Thermomechanical behaviour of composite polymer films obtained from poly(vinyl acetate) latexes sterically stabilized by poly(vinyl alcohol)

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Dynamic thermomechanical properties of composite polymer films obtained from poly(vinyl acetate) (PVAc) latexes which are sterically stabilized by poly(vinyl alcohol) (PVA) are investigated. These films exhibit dramatic changes in their dynamic mechanical response after annealing. The effects of various parameters (volume fraction and features of PVA in the latex, mean size of the PVAc particles) on this behaviour are discussed. The results are interpreted on the basis of a phase rearrangement during annealing, which results in a strong enhancement of the degree of connectivity of the PVA matrix within the films. Finally, it is shown that qualitative and semiquantitative information can be gained from inspection of dynamic thermomechanical spectra concerning, respectively, the features of the interphase between PVAc particles and the PVA matrix and the actual volume fraction of PVA involved in the continuous matrix.

(Keywords: poly(vinyl acetate); poly(vinyl alcohol); sterically stabilized latex; composite films; thermomechanical properties; multiphase system; phase rearrangement)

INTRODUCTION

Polymer blends or composites have come to be one of the most efficient ways to produce high-performance materials, because the immiscibility encountered for most polymer pairs makes it possible to combine attractive properties of each separate phase in a given range of temperature. As far as viscoelastic properties are concerned, simple volume-average mixing rules do not satisfactorily describe the physical behaviour of these systems, but phase geometry and morphology are known to play an important role[1]. Among the various polymerization methods, emulsion polymerization can be considered as a very versatile and well-suited process to achieve a peculiar composite morphology through the production of heterogeneous colloidal polymer particles[2,3]. Upon drying, these latexes can give rise to continuous multiphase films whose final morphology depends on the compatibility of the polymer phases, mobility of the chains and the thermal treatment of the samples[4]. Dynamic thermomechanical analysis has been extensively used for the characterization of heterogeneous polymer films obtained from poly(butyl acrylate)–poly(vinyl acetate) (PBA–PVAc) composite latexes[3,5,6]; the temperature dependence of the moduli has been satisfactorily fitted using Kerner's equation for a two-component composite. Moreover, correlations between features of the transitions and morphology of the two phases have been proposed. At the same time, an extensive qualitative description of the effects of thermal annealing and particle features on the final thermomechanical behaviour of polymer films obtained from polystyrene–PBA (PS–PBA) latexes has been provided by O'Connor and Tsaur[4]. Recently, we have also thoroughly investigated the dynamic micromechanical properties of copolymer latex films so as to probe the effect of gel content[7] and functional comonomer content[8] on their thermomechanical behaviour. In particular, incorporation of ionic functional groups at the surface of the particles has been shown to give rise to ionic macroscopic segregated phases or isolated multiplets owing to the incompatibility of the ionic species within the non-polar cores of the particles. This phase separation results in dramatic alterations of the viscoelastic properties of the composite films[8].

Now it seems to be of particular interest to focus on a new kind of latexes which have been so far poorly investigated for the thermomechanical behaviour of their films. These are aqueous dispersions of particles which are sterically stabilized by a water-soluble polymer[9] as opposed to the previous latexes whose stabilities were related to electrostatic repulsions between the particles[10]. Sterically stabilized colloids display many advantages compared to electrostatically stabilized ones: they are less sensitive to electrolytes, and exhibit better rheological properties[11]. Moreover, in composite polymer films obtained on drying these dispersions, the steric stabilizer is expected to fill the voids between the particles and achieve the development of cohesive strength by some kind of interstitial crosslinking process[12,13]. In the present work, we focus on the thermomechanical behaviour of multiphase polymer films obtained from poly(vinyl acetate) (PVAc) latexes, sterically stabilized by poly(vinyl alcohol) (PVA), a part of which can be introduced into the dispersion after polymerization. The PVA chains are anchored at the particle surface, either

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by physical adsorption or chemical grafting, and act as a steric stabilizing layer for the particles. This versatile system offers the opportunity of varying the total amount and features of PVA, and also the features of the particles, so as to study their effect on the thermomechanical behaviour of the films. A semiquantitative analysis of this thermomechanical behaviour will be proposed in terms of a polymer–polymer composite model based on the well-known Kerner equation. Then, information about the interphase region[14] between PVAc particles and PVA chains in the films will also be discussed.

Table 1 Main features of the series of PVAc latexes sterically stabilized by PVA

Latex	PVA volume fraction (%) Initial charge ϕ_i	Final addition ϕ_a	PVAc average particle size d (μm)	PVA viscosity grade[a] η (mPa s)	PVA hydrolysis level[a] (mol%)
A	3.15	0	0.7		
B1	5.2	0	1.2		
B2	5.2	3.6	1.2	25	88
C1	5.3	4	2	25	80
C2	5.3	4	0.55	25	80
C3	5.3	5.7	2	4	80
C4	5.3	5.7	0.55	25	80
C5	5.3	5.7	0.55	25	99
C6	5.3	5.7	0.55	4	80
D1	6.5	0	1.2		
D2	6.5	3.6	1.2	25	88
D3	6.5	7	1.2	25	88

[a] These are the features of the PVA added at the end of polymerization (final addition); η is the viscosity of a 4 wt% aqueous solution of PVA at 20°C

EXPERIMENTAL

Latex preparation

A series of emulsifier-free poly(vinyl acetate) latexes were prepared in a 25 l stainless steel reactor equipped with a condenser, using a semicontinuous emulsion polymerization process. The initiator was potassium persulfate (KPS). Vinyl acetate monomer from Rhône–Poulenc was fed in over a period of 5 h. Poly(vinyl alcohol) (PVA) from Rhône–Poulenc (Rhodoviol 25/140) was introduced in the initial charge of the reactor at various volume fractions (between 3.15 and 6.5%), together with an antifoaming agent, sodium acetate as a buffer, and 5% of the total vinyl acetate amount. The reaction started at 66°C and the temperature was then increased to 83°C and kept constant during the whole process.

Depending on the amount of PVA introduced in the initial charge, the particle size distribution of the latexes obtained in this way was found to be broad for the highest initial content and rather narrow for the lower ones; the average particle size was between 0.55 and 2 μm. The effects of the PVA volume fraction and features on the properties of the resulting polymer films were studied by varying the amount of PVA introduced in the dispersion after the polymerization (final addition), and also by varying the viscosity grade (η) and hydrolysis level (HL) of the added PVA. For this purpose, dilute aqueous solutions of PVA (15% weight content) were poured into the dispersions at a temperature of 75°C under stirring. It was checked that the solubility of the added PVA in water was acceptable under these conditions. Thus, our samples exhibited final PVA volume fractions ranging from 3.15 to 13.5%. The main data concerning the series of dispersions are given in *Table 1*.

Film formation

Polymer films used in the dynamic thermo-mechanical analysis (d.t.m.a.) studies were prepared by casting the latexes in silicon dishes of well-controlled depth and evaporating the water under ambient conditions over 48 h. They were then dried in an oven at 70°C for 30 min. Samples with a 1 mm constant thickness were then cut to dimensions of 5×1 cm^2 and stored under vacuum in a desiccating vessel prior to use.

Dynamic thermo-mechanical analysis (d.t.m.a.)

The dynamic thermomechanical behaviour of the films was investigated using the Rheometrix RDS-LA viscoelastometer described in previous work[7,8]. The isochronal temperature dependences of the storage modulus E', loss modulus E'' and loss tangent $\tan\delta$ were recorded over a wide temperature range (25–150°C). These variations were obtained for a frequency of 1 Hz at a constant heating rate of 1°C min^{-1} under a nitrogen atmosphere. Simple extension was chosen as the deformation mode. The strain amplitude was fixed at 10^{-3}; this value lies in the linear viscoelastic regime, where the moduli do not depend on the deformation amplitude. Under these conditions, the accuracy and reproducibility of the measurements were found to be satisfactory. The effect of annealing was studied by running the samples once, then annealing them at 150°C for half an hour under a nitrogen atmosphere, and finally running them again from 25 to 150°C. It was found that a longer treatment at 150°C did not induce any additional alteration of the viscoelastic behaviour of the samples. According to Marten[15], the thermal decomposition of PVA under a nitrogen atmosphere, i.e. in the absence of oxygen, only begins at 200°C through dehydration. So, the applied thermal treatment does not modify the chemical features of our system.

RESULTS

Effect of thermal annealing and PVA volume fraction

Figure 1 shows the typical isochronal temperature dependence of the storage modulus E' and loss tangent $\tan\delta$ recorded under the above conditions for latex film A, which exhibits the lowest PVA volume fraction in the series (3.15%). For comparison, spectra obtained for the same sample before and after thermal annealing at 150°C have been included in the same figure. Even after thermal annealing, d.t.m.a. spectra of the films are found to exhibit only a strong transition located at $\sim$35°C, which is assigned to the classical change from the unrelaxed glassy state in the low-temperature region to the rubber-like behaviour in the high-temperature range. This strong relaxation phenomenon is responsible for both the steady decrease of about three orders of magnitude in the storage modulus E' and the maximum in the $\tan\delta$ curve. The value of T_g, deduced from the maximum value of the loss modulus E'' of the films[2,7], appears in the expected region for bulk PVAc, i.e.

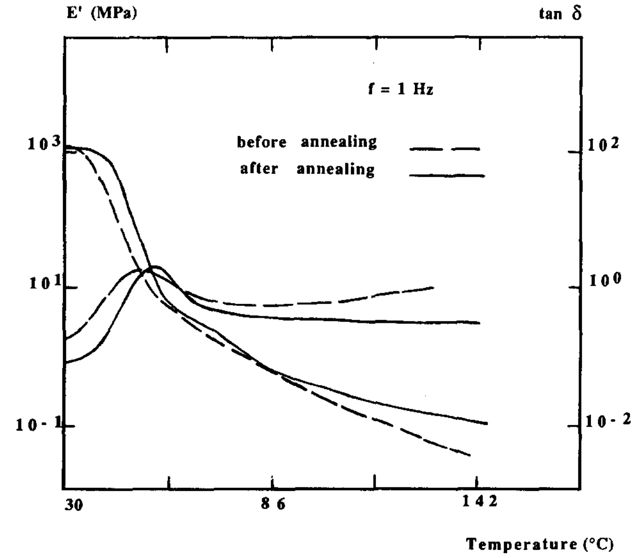

Figure 1 Typical isochronal ($f = 1$ Hz) temperature dependence of storage modulus E' and loss tangent tan δ obtained for latex film A before and after thermal annealing at 150°C

~32°C[16], whereas the T_g for PVA is expected to lie between 60 and 85°C, depending on its HL value and degree of polymerization (*DP*)[15]. Both spectra in *Figure 1* do not bear any clear witness to the presence of PVA in the film: only a slight shift is observed for the position of T_g compared to the value expected for pure PVAc samples[16], together with a slight hump in the storage modulus curve located between 55 and 70°C. Comparison of the spectra in *Figure 1* suggests that thermal annealing alters the d.t.m.a. spectra of film A only slightly. The main modification is the appearance of a rubbery modulus plateau in the temperature region located above 110°C, which is the signature of the formation of a rubber-like network; in addition, a little shift of ~6°C for the glass transition temperature T_g is also observed after annealing.

Figure 2 shows the typical isochronal temperature dependence of the storage modulus E' and loss tangent tan δ recorded under the above conditions for latex film D3, which exhibits the highest PVA volume fraction in the series (13.5%). Spectra obtained before and after annealing the sample at 150°C have been reported in the same figure to allow a detailed comparison. The temperature dependences of E' and tan δ obtained for sample D3 before annealing are quite similar to those obtained for sample A, except that the hump in E' located around 60°C is more pronounced. This hump is likely to be related to the existence of isolated PVA clusters in the film. As opposed to film A, it appears that annealing film D3 results in dramatic changes in its viscoelastic behaviour; apart from the main glass transition previously observed near 35°C, a second relaxation phenomenon clearly stands out at about 70°C after annealing. The appearance of this second transition is accompanied by an overwhelming increase in the storage modulus E' in the temperature range between the two transitions. In this zone, E' exhibits almost a plateau, or at least a smooth variation with temperature. In addition, after annealing, tan δ exhibits two well-identified loss peaks which are the signature of a phase-separated blend[4] since each component experiences its own glass transition. All these observations strongly suggest that after annealing the film contains two clearly distinct phases, which should consist of macroscopic domains of PVAc on the one hand and a PVA phase on the other. As will be discussed later, a phase rearrangement has likely taken place upon annealing, leading to an enhancement of the PVA phase connectivity. Comparison of *Figures 1* and *2* suggests that the volume fraction ϕ of PVA in the films is related to the key parameter for the appearance of an outstanding phase reorganization.

Figure 3 shows the typical isochronal temperature dependence of the storage modulus E' recorded after thermal annealing for latex films A, B2 and C4 which contain various PVA volume fractions ranging from 3.15 to 11%. Before discussing this diagram, it

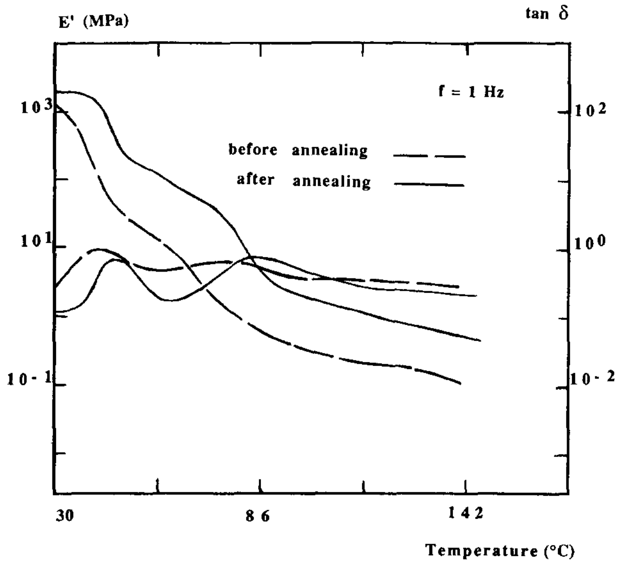

Figure 2 Typical isochronal ($f = 1$ Hz) temperature dependence of storage modulus E' and loss tangent tan δ obtained for latex film D3 before and after thermal annealing at 150°C. A second transition clearly appears around 70°C after thermal annealing, accompanied by a pronounced increase in the storage modulus E' between 40 and 70°C

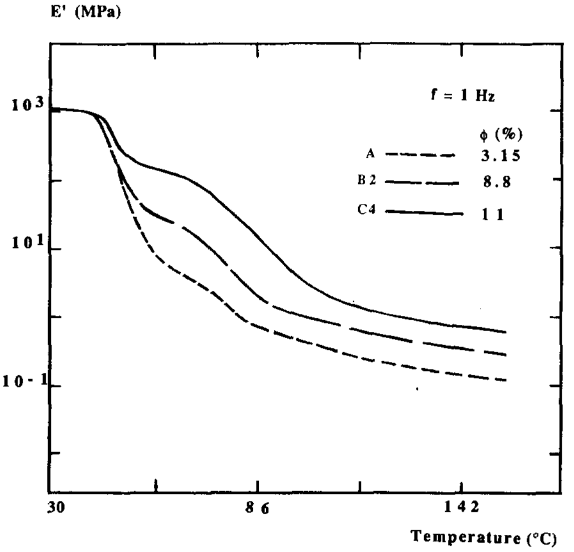

Figure 3 Typical isochronal ($f = 1$ Hz) temperature dependence of storage modulus E' obtained for latex films A, B2 and C4 after thermal annealing at 150°C. Notice that the spectrum obtained for latex film D1 ($\phi = 6.5\%$) under the same conditions (not included in the figure) is identical to that of sample A. The threshold value ϕ_t of the PVA volume fraction for the clear outset of phase rearrangement is thus experimentally found to lie between 6.5 and 8.8%

should be stressed that spectra recorded for samples B1 and D1, whose PVA volume fractions are 5.2 and 6.5%, respectively, have not been included in the figure because they are quite similar to that obtained for film A and they do not actually show any modification upon annealing. Inspection of *Figure 3* reveals that the value of E' in the temperature zone located between the two main transitions is dependent on the PVA volume fraction in a rather complicated way; qualitatively, *Figure 3* is most informative because it shows that there exists a threshold value[17] ϕ_t for the PVA volume fraction, above which the system undergoes a profound reorganization upon annealing. The value of $\phi - \phi_t$ appears to be a key parameter for a quantitative interpretation of the dependence of E' upon PVA content[17]. From inspection of *Figure 3*, it turns out that ϕ_t ranges from 6.5 to 8.8%. For a PVA content lower than ϕ_t, some changes may occur in the distribution of PVA in the films, but they do not significantly alter the thermomechanical properties.

A more complete analysis of the strong phase rearrangement observed in our composite films will be given in the third section, together with a semiquantative approach. It will be shown that the value of E' measured in the region located between the two transitions can be quantitatively related to the mechanically effective volume fraction of PVA involved in the segregated continuous phase formed upon annealing[1,3,4].

Effect of average PVAc particle size

Figure 4 shows the typical isochronal temperature dependence of the storage modulus E' and loss tangent $\tan\delta$ recorded for latex films C3 and C6 after annealing at 150°C. These films are obtained from latexes which exhibit the same PVA volume fraction (11%) but quite different average particle sizes, i.e. 2 μm for the former and 0.55 μm for the latter. Since their PVA contents are higher than ϕ_t, these samples have undergone the phase rearrangement discussed earlier. However, the phenomenon seems to be more pronounced for the latex having the highest average particle size, since the value of E' in the region between the two main transitions is found to be higher in the latter case. This behaviour is attributed to a larger mechanically effective PVA volume fraction involved in the continuous segregated phase for sample C3.

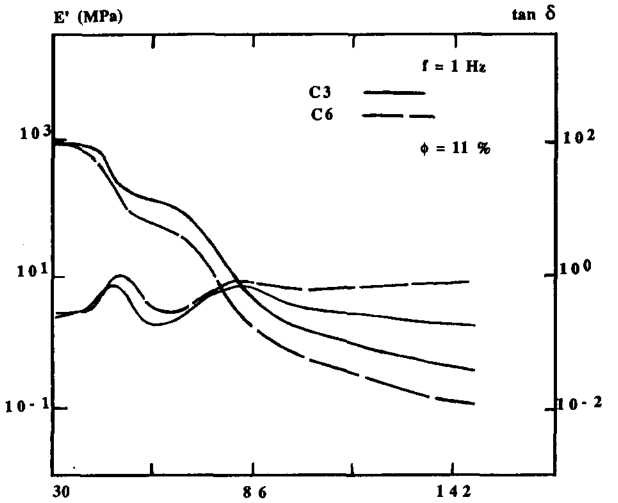

Figure 4 Typical isochronal (f = 1 Hz) temperature dependence of storage modulus E' and loss tangent $\tan\delta$ obtained for latex films C3 and C6 after thermal annealing at 150°C. The average particle size is 2 μm for the former and 0.55 μm for the latter. The PVA volume fraction (11%) and features are identical for the two samples (see *Table 1*)

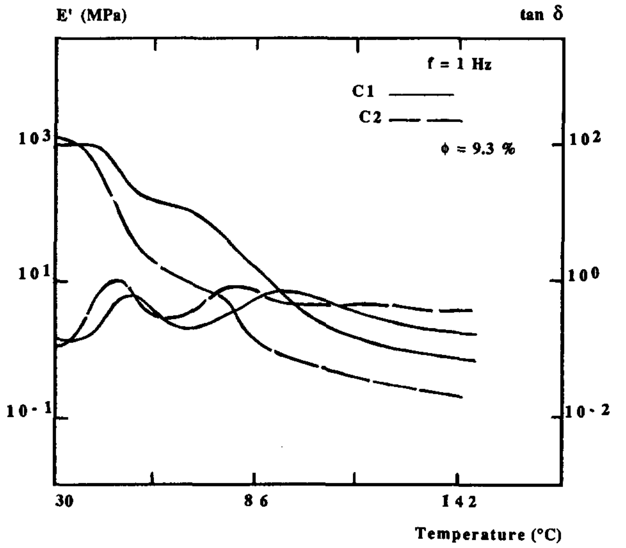

Figure 5 Typical isochronal (f = 1 Hz) temperature dependence of storage modulus E' and loss tangent $\tan\delta$ obtained for latex films C1 and C2 after thermal annealing at 150°C. The average particle size is 2 μm for the former and 0.55 μm for the latter. The PVA volume fraction (9.3%) and features are identical for the two samples (see *Table 1*). The effect of average particle size on phase rearrangement appears to be much more pronounced for a PVA volume fraction close to ϕ_t

Figure 5 shows the same kind of spectra as *Figure 4*, recorded for samples C1 and C2, whose PVA volume fractions are only 9.3%. This diagram entirely confirms the influence of average particle size on phase rearrangement. Moreover, comparison of these figures suggests that the particle size effect is probably enhanced markedly when the PVA volume fraction gets closer and closer to the threshold value for phase segregation ϕ_t. These observations lead us to conclude that $\phi - \phi_t$ is not the only parameter controlling the reorganization of the system and the viscoelastic features after annealing. Furthermore, an additional effect of the viscosity grade of the added PVA (4 mPa s for C3 and C6, 25 mPa s for C1 and C2) cannot be fully excluded, since the rate of reorganization of the phases during annealing could be limited by molecular diffusion and, hence, the molecular weights of the chains. This remark suggests that an interrelated effect of the parameter $\phi - \phi_t$ and the features of PVA could also take place. This point will be discussed in the next sections.

Effect of PVA features on phase rearrangement

PVA polymers can be obtained by controlled hydrolysis of poly(vinyl ester)s. Their main features are their hydrolysis level (HL) and their viscosity grade η, which mainly depend on their molecular weight and branching content. The latter is defined as the viscosity of a 4 wt% aqueous solution measured at 20°C, whereas the former is related to the content of hydroxy and acetate groups in the polymer[15]. In our study, η can take two distinct values, 4 and 25 mPa s, which correspond to a low nominal degree of polymerization (*DP*) ($\sim$500) and a medium one ($\sim$1500), respectively[15]. As for HL, its value ranges from 80 to 99 mol%.

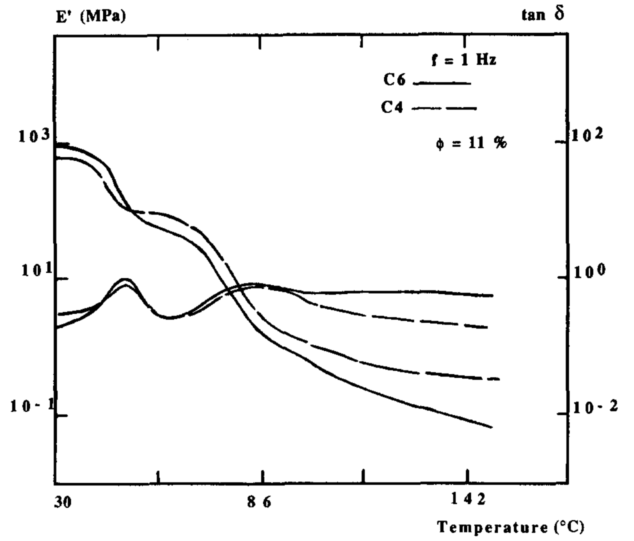

Figure 6 Typical isochronal ($f = 1$ Hz) temperature dependence of storage modulus E' and loss tangent $\tan\delta$ obtained for latex films C4 and C6 after thermal annealing at 150°C. The viscosity grade of the PVA added at the end of polymerization (25 mPa s and 4 mPa s for C4 and C6, respectively) does not affect the viscoelastic behaviour of the films

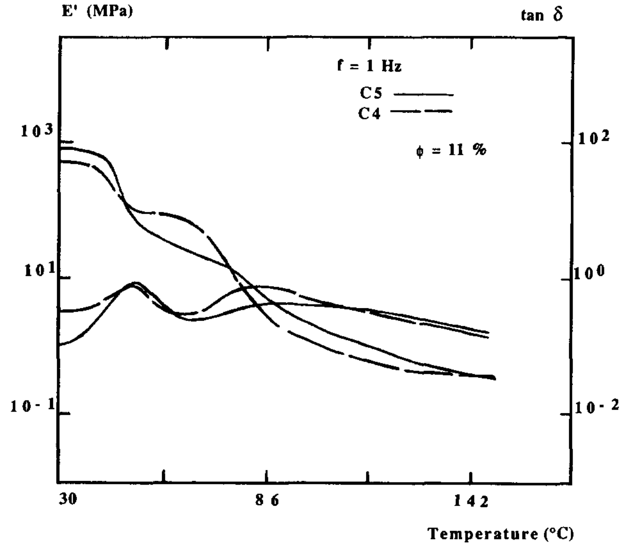

Figure 7 Typical isochronal ($f = 1$ Hz) temperature dependence of storage modulus E' and loss tangent $\tan\delta$ obtained for latex films C4 and C5 after thermal annealing at 150°C. The volume fraction of PVA involved in a continuous segregated phase after annealing appears to decrease markedly when the HL value is increased from 80 to 99%

Figure 6 shows the typical isochronal temperature dependence of the storage modulus E' and loss tangent $\tan\delta$ recorded for latex films C4 and C6 after annealing at 150°C. These samples contain the same PVA volume fractions, but the viscosity grade of PVA added at the end of polymerization is quite different. In the present case, it appears that the variation in η does not significantly affect the reorganization of the components upon annealing, since the films exhibit very similar viscoelastic behaviour over the entire temperature range. By focusing on the temperature region located between the transitions, it can be qualitatively inferred that the volume fractions of PVA involved in a segregated continuous phase after annealing are almost identical. However, no general conclusion can be drawn from the above single result; in particular, an effect might appear for PVA volume fractions closer to ϕ_t, as it has been previously observed for the effect of PVAc particle size.

As for the effect of the PVA HL value on the thermomechanical behaviour of the films, the typial isochronal temperature dependences of the storage modulus E' and loss tangent $\tan\delta$ have been recorded and compared for samples C4 and C5 (*Figure 7*). It turns out that increasing the HL value of PVA added at the end of polymerization from 80 to 99% results in a noticeable alteration of the thermomechanical behaviour of the annealed films. Firstly, the appearance of the second transition is obviously found to be less steady; secondly, the value of the storage modulus in the temperature range between the two transitions is almost one order of magnitude lower for sample C5 than for C4. These features are clearly indicative of a less mechanically effective PVA segregated phase built up upon annealing. This behaviour is not well elucidated, but it may be related to the distribution of PVA chains around the PVAc particles, and this is probably dependent on the emulsifying properties of PVA and hence its HL value.

Finally, it is worth noticing that the second glass transition temperature T_g, deduced from the maximum value of the loss modulus E'' of the films[2,7], is found to be 82°C for sample C5, which contains highly hydrolysed PVA (99 mol%), and 72°C for sample C4. This significant dependence of T_g (assigned to the PVA phase) on the HL value of PVA is quite consistent with literature data[15]; moreover, it brings out an additional argument to assign this transition to the continuous PVA phase formed upon annealing.

DISCUSSION AND CONCLUDING REMARKS

Firstly, as far as the effect of thermal annealing is concerned, the mechanical detection of the second phase after this treatment is likely to be related to an increase in the PVA domain size or degree of connectivity within the PVA phase. It should stem from a thermally induced coalescence of the PVA clusters initially contained in the films. An analogous phase rearrangement has recently been observed for films obtained from PS–PBA core–shell particles or homopolymer blends upon annealing at a temperature higher than the glass transition temperature for PS[4,18]. It has been attributed to a more or less extended coalescence of the PS phase at high temperature. In our case, we suggest that the molecular mobility probably becomes high enough at 150°C, i.e. well above the glass transition temperature for PVA, to allow the rearrangement of this phase via macromolecular diffusion. Furthermore, the resulting equilibrium morphology is expected to minimize the interfacial surface energy between the PVAc and PVA phases.

Besides the physical arguments on the driving force for reorganization, the occurrence of rearrangement could also be discussed using the formalism of bond percolation on a lattice[17]. In a very specific way for our sterically stabilized latexes, it is worth noticing that PVA is initially located in shells at the surfaces of the PVAc particles in the dispersion. Therefore, the initial morphology can be schematically described as a set of unconnected PVA clusters of finite size dispersed in the film. Then, the phase arrangement observed for ϕ higher than ϕ_t is likely to lead to the formation of a macroscopic infinite PVA cluster. In this description, ϕ_t appears to play the part of a percolation threshold[17]. At this step,

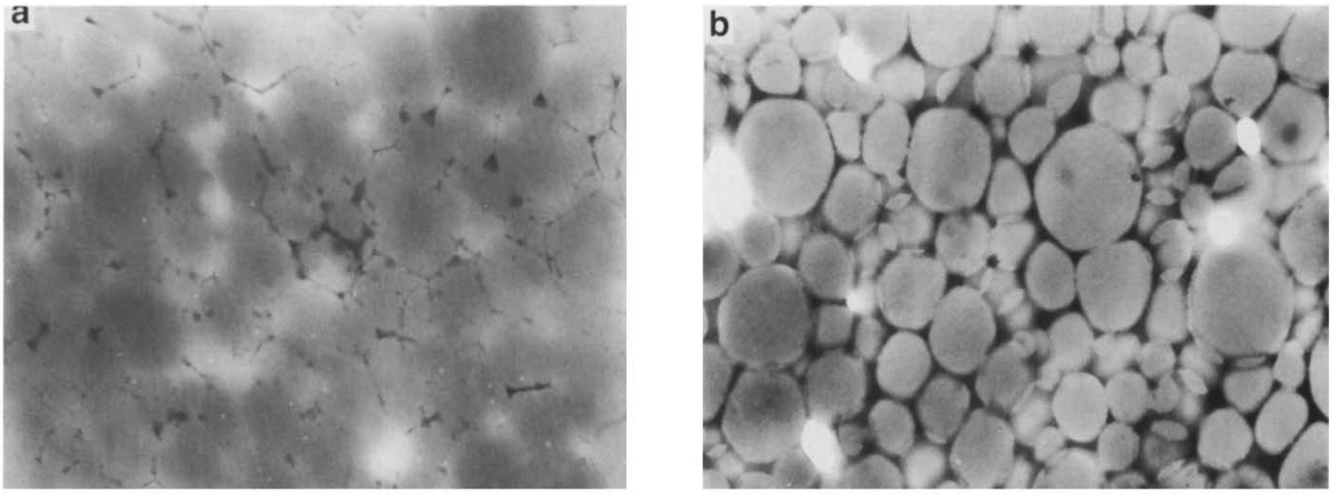

Figure 8 TEM photomicrographs of stained ultramicrotomed latex film D3 before (a) and after (b) thermal annealing. The PVA phase is selectively stained[12] with OsO_4. Comparison of the pictures gives clear evidence of a strong reorganization of the two phases, resulting in the formation of a continuous matrix (or lattice) embedding PVAc particles (magnification × 14000)

the exact morphology of the film, and more particularly the extent to which PVAc and PVA domains coalesce after annealing, remains unknown. However, using transmission electron microscopy (TEM) associated with a selective staining[12] of the PVA phase with OsO_4, this morphology can be revealed. Comparison of TEM photomicrographs taken on film D3 before and after annealing (*Figure 8*) clearly shows that the film consists of a PVA lattice or matrix in which PVAc particles are embedded and which is induced by annealing. Our results are then fully consistent with those reported by Kast[12], who has also found out such a film structure in the case of an ethylene–vinyl acetate copolymer latex sterically stabilized by PVA, and related it to the presence of two main relaxations in the d.t.m.a. spectra of the composite system. In addition, a careful inspection of the photomicrographs taken on annealed latex film D3 at a higher magnification (× 120000) enables us to estimate the thickness of the PVA shell surrounding the PVAc particles. The mean value of this thickness is estimated to be ~20 nm.

In a second step, we would like to stress that inspection of d.t.m.a. spectra provides fruitful information about the particle and film structure. In most of the storage modulus spectra reported above, a smooth decrease of E' in the temperature range between the two transitions has been singled out (see *Figure 2*, for instance). For the well-defined, phase-separated composite, the temperature dependence of E' in this region is expected to parallel that of the material forming the continuous phase[1] (PVA in our case), which is still in a glassy state in this zone. Therefore, the occurrence of a decrease in the storage modulus in this region is associated with a gradual relaxation of the composite system, and more particularly the somewhat heterogeneous zone located at the interface between PVAc and PVA. Considering the structure of the initial particles, there probably exists a more or less thick layer exhibiting a gradation of composition from pure PVAc to pure PVA with increasing distance from the core. Such a structure, which has already been proposed for heterogeneous acrylic polyblends[19], gives rise to a broadening of the transition regions. In our case, this interphase[14] should mainly consist of the PVA chains which have been grafted onto the PVAc particles during the polymerization. The relaxation mechanisms attributed to this interphase layer consistently appear in the temperature range between the transition temperatures of the two phases owing to a copolymerization effect and a restricted flexibility of the chains compared to pure PVAc. Following Theocaris and Spathis[14], it can also be inferred from our data that strong interactions between the PVA matrix and the PVAc particles are likely to take place in our films: in the d.t.m.a. spectra recorded after annealing, the positions of all the $\tan\delta$ maxima are found to be shifted towards the zone of higher temperature, which is indicative of good adhesion between matrix and inclusions[5,14]. This behaviour is quite consistent with some grafting of PVA chains onto PVAc particles, thus enabling good adhesion between the two components.

The effect of average PVAc particle size is rather unexpected *a priori*. When the PVAc particles get smaller, the PVA phase behaves as if it is markedly less spread out upon annealing (see *Figure 5*, for instance); on the other hand, for films built up from the largest PVAc particles it will be quantitatively shown later that almost all the PVA is involved in the continuous segregated PVA phase. Simple arguments would lead to the opposite conclusion: since the specific surface area of PVAc particles increases when their mean diameter decreases, it could be concluded that smaller particles should give rise to a continuous PVA matrix more readily, provided that the entire surfaces of the particles are actually coated with PVA. However, previous work has pointed out that a significant effect arises from the mean distance between the inclusions which are to coalesce under thermal treatment, rather than from their sizes[18]. Then, in our case, for a given PVA volume fraction, the mean thickness of the steric PVA shell adsorbed on the particles will decrease when the particle size decreases; on the other hand, the higher the PVAc particle size, the larger the mean effective section (or thickness) of the PVA lattice bond embedding these particles. Therefore, for a given degree of connectivity, the continuous PVA matrix resulting from the coalescence of these layers can exhibit quite different mechanically effective volume fractions of PVA involved in this phase. Summing up, the observed effect of particle size on phase reorganization is probably related to the initial distribution of PVA chains at the surface of the particles. However, inspection of *Figures 4* and *5* shows that a complete understanding of the effect of particle size is far from being reached, since it should also take into account the combined effects of both the PVA viscosity grade and the parameter $\phi - \phi_t$.

Concerning the effect of the PVA HL value, it has been clearly shown that increasing the HL value of PVA added at the end of polymerization results in a less mechanically effective PVA segregated phase built up upon annealing. This behaviour should be related to the effect of HL on the distribution and organization of PVA at the surface of the particles in the initial dispersion and then in the films before annealing. This distribution is probably dependent on the emulsifying properties of PVA and hence its HL value. More precisely, the increase in HL is expected to increase the incompatibility between the rather hydrophobic PVAc particles and the hydrophilic PVA chains added at the end of polymerization. For this reason, owing to it (probably) being chiefly present in the aqueous phase of the dispersion, highly hydrolysed PVA is expected to form more isolated clusters in the initial films (before annealing) than PVA, which exhibits a lower HL value. In the formalism of bond percolation, the probability of connection for these isolated clusters of bonds decreases with increasing intercluster distance. These arguments are consistent with a less easily built up PVA phase upon annealing, since macromolecular diffusion of PVA chains must occur over larger distances for effective coalescence. Nevertheless, no clear-cut evidence for the above initial structure of the films containing highly hydrolysed PVA can be put forward at present.

At this step, we should provide a more quantitative insight into the observed thermally induced phase rearrangement, and then derive the values of the mechanically effective volume fractions v_m of PVA involved in the segregated continuous phase after thermal annealing. Experimental data will be interpreted on the basis of a mechanical composite model which enables us to calculate the modulus of the multiphase system from the modulus of each constituent phase, provided that some microstructural prerequisites are fulfilled. The choice of a consistent model is not so easy, since exact calculation cannot generally be performed[3,20]. However, other work has suggested that a satisfactory description of the elastic behaviour of composite latex films can be provided using the Kerner equation. The main simplying assumptions which are required for applicability of this equivalent mechanical model are:

(i) that there is perfect adhesion between the two phases, which allows full transmission of stresses between the matrix and the inclusions; in our system, covalent grafting between PVAc and PVA should enhance interfacial adhesion;
(ii) the size and spatial distribution of the inclusions are random;
(iii) the composite system is of the general type, i.e. soft inclusions/hard matrix with spherical inclusions;
(iv) the effective properties of the individual phases can be taken to be the bulk properties of the pure constituents and phase volumes can be calculated from the overall composition; and
(v) interactions between inclusions can be ignored.

In the present case, conditions (ii) and (iii) are likely to be fulfilled, whereas no safe argument can be posited for conditions (i) and (iv). Now, concerning condition (v), it seems that this strongly restricts the applicability of the model to low volume fractions for inclusions. However, phenomenological corrections have been proposed to take into account the interaction effect and hence to avoid deviation from the model at too high inclusion contents[3,21,22]. This correction introduces an interaction parameter Ψ through the maximum packing volume fraction of the particles, which mainly depends on the size dispersity of the particles and agglomerate formation and shape. Specification of the actual value of the maximum volume fraction remains somewhat uncertain[3]. For this reason, it will be taken to be close to 0.72, i.e. the value usually found for monodisperse spherical inclusions. In this case, the correction factor can be taken equal to unity.

Under the above conditions, the Kerner equation for the storage modulus of the composite films can be written in the form

$$E'/E'_m = \frac{(1-v)E'_m + (\alpha + v)E'_i}{(1+\alpha v)E'_m + \alpha(1-v)E'_i} \tag{1}$$

where E'_m is the storage modulus of the matrix, E'_i is the storage modulus of the inclusions, and v is the volume fraction of the inclusions. The quantity α is a function of Poisson's ratio of the matrix ν_m, and can be expressed as

$$\alpha = 2(4 - 5\nu_m)/(7 - 5\nu_m) \tag{2}$$

With an appropriate choice of parameters[1], the general form of equation (1) can be directly obtained from rather simple equivalent mechanical models consisting of elements, connected partly in series and partly in parallel, which exhibit the elastic properties of the constituent phases of the composite[23]. Although a complete fit of our experimental mechanical data is not presented in this work, equation (1) offers the opportunity to derive the actual volume fraction of PVA involved in the continuous matrix after annealing. For a composite system, the temperature dependence of the storage modulus in the range located between the two transitions is expected to parallel that of the material forming the continuous matrix. This behaviour is indeed observed experimentally; in this temperature zone, the storage modulus of the inclusions E'_i is much lower than that of the matrix E'_m since the former have already experienced their glass transition (see *Figure 1*), whereas the latter is still in a glassy state. In this particular temperature range, where E' exhibits almost a plateau, equation (1) can be simplified to

$$E'/E'_m = \frac{(1-v)E'_m}{(1+\alpha v)E'_m} \tag{3}$$

This expression can be inverted to give

$$v = \frac{1 - E'/E'_m}{1 + \alpha E'/E'_m} \tag{4}$$

Finally, v_m can be expressed using

$$\begin{aligned} v_m &= 1 - v \\ &= \frac{(1+\alpha)E'/E'_m}{1 + \alpha E'/E'_m} \end{aligned} \tag{5}$$

Table 2 Values of the volume fraction v_m of the mechanically effective PVA, derived from the Kerner equation. This corresponds to the PVA fraction which is involved in the continuous segregated phase after thermal annealing of the film and gives rise to the enhancement of the storage modulus E' of the composite in the temperature range located between the two transitions

Latex	PVA volume fraction (%) Initial charge ϕ_i	Final addition ϕ_a	PVAc average particle size d (μm)	v_m[a] (%)
B2	5.2	3.6	1.2	5
C1	5.3	4	2	9
C2	5.3	4	0.55	3
C3	5.3	5.7	2	11
C4	5.3	5.7	0.55	11
C5	5.3	5.7	0.55	4
C6	5.3	5.7	0.55	10
D2	6.5	3.6	1.2	3
D3	6.5	7	1.2	9

[a] The accuracy of the values of v_m is estimated to be within 15%

For most polymers, Poisson's ratio ν_m is found to lie between 0.2 and 0.5. Following Dickie[1] and Jourdan *et al.*[3], we will take a constant value of 0.35 for ν_m, and hence a constant value of 0.86 for α. The values of v_m deduced from equation (5) for the samples which exhibit a profound alteration of their viscoelastic properties after annealing are gathered in *Table 2*. Because of the slow relaxation sometimes observed in this region, the accuracy of the determination is not very high (within 15%), but it allows a reasonable discussion of the results. Inspection of *Table 2* reveals that the whole fraction of PVA introduced into the film (ϕ) is not necessarily involved in the continuous matrix after annealing. More particularly, depending mainly on the size of the PVAc particles and the features of the PVA added at the end of polymerization, the value of v_m can correspond to only a small part of the total PVA content ϕ; in this case, it is found to be close to the volume fraction of PVA added at the end of polymerization (ϕ_a). This behaviour is not well understood at present. However, in many respects, even if each requirement for applicability of the model is not entirely fulfilled, these semiquantitative results are quite consistent with our previous qualitative analysis and emphasize the pronounced effect of PVAc particle size and PVA features on the elastic properties of our composite films.

In conclusion, we have discussed a coherent set of original d.t.m.a. results obtained for a composite system which exhibits a specificity owing to the initial locations of the two consistuents (PVAc, PVA) in the initial latexes. Our data clearly show that the spatial distribution of the constituents in the film undergoes a strong rearrangement upon thermal annealing at a temperature higher than both glass transition temperatures of the constituents. This phenomenon is intimately related to dramatic alterations of the viscoelastic behaviour of the composite film, which more precisely appear in the temperature range located between the two glass transition temperatures. The kinetics and detailed mechanism of this profound rearrangement are not known. However, the driving force could be the degree of incompatibility of the constituents and the mechanism could involve the enhancement of molecular mobility of PVA upon thermal annealing above its T_g. The phase rearrangement definitely results in the formation of a continuous PVA matrix embedding PVAc particles; it occurs upon thermally induced coalescence of unconnected PVA clusters which are initially contained in the film. The noteworthy versatility of the studied system has made it possible to reveal the main parameters which control the phase reorganization. These parameters are the PVA volume fraction ϕ, the size of the PVAc particles, the viscosity grade η and the hydrolysis level (HL) of PVA. A preliminary analysis of the phenomenon, involving the formalism of bond percolation on a lattice, has been proposed. The percolation threshold ϕ_t, according to this formalism, has been found experimentally to be between 6.5 and 8.8% in our system. Refined qualitative information about the particle and film structure has also been gained through inspection of the d.t.m.a. spectra. More precisely, the shapes of the spectra in the region located between the two glass transitions of some films have revealed a gradual relaxation of heterogeneous regions in the composite system. This phase is likely to exist at the interface between PVAc and PVA and consist of a layer exhibiting a gradation of composition from pure PVAc to pure PVA with increasing distance from the cores of the particles. Moreover, it should contain the PVA chains which have been grafted onto the PVAc particles during the polymerization and are responsible for the strong interactions between the PVA matrix and the PVAc particles. In addition, a quite informative semiquantitative analysis of our experimental data has been performed, based on a classical equivalent model for polymer–polymer composites and the correlative application of the Kerner equation. A complete fit of the experimental data is not included in this work, but a treatment of this equation, performed under simplifying assumptions, makes it possible to derive the value of the volume fraction v_m of PVA involved in the continuous matrix after annealing. The semiquantitative results obtained in this way are found to be quite consistent with the qualitative analysis.

However, much is still to be discovered concerning the actual combined effects of PVA features and volume fraction before a complete understanding of the viscoelastic behaviour of these systems can be reached. At the present time, no simple relationship between the viscoelastic features of the films and the key parameter $\phi - \phi_t$ can be established without taking into account the features of PVA. In other words, parameters which have an effect on the phase reorganization in the films do not appear to be independent of each other. A more complete analysis using the bond percolation formalism may shed light on this intricate problem, provided that the critical exponents of the system[17] depend on the PVA features. Besides, most important among other things to be investigated now is the effect of annealing on the cohesive strength of these films, since a significant enhancement of this property can be expected upon formation of the continuous PVA matrix[13]. For this purpose, investigations into the large strain ultimate mechanical properties of our composite films should be of particular interest.

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