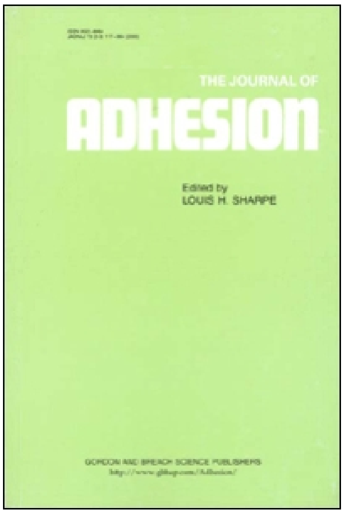

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Adhesion of Pure and $CaCO_3$ Filled Latex Films on Poly(ethylene terephthalate)*

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Adhesion to poly(ethylene terephthalate) of carboxylated styrene-butadiene latex films, filled with calcium carbonate particles, was studied in this work. The acid content (2, 4 or 6 wt%) the degree of crosslinking (25, 50 or 75 wt% of insoluble polymer) of the latex particles, and the percentage of filler (0, 20, 40, 60, 80 or 90 wt%) were varied. A peel test at 180° was used.

It was shown that, for the lowest filler percentages (up to 60 wt%), the films were non-porous and adhesion decreased when the peel rate, the percentage of filler, the degree of crosslinking and the acid content increased. Failure was always localized at the film-support interface (except at very low peel rate). At low peel rate, stick-slip was observed. The adhesion lowering can be explained by a decrease of the energy dissipation during peeling due to a reduced mobility of the polymeric chains. At high filler percentage (80 or 90 wt%), the films became porous and the level of adhesion very low. Failure occurred in the bulk of the latex film. The peel rate dependence was reversed; adhesion increased at higher speed. Owing to its marked importance in this system, the mechanism of the stick-slip phenomenon is especially discussed.

KEY WORDS: adhesion of latex films; carboxylated styrene butadiene; calcium carbonate; peel test; stick-slip

INTRODUCTION

Water-based polymeric dispersions (latexes or latices) are now extensively used in paint, paper and adhesive applications. These latexes are not pure but filled with mineral particles such as calcium carbonate, kaolin, talc, silica, and others. In all applications, one of the most important properties of the films made from the filled latexes is adhesion. That is the reason why we were interested in studying adhesion of filled latex films. However, these filled systems are most complicated. One difficulty, among many others, arises from the fact that the filler content can reach values as high as 80 or even 90 wt%. The properties of films containing low or high amounts of filler can be very different. In fact, the complexity of the problem of adhesion of a polymeric layer onto a support dramatically increases from the homogeneous film (deposited

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* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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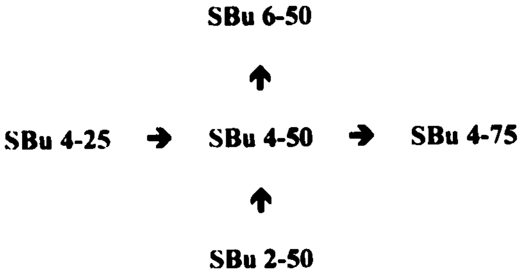
from a solution, for instance), to the pure latex film, and to the filled latex film with growing filler contents. Before tackling the problem of filled latex films, we studied adhesion of the corresponding pure latex films. It would even have been interesting to study "solution films". To prepare those, a latex film is dissolved in an appropriate solvent and a new, much more homogeneous, film is formed by evaporation of the solvent. These solution films have rheological and adhesion properties very different from the corresponding latex films.[1,2] This procedure is often extremely helpful for understanding the properties of latex films. Unfortunately, in this case, adhesion of solution films was too high to be measured by our testing method, namely a 180° peel test.

EXPERIMENTAL

Latexes

Five different carboxylated styrene butadiene latexes (Scheme 1) were used in this study. The styrene/butadiene weight ratio was 1.6. This leads to a glass transition temperature of 11°C. The carboxylic functions came from a 50 wt%-50 wt% mixture of acrylic and fumaric acids. The latexes were synthesized in a semi-continuous process. The mean particle diameter was 0.15 µm. The latexes differed in the degree of crosslinking of the chains in the particles (adjusted by the use of various amounts of transfer agent) and in the carboxylic acid content. Latexes with three degrees of crosslinking (25 wt%, 50 wt%, and 75 wt%; these percentages represent the amounts of insoluble material in the particles) and three total acid contents (2 wt%, 4 wt%, and 6wt%) were synthesized. All percentages refer to the dry material in the latex. The reference latex contains 4 wt% of acid monomers (2 wt% of acrylic acid and 2 wt% of fumaric acid), and 50 wt% of insoluble polymer. It is noted SBu 4-50; S and Bu stand for styrene and butadiene, respectively. The other available latexes are indicated in Scheme 1. The pH was adjusted at 8.5. The solids content was 50 wt%.

Calcium carbonate (Hydrocarb 90 from Omya, France) was used as a filler. Its purity is 99.75%. It has a density of 2.7 g/cm^3 and a specific surface area of 7 m^2/g. The shape



SCHEME 1 The five different pure latexes used in this work. S stands for styrene, Bu for butadiene. The first figure represents the acid content in weight percent, the second one the percentage of insoluble polymer in the particles. For instance, the reference latex, SBu 4-50, in the center of the scheme, contains 4 wt% of acid, and 50 wt% of insoluble polymer.

of the particles is rather spherical. The particle size distribution is broad, ranging from 0.1 μm to 5 μm. The mean diameter is 1.26 μm. The filled latexes were prepared by mixing one of the pure latexes described above with the $CaCO_3$ filler in the form of an aqueous dispersion, the solids content of which was 70 wt%, and stabilized by 0.3 wt% of the neutral sodium salt of a polycarboxylic acid (Dispex N40 from Allied Colloids). The weight percentages of filler in the latexes were 20, 40, 60, 80, or 90. The corresponding volume percentages are 8.5, 20, 35.5, 60, and 77, respectively.

Latex Film Characterization

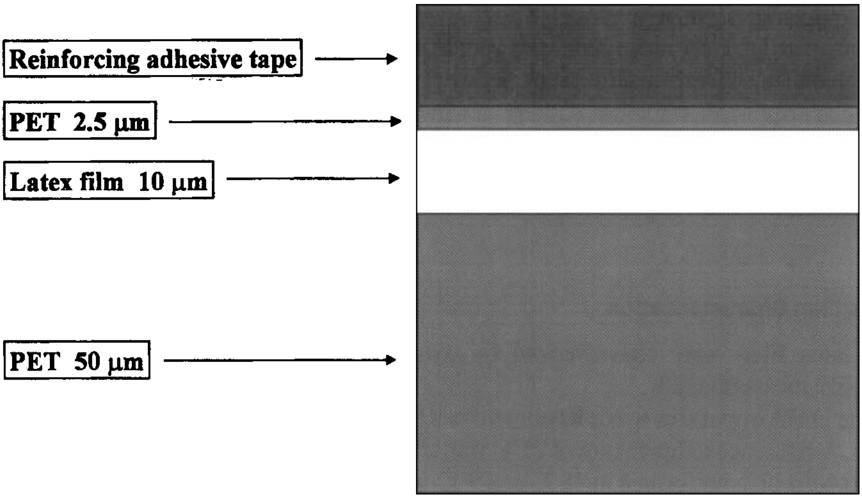
The latex films were characterized by dynamic mechanical analysis (DMA) and porosity measurements.

The DMA apparatus was a Rheometrics RSA II. The frequency range was 0.1 to 100 rad/s. A reference temperature of 23°C was chosen. Moduli *versus* frequency measurements were also performed at 18°C and 9°C. Master curves were constructed using the Williams, Landel and Ferry (WLF) law.[3] The shift factors were -0.87 at 18°C and – 2.78 at 9°C. For the films containing 0% and 20 wt% $CaCO_3$, measurements were performed in the tensile mode, whereas the dual cantilever mode was used for higher filler contents. The thickness of the sample was 1 mm. Porosity was determined by weighing the films in air and after dipping them for 3 days in a silicone oil of known density (0.98 g/cm^3). The density of the polymer is 1.07 g/cm^3. The error of this method is estimated at 5%.

Peel Test

The samples were prepared in the following way. The appropriate latex was cast onto a 50 μm thick poly(ethylene terephthalate) (PET) film (supplied by Rhône-Poulenc). A 2.5 μm PET film was then carefully deposited on top of the latex layer. This sandwich was dried in an oven at 70°C for 30 min. This fast drying step avoided sedimentation of the filler. The amount of latex was such that the dry latex film had a thickness of 10 μm. The sample was then further aged at 23°C and 50% relative humidity for 24 h. Before peeling, the thin PET layer was reinforced with a polypropylene adhesive tape. The sample is shown in Scheme 2.

The samples were peeled at an angle of 180°, in the T-configuration. All peel experiments were performed in a room conditioned at 23°C and 50% relative humidity. A Zwick tensile machine was used in the peel rate range of 1 to 600 mm/min. A few experiments were also carried out at lower rates (0.03 to 0.06 mm/min) with a home-made machine, and at higher rates (800 to 2000 mm/min) with an Instron 8031 apparatus. The width of the peeled sample was 1 cm. Its length, in the range of a few centimeters, depended on the peel rate. The error range was never more than 15% at low peel rates. It was around 10% at higher peel rates, above 250 mm/min. This is good for such kinds of mechanical measurements. It has to be stressed here that the peel strength at high filler contents (80, 90 wt%) becomes low and, taking into account the above mentioned error range, it is difficult to draw precise conclusions from the results concerning the heavily-filled latex films.



SCHEME 2 Sample used for the peel test.

In almost all peel experiments (see Figure 1a, for example), a stick-slip phenomenon was observed in a certain peel rate range. In the stick-slip zone, at a given peel rate, the peel force oscillates almost regularly with time between a maximum and a minimum value (sawtooth-shaped curve). These extreme values are indicated in the figures.

Determination of Loci Failure

Two techniques were used in order to determine the loci of failure, scanning electron microscopy (SEM) and contact angle measurements with water.

The SEM apparatus was a Stereoscan 120 from Cambridge Instruments, operated at 9 kV. A thin gold layer ($\approx 10\,\mathrm{nm}$) was vacuum deposited on the sample before observation.

The surfaces were also analyzed by measurements of contact angles of water. This technique provides information on the uppermost surface layer. Measurements were taken within 5 to 10 seconds of placing the drop. No detectable change in the drop shape occurred in the first 30 seconds. The contact angle measurements were made in a Spindler & Boyer (Germany) contact angle goniometer at a fixed temperature of 23°C. Freshly bidistilled water was used. The volume of the drop was 2 μl. Each contact angle value given in this article corresponds to an average of 10 measurements on the same surface. The error range was ± 2°. The effects of roughness differences between samples are neglected.

RESULTS

This section is divided into two parts, the first one devoted to pure (0% $CaCO_3$) latex films, and the second to $CaCO_3$-filled latex films.

I Pure Latex Films

Influence of peel rate

All pure latex films behave similary in the peel-rate range contained between 1 mm/min and 2000 mm/min. Only the Figure concerning the reference latex (SBu 4-50) is presented (Fig. 1). First, there is a stick-slip zone between 1 mm/min and 100 mm/min.

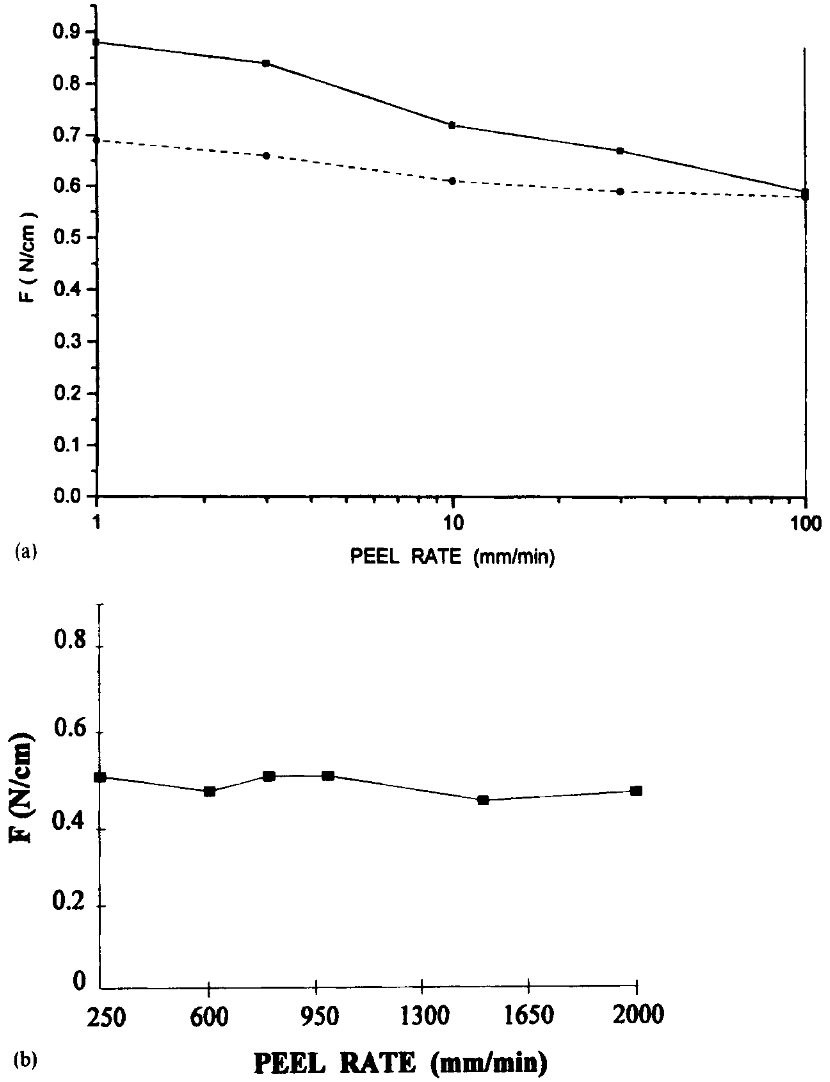


FIGURE 1 Peel force *versus* peel rate for unfilled SBu 4-50 latex films sandwiched between poly(ethylene terephthalate) films. a. Top. Stick-slip zone. The upper and lower lines represent the maximum and the minimum, respectively, of the oscillating peel force. b. Bottom. Outside of the stick-slip zone, the peel force remains constant with time.

A characteristic acoustic wave is emitted when stick-slip occurs. The amplitude of the oscillations of the peel force decreases when the peel rate tends towards 100 mm/min. The maximum peel force decreases faster than the minimum peel force with an increasing peel rate (Fig. 1a). After 100 mm/min, the peel force stabilizes and remains almost constant between 250 mm/min and 2000 mm/min (Fig. 1b).

Influence of acid content

Figure 2 shows the peel force *versus* peel rate for the pure latex films with increasing acid content, SBu 2-50, SBu 4-50, and SBu 6-50. The peel force decreases with increasing acid content. This is true inside and outside of the stick-slip zone.

Influence of crosslinking

The effect of increasing crosslinking on the peel force of the latex films is presented in Figure 3. Adherence decreases when the degree of crosslinking increases.

Loci of failure

In the range 1 mm/min to 600 mm/min, rupture is always interfacial, occurring at the interface between the latex film and the 2.5 μm PET film. This is shown by the contact angle values in Table I. Contact angles of water droplets are identical on the initial 2.5 μm PET film before formation of the sandwich and on the side of this film which was

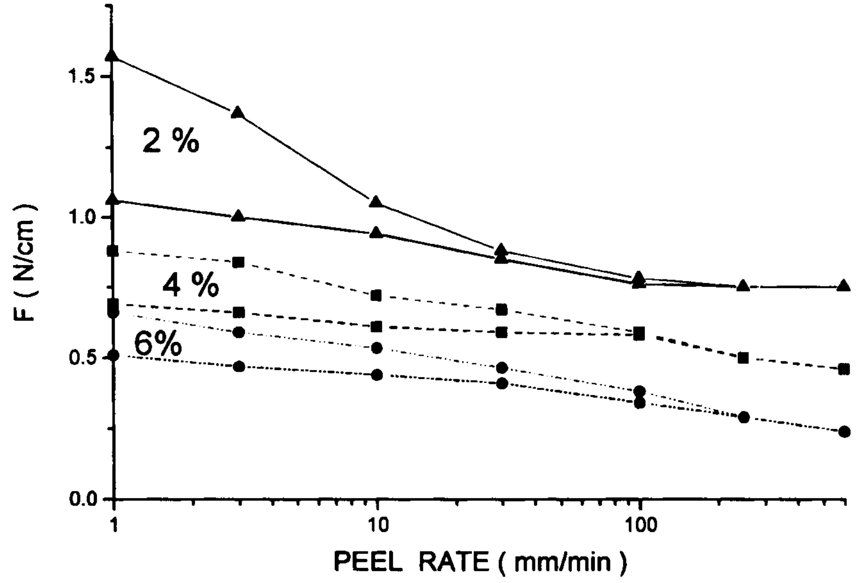


FIGURE 2 Peel force *versus* peel rate for unfilled latex films with increasing acid content, **SBu 2-50, SBu 4-50,** and **SBu 6-50,** sandwiched between PET films. The upper and lower lines represent the maximum and the minimum, respectively, of the oscillating peel force in the stick-slip zone.

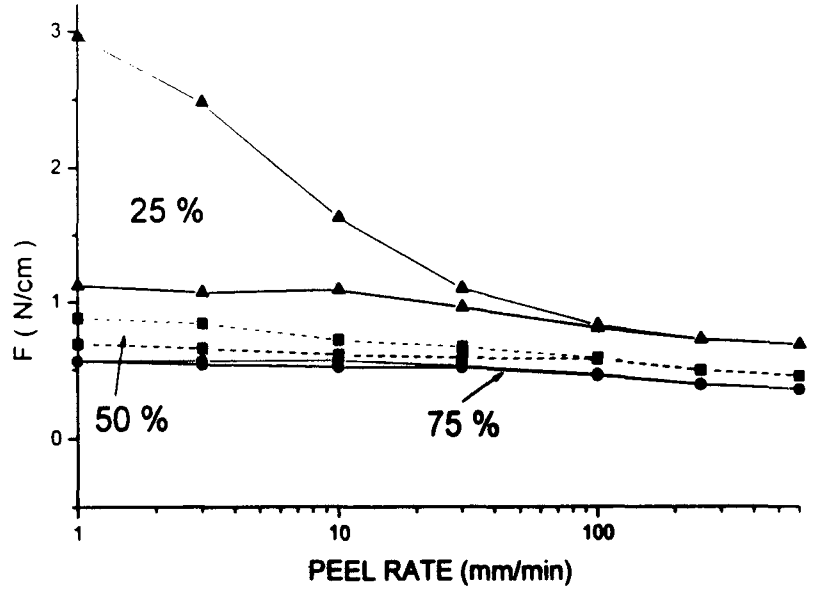


FIGURE 3 Peel force *versus* peel rate for unfilled latex films with increasing degree of crosslinking, SBu 4-25, SBu 4-50, and SBu 4-75, sandwiched between PET films. The upper and lower lines represent the maximum and the minimum, respectively, of the oscillating peel force in the stick-slip zone.

TABLE I
Contact angles of water

	PET 2.5 μm before peeling	PET 2.5 μm after peeling	Latex film
Contact angle	77°	78°	70°

in contact with the latex film after rupture of the sample. The contact angle on the latex film is significantly different. Electron micrographs of the surfaces revealed after peeling do not present any special feature.

At very low peel rate, between 0.03 and 0.06 mm/min, the locus of failure depends on the degree of crosslinking of the latex. For the latex with the higher degree of crosslinking (SBu 4-75), rupture remains interfacial between the latex film and the 2.5 μm PET film. For all other latexes with lower degrees of crosslinking, rupture becomes cohesive in the latex film as shown by scanning electron micrographs in Figure 4.

II Filled Latex Films

Dynamic mechanical analysis

The pure latex films present the typical characteristics of viscoelastic materials, low moduli at low frequencies and high moduli at high frequencies. Addition of the $CaCO_3$ filler progressively increases the moduli. However, the moduli increase faster at low

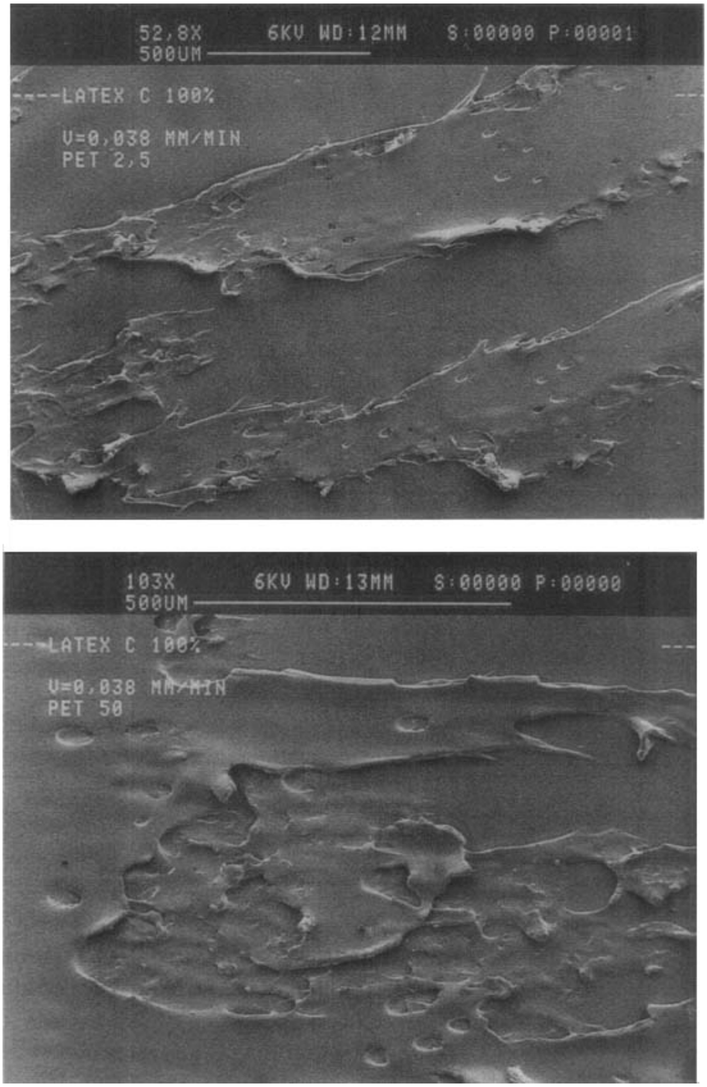


FIGURE 4 Scanning electron micrographs of the surfaces revealed after peeling. Pure SBu 4-50. Peel rate 0.038 mm/min. a. Top. 2.5 μm PET film side. b. Bottom. 50 μm PET film side.

frequencies than at high frequencies. Consequently, at high filler contents, 80 and 90 wt%, moduli become almost independent of the frequency. See the example of the SBu 4-75 latex films in Figure 5a. The loss factor tan δ flattens out with increasing filler content and shifts slightly towards higher frequencies (Figure 5b).

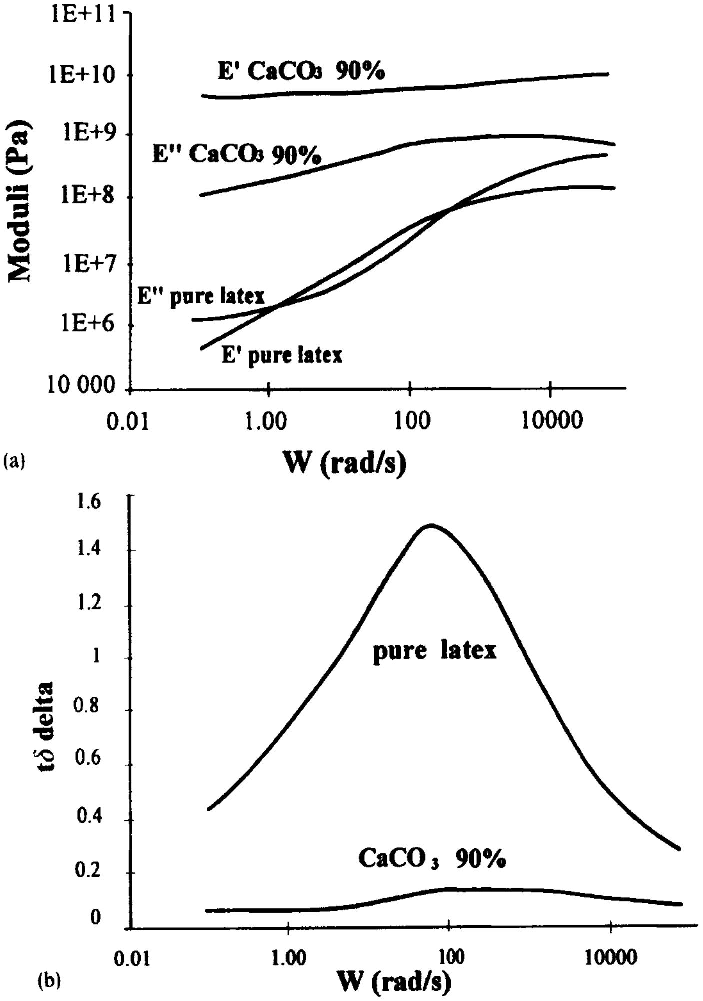


FIGURE 5 Moduli and loss factors *versus* frequency for **SBu 4-75** latex films, unfilled or filled with 90 wt% $CaCO_3$. a. Top. Moduli. b. Bottom. Loss factors.

Porosity measurements

Porosity measurements have been performed on the SBu 4-75 and SBu 4-50 latex films (Table II) Taking into account the error range of the method (5%), the porosity becomes significant only above 80 wt% of filler.

Influence of the filler on the peel strength

Figure 6 displays the peel strength *versus* peel rate results for SBu 4-50 films containing increasing amounts of $CaCO_3$. The peel forces decrease with increasing filler contents.

TABLE II
Porosity measurements
SBu 4-75

$CaCO_3$	0%	20%	40%	60%	80%	90%
Pore Vol	2%	4%	7%	5%	7%	30%

SBu 4-50

$CaCO_3$	0%	20%	40%	60%	80%	90%
Pore Vol	1%	1%	2%	2%	8%	25%

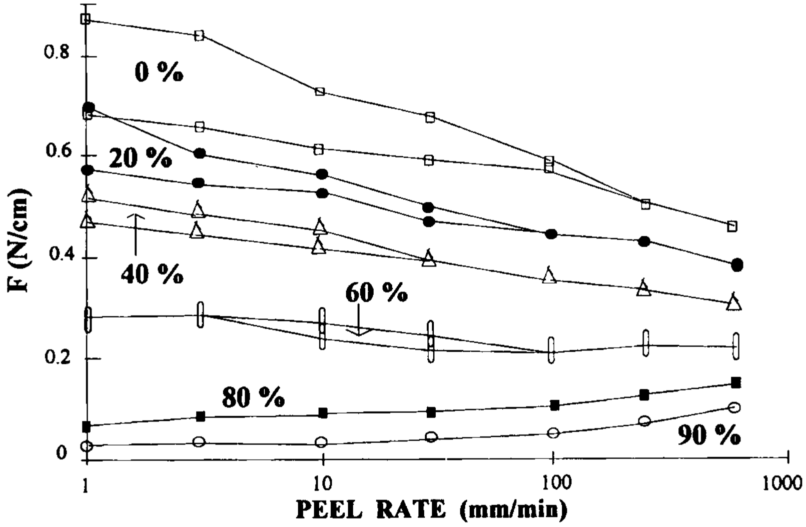


FIGURE 6 Peel force *versus* peel rate for $CaCO_3$ filled **SBu 4-50** latex films with increasing filler content.

The importance of the stick-slip decreases when more $CaCO_3$ is present in the latex film; with 80 and 90 wt% CaCO3, there is no longer any stick-slip. It can also be seen in Figure 6 that, at high filler contents (80 and 90 wt%), the peel strength increases with peel rate.

Loci of failure

An increase of the filler content changes the loci of failure. At low filler contents, up to and including 60 wt%, rupture is interfacial between the latex film and the thin PET film. Above 60 wt% of filler, rupture becomes slightly cohesive. Traces of residues of the filler latex film appear on the PET film. Scanning electron micrographs of SBu 4-50 systems containing 80 wt% and 90 wt% of $CaCO_3$ are shown in Figure 7.

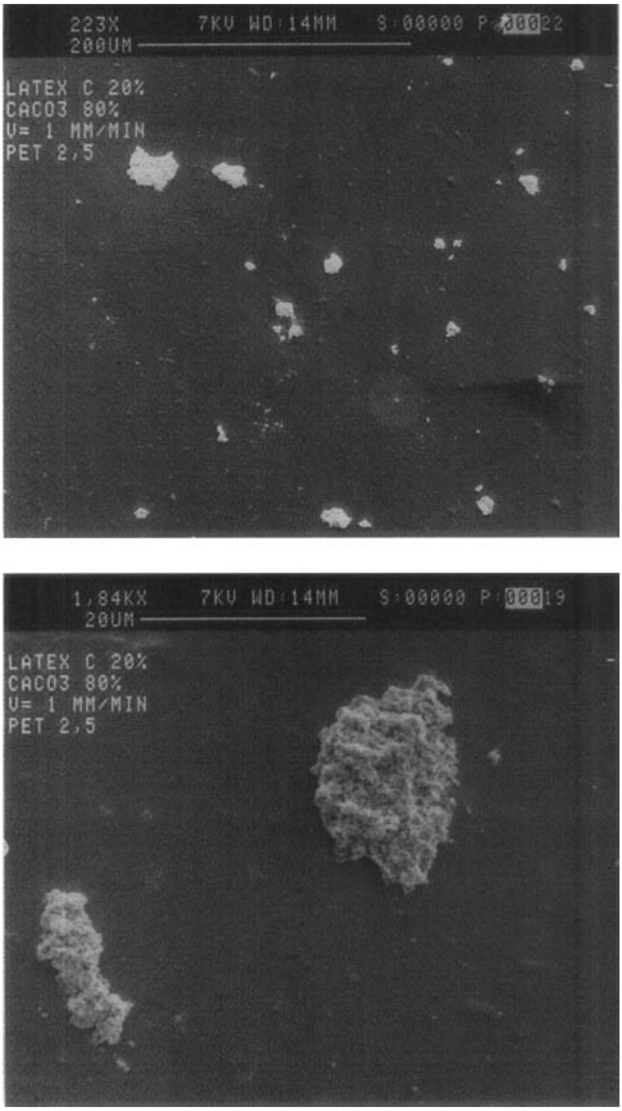


FIGURE 7 Scanning electron micrographs of the 2.5 μm PET film after peeling. $CaCO_3$ filled **SBu 4-50**. Peel rate 1 mm/min. a. Top. 80 wt% of $CaCO_3$. b. Middle-top 80 wt% $CaCO_3$, higher magnification. c. Middle-bottom. 90 wt% $CaCO_3$. d. Bottom. 90 wt% $CaCO_3$, higher magnification.

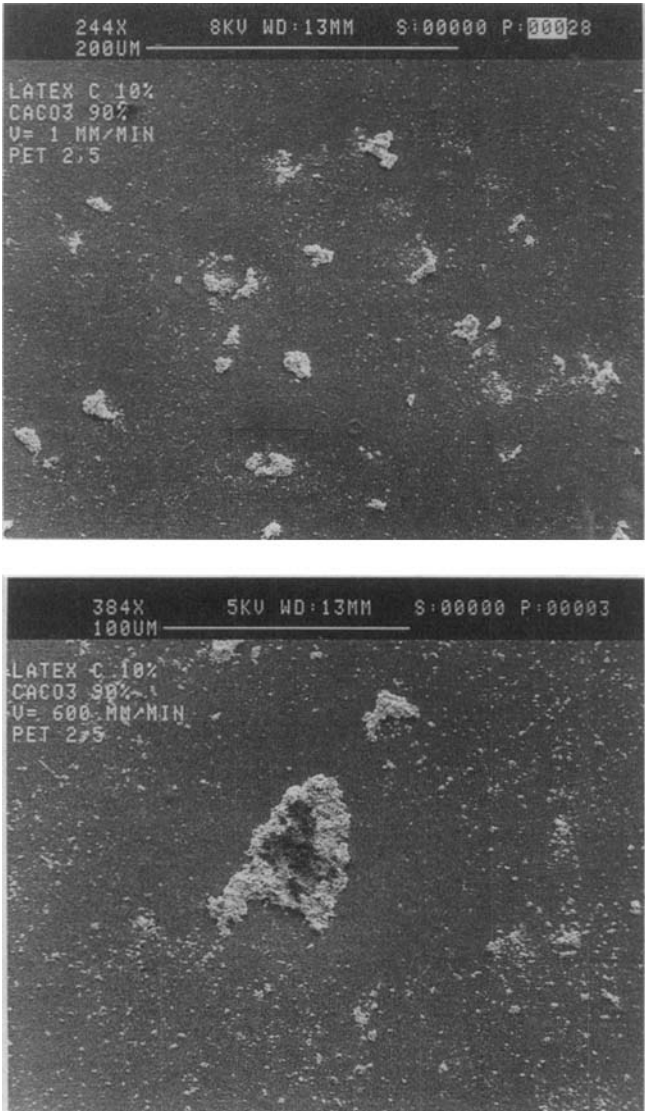


FIGURE 7 *(Continued).*

Influence of the filler on the dependence of the peel strength on the acid content and degree of crosslinking

Adding $CaCO_3$ to the latex film does not change the acid and crosslinking effects which were shown in pure latex systems (Figures 2 and 3). Whatever the filler content, increasing the acid content results in a decrease of the peel strength (an example for films containing 40 wt% $CaCO_3$ is shown in Fig. 8). Similarly, an increase in the degree of crosslinking decreases the peel strength at all filler percentages, although the differences between the systems with different degrees of crosslinking become less visible at higher filler contents (Fig. 9). Figure 9b shows an increase of the peel force with peel rate for heavily-filled (80 wt%) systems.

DISCUSSION

Influence of Peel Rate on Peel Energy. Stick-Slip

Generally, peel strength or peel energy increases with peel rate at constant temperature (or peel energy increases with decreasing temperature at constant peel rate). This is largely due to the viscous loss effects associated with peeling of polymeric films. This velocity dependence appears in many expressions of the peel or fracture energy.[4-7] A power 0.6 dependence is often found,[5, 8-10] although other exponents are also reported in the literature, for example 0.17 for PMMA[11] or 0.35 for peeling an adhesive tape from a roller.[12] However, complications arise from the existence of transitions and instabilities (stick-slip) occurring as peel rate or fracture velocity increases. The most important transition, analyzed by Gent and Hamed,[13, 14] takes place when rupture evolves from cohesive to adhesive. At low velocity, chains have time to disentangle; they move over large distances (on a molecular scale) as peeling proceeds. These motions give rise to important friction losses, the energy dissipated strongly increasing with rate of separation. Rupture is cohesive. As velocity increases, a sharp transition takes place. Chains no longer have time to disentangle, motions are much more limited, peel energy drops because of a drop in the energy dissipated by viscous losses and rupture becomes adhesive. As the peel rate further increases, peel energy starts to increase again, but this increase in much less marked than in the cohesive rupture zone. Eventually, a second transition arises, corresponding to a glass transition, after which the peel energy decreases again.[14]

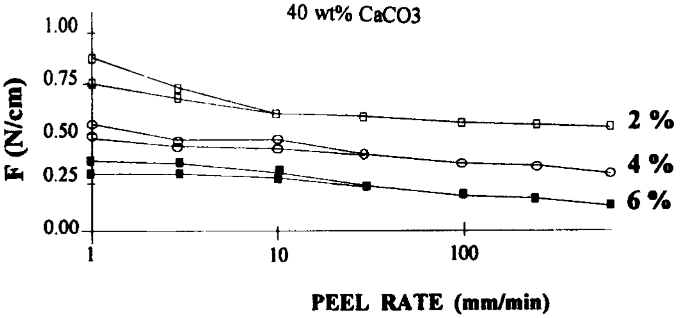


FIGURE 8 Peel force *versus* peel rate for latex films containing 40 wt% $CaCO_3$ and increasing amounts of acid: **SBu 2-50, SBu 4-50, SBu 6-50.**

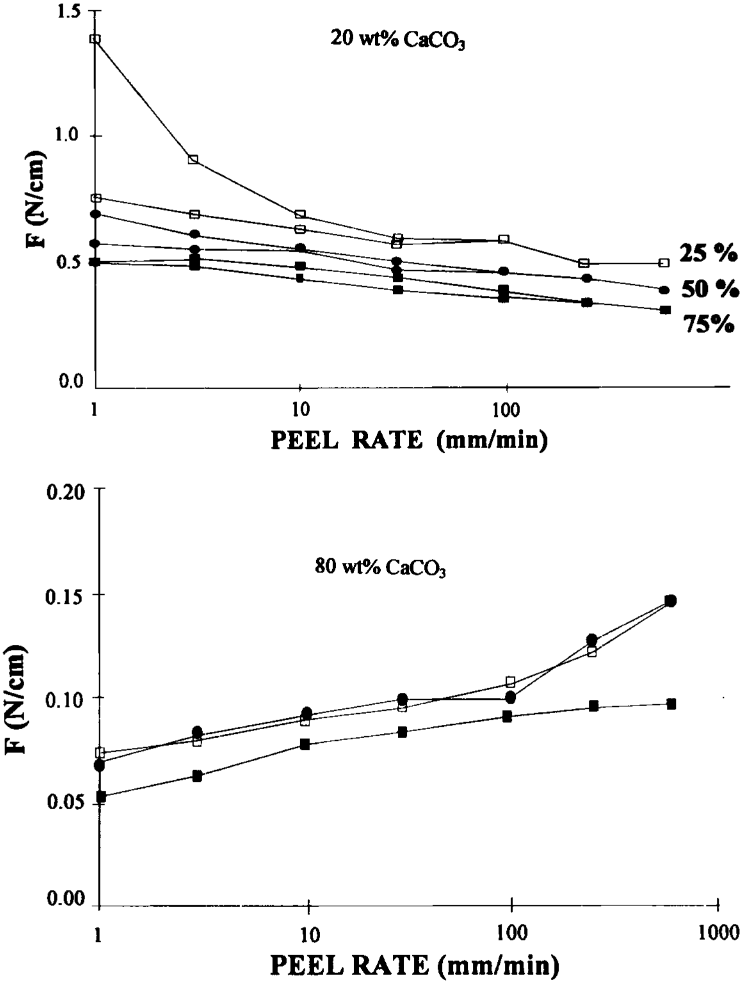


FIGURE 9 Peel force *versus* peel rate for filled latex films with increasing degrees of crosslinking. □ **SBu 4-25**; ● **SBu 4-50**; ■ **SBu 4-75**. a. Top. 20 wt% $CaCO_3$. b. Bottom. 80 wt% $CaCO_3$.

In our systems, an increase of the peel energy with peel rate is only observed in heavily-filled films (80 or 90% of filler) (see Figs. 6 and 9b). In all other cases, outside of the stick-slip zone which will be discussed below, the tendency is rather to decrease the peel energy or to maintain it constant as peel rate increases. In Figure 1b, it is shown that peel energy remains constant as peel rate increases over an order of magnitude. Let us recall that rupture is adhesive in all cases discussed here. These results can be interpreted in terms of viscous losses taking two facts into account. The chain motions occurring in a peel experiment, either in the whole bulk of the sample or specifically in the vicinity of the propagating crack, are characterized by the amplitude of the movement, *i.e.* the distance covered by a given chain segment, and the velocity of this motion. When peel rate increases, the velocity of the chain segments increases and consequently viscous losses increase. However, a peel rate increase can also have the consequence of decreasing the amplitude of the chain movements and thus the friction losses. If this second effect dominates, the peel energy can decrease with increasing peel rate. If they more or less compensate, the peel energy can remain constant over a relatively wide range of peel rates. A more quantitative analysis of these phenomena could be undertaken in the framework of de Gennes' theory of reptation.[15] The chain motions considered here are the motions relative to the matrix of surrounding chains. A chain can move in a cooperative way with other chains; this does not give rise to viscous energy dissipation. A proper modeling of energy dissipations on the molecular scale during a peel experiment necessitates a knowledge of the relationship between macroscopic motions and corresponding chain motions. This is out of reach at present but constitutes a stimulating research challenge for coming years.

Let us now discuss the results in the stick-slip zone. A very interesting general presentation of the stick-slip phenomenon was made by Maugis.[16] In the stick-slip zone, the crack velocity jumps periodically from a high value to a low one and to the high one again. These velocity jumps can be of several decades.[17] They are due to a discontinuity in the strain energy release rate (G) *versus* velocity (v) curve. According to Maugis,[16] this discontinuity is, in fact, a negative branch in the $G(v)$ curve which cannot be observed and arises from a broad peak due to viscoelastic losses superposed on the increasing elastic solution. Other interpretations of the discontinuity are also possible.

The stick-slip zone is often considered as the transition between cohesive and adhesive rupture. It is clearly the case in some elastomer/glass systems, as shown by a careful AFM analysis of the loci of failure by Ryschenkow *et al.*[18] However, it is not a general rule. In the work done by Maugis and Barquins[12,19] on adhesive tapes, the cohesive/adhesive transition took place on the low velocity side of the stick-slip zone, without a slope change in the $G(v)$ curve. This is in agreement with observations by Aubrey and Sherriff[20] who studied peel adhesion and viscoelasticity of rubber-tackifier resins blends in pressure sensitive adhesives. These authors only observed a very small slope change at the cohesive/adhesive transition. Stick-slip occurred at higher pulling rates and was attributed to a transition between a rubbery and glassy response of the adhesive during peeling.

In our systems, rupture is also always adhesive in the stick-slip zone, except when the filler content exceeds 60 wt%. The cohesive/adhesive transition takes place at rates below those corresponding to stick-slip, somewhere between 0.05 and 1 mm/min. Whether there is a slope change at the transition in the $G(v)$ curves in our systems is not known.

In the classical explanation of stick-slip,[16,21] the maximum and minimum peel energies should remain constant in the stick-slip zone whatever the pulling rate. This is obviously not the case, neither in our systems (see Figs. 1a, 2, 3, 6, 8, 9a) nor in the literature results.[2,19,20,22] Usually, the amplitude of the oscillations decreases with increasing rate, as in the present results. However, it can also increase and reach a plateau, as was observed in an adhesion study of acrylic latex films onto PET.[2] The amplitude changes in the stick-slip zone can be explained by taking into account inertial effects when the crack accelerates or decelerates.[16] In the analysis presented in Reference 16, Maugis makes the assumption that the peel angle remains constant. When the variation in peel angle is accounted for, a supplementary degree of freedom is introduced which can lead the system into a chaotic regime.

Influence of Acid Content and Degree of Crosslinking

The effect of increasing the acid content of the film or its degree of crosslinking is basically the same (Figs. 2 and 3); it decreases the peel strength and the filler does not change the situation (Figs. 8 and 9). The same interpretation holds in both cases.

Adding an acidic monomer to an acrylic copolymer is often thought to have the effect of increasing adhesion. This can be true when specific (*e.g.*, acid-base) interactions can develop between carboxylic groups and some functionalities at the surface of the support. In our case, latexes are at a pH of 8.5 where organic acid groups are in the form of carboxylates which do not strongly interact with ester functions of poly(ethylene terephthalate). Films made from lower pH latexes would perhaps lead to different results.

We also considered the possible contribution of water-soluble species formed during the course of the latex synthesis. The amount of such species increases when the acid content increases. They could segregate towards the film-support interface and build up a weak boundary layer. This could be a partial explanation of the decrease in peel strength with increasing acid content. In order to check this hypothesis, two latexes, SBu 2-50 and SBu 6-50, were purified by the serum replacement technique.[23] After purification, the content in soluble species dropped from 4.1% to 0.2% for SBu 6-50, and from 3.1% to 0.1% for SBu 2-50. However, the peel test measurements were not affected. Thus, the soluble species do not influence the peel strength of the films.

The acid content effect can be explained by a reduction of the chain mobility, and thus a decrease of the energy dissipation by viscoelastic losses during peeling, as the acid content increases. Acid groups act as physical crosslinking knots through hydrogen bonding in the carboxylic form or through ionic dipolar interactions in the carboxylate form. This was shown by a dynamic mechanical analysis of systems very similar to ours by Richard and Maquet.[24] Acid groups are mainly located at the interfaces between particles. The crosslinking knots are thus not homogeneously distributed in the film but concentrated in what can be considered as a continuous, interparticulate phase. Their effect on the chain mobility is, therefore, not straightforward. They can also limit it via a restriction in the motion of the particle cores as a whole.

There is one other example in the literature of the reduction of the peel strength of acrylic latex films when the acid content is increased. Seghal and Basset[25] have studied the effect of various functional groups, including carboxylic ones, on the peel adhesion of water-borne acrylic pressure sensitive adhesive. On stainless steel, the peel strength decreased from 626 g/cm, to 528 g/cm, 487 g/cm, and 447 g/cm when the carboxylic group content was raised from 0 to 3%, 6% and 10%. Hydroxyl and amino groups had similar effects.

Let us now discuss the case of chemical crosslinks, which is very similar. It can now be considered as a classical result that increasing the degree of crosslinking decreases the peel energy. Twenty years ago, Ahagon and Gent[26] showed that the strength of adhesion decreased with increasing crosslinking. This was regarded as a confirmation of the Lake and Thomas hypothesis[27] which stated that many molecular bonds must be stressed in order to detach or rupture one. Gent and coworkers[28] confirmed their earlier results a few years later on polybutadiene and ethylene-propylene elastomers of various degrees of crosslinking. Carré and Schultz[29] proposed that the adhesive strength of model elastomer/treated aluminum assemblies could be described by a product of three terms: the reversible energy of adhesion or cohesion, - a macroscopic dissipation factor due to viscoelastic losses, and a molecular dissipation factor related to the degree of crosslinking of the elastomer. The molecular dissipation factor, $g(M_c)$, was an increasing function of the average molecular weight between crosslinks, M_c. It was shown later on,[30] using the JKR technique,[31] that $g(M_c) = M_c^{\alpha}$, with α being either 1/2 or 1.

The above statement that increasing crosslinking decreases adhesion is not perfectly general. In the case of a polymer which has an extremely low cohesive strength under the conditions of the adhesion measurement, it can be beneficial to introduce crosslinks. For such kinds of materials, an increase in the degree of crosslinking increases the adhesive strength, via an increase of the cohesion, until an maximum is reached after which adhesion decreases again. An example of this behavior is given by Zosel[32] for poly(dimethyl siloxane).

Influence of Filler

Adding a filler to a polymeric film alters its adhesion characteristics in a complex way. The filler influences both the structure of the film-support interface and the rheological and mechanical properties of the bulk. At the interface, the presence of the filler is generally unfavorable to adhesion because it limits the contact of the polymeric matrix and the support. The effect of the filler on the bulk properties is more complex. An important parameter is the nature and the intensity of the matrix-filler interactions. These interactions are currently specifically studied. Reference 33 is a recent example of this kind of research, using atomic force microscopy. If interactions are strong, mobility of the chains in contact with the filler can be much reduced, possibly leading to a layer of polymer in a glassy state even for an elastomeric matrix. In a carboxylated styrene-butadiene/calcium carbonate system, Parpaillon *et al.*[34] showed that increasing the filler content shifted T_g towards higher temperatures and lowered the intensity of the tan δ peak. In this case, adhesion is lowered by the filler. However, the presence of the filler can also lead to specific dissipative processes. Dewetting of polymer from the filler particles can occur and lead to vacuole formation (cavitation process).[14, 35, 36] Internal friction between particles and separation of mutually adhering particles are other possible energy consuming phenonema.[14]

The consequence is that the introduction of a filler in a polymeric film can have several possible effects on the adhesion performances of the film. Adhesion can decrease, increase, or go through a maximum with increasing filler content. Examples of all these behaviors exit in the literature. Reegen[37] has studied the peel strength of polyurethane films filled with either $CaCO_3$ or chromium oxide *versus* filler content. He showed that peel strength goes through a maximum (around 15 wt%) with $CaCO_3$, whereas it decreases linearly with chromium oxide. In a silica/natural rubber system, Morris[38] observed an increase of peel strength with filler content.

In our case, the presence of the filler decreases adhesion (Fig. 6). The most straightforward interpretation is the following. First, the filler decreases the polymer-support contact. This phenomenon is amplified by a likely decantation of the filler particles during the film formation process. Second, there is probably a strong interaction between the polymer and the filler. This is confirmed by a NMR study by Parpaillon *et al.*[34] in a very similar system. The mobility of the chains in contact with the filler is then reduced and, correlatively, viscoelastic losses decrease. The diminution of the viscoelastic character of the film is shown by dynamic mechanical analysis results (Fig. 5). The decrease of the intensity of the tan δ peak (Fig. 5b) is particularly illustrative. The increase of the filler content also has the effect of decreasing the cohesion of the film. This is evidenced by the change in the locus of failure, from adhesive to slightly cohesive above 60 wt% (Fig. 7). It is not surprising, taking into account the appearance of porosity above 80 wt% of filler (Table II). Adhesion of films with high filler contents thus becomes extremely low.

CONCLUSION

This work must be considered as preliminary. Results concerning the influence of peel rate, acid content, degree of crosslinking, and presence of a filler on the peel strength are qualitatively more or less understood. The importance of chain mobility and corresponding viscoelastic losses has been abundantly stressed. It is, indeed, a key factor in the field of adhesion. However, a more quantitative knowledge of the phenomenon is needed. Macromolecular dynamics and molecular friction coefficients should be much better known. Ways exist to get better insight into these parameters, such as employment of NMR and dynamic mechanical analysis (DMA). The difficulty is to transfer NMR or DMA data to peel test experiments.

Filled films are very difficult to study. In our opinion, it is preferable, at the present stage, to first seek a better understanding of the adhesion behavior of unfilled latex films before tackling the problem of filled films, even if they are very important from a practical point of view.

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