Dynamic micromechanical investigations into particle/particle interfaces in latex films

J. Richard* **and J. Maquet**
Rhône-Poulenc-Recherches, Centre de Recherches d'Aubervilliers, 52 Rue de la Haie-Coq, 93308 Aubervilliers Cedex, France

(Received 9 September 1991; revised 16 January 1992; accepted 18 February 1992)

This paper is aimed at working out the part played by particle/particle interfaces in the viscoelastic behaviour of latex films. More precisely, a thorough analysis of the effect of neutral or ionized carboxyl functional groups, chemically incorporated in the latex particles and at the surface of the particles, is provided. The tensile micromechanical properties of styrene–butadiene copolymer latex films, with various carboxyl group contents and various neutralizing agents, are studied using dynamic mechanical analysis. Then, the structure of the latex films is investigated, using transmission electron microscopy (TEM) performed on stained ultramicrotomed films. The features of the interfacial crosslinking which result from ionic or hydrogen bonding interactions at the particle/particle interfaces are shown up, in close correlation with structural information gained from TEM investigations. The opportunity offered by the combination of the techniques used in this work, for a comprehensive prediction of the cohesive strength of the latex films is emphasized.

(Keywords: micromechanical properties; latex films; particle/particle interfaces)

INTRODUCTION

Emulsion polymers are mainly used for applications which require the formation of a continuous film with good cohesive properties. These applications encompass various fields such as water based adhesives, paints and coatings. The final strength properties of the polymer film should depend strongly on the film formation process, and more particularly on the features of the particle boundaries resulting from the coalescence mechanism. It is currently thought that the development of cohesive strength in latex films can be achieved through the molecular interdiffusion of polymer chains between adjacent particles[1,2]. The manipulation of the boundary region between polymer particles by incorporating functional moieties capable of undergoing chemical or physical crosslinking through covalent, ionic or hydrogen bondings, has also been suggested as a convenient way to achieve good film strength[3–5].

Obviously, the structure of the dried film and the ripening of particle boundaries under controlled ageing or curing conditions appears to be of critical importance; as a matter of fact, the last few years have witnessed a great deal of research carried out in this field[6–10], using well-suited techniques such as small angle neutron scattering (SANS) or transmission electron microscopy (TEM). Surprisingly, investigations into the contribution of particle boundaries to the dynamic micromechanical behaviour of latex films remain rather scarce, although in many ways, dynamic micromechanical analysis (d.m.a.) should be considered as a powerful non-destructive means for probing molecular interactions and the degree of crosslinking in latex films[11,12].

Recently, d.m.a. has been successfully used to gain a quantitative insight into the molecular dynamics of the polymer network within styrene–butadiene (SB) latex films[13]. More particularly, the key parameters which describe the effects of crosslinking and molecular interactions on the viscoelastic properties of the film have been investigated on different scales (macroscopic, molecular and local). However, the heterogeneous structure of the films arising from the preservation of particle boundaries due to incompletely achieved coalescence has not been taken into account in this previous work[13].

In the present paper, we focus on the exact part played by the network of particle boundaries in the viscoelastic behaviour of latex films. Dynamic micromechanical investigations are carried out, so as to probe molecular interactions in these interfacial zones, which should greatly affect the cohesion properties of the films. D.m.a. studies are performed using the same experimental and theoretical tools as those developed in our previous work[13]. The system chosen consists of SB copolymer latexes, which contain various amounts of a copolymerized acrylic type comonomer. Due to the hydrophilic character of this monomer, a large amount of carboxylic functional groups is incorporated at the surface of the particles. In the dried films, these groups give rise to hydrogen bonding interactions, which may act as bridges between adjacent particles, and therefore enhance the cohesive strength of the films. In the same way, for a given concentration of carboxylic groups present at the

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* To whom correspondence should be addressed

0032-3861/92/194164-10

surface of the particles, the influence of the neutralization of these acid functions is studied using d.m.a. In this case, physical crosslinking may occur in the interfacial zones between adjacent particles, through ionic dipolar interactions: due to the large difference in polarizability between the SB matrix and the hydrophilic surface layers, ionized groups arising from neutralized acid functions should tend to associate into multiplets or even larger domains[14]; then, they act as additional crosslinking knots. It will be shown that the viscoelastic properties of the latex films strongly depend on the nature of the counterion brought by the neutralizing agent. A refined analysis of this behaviour will be provided; it will be based on the structural information obtained from TEM investigations, which have been performed on strained ultramicrotomed films.

EXPERIMENTAL

Latex preparation

Two series of SB copolymer latices having the same composition of styrene and butadiene comonomers were prepared using a semicontinuous emulsion polymerization process described elsewhere[15]. The initiator was ammonium persulphate. A chain transfer agent was used so as to restrict covalent crosslinking of the chains within the particles, because it is assumed that the effect of molecular interactions in the boundary regions between adjacent particles will be more easily pointed out in a weakly crosslinked system. The first series consists of SB latices (glass transition temperature, $T_g = 30°C$) having the same gel fraction and different contents of an acrylic type comonomer. The amount of carboxylic groups located at the surface of the particles was determined by the conductimetric titration method. The second series is based on a single carboxylated SB latex ($T_g = 23°C$), whose pH has been adjusted to different values with various neutralizing agents such as: ammonia, sodium hydroxide, a diaminopolyoxyethylene (DAPOE) of low molecular weight ($600\,g\,mol^{-1}$) or an amino alcohol (AMA). The amount of carboxylic groups located at the surface of the particles was found to be $\sim 200\,\mu mol$ per dry polymer volume unit (cm^3) for the second series of products. In addition, for both series, the average particle size of the latices was determined using a classical turbidimetric method and was found to be close to $0.18\,\mu m$. This average diameter together with the narrow width of the corresponding size distribution were checked using TEM. The gel fraction values (G) of the two series of products were measured under mild conditions in $CHCl_3$ using the experimental procedure described previously[11]. They were found to be close to 20% for the first series of latices and 15% for the second series.

Table 1 Main features of the first series of latex particles

Latex	Average S:B composition (wt%)	Total carboxylic group content, Q_{COOH} ($\mu mol\,cm^{-3}$ polymer)	Surface carboxylic group content, Q^{S}_{COOH} ($\mu mol\,cm^{-3}$ polymer)
A	69:27	470	174
B	69:27	780	188
C	69:27	1090	461

Average particle size = $0.18\,\mu m$, gel fraction $G = 20\%$

Table 2 Main features of the second series of latex particles, based on a single carboxylated SB copolymer, whose pH has been adjusted to 4.5 or 9 with different neutralizing agents

	Neutralizing agent		
Latex	Type	pK_a[a]	pH
D	Ammonia	9.25	4.5
E	Ammonia	9.25	9
F	Sodium hydroxide	—	9
G	AMA	9.72	9
H	DAPOE	9.48	9

S = 69, B = 27, $Q_{COOH} = 600\,\mu mol\,cm^{-3}$ polymer, $Q^{S}_{COOH} = 200\,\mu mol\,cm^{-3}$ polymer, gel fraction $G = 15\%$, average particle size = $0.18\,\mu m$

[a] Values given for weak bases only in water at 25°C

The main data concerning both series of dispersions are given in *Tables 1* and *2*.

Film formation

Polymer films were prepared by casting the above products in silicon dishes of well-controlled depth and evaporating water at a temperature of 35°C until homogeneous, transparent, solid films were obtained. Samples exhibiting a constant thickness (ranging between 0.6 mm and 1.3 mm) were then cut to typical dimensions of $5 \times 1\,cm^2$ for d.m.a. experiments[13]. They were stored away from light under vacuum in a dessicating vessel prior to use.

D.m.a. experiments

The dynamic micromechanical behaviour of the films was investigated using the same experimental set-up (Rheometrics RDS-LA viscoelastometer) and procedure as described in our previous work[13]. The isothermal frequency dependence of the storage modulus (E'), the loss modulus (E'') and the loss tangent ($\tan\delta$) was deduced by sweeping the pulsation of the oscillating deformation between $10^{-1}\,rad\,s^{-1}$ and $500\,rad\,s^{-1}$ at different temperatures close to the T_g of the samples. Recorded spectra were then superimposed by simply shifting them along the frequency axis. For each sample, criteria of applicability of the method of reduced variables were checked to be fulfilled, as will be discussed later. The measurements were performed in a simple extension mode of deformation, whose amplitude ε ranged between 5×10^{-4} and 3×10^{-3}. In order to provide a more complete analysis, the isochronal temperature dependence of the viscoelastic variables E', E'' and $\tan\delta$ was also recorded at a frequency of 1 Hz and a constant heating rate of $2°C\,min^{-1}$ under a nitrogen atmosphere.

TEM experiments

TEM experiments were performed using a Philips CM12 transmission electron microscope. For TEM experiments, samples must be very thin ($\sim 10^3$ Å thick), dried and stained in order to reveal the edge of the particles by enhanced electron scattering. They were prepared through cryoultramicrotomy of films formed under the conditions described above. First, a small piece of dry film was cut with a razor blade and glued on a stand. Then, it was cooled to $\sim -50°C$ and sliced ($0.1\,\mu m$ thick) with an ultramicrotome apparatus. Finally, the slice was mounted on a copper grid and stained by contact with an aqueous solution of 1% uranyl acetate; the excess salt was washed by contact with drops of pure

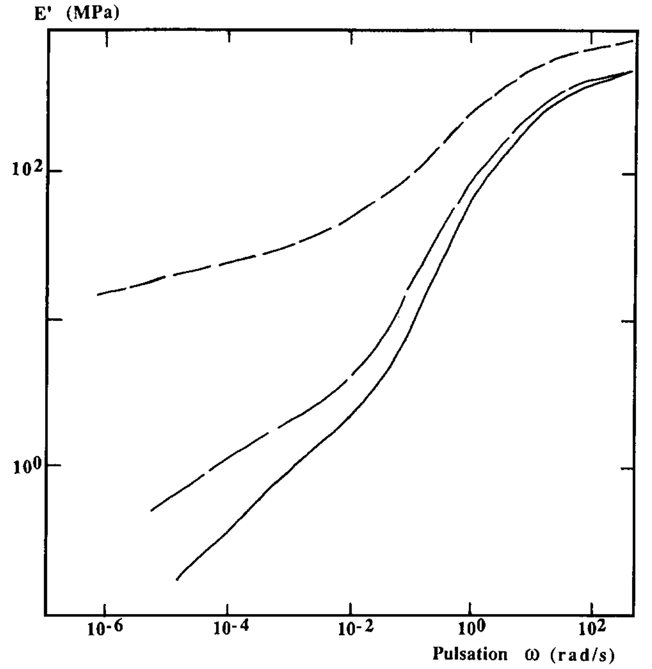

Figure 1 Log–log plot of the isothermal master curves obtained for E' of the first series (A–C) of latex films at $T_0 = 28°C$. The position of the transition zone on the frequency scale appears to be independent of ϱ_{COOH}, whereas E'_r in the low frequency region is very sensitive to this parameter. ϱ_{COOH} (μmol cm^{-3} polymer): (——) 470; (— —) 780; (- - -) 1090

water. The uranyl acetate stained the hydrophilic material in the film, and, more precisely, the carboxylic groups which form the hydrophilic boundary membranes between the original latex particles.

RESULTS AND DISCUSSION

Interfacial crosslinking due to carboxylic functional groups

Concerning the first series of latex films, isothermal master curves obtained for the frequency (or pulsation) dependence of the E' values are shown in *Figure 1*. The data are represented graphically after reduction to the reference temperature $T_0 = 28°C$. The empirical principle of time–temperature superposition (or method of reduced variables)[16,17] is checked to be valid for the whole series of samples and the temperature dependence of the frequency shifts is found to obey the well-known Williams–Landel–Ferry (WLF) equation[16,17]:

$$\log a_T = -c_1^0(T - T_0)/(c_2^0 + T - T_0)$$

where c_1^0 and c_2^0 are constants taken at $T_0 = 28°C$. c_1^0 and c_2^0 values, which have been derived for the first series of latices, are given in *Table 3*. They are found to be in the same order of magnitude as constants obtained for bulk samples of vinylic polymers containing carboxylic groups[16–18].

As previously described, the main feature of the isothermal master curves (*Figure 1*) is a strong relaxation phenomenon from a glass-like behaviour in the high frequency region to a rubber-like one in the lower range. Through this transition, the E' of the films strongly decreases from a value of $\sim 5 \times 10^2$–8×10^2 MPa to a much lower value, which markedly depends on the carboxylic group content in the copolymer. The viscoelastic behaviour of the films in the low frequency rubbery region, which corresponds to a more or less well-defined plateau of E', is related to slow relaxation phenomena due to the presence of the polymer network[13,16,17]. From a qualitative point of view, three findings are worth noticing in *Figure 1*:

1. Even when the content of copolymerized carboxylic groups is high (latex C), the d.m.a. spectrum exhibits only a single relaxation phenomenon (from glass-like to rubber-like behaviour). This result brings out strong arguments against the formation of a segregated carboxylic phase within the film. Otherwise, a second transition related to this polycarboxylic acid phase would have appeared in the spectrum. However, as the T_g of the corresponding polycarboxylic acid species is known to be high (> 100°C), we cannot completely eliminate the hypothesis by which the relaxation of this phase would be rejected to a domain of much lower frequency. Fortunately, TEM experiments performed on stained samples of latex films A, B and C clearly show that no segregated carboxylic phase exists in this system: as a matter of fact, only thin interfacial membranes located at the boundary between particles can be observed in the photomicrographs of stained ultramicrotomed samples (*Figure 2*).
2. The position of the transition zone does not significantly shift on the frequency scale, when the content of copolymerized carboxylic groups in the latex is varied. This zone is located between 10^{-2} rad s^{-1} and 1 rad s^{-1} in the present case, for spectra recorded at $T_0 = 28°C$. It has previously been shown that this position reflects local segmental

Table 3 c_1^0 and c_2^0 values measured for SB latex films with different contents of carboxylic groups (films A–C, see *Table 1*)

Latex film	Total carboxylic group content, ϱ_{COOH} (μmol cm^{-3} polymer)	c_1^0	c_2^0 (°C)
A	470	18	40
B	780	20	50
C	1090	25	63

The reference temperature $T_0 = 28°C$. The accuracy on the values of c_1^0 and c_2^0 is estimated to be within 10%

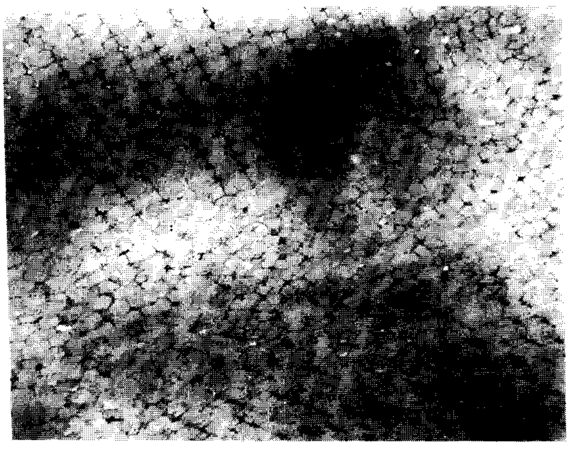

Figure 2 TEM micrograph of stained ultramicrotomed latex film C. Thin ordered interfacial layers are still present in the sample and form a network of hydrophilic boundaries between particles. However, no segregated carboxylic phase can be observed (magnification × 22 000)

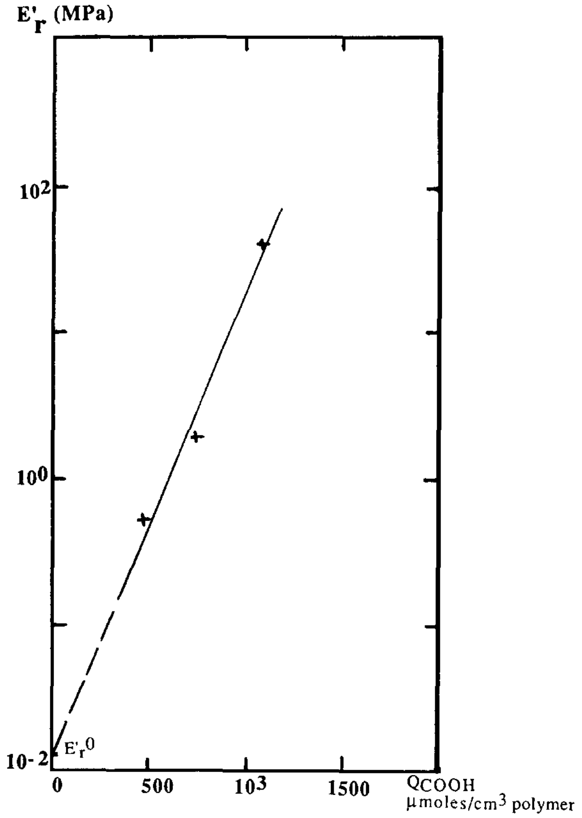

Figure 3 Plot of E'_r *versus* Q_{COOH}. Extrapolation of the curve towards a zero value for Q_{COOH} provides the value of $E_r'^0$

mobility of the chains within the polymer network[13]. Hence, the above observation strongly suggests that the copolymerization of carboxylic groups does not affect the local monomer dynamics, at least as far as concentration of this species is ranging between 460 μmol and 1090 μmol cm^{-3}.

3. The value of the rubbery storage modulus E'_r in the low frequency region is strongly dependent on the content of carboxylic groups in the polymer. This behaviour brings out clear evidence of the specific interactions between carboxylic groups which contribute to increase the density of coupling loci between the chains of the polymer network. These interactions likely find their origin in the hydrogen bonding between carboxylic groups, leading to the formation of dimers[19]. However, it is worthwhile noticing that the creation of these coupling loci does not lead to a sufficiently high increase of the tightness of the network for the local segment dynamics to be perturbed. In other words, the polymer network remains rather loose, although new physical crosslinking knots are created by carboxylic groups. The d.m.a. method likely gives average information over the sample, but the monomer dynamics must obviously be perturbed in the interfacial zones.

We would like now to provide a more quantitative insight into the contribution ν_H brought by interactions between interfacial carboxylic groups to the density of network strands ν_c, that has been defined in our previous work[13]. The methodology used so as to derive ν_H is described below: first, the value $E_r'^0$, that E'_r should display for a SB copolymer latex without copolymerized carboxylic groups, can be determined. In fact, $E_r'^0$ corresponds to the contribution of the only covalent coupling and physical entanglement knots. It can be deduced by plotting the dependence of E'_r upon the total carboxylic group content Q_{COOH} of the sample and extrapolating it towards a zero value for Q_{COOH} (*Figure 3*). In this process, it is assumed that variations of E'_r against Q_{COOH} obey the same law in the low range of acid contents. Second, as the equilibrium E'_r is related to the moles of network strands per volume unit ν_c by the classical relationship[17]:

$$E'_r = 3\nu_c RT \qquad (1)$$

then we can obtain ν_H by simply subtracting $E_r'^0$ from E'_r, and finally writing the expression:

$$\nu_H = (E'_r - E_r'^0)/3RT \qquad (2)$$

The value of E'_r can be deduced using the procedure given in reference 13, i.e. deriving this parameter from the peak value of the loss compliance J''_m. The plot of ν_H obtained in this way *versus* Q_{COOH} is given in *Figure 4*. This diagram clearly shows that ν_H can increase rapidly as Q_{COOH} varies. Moreover, it can reach very high values, close to 4×10^3 μmol cm^{-3} for Q_{COOH} of $\sim 10^3$ μmol cm^{-3}. It is worthwhile noticing that this value is nearly one order of magnitude higher than the value of the density of network strands obtained for the most covalently crosslinked SB latex that has been studied in our previous work[13].

Hence, it turns out that the interactions between carboxylic groups contribute very efficiently to the viscoelastic behaviour of latex films. Furthermore, a semiquantitative analysis can be provided by comparing the plot of *Figure 4* (solid line) with a theoretical plot

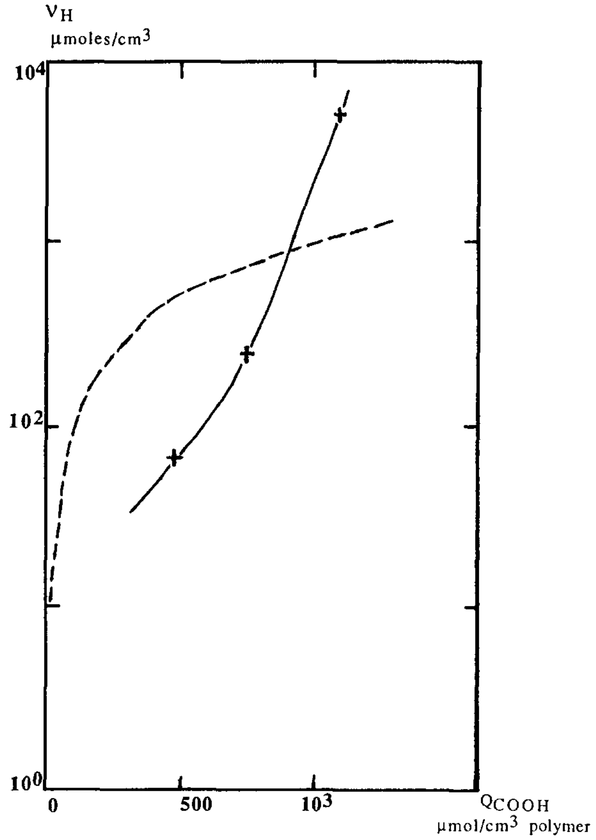

Figure 4 Plot of ν_H *versus* Q_{COOH} (——). This plot can be compared with the theoretical prediction (– – –) obtained by assuming that each carboxylic group is involved in an acid dimer

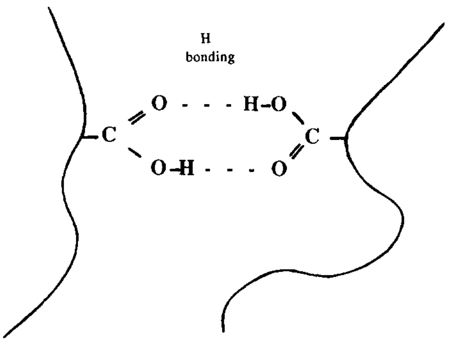

Figure 5 Schematic view for the formation of a carboxylic dimer through H bonding between two acid groups

(broken line), arising from a calculation performed under the following conditions: as far as the content of carboxylic groups remains rather low, interactions among these species are likely to give rise to acid dimers[19] through hydrogen (H) bonding (*Figure 5*); the polymer network consists of tetrafunctional knots from which four strands radiate. Then, comparison of experimental and theoretical plots brings us to the following conclusions:

1. as far as Q_{COOH} remains $< \sim 900\,\mu$mol cm^{-3}, each carboxylic group is not involved in H bonding;
2. for Q_{COOH} values close to 900 μmol cm^{-3}, the polymer film behaves as if each carboxylic function were included in a dimer through H bonding;
3. the steady increase in ν_H for Q_{COOH} values $>900\,\mu$mol cm^{-3}, might arise from a change in the structure of the coupling loci introduced by the carboxylic groups. More precisely, when the content of this species becomes higher and higher, clustering is more and more likely to occur, provided that the difference in polarizability between the SB copolymer and the carboxylic groups is large. Then, the carboxylic groups are likely to aggregate in separated microphases, and our model can no longer be applied correctly. However, another possible explanation could be an increase in the density of coupling knots due to the trapping of chain loops in the network formed by the chains bearing acid groups[20].

Unfortunately, the above description does not give a complete understanding of the actual part played by the carboxylic groups in the cohesive strength of the films, because it does not take into account the exact distribution of this species in the core and at the surface of the particles. In order to overcome this drawback, we will now focus on the relationship that can be established between ν_H and the surface content of carboxylic groups Q^S_{COOH} (*Figure 6*). We will then compare it with the theoretical prediction, assuming that each carboxylic group incorporated at the surface of the particles is involved in an acid dimer. Provided that particle interfaces are preserved within these films (*Figure 2*), it can be predicted that the probability for dimer formation is likely to be close to 1 in the boundary zones due to the high density of carboxylic groups in these regions, and conversely lower in the core of the particles. For this reason, carboxylic groups will obviously achieve cohesive strength within the film through interfacial crosslinking (H bonding) at particle boundaries. From a more quantitative point of view, it turns out that each carboxylic group is indeed included in a dimer for Q^S_{COOH} values close to 200 μmol cm^{-3}. In our polymerization process, this amount corresponds to a Q_{COOH} value of $\sim 600\,\mu$mol cm^{-3}. Then, it is worthwhile noticing that, for higher values of this latter parameter, the contribution of carboxylic groups buried in the core of the particles increases rapidly. This behaviour is likely to be related to the increase of the probability for acid dimer formation in the core of the particles, as Q_{COOH} becomes higher than 600 μmol cm^{-3}. Hence, it can be concluded that there exists a threshold value for Q_{COOH}, above which extra carboxylic groups do not achieve cohesive strength of the latex films any more, although they are still responsible for the increase in E'_r. Thus, these extra carboxylic species do not participate in interfacial crosslinking, but only in coupling knots located in the core of the particles.

Hence, our thorough analysis has enabled us to give a good description of the part played by copolymerized carboxylic groups in both the viscoelastic behaviour and cohesive strength properties of latex films, in close correlation with the exact distribution of these species in the core and at the surface of the particles.

Interfacial crosslinking due to ionic groups

Increasing the pH of latices above the pK_a of the copolymerized carboxylic groups present at the surface of the particles, results in dramatic changes in the structure of the films obtained from these dispersions[8]. In particular, in the case of these low gel content SB latices, SANS results seem to show that an organized network of interfaces can be preserved in the films when the latex is neutralized, whereas it almost completely vanishes otherwise. This behaviour is likely to be related to the presence of ionic groups located at the boundaries

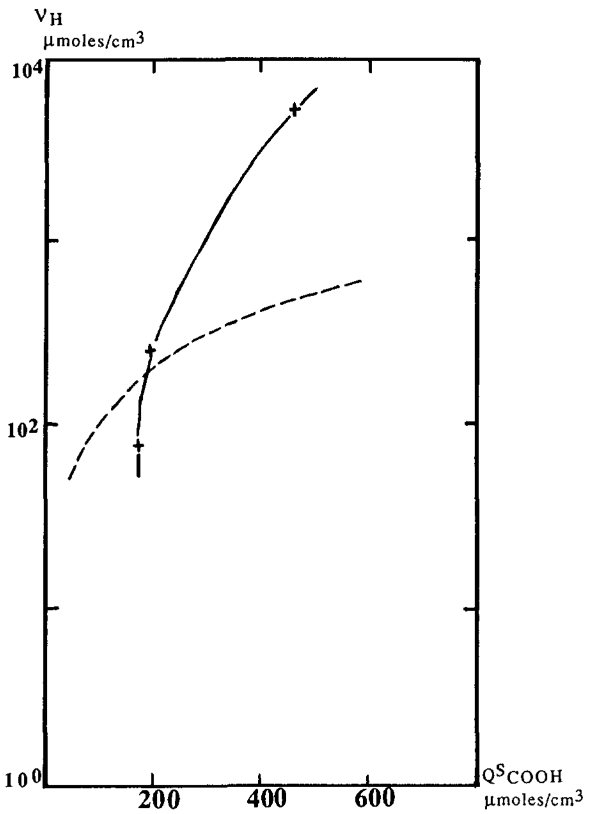

Figure 6 Plot of ν_H *versus* Q^S_{COOH} (——), compared with the theoretical prediction (– – –) assuming that each copolymerized function is involved in an acid dimer

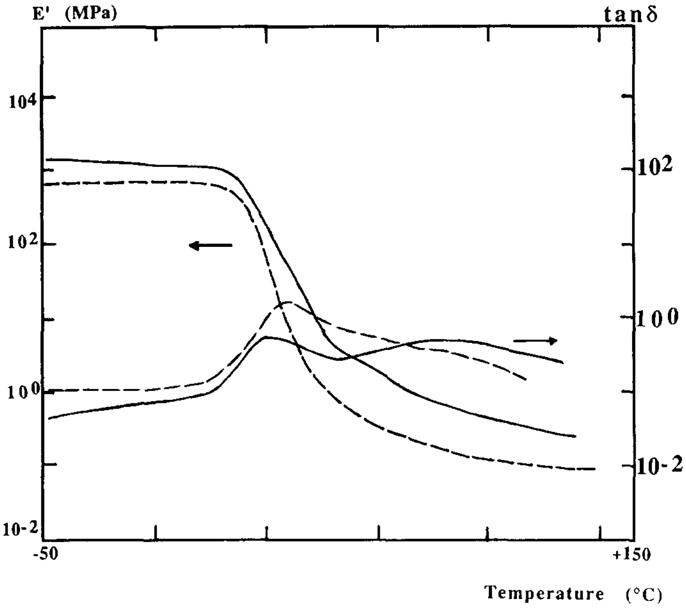

Figure 7 Isochronal ($f = 1$ Hz) temperature dependence of E' and tan δ, recorded for latex films D (– – –) and E (——). The level of E'_r is found to depend markedly on the neutralization of the latex

between particles. These groups should give rise to dipolar interactions, which create physical crosslinking knots, and thus enhance both the rubbery storage behaviour and cohesive strength properties of the latex films. As a matter of fact, in the case of bulk ion-containing polymers, it is well known that, because of the low polarizability of the surrounding matrix, ionic species tend to form dipoles or multiplets, or even to cluster into larger domains which link the chains together[19,21]. Thus, it appears to be of particular interest to probe the viscoelastic behaviour and morphology of ion-containing latex films at the same time, so as to try to understand how this phenomenon can alter the properties of the films.

Figure 7 shows the isochronal temperature dependence of E' and tan δ, recorded for samples D and E under conditions described in the Experimental section. Let us recall that the samples are issued from the same dispersion whose pH has been adjusted to two different values (4.5 and 9) with ammonia. The increase of pH above the pK_a of the copolymerized carboxylic groups results in two alterations in the d.m.a. spectra of the films, which are to be related to the creation of ionic moieties at the boundaries between particles. First of all, concerning the transition zone from the low temperature glass-like behaviour to the high temperature rubbery region, it appears that the maximum value for tan δ is significantly decreased when the latex is neutralized, indicating that viscous loss is restricted in the sample, due to the presence of new ionic crosslinking knots. Surprisingly, the position of the transition zone on the temperature scale is only slightly affected by this phenomenon; this behaviour could stem from the fact that only a small amount of the whole sample is concerned with the ionic crosslinking process. Second, concerning the high temperature rubbery region of the samples, the E' obtained for the neutralized latex films exhibits a much higher value (about one order of magnitude) than the value obtained for the low pH (4.5) latex films. Now, comparison of TEM micrographs taken on both samples shows an enhancement of particle boundary preservation upon neutralization of the latex, although some particles may have coalesced even in the neutralized latex film (*Figure 8*). Hence, an unambiguous correlation can be drawn between the structure of the latex films and their stiffened rubber behaviour.

Crosslinking effect induced by ionic interactions in the boundary regions between particles can be more readily observed in the isothermal frequency dependence of E' (*Figure 9*). *Figure 9* is obtained by applying the method of reduced variables at $T_0 = 28°C$. Criteria of applicability of the method were checked to be fulfilled for both non-neutralized and neutralized samples, since no general rule seems to be valid for ion-containing polymers[18,22,23]. In particular, breakdown in frequency–temperature superposition may occur due to the temperature-dependent morphology of the ionic multiplets or clusters[23]. In the present case, the shift factors for the frequency scale log a_T were found to obey a law of the WLF type, with values of the c_1^0 and c_2^0 constants equal to 8 and 32°C, and 10 and 35°C for the non-neutralized and neutralized samples, respectively. These values are typically in the same order of magnitude as the c_1^0 and c_2^0 values given in the literature for ion-containing acrylo-vinylic bulk copolymers[18]. Furthermore, using the methodology developed in reference 13, it can be shown that the E'_r of the neutralized sample exhibits a value ~50 times higher than that determined for the non-neutralized

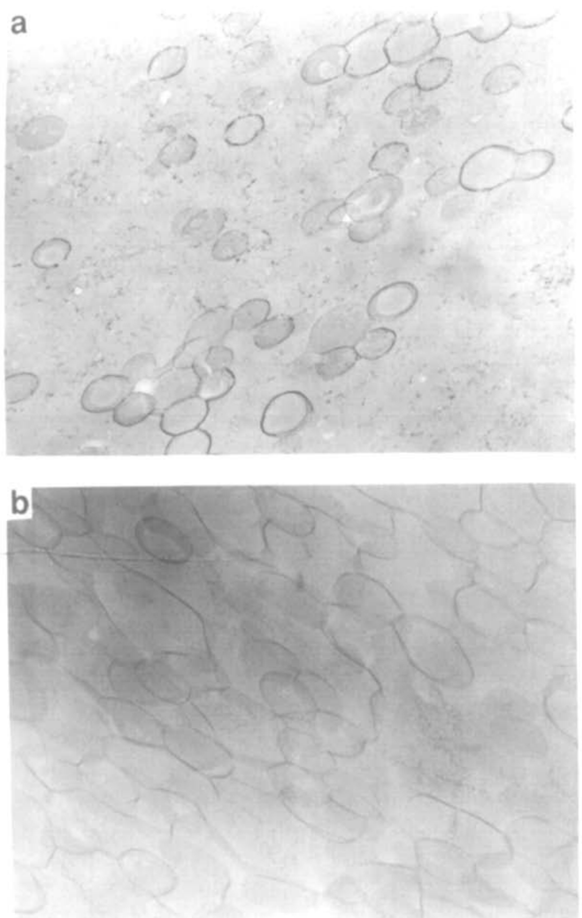

Figure 8 TEM micrographs of stained ultramicrotomed latex films D (a) and E (b). Comparison of these pictures brings out evidence of the enhancement of particle boundary preservation and particle ordering upon neutralization of the latex (magnification ×35000)

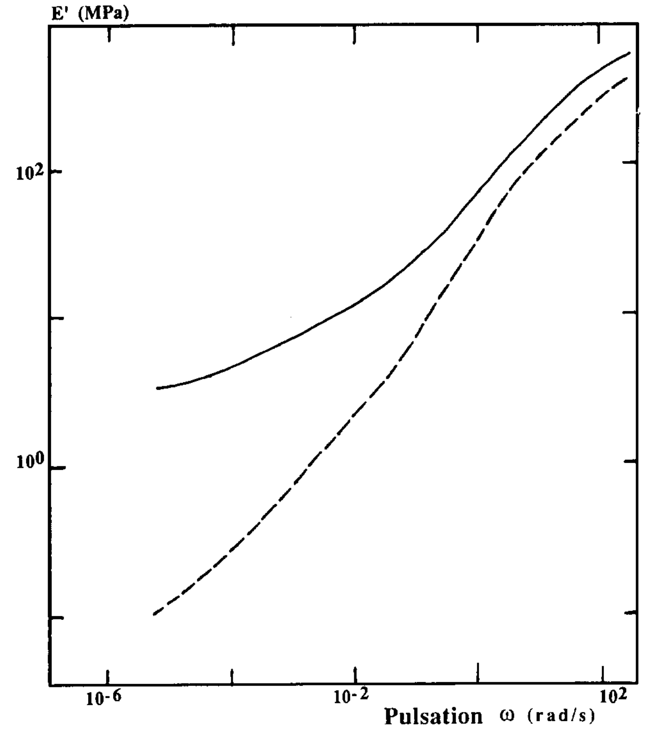

Figure 9 Log–log plot of the isothermal master curves obtained for E' of latex films D (– – –) and E (——) at $T_0 = 28°C$. A strong crosslinking effect appears in the low frequency region upon neutralization of the latex

one. Thus, the crosslinking effect is quite similar to the ionomer process in a polymer matrix of low polarizability bearing ionic inclusions. Moreover, as the ionic crosslinking knots are introduced at the boundaries between particles, it can be inferred that they will contribute to the cohesive strength of the latex films. Finally, it is worthwhile noticing that this ionomer effect has been found to be very sensitive to the presence of water (even in the vapour form) in the films: for non-well-dessicated samples, the E'_r of the films obtained from the neutralized latex comes back to the value determined for the non-neutralized film.

At this stage, it should be stressed that interfacial crosslinking can occur even when the cation brought by the neutralizing agent is monovalent[18,23,24]: ionic multiplets then stem from ion pair interactions through electrostatic mechanisms, and they are confined in polar interfacial membranes dispersed in the SB matrix of low polarizability. In these multiplets, charge distribution is fixed by both electrostatic potential, steric factors and constraints arising from the fact that each ion pair is linked to the polymer backbone. In this process, it has been shown that the nature and the size of the neutralizing agent should play a major part. According to Navratil *et al.*[18], the counterion size seems to have some effect on the stability of the ion multiplets. The ease with which multiplets dissociate is a function of the inter-ion distance in such a multiplet: the larger the inter-ion distance, the lower the energy required to remove an ion pair. So, it seems to be of particular interest to check whether this behaviour is still valid in latex films. For this purpose, the isochronal viscoelastic properties of films obtained from latices whose pH have been raised to 9 using various neutralizing agents were investigated. *Figures 10* and *11* show the ischronal temperature dependence of E' and tan δ recorded for samples F and G, respectively. In both figures, the corresponding curves recorded for the non-neutralized sample D have also been reported. It appears that, concerning samples F and G, neutralization of the carboxylic groups with sodium hydroxide and AMA, respectively, has given rise to a strong ionomer effect, resulting in an overwhelming increase in the E'_r, for sample F particularly. Besides, the main T_g of the films is not affected by neutralization. However, these films exhibit a second relaxation phenomenon located around 55°C, which is responsbile for a second transition

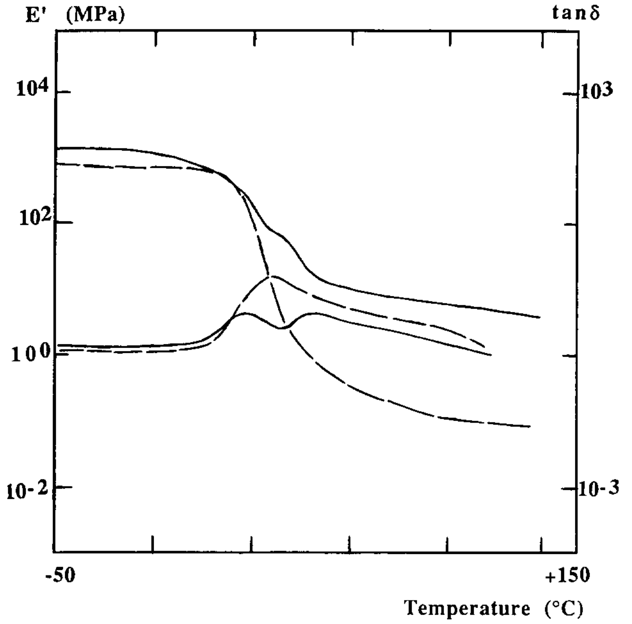

Figure 10 Isochronal ($f = 1$ Hz) temperature dependence of E' and tan δ, recorded for latex film F (——). A second transition of low amplitude appears in both the E' and tan δ curves. The corresponding curves recorded for the film issued from the non-neutralized latex are also shown for comparison (– – –)

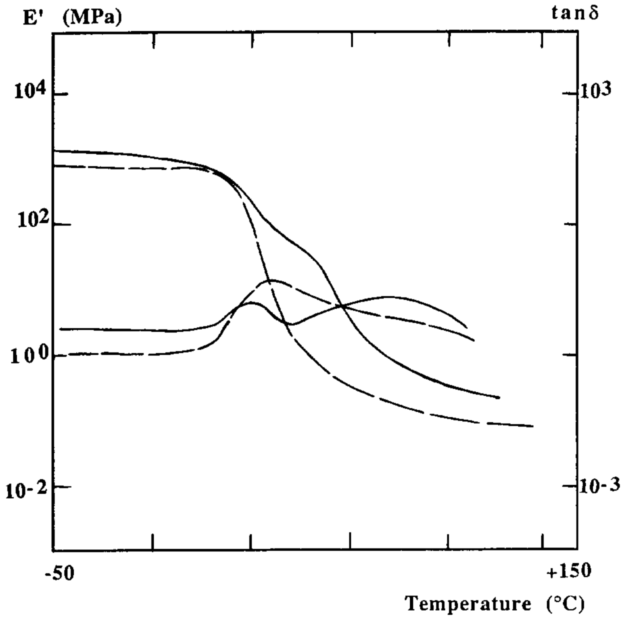

Figure 11 Isochronal ($f = 1$ Hz) temperature dependence of E' and tan δ, recorded for latex film G (——). A second steady transition appears at ~55°C in both the E' and tan δ curves. The corresponding curves recorded for the film issued from the non-neutralized latex are also shown for comparison (– – –)

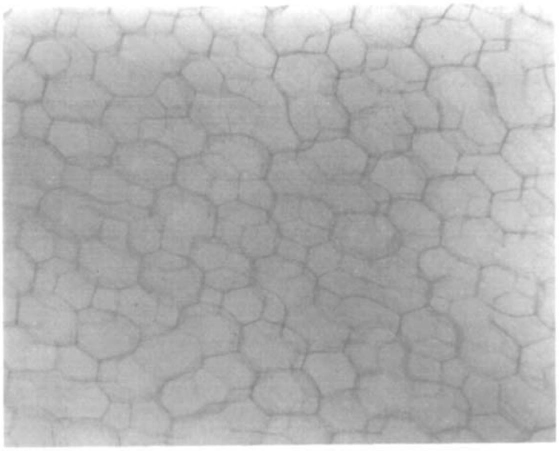

Figure 12 TEM micrograph of stained ultramicrotomed latex film F. The stained network of hydrophilic interfaces appears to be regular and well-defined (magnification ×60000)

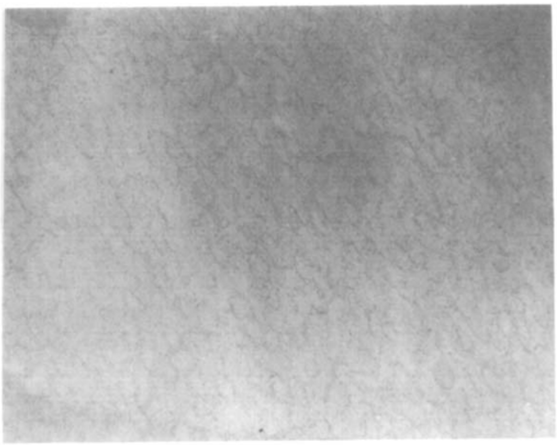

Figure 13 TEM micrograph of stained ultramicrotomed latex film G. The stained network of hydrophilic interfaces appears to be very dense, but only in the form of thin dotted layers (magnification ×22000)

of low amplitude appearing in both the E' and tan δ curves in *Figures 10* and *11*. This transition should be considered as the signature of a segregated phase consisting of an interfacial network of ionic clusters, whose relaxation is quite different from that of the core of the particles. Furthermore, in the case of film F, its steady shape brings out evidence of the rather high degree of connectivity of this phase. In a simplified scheme, the polymer film should be considered as an SB elastomer, whose T_g is close to 20°C, and which contains a three-dimensional honeycomb-like network of thin interfaces, these membranes acting as a strengthening architecture. When the second transition does not appear, as in the case of sample E (*Figure 7*), it can be inferred that ionic groups remain likely in the form of isolated aggregates or multiplets, without giving rise to a macroscopic phase. Then, they only behave as additional crosslinking knots and not as a different segregated phase.

Detailed information about the morphology of the films, in close correlation with the strong changes observed in the d.m.a. spectra, can be brought out by inspection of TEM micrographs taken on samples F and G (*Figures 12* and *13*). The stained network of strongly polar interfaces seems to be rather regular and well-defined for sample F, whereas it appears only in the form of thin dotted layers in the case of sample G. This behaviour is not well-elucidated, but it may arise from a difference in the morphology of the ionic multiplets within the interfacial layers: considering the viscoelastic behaviour of both films, more clustering is likely to occur upon neutralization with AMA. Another possible explanation, which remains more unlikely, could be a difference in the affinity of these layers for the staining agent. Nevertheless, the morphology of films F and G is clearly found to be different from that previously observed for films D and E. More precisely, the former films obviously exhibit a much more well-ordered structure than the latter ones, with a much higher density of the interfacial network. These observations can thus be satisfactorily correlated to the above modifications in the viscoelastic properties of the films.

At this point, it has been clearly shown that introduction of ionic groups at the boundaries between particles leads to a noticeable increase in the E'_r of the films, due to either the presence of new physical ionic crosslinking loci or the creation of a segregated phase of ionic clusters. In both cases, cohesive strength of the films is likely to increase compared to that of the non-neutralized latex films. Moreover, as manifested in the wide well-defined rubber-like plateau observed in *Figure 10*, Na^+ counterions are found to form very stable crosslinks over a large temperature range. In this respect, the behaviour of latex films containing carboxylic ionomers is identical to that of bulk ionomers of the same type[18]. In fact, ionomer formation effect in latex films has been evidenced for small-sized neutralizing agents, such as ammonia, sodium hydroxide or even AMA. In contrast, concerning the neutralizing agent DAPOE which has a much larger size, a quite different behaviour is expected due to the polymeric nature of this species. *Figure 14* shows the isochronal temperature dependence

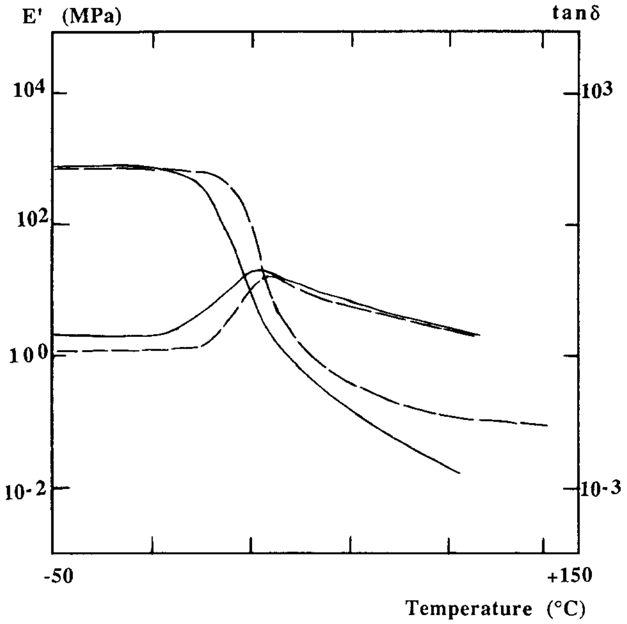

Figure 14 Isochronal ($f = 1$ Hz) temperature dependence of E' and tan δ, recorded for latex film H (——). The position of the glass transition zone is shifted towards the low temperature region by ~ 12°C, and modulus E'_r is greatly reduced, indicating a pronounced plasticization effect. The corresponding curves recorded for the film issued from the non-neutralized latex are also shown for comparison (– – –)

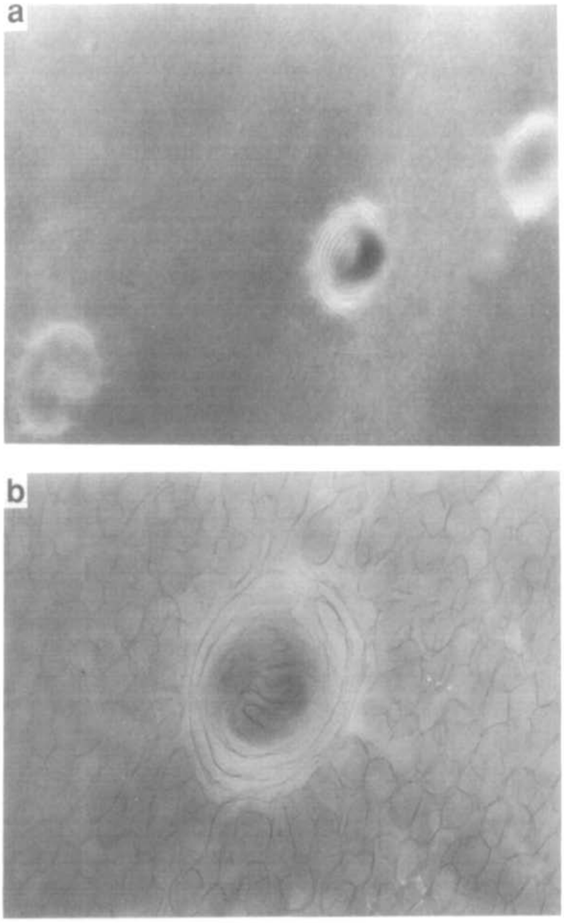

Figure 15 TEM micrographs of stained ultramicrotomed latex film H. Beside the well-ordered structure of close-packed individual particles, large hydrophilic coiled lamellar aggregates can be observed (magnification: (a) ×10000; (b) ×35000)

of the E' and tan δ recorded for film H; the corresponding curves for the non-neutralized sample D have also been reported for comparison. Two main alterations in the spectra are worth noticing. First, the position of the glass transition zone is strikingly shifted towards the low temperature region by $\sim 12°C$. Second, E' practically does not show any rubbery behaviour, and seems to rapidly decrease after the transition zone, towards values typically reported for viscous liquid-like polymers. In fact, these two phenomena are the signature of some kind of plasticization of the latex film induced by DAPOE, which corresponds to a totally opposite effect compared to the previous ionomer one. It must arise from the size and polymeric nature of the neutralizing agent, which can give rise to particular non-ionic interactions with the chains belonging to the latex particles. The presence of DAPOE is likely to greatly reduce the intermolecular forces among carboxylic moieties. The same effect has been observed in bulk carboxylic ionomers based on styrene–methacrylic acid copolymers, plasticized by alkyl phthalates[18,25]. However, a more fruitful discussion can be constructed upon inspection of the morphology on the films. *Figure 15* shows TEM photomicrographs taken of film H. It appears that the films exhibit a two-phase structure: besides a well-ordered structure stemming from the close-packed stacking of individual particles, large lamellar objects whose size scales ~ 10 times the diameter of the latex particles, can be observed. These lamellar objects are hydrophilic, since they can be stained by uranyl acetate. For this purpose, it is suggested that they likely arise from the segregation of the DAPOE molecules, which are hydrophilic due to their oxyethylene groups and which can organize in the form of coiled lamella in the film. SANS experiments performed on this sample confirm all these results[26]. However, whether these aggregates form during the coalescence of the particles (dehydration process), or in the dried film, cannot be decided at this point. Nevertheless, the plasticization effect appearing in the micromechanical behaviour of the films, can be related to the presence of these large lamellar DAPOE aggregates dispersed in the films, although the exact mechanism is not well understood. Obviously, these aggregates will not enhance the cohesive strength of the films, since they tend to considerably lower the elastic behaviour of the films towards a liquid-like behaviour (above their T_gs).

CONCLUSIONS

This paper gives a thorough investigation into particle/particle interfaces in films obtained from aqueous polymer dispersions. A refined analysis of the part played by boundary regions between particles in the micromechanical behaviour of latex films has indeed been provided by combining d.m.a. and TEM techniques. In many ways, it appears once again that working out relationships between the morphology of the films and their viscoelastic properties should be considered as a powerful means for gaining safe and reliable information[9,10,12,13]. Our present work mainly brings out strong evidence of the major part played by particle interfaces in the viscoelastic properties of latex films. Furthermore, it can be considered as a first approach to the cohesive strength properties of the films, since it enables the formation of links between particles, acting as strengthening bridges, to be predicted. In our system, the boundary regions between polymer particles have been manipulated by incorporating non-neutralized or neutralized carboxylic functions at the surface of the particles. The presence of these groups results in interfacial crosslinking due to either H bonding or ionic dipolar interactions. In the case of non-neutralized functional groups arising from a copolymerized carboxylic acid, interactions among these groups have been shown to contribute efficiently to the viscoelastic properties of latex films, although they are not found to form a segregated phase, even at high content. Moreover, a semiquantitative analysis has enabled us to single out a threshold value for Q_{COOH}, over which extra carboxylic groups are not likely to achieve any further cohesive strength, since they cannot participate in interfacial crosslinking. However, these extra carboxylic functions are still responsible for the increase in the E'_r, because they are included in coupling knots located in the core of the particles. Concerning ionic groups incorporated at the surface of the particles upon neutralization of carboxylic functions, these species give rise to dipolar interactions, which result in additional physical crosslinks. Due to the low polarizability of the core of the particles, ionic species tend to form isolated multiplets, or even to cluster into larger domains. In the case of our ion-containing latex films, the former morphology is induced by neutralization with ammonia, whereas the latter is likely to appear when sodium hydroxide or AMA are used as neutralizing agents. Comparison of d.m.a. spectra obtained for both kinds of samples brings out strong arguments in favour of such a difference in the structure of the interfacial ionic layers: clustering of ions in a segregated phase gives rise to a pronounced second relaxation phenomenon, located at a temperature higher than the main T_g; on the contrary, when ions remain in the form of isolated aggregates or multiplets, this second transition does not appear. Furthermore, TEM observations can be correlated to the modifications appearing in the viscoelastic properties of the films: the enhancement of the rubbery elastic behaviour is clearly related to the order and the density of the interfacial network. Finally, it has been shown that, depending on the nature and the size of the neutralizing agent introduced in the dispersion, either an ionomer effect or a totally opposite plasticizing effect can be obtained. The latter effect is thought to stem from a reduction of the intermolecular forces among carboxylic moieties, due to the macromolecular nature of the neutralizing agent (DAPOE) used. More precisely, TEM experiments have evidenced a segregation of the neutralizing molecules into large coiled lamella, which are likely responsible for the plasticization effect. As far as cohesion strength is concerned, it can be predicted that the ionomer effect is likely to enhance this feature, whereas plasticization will decrease it markedly.

Hence, our work as a whole, including both our previous study of the covalent crosslinking and molecular interactions effects[13] and the present investigation into the part played by particle/particle interfaces, provides a comprehensive description of the viscoelastic behaviour of latex films. All our results and the information gained are based on dynamic microstrain experiments, which are experiments performed in a thermodynamic state close to quasi-equilibrium. Now, it seems to be of particular interest to probe large strain ultimate properties, so as to obtain a more complete picture of the mechanical properties of the system and, more precisely, to check whether our predictions concerning cohesive strength of the films are confirmed.

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