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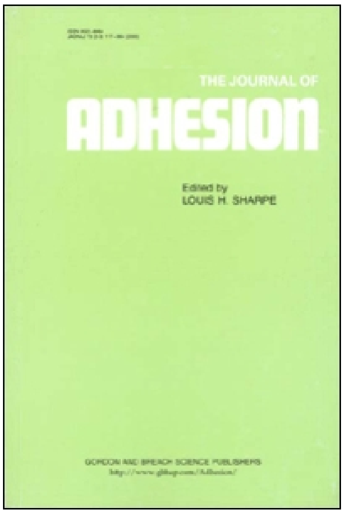

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The Influence of Surfactants on the Peel Strength of Water-based Pressure Sensitive Adhesives*

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In order to study the effect of surfactants on the adhesive properties, peel measurements were performed with two series of model polymers of ethylhexylmethacrylate (PEHMA), the first prepared by emulsion polymerization with four anionic surfactants, and the second by post-adding the same surfactants to a surfactant-free latex. Cohesive fracture is observed at low peel rates; the peel strength depends on the bulk mechanical properties and is independent of the emulsifier. A transition to another type of separation occurs at higher peel rates, which seems to be an interfacial failure by visual inspection. Surface analytical studies, however, give evidence that this "interfacial" failure is, in fact, a mixed failure, leaving traces of the polymer on the substrate surface. The peel rate at this transition as well as the peel strength at mixed fracture are influenced by the surfactants. Large differences were observed between the four surfactants as well as between both series of polymers, leading to the conclusion that the surfactants have a different mobility within the film. This is also reflected by a different aging behaviour of the films.

Keywords: Peel strength; emulsion polymer; pressure sensitive adhesive; surfactant

1. INTRODUCTION

Surfactants are used in emulsion polymers for a number of reasons; for example, in order to control particle formation, to stabilize the aqueous dispersions, and to improve their wetting properties on substrates. These

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surfactants, of course, remain in the latex film after film formation and may affect its properties. Accordingly, questions connected with the distribution of surfactants in the film and their influence on the film properties have early attracted attention, as can be concluded from papers of Voyutskii and Vanderhoff, for instance [1, 2]. These questions have become even more important with the increasing use of emulsion polymers in adhesives, above all pressure sensitive adhesives, as one can expect the adhesive behaviour to be especially sensitive to the presence of surfactants in surfaces and interfaces.

Surfactants can have two major effects on the adhesive properties, the first of which is connected primarily with the interfacial and surface properties. It is caused by an enrichment of the surfactants at the film surface, possibly leading to the formation of a weak boundary layer, which may deteriorate the adhesion performance. This has been shown by Delgado *et al.* [3] who found a decrease of peel adhesion with increasing surface concentration of alkyl and perfluoroalkyl sulfates as surfactants. It follows from studies of Holl and coworkers in Strasbourg, that the curves of peel strength *versus* surfactant concentration can show a maximum or a minimum, depending on the nature of the surfactant [4–6]. Another effect to be taken into account for some surfactants, which are compatible with the polymer to a certain extent, is a plasticizing of the emulsion polymer by the surfactant, which can enhance the peel strength but reduce the shear resistance [3].

The second major effect addressed is related to the fact that surfactants, present in the polymerization process, can influence the molecular structure of the emulsion polymers, *e.g.*, their molecular mass, their gel content and their comonomer distribution and, in this way, influence the bulk mechanical properties of the films. As the adhesive fracture energy is governed by surface effects as well as by viscoelastic energy dissipation in the bulk material, it is not easy to identify in which manner a surfactant influences the adhesion behaviour of a latex film.

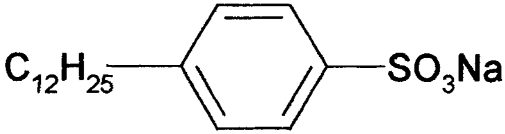
2. EXPERIMENTAL

2.1. Emulsion Polymers, Surfactants

In order to study both effects, peel measurements were performed with model polymers of ethylhexylmethacrylate (EHMA). This monomer has the advantage of forming uncrosslinked polymers in emulsion polymerization, leading to simpler model polymers than the acrylates which are more interesting for the use as pressure sensitive adhesives but tend to form gel-containing polymers.

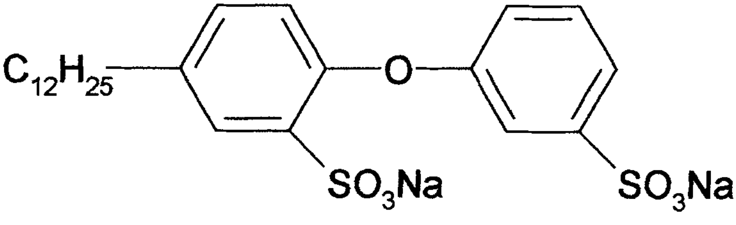
Two series of homopolymers were prepared, the first of which was obtained by emulsion polymerization of EHMA with four anionic surfactants with an equal molar concentration of 2×10^{-3}. These surfactants are sodium dodecyl sulfate (SDS),

Sodium dodecyl phenyl sulfonate (SDPS):



SCHEME 1

Sodium dodecyl diphenyl ether disulfonate (SDED):



SCHEME 2

and ethoxylated alcohol sulfate with 30 ethoxy groups and a dodecyl group as a hydrophobic tail. The surfactants were commercially available products which were used as received.

The latices were prepared by a seeded semi-batch polymerization process at 85°C and all have a similar particle size of about 160 nm.

For the second series we polymerized a surfactant-free PEHMA latex to which the same surfactants were added after polymerization in the same concentration as in the first series. Measurements with these two series of samples will additionally allow one to distinguish between the effect of surfactants present during polymerization or added after the polymerization. Films were formed from the latices at 23°C.

2.2. Experimental Techniques

The emulsion polymers were characterized by measurements of the dynamic shear modulus, *i.e.*, the storage modulus, G', and the loss modulus, G'', as a function of temperature and frequency by means of a dynamic mechanical analyzer with parallel plates. Master curves of G' and G'' at a reference temperature of 60°C were evaluated from the modulus *versus* frequency curves, measured at various temperatures. The zero shear viscosity, η_0, of uncrosslinked polymers can be calculated from the G'' *versus* frequency plot. The glass transition temperature, T_g, was determined as the temperature of the loss modulus maximum by measuring the dynamic shear modulus as a function of temperature at a frequency of 1 Hz. The weight average molecular mass, M_w, was obtained from gel permeation chromatography.

The adhesion of the latex films was measured using peel tests with an angle of 180°. These tests were performed at 60°C, *i.e.*, about 65°C above the glass transition temperature of PEHMA (Tab. I). This temperature was chosen for two reasons: firstly, the transition from cohesive to interfacial failure falls into the experimentally accessible range of peel rates at 60°C and, secondly, a temperature about 60°C above T_g accords with the behaviour of "real" pressure sensitive adhesives with a lower T_g than PEHMA at room temperature.

The adhesive layers for these measurements were formed on 30 μm thick polyester films as a reinforcing backing. The PEHMA layers had a thickness of about 150 μm; they were dried at 23°C and 50% relative

TABLE I Characterization of the polymers

Surfactant	M_w [10^5 *g/mole*]	η_0 *at* 60A°*C* [10^7 *Pa s*]	T_g [°*C*]
Without surfactant	3.8	4.3	−5
Alkyl aryl sulfonate	3.6	4.1	−7
Sodium dodecyl sulfate	3.7	4.3	−6
Dodecyl diphenyl disulfonate	4.3	38.0	−5
Ethoxylated alcohol sulfate	2.6	1.1	−5

humidity for 24 h and under vacuum for 4 h. Strips with a width of $b = 15$ mm were cut and bonded to stainless steel plates at 60°C under a defined contact pressure. A short time, *i.e.*, approximately 10 min, after bonding, the peel force, F, was measured as a function of the peel rate, v, in a wide range between 1×10^{-3} and 1×10^{1} mm/s. It took only some minutes to measure the peel strength over the whole range of peel rates above 1×10^{-1} mm/s. The measuring time was, of course, longer (about 10 to 20 min) at the lowest peel rates; but here surfactant diffusion during the measurement should not play a great role due to the separation by cohesive failure. The peel strength is given by the ratio of the peel force and the width of the peeled-off strip. Additional information about the adhesion behaviour can be obtained from the locus of failure which was primarily identified by visual inspection of the substrate, *i.e.*, the steel surface.

3. RESULTS

3.1. Characterization of the Polymers

Figure 1 shows the master curves of the storage modulus, G', and the loss modulus, G'', *versus* the angular frequency, ω, at 60°C for polyethylhexylmethacrylate, polymerized surfactant-free and with SDED and the ethoxylated alcohol sulfate, respectively. One finds the glass transition range at angular frequencies above about 10^{-1} s^{-1}, a not very pronounced plateau range, and a decrease of both moduli at low ω which indicates that the samples are uncrosslinked and reveal viscous flow. According to the relation $\eta_0 = G''/\omega$[7], the zero-shear viscosity, η_0, can be calculated. The calculations are summarized for all PEHMA samples in Table I. It is remarkable what large differences in η_0 and in the master curves are obtained simply by changing the surfactant. It follows from Table I, which also presents the weight average molecular masses, M_w, and the glass transition temperatures, that three materials have approximately the same molecular mass and viscosity. The PEHMA with the ethoxylated alcohol sulfate has the lowest M_w and η_0; the highest values for both quantities are found for the sample with SDED, for which η_0 is by a factor of 5 higher than one would expect from its molecular mass.

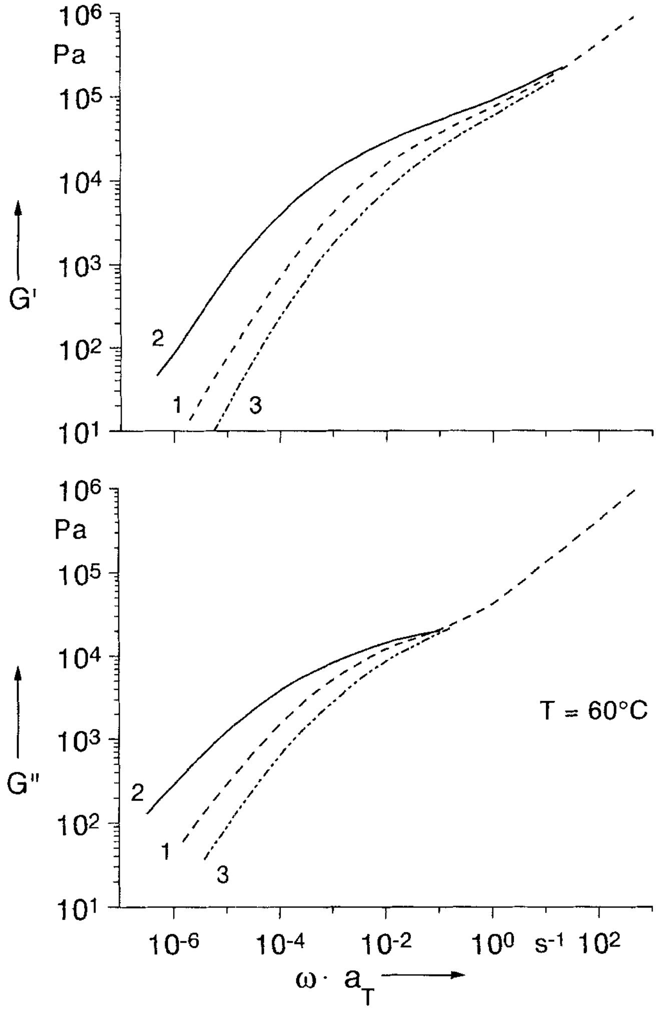


FIGURE 1 Master curves of the dynamic shear modulus (storage modulus, G', loss modulus, G'') as a function of the angular frequency for polyethylhexylmethacrylate at 60°C. 1. without surfactant, 2. with sodium dodecyl diphenyl ether disulfonate (SDED), 3. with ethoxylated alcohol sulfate.

The glass transition temperatures, obtained from the maximum of the loss modulus, vary between − 7 and − 5°C. This means that the surfactants studied in this work do not plasticize PEHMA significantly.

3.2. Effect of Surfactants on Peel Strength

The peel strength, F/b, of the surfactant-free PEHMA film is plotted *versus* the peel rate, v, on a double logarithmic scale in Figure 2. The rate dependence of the peel strength is typical of that for many uncrosslinked polymers [8]. One observes cohesive fracture at low peel rates, where F/b increases in proportion to v^n with an exponent of $n = 0.6$ which is in good agreement with results of Maugis and Barquins for the interfacial separation of polyurethanes from glass [9].

A transition from cohesive to interfacial (adhesive) separation occurs in a small range of the peel rate around 0.15 mm/s which is connected with an abrupt decrease of the peel strength. This effect has been related to the transition from the terminal to the plateau range of the viscoelastic spectrum [8]. F/b increases again with the peel rate above this transition, in this case with a lower exponent of 0.25. At still higher peel rates, slip-stick behaviour is observed, which is not to be discussed in this paper. Extensive studies have recently related the peel behaviour shown in Figure 2 to different mechanisms of deformation which could be made visible by a video-optic technique [10, 11]. The error bars at the left and the right side of Figure 2 represent the typical standard deviation for cohesive and interfacial separation, respectively.

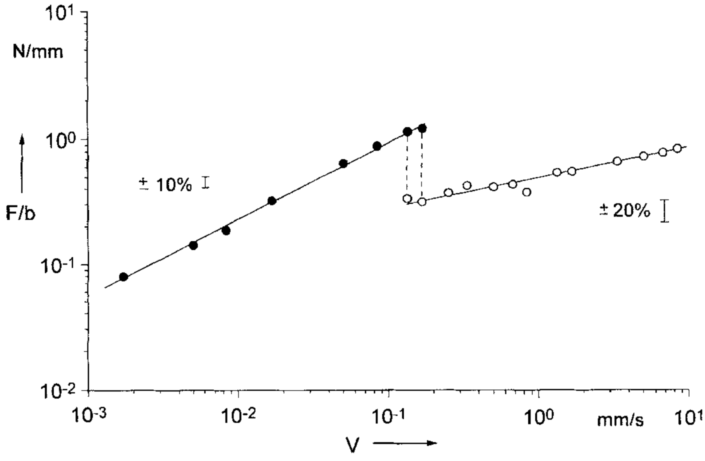


FIGURE 2 Peel strength F/b as a function of peel rate v for Polyethylhexylmethacrylate without surfactant, $T = 60°C$. ● cohesive fracture, ○ interfacial fracture. In the Figures 2 to 8, closed symbols mean cohesive, open symbols mean "interfacial" fracture.

It was mentioned before that the type of failure was primarily identified by visual inspection of the steel surface which appears bright and highly reflective after peeling at high rates. This visual inspection was very recently supplemented by surface analytical studies which give new insight into the "interfacial" failure at high peel rates. Silicon wafers were contacted with PEHMA films and tested in peel experiments. After peeling, the surface of the wafer was analyzed with TOF-SIMS. On silicon surfaces which seemed to have been separated from the polymer by an interfacial fracture, we found the spectra for silicon as well as for PEHMA. That leads to the conclusion that the "interfacial" separation, observed by visual inspection, in fact is a mixed interfacial and cohesive fracture which leaves spots or areas covered with PEHMA on the surface. A further characterization of this failure type needs more extensive studies which are in progress. Nevertheless, we indicate this failure mode as "interfacial failure" in this paper in order to distinguish it from the obvious cohesive fracture at low peel rates. One should, however, keep in mind the real nature of this separation mechanism.

Figure 3 compares the peel strength of the surfactant-free PEHMA sample, already shown in Figure 2, and the PEHMA polymerized with sodium dodecyl phenyl sulfonate. Both polymers have the same cohesive strength at low peel rates. It is determined by the mechanical properties of the polymers only, especially by their viscosity which is similar for both samples according to Table I. The transition to "interfacial" separation, however, occurs for the PEHMA with the surfactant at a peel rate which is nearly one order of magnitude lower, and the interfacial peel strength is considerably lower than that for the surfactant-free sample. The difference between the interfacial peel strength of both samples is largest at low peel rates and becomes smaller with increasing rates, as F/b for the PEHMA with SDPS increases with the peel rate with a higher exponent of about 0.4 than for the surfactant-free sample.

Figure 4 shows plots of the peel strength *versus* peel rate for the three samples, characterized by their shear moduli in Figure 1, *i.e.*, polymerized without surfactant and with SDED and the ethoxylated alcohol sulfate, respectively. There are large differences between the cohesive strengths, as one would expect on account of the different molecular masses and viscosities of the three polymers. The highest

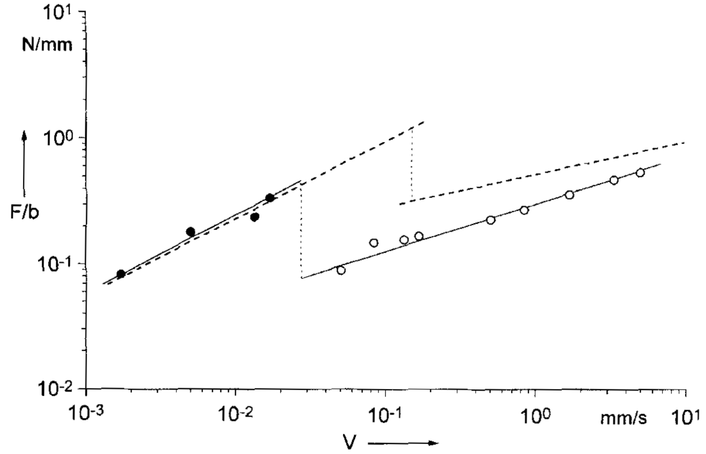


FIGURE 3 Peel strength as a function of peel rate for PEHMA without surfactant (– – –) and with dodecyl phenyl sulfonate (•, ○), $T = 60°C$.

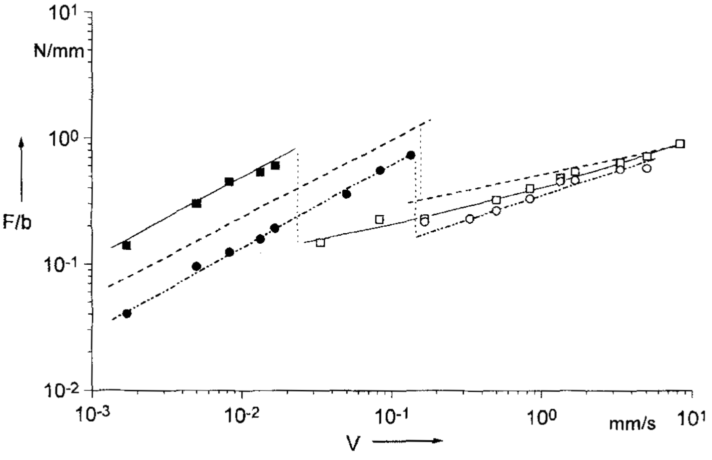


FIGURE 4 Peel strength as a function of peel rate for PEHMA without surfactant (– – –), with SDED (■, □) and ethoxylated alcohol sulfate (•, ○).

cohesive peel strength is observed for PEHMA with SDED which has the highest viscosity according to Table I; the lowest cohesive strength is found for the sample with the ethoxylated alcohol sulfate with the lowest viscosity and molecular mass of the three polymers.

The transition to "interfacial" separation occurs at the lowest peel rate for PEHMA with SDED which may be due to the higher "stiffness" of this material as well as to a direct influence of the surfactant in the interface. Interfacial fracture starts at about the same peel rate for PEHMA with the ethoxylated alcohol sulfate as for the surfactant-free film. The peel strength at interfacial separation is lower for both polymers with surfactants compared with the surfactant-free material, but the differences are smaller than for SDPS in Figure 3. Again, the difference is largest at low peel rates and becomes smaller with increasing v, as F/b increases more strongly for both PEHMA with surfactants than for the surfactant-free PEHMA. There is even no significant difference between the three samples in Figure 4 at the highest peel rates.

The results for the sample polymerized with SDS are similar to those for the polymers, shown in Figures 3 and 4, with a transition from cohesive to "interfacial" separation at about 1×10^{-1}mm/s.

3.3. Surfactant Addition During or After Polymerization

The influence of a surfactant on peeling can be different according to the manner of addition in the polymerization process, *i.e.*, during or after polymerization. That will be demonstrated in this section. It follows from Figure 5 that the ethoxylated alcohol sulfate leads to PEHMA films with a comparatively high peel strength when it is present in the emulsion polymerization process. Adding this surfactant to a surfactant-free latex after polymerization, however, results in films with a very low interfacial peel strength. The transition from cohesive to adhesive separation is found at a peel rate, v, which is more than one order of magnitude lower, and also F/b is much lower than for the polymer prepared in presence of this surfactant. Here, again, the differences between the interfacial peel strength of both samples are much larger at low peel rates and seem to disappear at high v.

A different behaviour is found for SDED (Fig. 6). The two samples, obtained by addition of the surfactant during or after polymerization respectively, have a rather different cohesive strength due to the differences in the molecular masses of both polymers. The cohesive to interfacial transition occurs also at different peel rates which, in this case, may also be caused by the differences in the stiffness of both

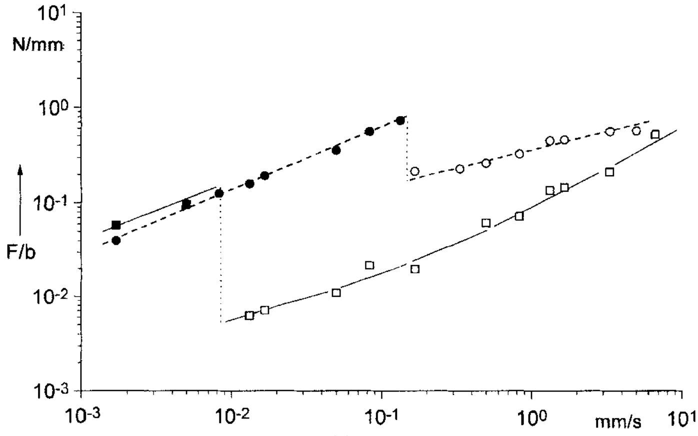


FIGURE 5 Peel strength as a function of peel rate for PEHMA with ethoxylated alcohol sulfate, present during polymerization (•, o) and added after polymerization (■, □).

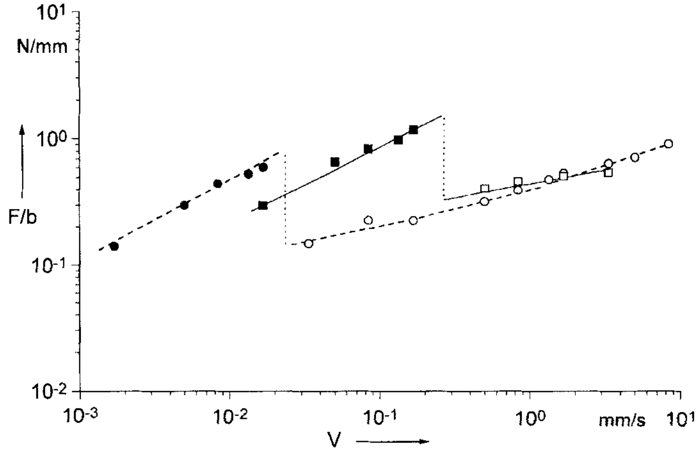


FIGURE 6 Peel strength as a function of peel rate for PEHMA with SDED, present during polymerization (•, o) and added after polymerization (■, □).

samples. The peel strength at interfacial separation, however, is more or less equal, *i.e.*, the manner of surfactant addition does not influence the adhesive strength significantly.

The two other surfactants, SDS and SDPS, show a behaviour between that of the two extreme surfactants, SDED and the ethoxylated alcohol sulfate. In order to compare the four surfactants, the peel rate of the cohesive to interfacial transition, V_c, the peel strength at this peel rate which is the lowest interfacial peel strength of the sample, and the peel strength at a high rate, 5 mm/s, are listed in Table II.

3.4. Effect of Aging

Films from the PEHMA latices were formed at 23°C, as already mentioned. There seems to be no significant diffusion of surfactant molecules to the film surface within storage times up to 3 days at 23°C, *i.e.*, about 30°C above the glass transition temperature, as was verified by peel measurements. However, this is expected to change at higher temperatures. In order to study the effect of surfactant diffusion to the film surface, films were annealed at 60°C for one and two hours and subsequently tested.

Figure 7 shows the peel strength for PEHMA, polymerized with SDPS. After an annealing time of 2 h, the peel strength is reduced drastically and the transition from cohesive to adhesive separation is shifted to very low peel rates, not accessible to our measurements. This means that this surfactant apparently diffuses rather easily to the surface and reduces its interfacial strength.

TABLE II Effect of surfactant addition

Surfactant		v_c [*mm/s*]	*F/b at* v_c [*N/mm*]	*F/B at* 5 *mm/s* [*N/mm*]
SDPS	1	0.03	0.09	0.55
	2	0.02	0.04	slip-stick
SDS	1	0.07	0.19	0.70
	2	0.04	0.10	0.45
SDED	1	0.03	0.15	0.75
	2	0.20	0.31	slip-stick
Ethoxylated alcohol sulfate	1	0.15	0.20	0.65
	2	0.01	< 0.01	0.35

1: Surfactant present during polymerization; 2: Surfactant added after polymerization.

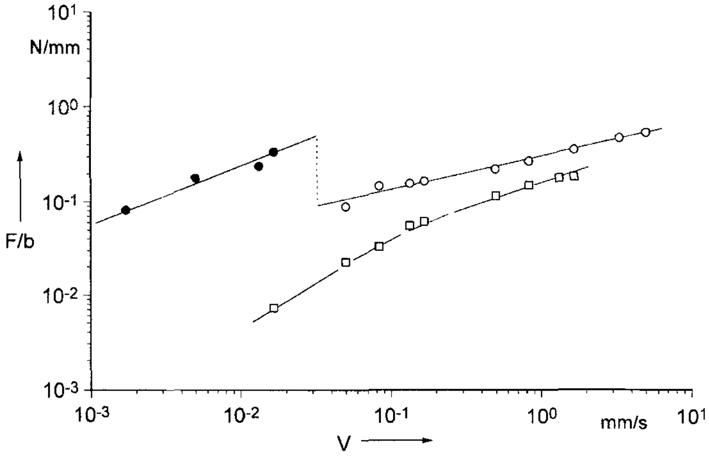


FIGURE 7 Peel strength as a function of peel rate for PEHMA with SDPS, unnealed (•, o) and annealed 2 h at 60°C (■, □).

Another behaviour is found for SDED. It follows from Figure 8 which shows the peel strength for PEHMA, polymerized in the presence of this surfactant, that *F*/*b* has the same values for the original and the annealed films over the whole range of peel rates. SDED is thus immobile at 60°C, and no deterioration of the surface is observed. A similar behaviour is found for the sample polymerized with the ethoxylated alcohol sulfate, which also shows the same peel strength independent of the annealing time. SDS, on the other hand, behaves very similar to SDPS.

The effect of annealing at 60°C is summarized in Table III, which lists the peel strength at a rate of 0.2 mm/s for the PEHMA samples, polymerized with the four surfactants. Additionally, it shows the annealing effect on the samples with added surfactants. Generally, the diffusion seems to be higher when the surfactant is added to the latices after polymerization than when it is present during the polymerization process. The surfactants partly behave in a very different manner, an observation which is also valid for other effects and which will discussed in the next section of this paper.

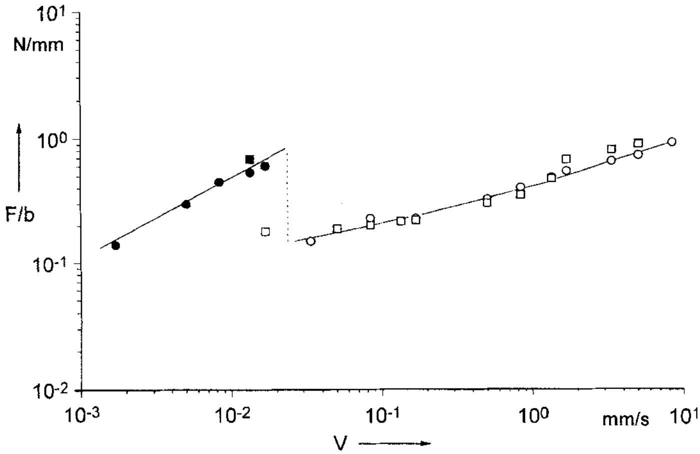


FIGURE 8 Peel strength as a function of peel rate for PEHMA with SDED, unnealed (•, ○) and annealed 2 h at 60°C (■, □).

TABLE III Effect of annealing at 60°C

Surfactant		*F/b at* 0.2 *mm/s* [*N/mm*]		
		Not annealed	1 *h* 60°C	2 *h* 60°C
SDPS	1	0.17		0.06
	2	0.11	0.05	0.02
SDS	1	0.26	0.05	
	2	0.15	0.04	0.04
SDED	1	0.26	0.24	0.24
	2	1.20[a]	0.15	0.15
Ethoxylated alcohol sulfate	1	0.20	0.20	
	2	0.03		

1: Surfactant present during polymerization; 2: Surfactant added after polymerization.
[a] Cohesive fracture.

4. DISCUSSION

The PEHMA samples studied in this work show a peel behaviour typical for homogeneous, uncrosslinked polymers: cohesive fracture at low peel rates, a transition from cohesive to "interfacial" separation with an abrupt decrease of the peel strength, and "interfacial" fracture at high peel rates. The cohesive peel strength is governed by the bulk mechanical properties, *e.g.*, the viscosity, of the polymers. F/b increases in proportion to $v^{0.6}$ with the peel rate. The transition from cohesive to "interfacial" failure and the interfacial peel strength are determined by the mechanical as well as the interfacial properties.

The four surfactants studied in this work partly show a different behaviour. PEHMA polymerized with the ethoxylated alcohol sulfate has an interfacial peel strength which is not much lower than that of the surfactant-free polymer. It is not significantly reduced upon annealing the films at 60°C. Surfactant-free PEHMA with which the ethoxylated alcohol sulfate has been admixed after polymerization, however, has a peel strength which is nearly one order of magnitude lower in the regime of interfacial separation. This means that the ethoxylated alcohol sulfate is immobilized on the particle surfaces in the polymerization process and, thus, unable to diffuse to the film surfaces at higher temperatures, but it is not immobilized by post-adding. A possible explanation, which has not been verified yet, is that the surfactant is grafted on the emulsion polymer. This point, of course, deserves further studies.

The peel strength at interfacial separation decreases only weakly for the PEHMA polymerized with SDED, also. Likewise, addition of SDED to the surfactant-free latex has no strong effect on the interfacial strength. This surfactant, too, is immobile, as F/b is not reduced at all by annealing at 60°C. As this effect is independent of the way it is introduced into the latex, this surfactant apparently is not grafted on to the particle surface during polymerization. Possibly, the two ionic groups of SDED, which may give rise to a kind of network structure, are the origin of this stability. This assumption is also not proven.

The two other surfactants, SDS and SDPS, behave rather similarly. They reduce the interfacial strength significantly in comparison with the surfactant-free film; and this reduction is even more dramatic when they are admixed with the surfactant-free latex after polymerization. Annealing leads to a strong decrease of F/b, as well. This means that both surfactants are not strongly anchored on the particle surfaces but rather mobile to migrate easily into surfaces or interfaces. It is, thus, dependent on the nature of the surfactants and their interaction with the polymer in which way the peel behaviour of emulsion polymers is affected.

Concerning interfacial separation on observation is made which needs further clarification. It is found that the *F/b versus v* plots for the PEHMA samples have different slopes, and that the slope is higher for samples with low interfacial peel strength, leading to the effect that the differences in *F/b* are more pronounced at low peel rates and tend to disappear at high rates.

According to Andrews and Kinloch [12] and Gent and Schultz [13], the adhesive fracture energy, G_a, can be written as

$$G_a = W_0[1 + \Phi(T, v)] \tag{1}$$

where W_0 is the energy expended to create free fracture surface, *i.e.*, the thermodynamic work of adhesion for van der Waals interactions, and Φ is a viscoelastic function, characterizing the energy dissipation. As, under some restrictions, the peel strength corresponds to the fracture energy,

$$F/b = G_a/2 \tag{2}$$

for a peel angle of 180° [14], also *F/b* should follow this relation.

If we compare two polymers with equal bulk mechanical but different surface properties, as it is the case in Figures 3 and 5 for instance, one would expect that the differences in the peel strength are only caused by different values of W_0. This means that the *F/b versus v* plots should be parallel in the double logarithmic diagrams in the regime of "interfacial" separation; this, however, is clearly not the case.

An explanation for these discrepancies may ensue from the surface analytical studies which have been mentioned in Section 3.2. These lead to the conclusion that the failure at high peel rates is a mixed interfacial and cohesive fracture with spots covered with PEHMA on the surface. There is some evidence from these studies that the contributions of both failure types to the fracture energy, *i.e.*, the peel strength, are dependent on the peel rate. Accordingly, we cannot expect Eq. (1) to be valid, as the surface energy term depends also on the peel rate.

Acknowledgements

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