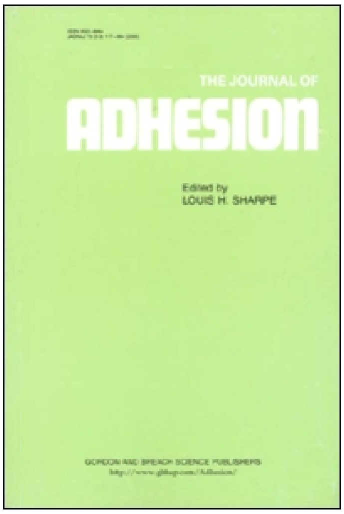

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Rheology and Adherence of Pressure-Sensitive Adhesives

G. Marin[a]; C. Derail[a]
[a] Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067, Université de Pau et des Pays de l'Adour, Pau, France

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Rheology and Adherence of Pressure-Sensitive Adhesives

G. Marin
C. Derail
Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067,
Université de Pau et des Pays de l'Adour, Pau, France

We have studied the relationship between rheological and peeling properties for hot-melt pressure-sensitive adhesives based on homopolymers or copolymers blended with tackifying resins. In this article, we particularly try to demonstrate that it is possible to define a quantitative link between rheology and adherence when the model formulations are deposited on substrates with strong (thermodynamic) adhesion. We describe the experimental results obtained on these model formulations and discuss the quantitative relationships obtained. In the case of "adhesion modulation" (derived from different treatments of the substrates), we show that the relationships become much more complicated, even with the same model adhesives. At the end, we discuss on the competition between adhesion and dissipation in the case of poor adhesion.

Keywords: Block copolymers; Homopolymers; Hot-melt pressure-sensitive adhesive; Master curve; Noise; Peeling properties; Pressure-sensitive adhesive; Rheological properties; Stick–slip; Tape; Terminal relaxation time; Time–temperature equivalence

INTRODUCTION

Since the pioneering work of Kaelble [1] and Gent and Petrich [2], it has been confirmed that there is a strong link between rheological behavior and adherence properties particularly for soft adhesives presenting high adhesion with a solid surface [3–5] or a flexible surface [6].

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Address correspondence to Gérard Marin, Laboratoire de Physico-Chimie des Polymères, UMR-CNRS 5067, Université de Pau et des Pays de l'Adour, BP 1155, F-64013 Pau, France.

Pressure sensitive adhesives (PSAs) or hot-melt pressure-sensitive adhesives (HMPSAs) are typical examples of such materials. Basically made from a blend of a polymer(s) base, tackifying resin(s), and other components (oil, fillers, antioxidants), the final formulation dedicated to a given application remains mainly empirical because it is difficult to establish quantitative relations that take into account both type of properties governing adherence properties [7]: surface properties (interfacial energy, roughness) and rheological properties of the adhesive (energy dissipation). It is important to recall that the rheological and adherence master curves can be built with the same time–temperature shift factors in the present case (high adhesion, high dissipation); more precisely, Derail *et al.* [3] have shown that the relaxation time of the terminal relaxation domain is the relevant parameter to establish a quantitative relation in the cohesive domain for peeling properties. This quantitative relation has been demonstrated for model adhesives [3] and has been confirmed recently for different systems [5,8].

Several authors [9–12] have recently reported that the rheological behavior of copolymer-based adhesives presents a strong link with adherence properties. In the case of PSAs based on EVA (polyethylene vinyl acetate) random copolymers, Gibert *et al.* [9] have demonstrated that the cohesive-to-interfacial transition observed on a peeling curve appeared at the same time (crystallization time) as the liquid-like to solid-like transition induced by crystallization of the EVA. In the case of HMPSAs based on block copolymers (styrene–isoprene type), one can demonstrate that the ratio between the triblock and diblock copolymers is a key parameter to control their rheological behavior [10,11] and, consequently, their tack properties [12]. For pure diblock systems, it has been shown that the cubic ordered phase seems to give better tack and adherence properties [13,14].

It is possible to describe the rheological behavior of these systems through molecular models derived from the reptation concept of de Gennes [15]; this predictive approach leads directly to macromolecular design of polymers dedicated to adhesive formulation. Hence, it is possible to synthetize new copolymers [16] that would mimic the rheological behavior of copolymer blends and allow formulators to simplify existing full formulations by decreasing the number of components, for example. In these systems based on block copolymers, the organized phase is responsible for the solid-like behavior of the material, which is a key parameter for nonflow of the adhesive at long times (shear/creep behavior improvement).

However, it is important to point out that even if (i) linear viscoelastic properties are relevant to adherence control, the understanding of adherence and adhesion depends also on (ii) nonlinear rheological properties [12,17,18] when large deformations are involved and (iii) the physical way stresses are transmitted between the adhesive and the substrate.

In this article, we focus on the relation between adherence and rheological behavior for model adhesives based on homopolymers or copolymers blended with one or two tackifying resins. We demonstrate that it is possible to define a quantitative link between rheology and adherence when a strong (thermodynamic) adhesion is present. The relationship is much more complicated in the case of adhesion modulation, *i.e.*, in the case of competition between adhesion and dissipation (poor adhesion).

In the first part we recall some important results regarding quantitative relations between rheological properties and peeling behavior. In the second part we give an example of an application of this quantitative approach: it is possible to eliminate the "noise" during peeling by playing with the formulation, with a quantitative result in the case of strong adhesion and interesting qualitative trends in the case of peeling on a nonadhesive (release) substrate.

EXPERIMENTAL

Adhesives

The homopolymers are quasi-monodisperse anionic polybutadiene samples synthetized by the Michelin Company (Clermond-Ferrand, France), blended with a Dertophene T® terpene-phenolic tackifying resin manufactured by DRT (Dax, France). The copolymers are commercial triblock Vector® grades (V4111 and V4113) provided by ExxonMobil Chemical (Houston, TX, USA) blended with different commercial tackifying Escorez® 2203 and/or ECR® 185 resins from ExxonMobil Chemical (Houston, TX, USA) and/or Wingtack® 10 resin from the Chemical Division of the Goodyear Tire and Rubber Company (Akron, OH, USA). The characteristics of the samples and formulations are shown in Table 1. In the case of the copolymer-based formulations, the aliphatic resins are typically compatible only with the elastomeric part (polyisoprene part) [10].

Rheological Experiments

Measurement of complex shear modulus (G′, storage modulus, and G″, loss modulus) as a function of circular frequency, ω, has been performed at various temperatures in the linear domain, in the

TABLE 1 Characteristic Parameters of the Different Components of the Formulations

Name	Polymer or copolymer	Resins
B1_ratio (B1/Resin1)	Polybutadiene (denoted B1) $M_w = 150\ 000\,\mathrm{g \cdot mol^{-1}}$	Dertophene T (denoted Resin1) $T_g = +38^\circ\mathrm{C}$
B2_ratio (B2/Resin1)	Polybutadiene (denoted B2) $M_w = 65\ 000\,\mathrm{g \cdot mol^{-1}}$	Dertophene T (denoted Resin1) $T_g = +38^\circ\mathrm{C}$
SIS + SI_ratio (SIS + SI/Resin2/Resin3)	SIS V4113 $M_w = 154\ 000\,\mathrm{g \cdot mol^{-1}}$ $\%S = 15\%$	Escorez 1310 (denoted Resin2) $Tg = +47^\circ\mathrm{C}$ Wingtack 10 (denoted Resin3) $Tg = -27^\circ\mathrm{C}$
SIS_1_ratio (SIS/Resin4)	SIS V4111 (denoted pure SIS) $M_w = 118\ 000\,\mathrm{g \cdot mol^{-1}}$ $\%S = 18.2\%$	Escorez 2203 (denoted Resin4) $T_g = +47^\circ\mathrm{C}$
SIS_2_ratio (SIS/Resin5)	SIS V4111	Escorez 185 (denoted Resin5) $T_g = +7.5^\circ\mathrm{C}$

Ratio–Volume Fraction in the Blend

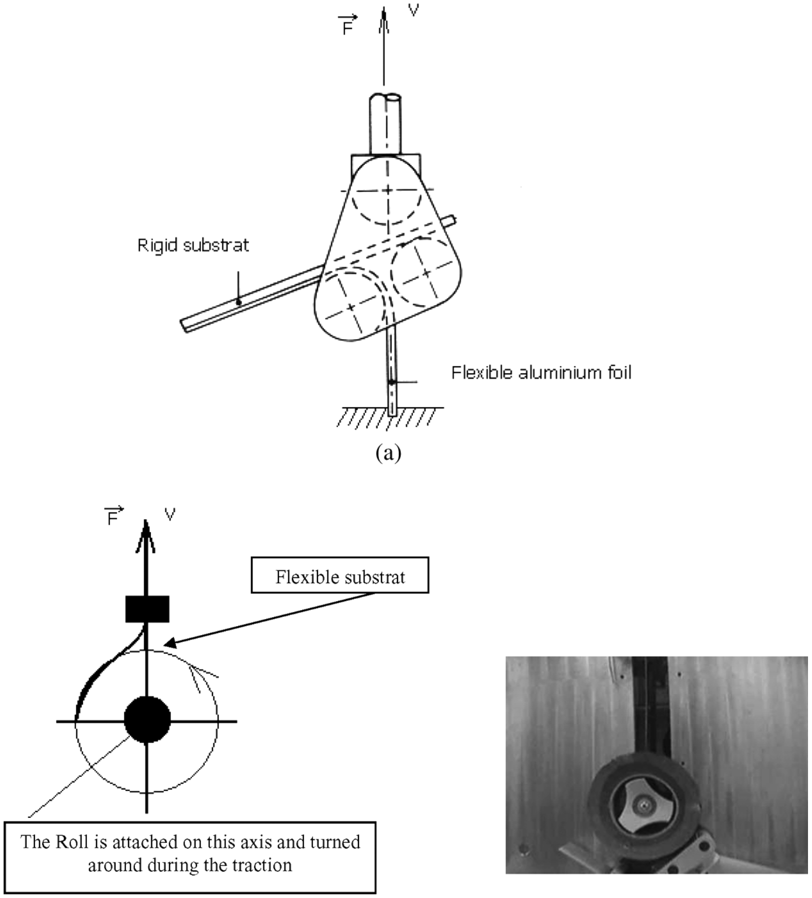
frequency range 10^{-2} to $100\,\mathrm{rad \cdot s^{-1}}$, using different rotational rheometers in different geometries (parallel plates, cone-plate, rectangular torsion). The time–temperature superposition principle applies as a first approximation and has been used to build the master curve at room temperature. For the block copolymers, the reference temperature must be chosen according to the order–order or order–disorder temperatures [19].

All the rheological results presented in this article have been performed in the linear domain determined by a strain sweep.

Peeling Experiments

All isothermal peeling experiments were performed on a tensile machine (Adamel Lhomargy, DY30, Roissifen Brie, France) by measuring the peeling force as a function of peeling rate at various temperatures ranging from −50 to 100°C. Two different geometries (Figure 1) for peeling tests were used:

1. *Floating rollers peel test (ASTM D 3167-76)*: In this case, we have used sandwich-type probes made of three parts. The adhesive part



(a)

(b)

FIGURE 1 Peeling experiments using a floating roller test (a) or directly on an adhesive roll (b).

is pressed between a flexible aluminium foil (104 μm) cleaned with acetone and a rigid aluminium one (2 mm), which was sanded in a controlled way.

2. *Peeling on a roll of adhesive*: we have directly installed a roll of adhesive on the tensile machine as presented in Figure 1. In this case, the geometry is not well defined, but it is possible to work directly on the tape used by the consumer. It is possible to modify the nature of the surface by an antiadhesive treatment, which changes the adhesion properties of the substrate.

RESULTS AND DISCUSSION

We recall results obtained on model adhesives based on homopolymers and detail original results for formulations based on copolymers and resins.

Blends Based on Homopolymer and Resin: Important Features

It is now well accepted that it is possible to apply time–temperature equivalence on experimental peeling results in the same way as for rheological properties. As the first approximation, the shift factors are the same in both cases (Figures 2 and 3) [3]. This description remains qualitative. It is possible to define quantitative relations in studying the cohesive fracture domain of the peeling curve. In Figure 4a one can observe the variation of the peeling force as a function of peeling rate for different blends based on B1 and B2 homopolymers (see Table 1). One can notice the effects of the polymer/resin ratio and of the effect of the molecular weight of the polymer (B1 or B2):

1. For the same peeling rate, one can observe that the peeling force increases when the resin volume fraction increases in the blend (B1-based blends). In this case, the evolution of the peeling force is a function of the topological and thermodynamical effects of the resin, which are well described elsewhere [3].
2. When B2 is used (M_w B2 $<$ M_w B1), one can observe a decrease of the peeling force at same resin volume fraction.

In the terminal region of relaxation of the rheological behavior (low frequencies), it has already been shown that it is possible to build a master curve independent of molecular weight and polymer volume fraction [3, 20]. In this way, one can notice on Figure 4b that the terminal relaxation time, denoted τ_0, is a reducing parameter for the peeling curves in the cohesive peeling domain. We recall that the terminal relaxation time is given by:

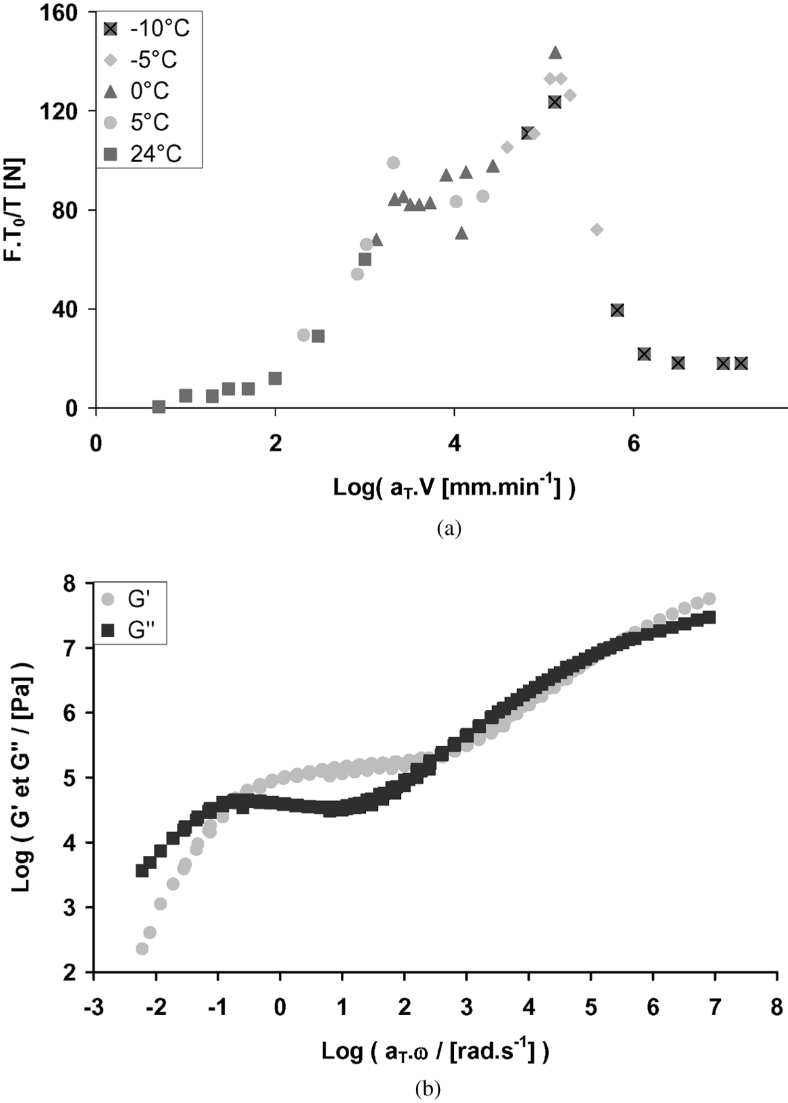
$$\tau_0 = \eta_0 \cdot J_e^0, \tag{1}$$

where η_0 is the zero-shear viscosity:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{2}$$

and J_e^0 the recoverable compliance:

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2}. \tag{3}$$



(a)

(b)

FIGURE 2 Master curves at $T_{\text{ref}} = 20^\circ\text{C}$ for B1_(35/65): (a) peeling force *versus* peeling rate, and (b) G′ (elastic modulus) and G″ (loss modulus) *versus* frequency.

One can determine these parameters, at T_{ref}, on the rheological master curve of each blend. The values of τ_0 are reported in Table 2.

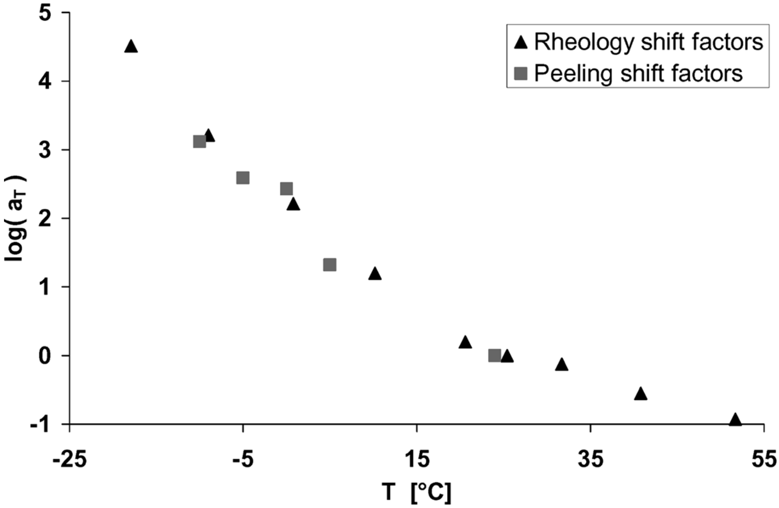


FIGURE 3 Comparison of time–temperature shift factors derived from peeling and rheological experiments.

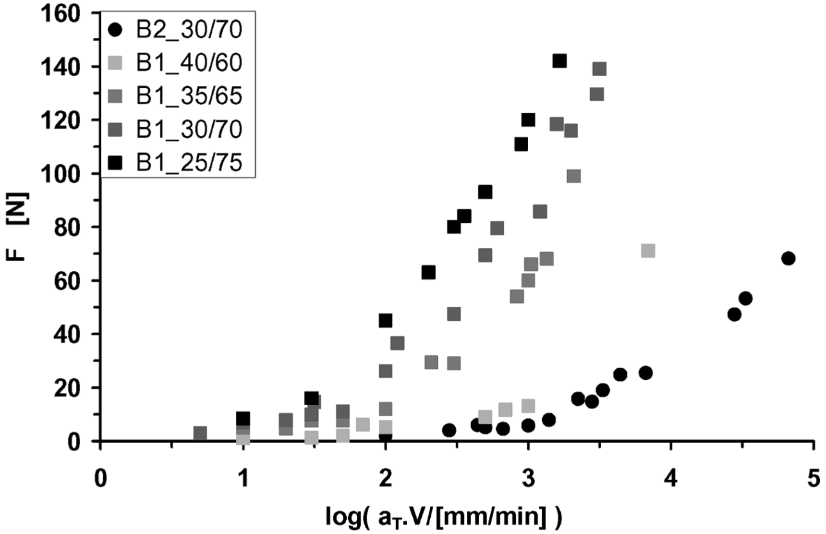
As far as peeling properties are concerned in the cohesive fracture domain, one can extend the time–temperature equivalence to time–molecular weight or time–concentration equivalence as presented in Ref. 21. This feature has been recently confirmed on different PSAs based on acrylic or acrylate polymers [5,8].

Application to the Copolymer Formulations

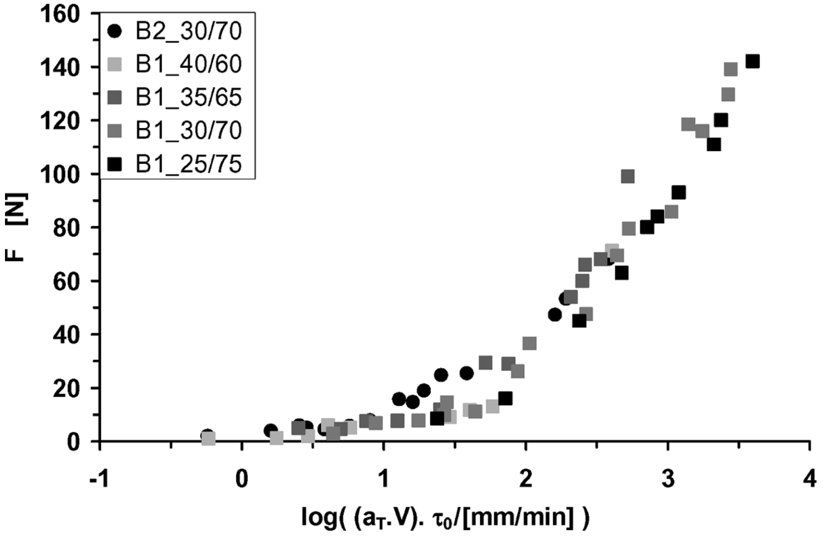
We have extended the relations established previously on model formulations to commercial-type HMPSA formulations based on a blend of block copolymers (triblock + diblock) and two tackifying resins and on a simplified formulation based on a triblock copolymer and a single tackifying resin. The rheological behavior of this type of block copolymers is well described elsewhere [10,11,16].

Commercial Copolymer-Based Adhesive

We have performed some peeling experiments on a typical formulation based on a blend of block copolymers (V4113–triblock [SIS] and diblock [SI]). In this case, the adhesive exhibits a solid-like viscoelastic behavior as can be observed on the rheological master curve in Figure 5. According to the previous description (the case of EVA), it is impossible to reach the cohesive fracture domain on this system



(a)



(b)

FIGURE 4 Cohesive fracture domain for formulations based on B1 polymer (25 to 40/75 to 60) and B2 polymer (30/70) ($T_{\mathrm{ref}} = 20°\mathrm{C}$): (a) peeling force *versus* peeling rate, and (b) peeling force *versus* reduced peeling rate (peeling rate × terminal relaxation time).

TABLE 2 Values of Relaxation Time (T = 20°C) for Each Blend Based on B1 and B2 Homopolymers

Blend	Relaxation time τ_0 (min)
B1_25/75	2.38
B1_30/70	0.88
B1_35/65	0.25
B1_40/60	0.058
B2_30/70	0.0057

(no flow region). We have compared the signature obtained on the tensile machine and the rheological behavior at the same temperature. We have represented in Figure 5 the rheological behavior at different temperatures and the corresponding peeling curves. The terminal domain of relaxation corresponds to an interfacial fracture with a crack localized between the adhesive and the rigid substrate. In the intermediate domain (transition region), one can observe a stick–slip behavior and, finally, at very low temperatures, the crack is localized between the adhesive and the flexible substrate with a very low peeling force. One can conclude that the propagation of the crack, as well as the value of the peeling force, depends largely on the rheological behavior of the adhesive, which is itself linked to the temperature and/or the peeling rate.

Model Copolymer-Based Adhesive

The aim of this section is to describe the relationship between rheological properties and peeling properties in the vicinity of the interfacial fracture and stick–slip transition where adhesion properties are very important. We have used a pure triblock copolymer, which has been independently formulated with two tackifying resins that have different glass-transition temperatures (see Table 1).

The pure [SIS] triblock exhibits a solid-like viscoelastic behavior (Figure 6). Let us recall that (i) these copolymers are organized according to a phase diagram depending on the length and type of monomer of each block [19], (ii) the polystyrene part plays the same role as a filler for the elastomeric part (polyisoprene), and (iii) the α transition exhibited on the master curve (Figure 6) is, as a first approximation, very close to what is observed for the polyisoprene block [10]. One can notice in the same figure the effects of the tackifying resins on the rheological behavior of the pure triblock. The volume fraction of the resin is the same for the two blends (50/50). One can observe that the topological effect (level of plateau modulus, shape of the curves)

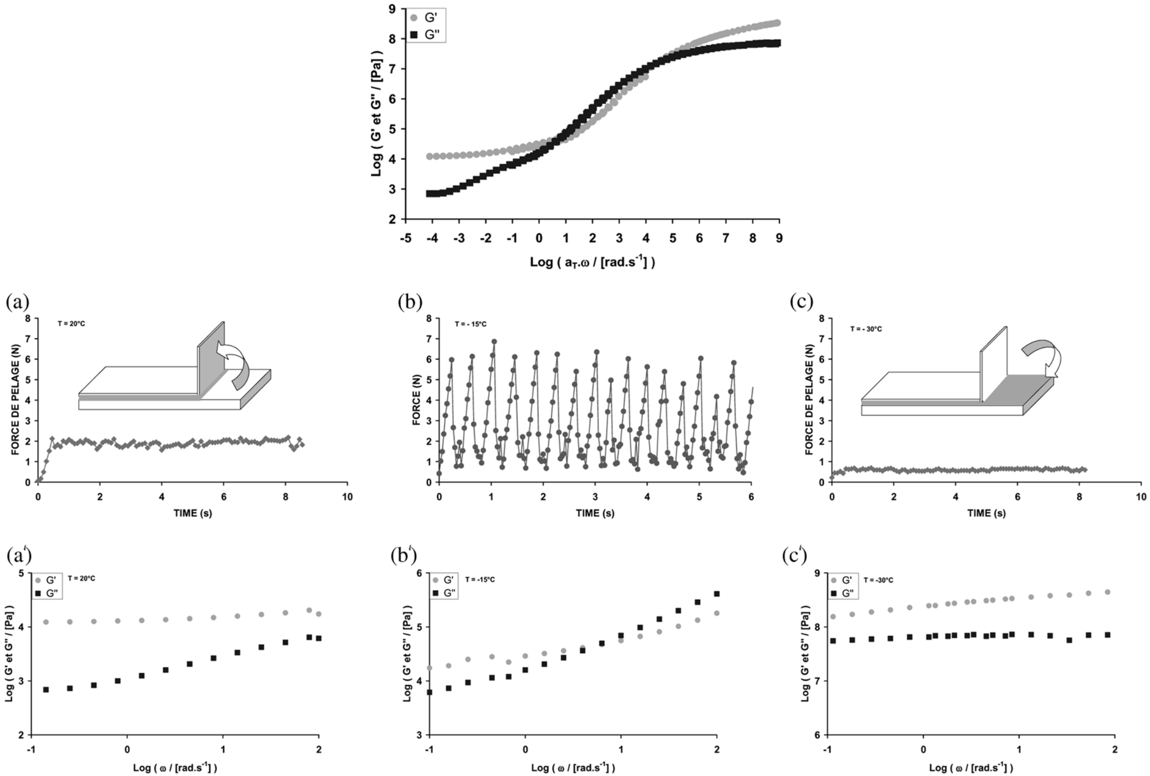


FIGURE 5 G′, G″ *versus* frequency for SIS + SI_31/42/27 ($T_{\mathrm{ref}} = 20°\mathrm{C}$) and peeling curves measured on the tensile machine at various temperatures: (a) terminal domain (rubbery plateau) (20°C); (a′) adhesive fracture (20°C); (b) transition region (alpha region) (−15°C); (b′) stick–slip (−15°C); (c) glassy domain (−30°C); and (c′) glassy fracture (−30°C).

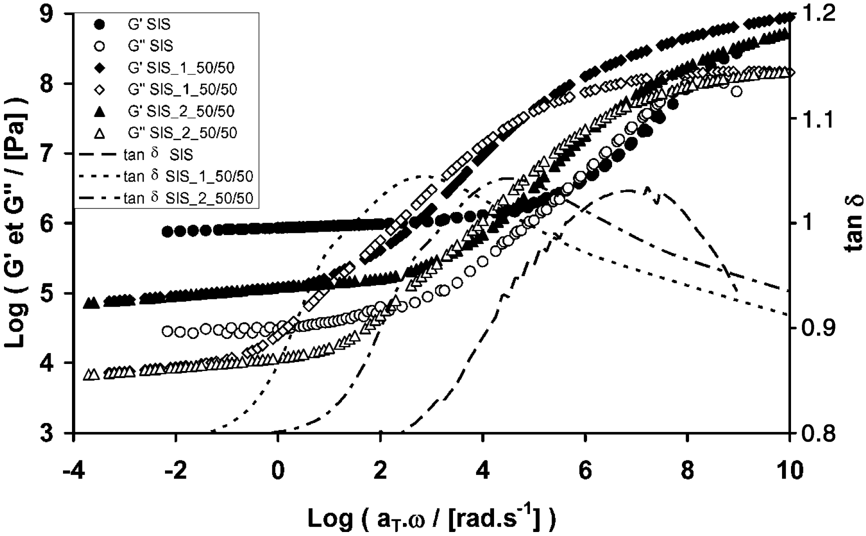


FIGURE 6 G′ and G″ and tan δ *versus* frequency for SIS and SIS_1_50/50 and SIS_1_50/50 at $T_{\mathrm{ref}} = 20°\mathrm{C}$.

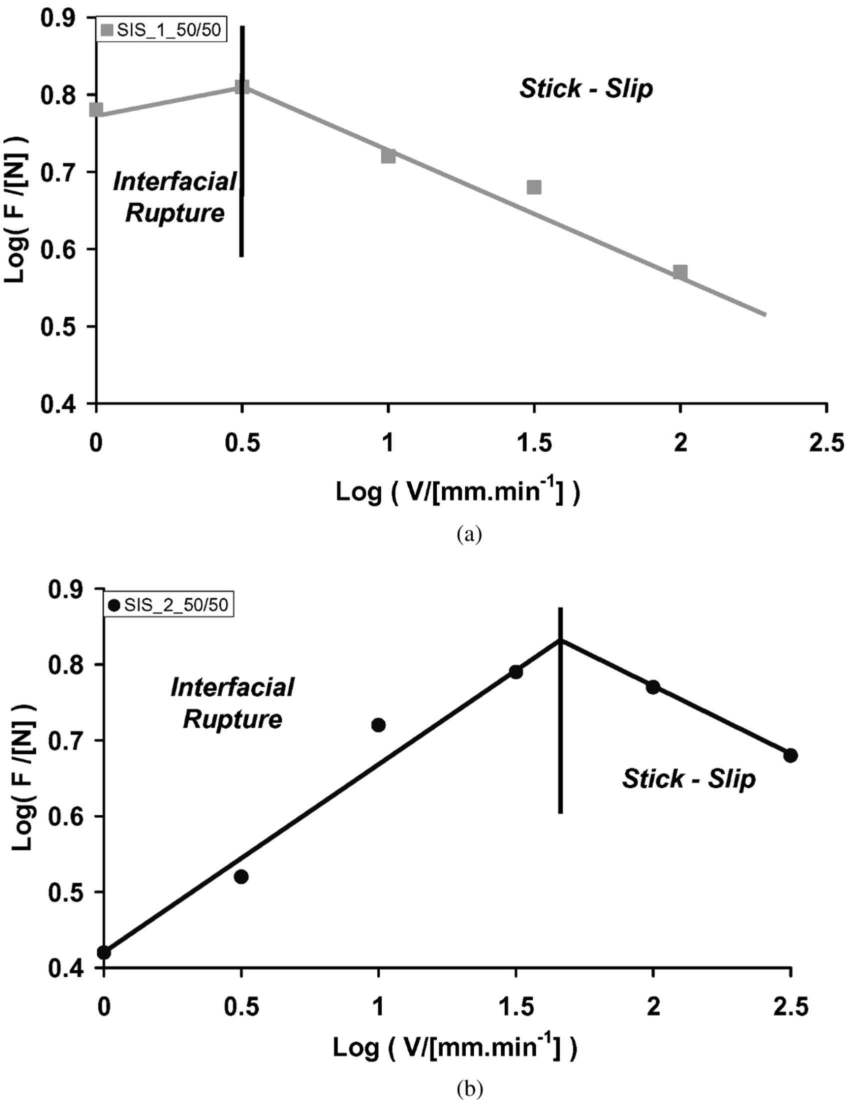
is exactly the same for the two resins. Indeed, these tackifying resins swell only the entanglement network of the elastomeric part. The resin acts like a solvent on the isoprene part of the copolymer [10], and this effect can be described, independently of the nature of the resin, by the power law:

$$G_{\mathrm{n}}^{0}(\mathrm{blend}) = G_{\mathrm{n}}^{0}(\mathrm{copolymer}) \cdot \Phi^{2}, \tag{4}$$

where G_{n}^{0} (blend) and G_{n}^{0} (copolymer) are, respectively, the rubbery plateau for the full formulation and for the pure copolymer, and Φ is the volume fraction of the elastomer part in the block copolymer within the formulation.

The thermodynamical effect (antiplasticizing effect: shift of T_{g}) can be also observed in Figure 6. The master curves of the formulations are horizontally shifted to lower frequencies. The frequency range of the α relaxation (glass transition) is higher for the formulation based on Resin5 (SIS_2_50/50) than the formulation based on Resin4 (SIS_1_50/50) because the glass-transition temperature of Resin5 is lower than the glass-transition temperature of the Resin4 (T_{g} Resin5 < T_{g} Resin4).

We have performed peeling experiments with these adhesives by using the roll test. The adhesive is deposited on a classical substrate



(a)

(b)

FIGURE 7 Peeling force *versus* peeling rate (double logarithmic scale): (a) SIS_1_50/50, and (b) SIS_2_50/50.

used for tape application. One can observe (Figure 7) that there is a shift of the transition between interfacial fracture and stick–slip between the two formulations. The transition peeling rate is higher for the formulation based on Resin5 (SIS_2_50/50) than for the

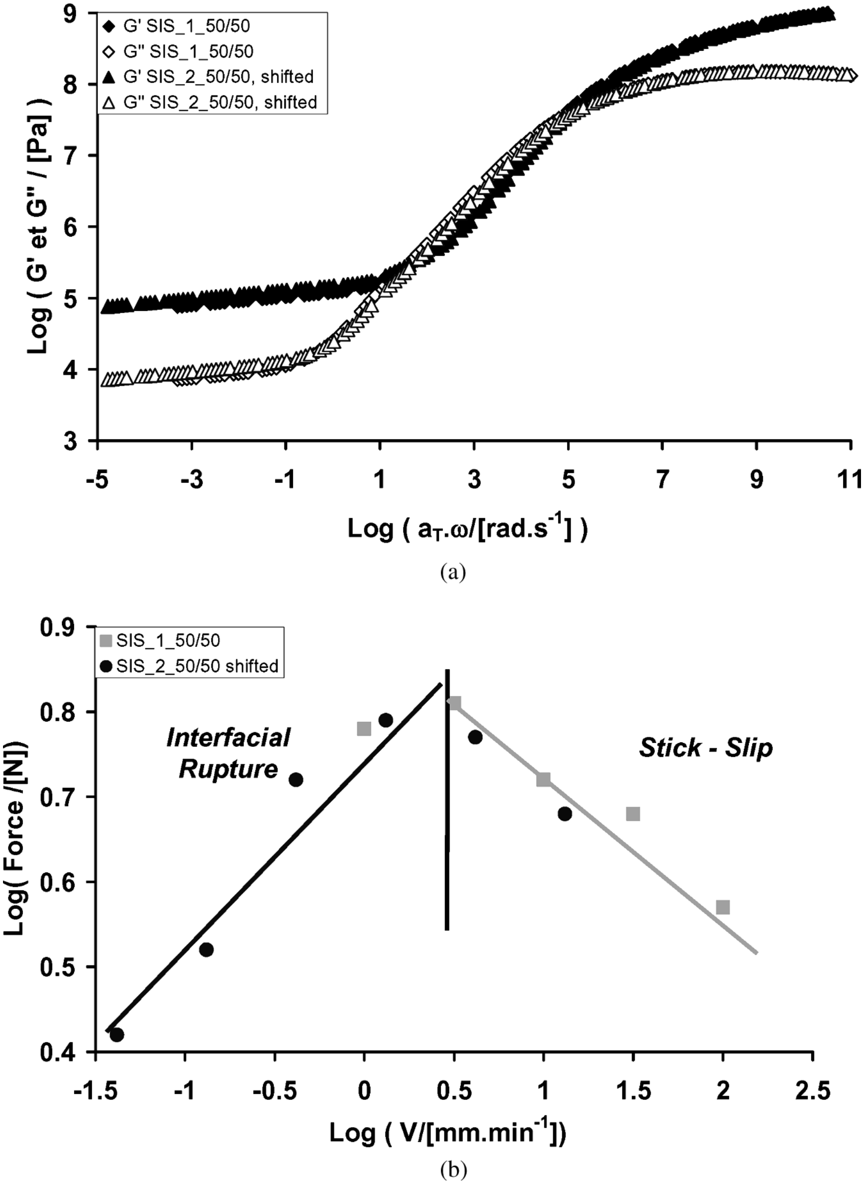
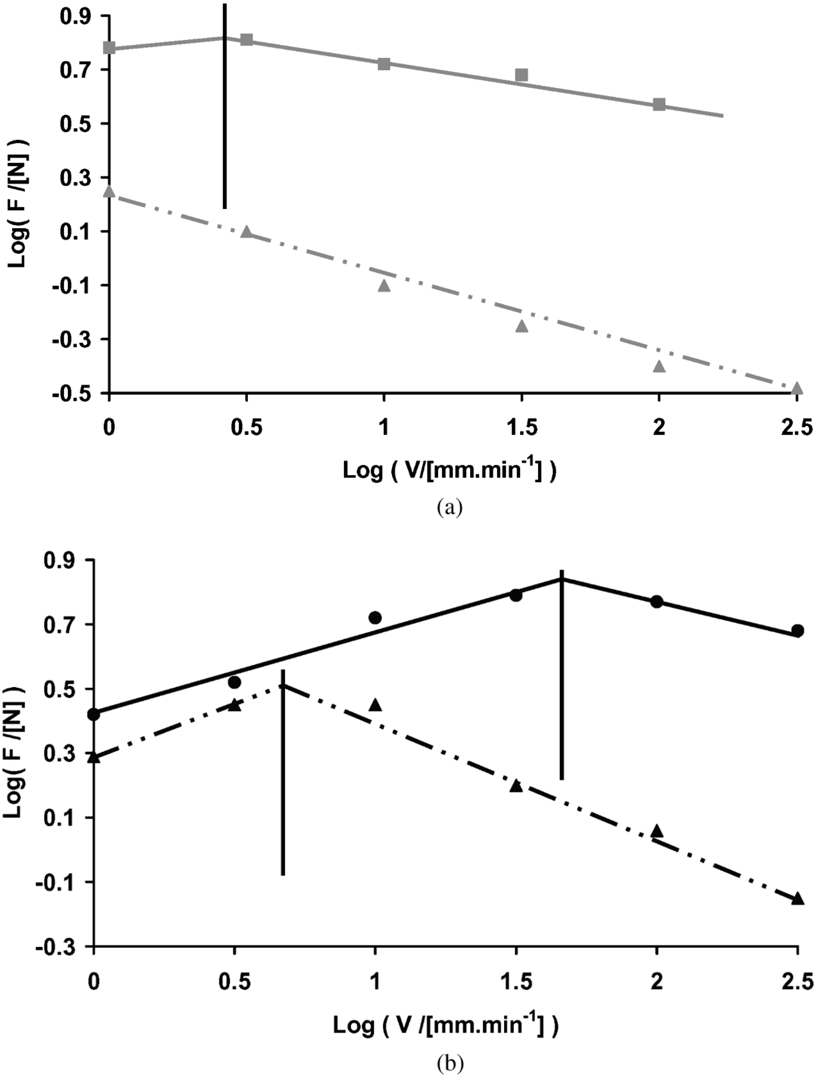


FIGURE 8 Superimposition for the rheological master curve (a) and peeling master curve (b) for SIS formulations (same horizontal shift for rheological and peeling properties of SIS_2_50/50).



(a)

(b)

FIGURE 9 Peeling force *versus* peeling rate (double logarithmic scale): (a) SIS_1_50/50 on two different substrates (full line: substrate without treatment, broken line: substrate with treatment); and (b) SIS_2_50/50 on two different substrates (full line: substrate without treatment, broken line: substrate with treatment).

formulation based on Resin4 (SIS_1_50/50). Moreover, it seems that it is possible to build a master curve by shifting the two curves.

In Figure 8 we show that one can obtain a master curve by shifting one curve onto the other. We have applied exactly the same horizontal shift, equal to about 30 for these systems, on the rheological master curve, and we notice also a good superimposition in the same way as for peeling properties.

As a first approximation, this original feature shows that when there is an aggressive adhesion between adhesive and substrates, the rheological behavior of the adhesive governs the peeling properties to a large extent. These results confirm the results obtained on model adhesives and on EVA-based PSAs [3,9].

This quantitative approach of predictive formulation is, however, limited to the case of strong adhesion, where there is a separation of variables between adhesion (interfacial properties) and adherence (viscoelastic losses) as presented in the next section.

Modification of the Adhesion by Antiadherent Treatment

In the case of surfaces prepared with antiadherent treatment, one can observe (Figure 9) that the force levels decrease for both adhesives (with both resins); in the same way, the peeling rate for the interfacial to stick–slip transition is changed. This last point shows that for an adhesion lower than the previous examples, there is a competition between the viscoelastic losses and the interfacial properties.

CONCLUSIONS

We have focused on the strong relationship between rheological and adherence properties in the case of strong adhesion between adhesives and substrates. We have shown that this relationship obeys general physical rules, for model adhesives as well as commercial-type adhesives, in agreement with recent models of molecular rheology. Because linear viscoelastic properties may be derived from molecular parameters, this approach leads to a direct link between molecular structure and adherence properties. To the end, we have clearly shown that in decreasing the affinity between the adhesive and the substrate by an antiadherent treatment, the law applied for the strong adhesion case is not valid. So, in this last example, rheological behavior of the adhesive is not the only relevant parameter to control adherence properties.

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