases.

In the cohesive domain (before the transition), the peeling force increases slowly when the hydrocolloid filler content increases from 0% to 40% (for a given peeling rate), whereas the peeling force decreases for the highest content (M5, 50%). We clearly have a competition between dissipation and elasticity. One can expect that, as the elastic modulus of the adhesive increases with peeling rate, the fibrils that appear during cohesive failure break at a lower strain for higher

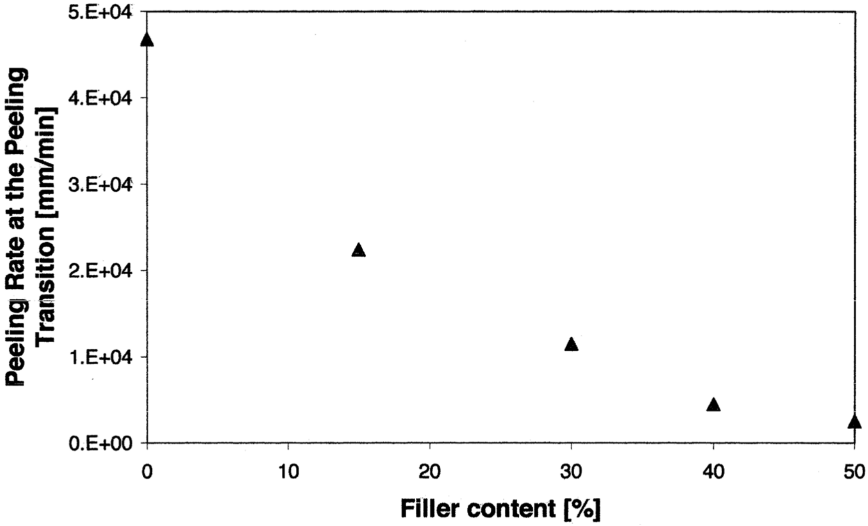

FIGURE 5 Evolution of the peeling rate at the cohesive-interfacial or stick–slip transition *versus* filler content.

peeling rates so the dissipated energy will be lower. At the same time, however, the peeling force to deform the adhesive is higher because the elastic modulus increases with filler content.

Finally, as this competition is also affected by the deformation of the substrate, it is difficult to give a clear explanation of the overall behavior. Hence, we have carried out peeling experiments on different systems to understand these features and, particularly, the transition from cohesive to interfacial fracture or stick–slip, as a function of filler content.

Peeling Properties as a Function of Peeling Rate on Different Systems

We have used a classical system (rigid aluminum–adhesive–flexible aluminum). By using formulation I1, which is close to M5 for the filler content but with a lower polymer content, one can observe in Figure 6 that we get the full range of peeling domains described previously [4]. We have performed similar tests with the viscoelastic substrate stuck on the rigid aluminum foil using a hard adhesive exhibiting negligible deformation. In this case, the viscoelastic film cannot be deformed during the peeling experiments. The data obtained with formulation I1 are reported in Figure 7. The results are close to the previous

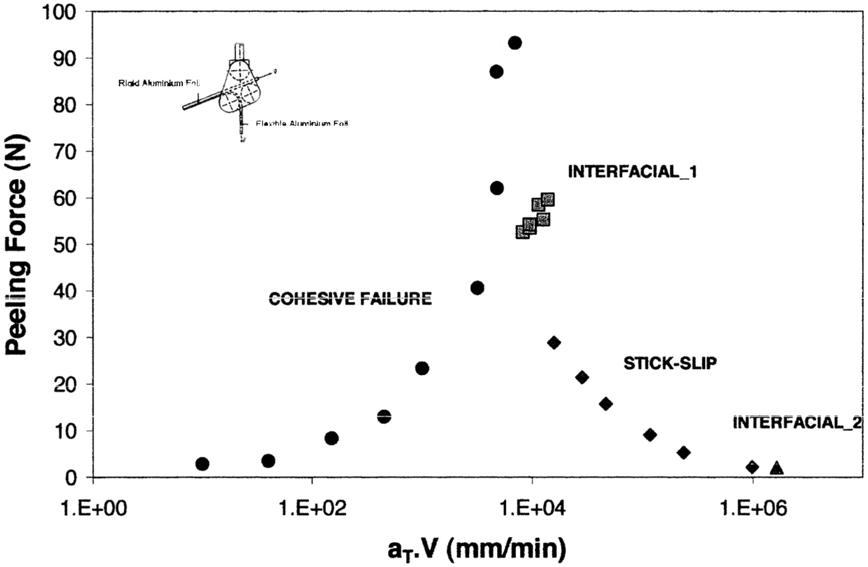

FIGURE 6 Peeling force *versus* peeling rate on a semilogarithm scale ($T_{ref} = 33°C$) for I1 formulation for rigid aluminum–adhesive–flexible aluminum and floating roller peel test.

system. Finally, we performed a peeling test at a fixed angle with the viscoelastic substrate free to deform during the peeling experiment. One can notice in Figure 8 that the results are different there. In particular, the interfacial failure domain has disappeared, and we only see the cohesive domain, the stick–slip domain, and the glassy domain at the highest peeling rate (or lowest temperatures).

DISCUSSION: A "FAILURE TRANSITION DIAGRAM" TO DESCRIBE THE FAILURE TYPE

When using model formulations such as Mi (Figure 4) and/or different systems with different nature of substrates (Figures 6–8), we have clearly shown that peeling properties are governed by the viscoelastic properties of the adhesive as well as the nature of the substrate. In the first case, we have modulated the viscoelastic behavior of the adhesive (for Mi formulations) deposited on the viscoelastic substrate; in the second case, we have changed the nature of the substrate with the same adhesive (I formulation). The transition between the cohesive domain and the interfacial or stick–slip domain depends on these

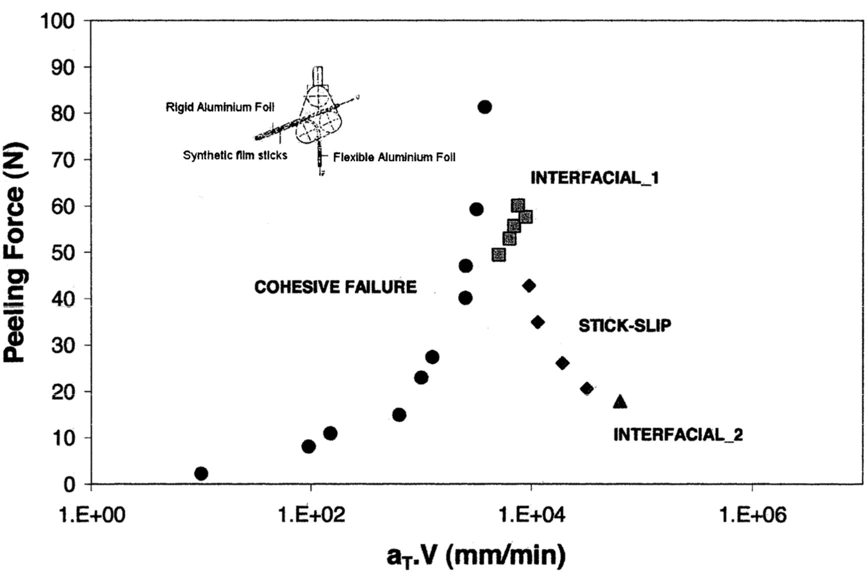

FIGURE 7 Peeling force *versus* peeling rate on a semilogarithm scale ($T_{ref} = 33°C$) for I1 formulation for rigid aluminum–viscoelastic substrate stuck on rigid substrate–adhesive–flexible aluminum and floating roller peel test.

changes. It is particularly interesting to notice that when the adhesive and the substrate exhibit similar types of viscoelastic behavior, one can observe the disappearance of the interfacial failure domain. In the case of model formulations deposited on a viscoelastic substrate, we have shown that the peeling interfacial domain disappears for the lower filler contents (M1 to M4); in the case of the I formulation, the peeling interfacial domain disappeared also when we used the viscoelastic substrate. We wished to demonstrate that the interfacial domain seems to disappear when there is a competition between the viscoelastic properties of the adhesive and the substrate. In this case, we have just observed a transition to a stick–slip domain. In other words, the interfacial domain appears when the substrate is rigid enough so that energy dissipation occurs mainly within the adhesive. In this way, we have built a failure transition diagram to estimate the type of transition obtained in the case of a viscoelastic substrate as a function of peeling rate. We are using here the results obtained with the Mi formulations (Figure 4). We have reported the value of the elastic moduli of the adhesive and synthetic film at the peeling transition on the vertical axis of Figure 9. We have estimated the

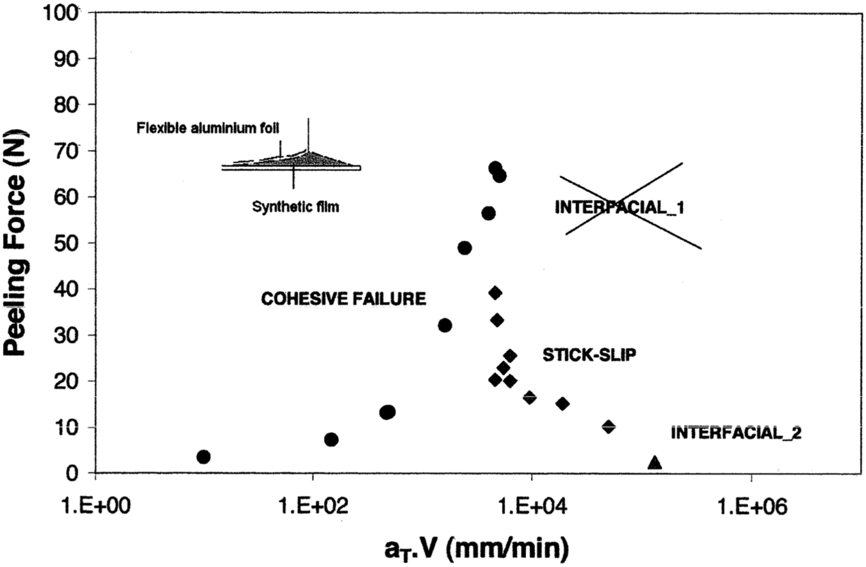

FIGURE 8 Peeling force *versus* peeling rate on a semilogarithm scale ($T_{ref} = 33°C$) for I1 formulation for viscoelastic substrate–adhesive–flexible aluminum and peeling test at fixed angle (90°).

frequency ($\omega_{\text{peeling transition}}$) corresponding to the peeling transition rate ($V_{\text{peeling transition}}$) as

$$\omega_{\text{peeling transition}} = \frac{V_{\text{peeling transition}}}{\text{thickness}_{\text{adhesive}}} \tag{1}$$

On the horizontal axis of Figure 9, we have reported the peeling transition rate (given by Figure 4), which depends on the filler content. We have represented these values with a standard deviation of 20% to take into account the errors in the real frequency applied on the adhesive and substrate. We have also reported on this graph the value of the elastic modulus of the viscoelastic substrate at the estimated transition frequency by using the same Eq. (1). We have also reported a standard deviation equal to 20% and so built a window for the estimated values. It is possible to differentiate between the two domains of transition on this failure transition diagram, which finally quantifies the competition between the viscoelastic properties of the adhesive and substrate. In the case where the elastic moduli of the adhesive and substrate are of the same order of magnitude, we obtain a transition from cohesive to stick–slip. In other cases, we obtain a transition from cohesive to interfacial, as discussed previously.

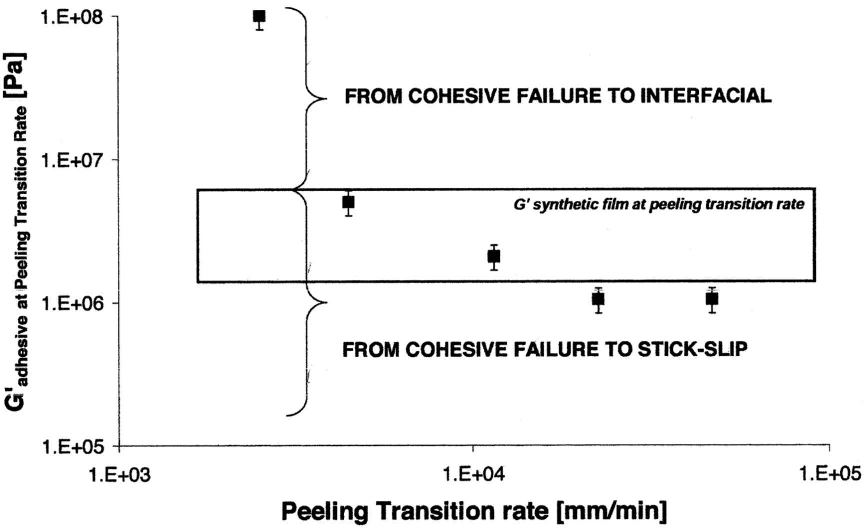

FIGURE 9 Transition diagram: G′ of the adhesive at the characteristic frequency obtained from Eq. (1) as a function of peeling transition rate. Comparison with the G′ values of the synthetic film at the same frequencies represented by the rectangle. The different domains describe the nature of the transition in the peeling experiments.

CONCLUSION

To better control adhesion on human skin for medical applications, one has to understand the adhesion mechanisms and especially identify the relative contribution of each element of the system in a peel experiment. In the present case, an adhesive tape is stuck on a viscoelastic substrate, which may mimic the properties of human skin. All the experimental results presented have been discussed to understand the competition between the deformation of the adhesive and the adherend, the effects on the failure location, and the relative level of the peeling force. We have shown with different systems that the deformation of the substrate causes important differences in the peeling behavior. Particularly, we have shown that the transition between the failure domains is partially governed by the competition between the viscoelastic behaviors of the adhesive and the substrate.

Finally, we have established a relationship between the rheological behavior of the adhesive and the rheological behavior of the substrate and we have proposed that this competition could be described in a failure transition diagram. This last point has to be confirmed on various substrates exhibiting different types of viscoelastic behavior.

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