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Influence of Cross-Linking on Structure, Mechanical Properties, and Strength of Latex Films

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ABSTRACT: Two series of emulsion polymers with *n*-butyl (meth)acrylate and the bifunctional monomer methallyl methacrylate were prepared, covering the whole range from un-cross-linked to highly cross-linked particles. Dynamic mechanical measurements showed that films from slightly or moderately cross-linked particles behave like homogeneous networks in the linear viscoelastic range. Measurements of the fracture energy per unit volume, W_B, of poly(butyl methacrylate) films gave insight into the development of mechanical strength by interdiffusion across particle boundaries. When annealed above T_g, un-cross-linked films show a transition from brittle to tough fracture at short annealing times, followed by a further gradual increase of W_B linear with the square root of the annealing time. On the basis of these measurements and small-angle neutron scattering experiments on the same samples,[7] a three-stage process is proposed for the development of film strength. Films from particles so highly cross-linked that the mean molecular mass between cross-links becomes smaller than the entanglement length M_e remain brittle upon annealing. Interdiffusion and the formation of interparticular entanglements are impossible in these latex films.

1. Introduction

The elastic properties of homogeneously cross-linked polymers have been thoroughly investigated over a long time and are well described by molecular theories of rubber elasticity [e.g., refs 1–3]. In latex films, however, it seems rather improbable that homogeneous networks occur due to the origin of these films from aqueous dispersions, i.e., isolated particles. Cross-linking of emulsion polymers, thus, has open questions with respect to network structure. Two limiting cases of network models can be imagined to occur in latex films, namely, (1) films from un-cross-linked particles which are interparticularly cross-linked across particle boundaries during or after film formation, e.g., by hydrophilic bifunctional monomers (networks of this type often show a strong chemical heterogeneity [4]); (2) films formed from pre-cross-linked particles without any additional cross-linking across particle boundaries.

The second model covers the largest part of this paper which mainly deals with the transition from un-cross-linked to cross-linked films, characterized by swelling and mechanical measurements, and the film formation from latices with cross-linked particles.

Cross-linking of latex films is of interest for various reasons. Many emulsion polymers are naturally cross-linked, as some monomers such as acrylates and butadiene tend to cross-link and form microgels during emulsion polymerization. Another more important reason is that latex films have to be cross-linked in various fields of application in order to reach a satisfactory level of performance. An insight into the basic concept of cross-linking and structure–property relations of cross-linked emulsion polymers can, thus, be helpful in developing new products.

Homogeneous networks can be characterized by measurements of the linear viscoelastic behavior, e.g., by dynamic mechanical experiments. With some assumptions and simplifications, found in various textbooks[1,2] but not to be discussed here, the storage modulus G' of a polymer in the rubberlike state, which is independent of frequency, is related to the cross-link density ν, i.e., the molar concentration of network chains, or to the mean molecular mass between two cross-links, M_c, by the equation

$$G' = \nu RT = (\rho/M_c)RT \qquad (1)$$

where ρ is the density, R is the gas constant, and T the temperature in Kelvin.

Another well-established method for characterizing networks is swelling measurements in a solvent for the corresponding un-cross-linked polymer. The swelling is governed by the well-known Flory–Huggins equation[5,6]

$$\ln(1 - \upsilon_p) + \upsilon_p + \chi\upsilon_p^{\,2} + \nu V_1(\upsilon_p^{\,1/3} - \upsilon_p/2) = 0 \qquad (2)$$

υ_p is the volume fraction of the polymer in the swollen gel, V_1 the molar volume of the solvent, and χ a parameter describing the interaction between polymer and swelling agent.

2. Experimental Section

2.1. Model Polymers. In this work model emulsion polymers of two monomers, *n*-butyl acrylate (BA) and *n*-butyl methacrylate (BMA), and the cross-linking monomer methallyl methacrylate (MAMA) are studied. As BA forms microgels already in homopolymerization, some latices have been prepared in the presence of small amounts of *tert*-dodecylmercaptan (DMCT) as a chain-transfer agent in order to get un-cross-linked PBA, too. The *n*-butyl methacrylate homopolymer is completely soluble in tetrahydrofuran and free of microgel.

The latices were prepared using the following formulation or a scaled version of it: 950 g of distilled water, 4 g of sodium laurylsulfate (Merck), eventually *tert*-dodecylmercaptan, and 450 g of the monomer (mixture) were placed into an all-glass polymerization reactor equipped with thermometer, stirrer, N_2 gas inlet, and reflux condensator. The mixture was stirred under a gentle N_2 stream and heated to 80 °C. A total of 15 min after reaching this temperature, a N_2-deaerated solution of 4 g of sodium peroxydisulfate in 100 g of distilled water was added "in one shot". The temperature was maintained for 5 h at 80 °C. Then the latex was cooled down and filtered through a 120-μm sieve. The latices typically had a solid content of about 30% by weight, a pH of about 2, and a mean particle diameter of about 60 nm as determined by dynamic light scattering.

Films were cast from these latices at room temperature, resulting in two series of samples which cover the whole range from un-cross-linked to highly cross-linked polymers. As poly(*n*-butyl acrylate) has a glass transition temperature of T_g = −42 °C, determined by dynamic mechanical measurements with a frequency of 1 Hz,[4] the PBA series represents "soft" polymers at

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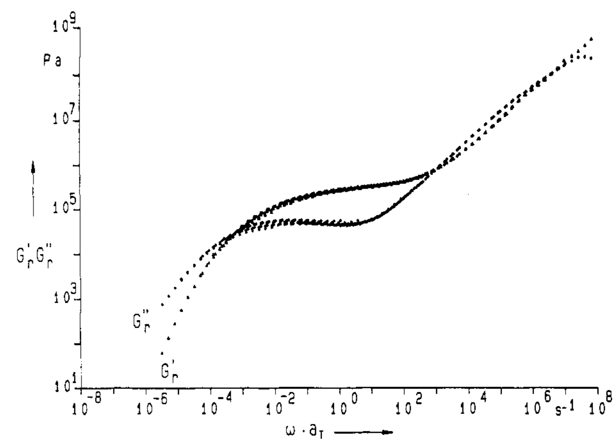

Figure 1. Storage modulus G' and loss modulus G'' as a function of the angular frequency for an un-cross-linked polymer (polyisobutylene), T_0 = 23 °C (own unpublished data).

room temperature. PBMA, on the other hand, has a T_g of 29 °C, giving rise to a series of polymers which are "hard" at 23 °C.[7] In spite of its T_g, PBMA forms clear, coherent, though very brittle, films at 23 °C.

2.2. Experimental Methods. The mechanical data given in this paper have been obtained by shear measurements with a commerical dynamic mechanical analyzer in a parallel-plate geometry. With these measurements, the dynamic shear modulus of the sample which consists of the storage modulus G' and the loss modulus G'' can be determined. All measurements were performed in the linear viscoelastic regime, i.e., at sufficiently small strain so that G' and G'' are independent of the applied strain. The moduli were measured as a function of frequency at various, i.e., up to eight temperatures between the glass transition temperature and about 180 °C. The modulus versus frequency curves at the different temperatures were subsequently superimposed to master curves at a reference temperature T_0 = 23 °C by use of the well-known method of frequency/temperature superposition.[8]

Swelling measurements of films were performed with tetrahydrofuran (THF) which is a gold solvent for PBMA as well as PBA. The degree of swelling, defined as the weight ratio of the swollen and the unswollen sample, and the fraction of the soluble polymer are determined. The weight ratio can easily be transformed to the corresponding volume ratio Q which is shown in Figures 3 and 4. The results are compared with swelling measurements on latex particles with the analytical ultracentrifuge (AUZ).[9]

The mechanical strength of the films is characterized by stress/strain mesurements in uniaxial tension with a tensile tester. A crosshead speed of 1.67 mm/s and a sample length of 24 mm were employed.

3. Shear Modulus of Un-Cross-Linked Polymers

A typical example for the master curves of G' and G'' of an un-cross-linked polymer, polyisobutylene, is given in Figure 1. The curves show three frequency ranges with different viscoelastic behavior: (1) the glass transition range at high frequencies where both G' and G'' increase with the angular frequency; (2) the plateau range between 10^{-3} and 10^3 s^{-1} where both moduli are only slightly frequency dependent; (3) the terminal zone at low frequencies where the mechanical behavior is increasingly governed by viscous flow.

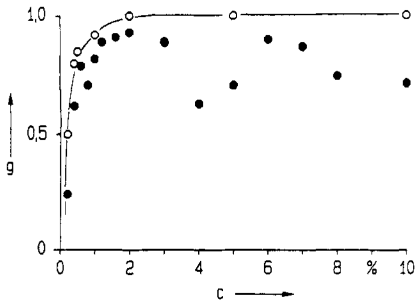

Figure 2. Fraction of insoluble poly(butyl methacrylate) (PBMA), g, versus the molar concentration of methallyl methacrylate (MAMA): (○) particles; (●) films.

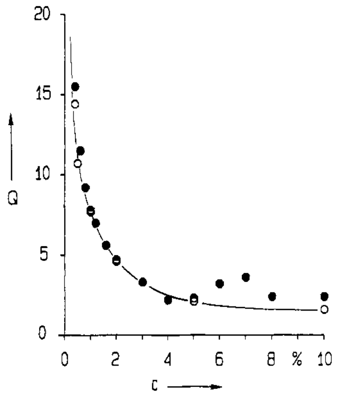

Figure 3. Degree of swelling (by volume), Q, vs the concentration of MAMA for PBMA: (○) particles; (●) films.

In the plateau range, the polymer is predominantly elastic as G' is larger than G'', and the viscoelastic behavior is determined by the entanglement network. If G' becomes independent of ω in this frequency range, the mean molecular mass M_e between two entanglements can be calculated from this plateau modulus $G_{eN}°$, the pseudoequilibrium modulus of the entanglement network, by an equation similar to eq 1:[10]

$$G_{eN}° = (\rho/M_e)RT \tag{3}$$

If G' is not independent of ω, $G_{eN}°$ can be evaluated by various approximations.[10] In this work the approach of Marvin and Oser has been applied.[11]

In the terminal range G'' is larger than G' and related to the zero-shear viscosity by the equation

$$G'' = \eta_0\omega \tag{4}$$

while G' is proportional to ω^2. It is, thus, possible to unambiguously decide if a polymer shows viscous flow and is, accordingly, un-cross-linked.

4. Viscoelastic Behavior and Swelling of Films from Cross-Linked Particles

The swelling measurements on the PBMA particles and films are summarized in Figures 2 and 3, showing the gel fraction g and the degree of swelling Q as a function of the molar concentration c of the bifunctional monomer MAMA. The gel fraction g increases with increasing concentration of MAMA. The agreement between the results for the particles and the films is very good at concentrations below about 2% MAMA, taking into account the very different methods. At higher concentrations, the gel fraction of the particles determined with the AUZ is above 98%, but the gel content of the films seems to decrease with increasing c and shows a rather large scatter. That may be due to the fact that the swollen films of the highly cross-linked particles are very fragile and difficult to handle. Another possible explanation is that particles or aggregates of particles are dissolved from these very highly cross-linked films. The gel point, i.e., the cross-linker concentration at which at first a measurable gel content is observed, is found between 0.06 and 0.08% MAMA for the particles as well as the films. The degree of swelling strongly decreases with increasing MAMA concentration (Figure 3). Here, too, the scattering

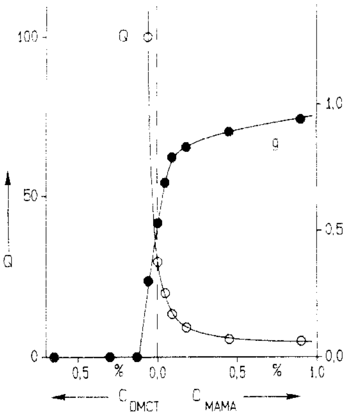

Figure 4. Degree of swelling Q and gel fraction g for poly(butyl actylate) (PBA) plotted versus the molar concentration of MAMA and DMCT (*tert*-dodecylmercaptan), respectively.

of the film swelling data is larger at higher MAMA concentrations.

Similar results have been obtained for the PBA series. Figure 4 shows the gel content and the swelling ratio for the films dependent on the molar concentration of MAMA, plotted to the right, and DMCT, respectively, plotted to the left. For PBA the gel point is found at about 0.08% DMCT, whereas the pure PBA already has a gel fraction of about 0.5 and a swelling ratio of 30. The BMA and the BA emulsion polymers can, thus, be divided into three groups according to their swelling behavior: (1) no gel content, i.e., no cross-linking, below the gel point; (2) a rapid increase of g and a strong decrease of Q in a small concentration range of MAMA and DMCT, respectively, above the gel point; (3) a high gel fraction between 0.8 and 1 connected with a small swelling ratio at MAMA concentrations above about 1 for PBMA and 0.1 for PBA.

Figure 5 shows the master curves of G' and G'' for the PBA series with molar concentrations of DMCT between 0 and 0.65% and of MAMA between 0.09 and 0.9%. In order to avoid too much overlap of the curves, the G' and G'' plots for the various samples have been shifted horizontally what is indicated by the quantity A in the figure. Un-cross-linked behavior with viscous flow is found for the PBA with 0.3 and 0.65% DMCT. This can be concluded from the dependence of G'' and G' on ω at low frequencies, which can be approximated by the two lines with slopes of 1 and 2, respectively, drawn in Figure 5. A very interesting behavior is exhibited by the sample with 0.06% DMCT, a concentration which is near the gel point. G' and G'' are nearly equal and increase proportional to $\omega^{1/2}$ over a frequency range of about 4 orders of magnitude, as can be concluded from the line with a slope of $^1/_2$ in the figure. This agrees with investigations of Winter et al.[12-14] who were the first to find that G' and G'' of polymers at the gel point are congruent and proportional to $\omega^{1/2}$. The PBA made without any additive is slightly cross-linked; i.e., G' has higher values than G''. The polymers with MAMA reach a constant value of the storage modulus in the limit of low frequencies, as it is predicted by the theory of rubber elasticity, and G'' is much smaller than G'.

A similar viscoelastic behavior is observed for PBMA for which a reference temperature of 100 °C has been chosen (Figure 6). In this case the gel point is near 0.06% MAMA which again is in good agreement with the swelling measurements on particles as well as films. The PBMA samples with lower MAMA concentration show viscous flow and those with higher concentrations rubberlike behavior at low frequencies.

The shift factors a_T which are not shown here follow a WLF reaction, as common. They are the same for all samples of each polymer with the exception that, at the higher temperatures, the shift factors for the highly cross-linked samples possibly are larger than the corresponding factors for the un-cross-linked samples. This conclusion, however, is not very reliable, as it is rather difficult to determine the shift factors for the flat modulus versus frequency curves of the cross-linked samples with sufficient accuracy. From the dynamic mechanical measurements, too, the polymers of the two series can be divided into three groups, which is in agreement with the classification by swelling: (1) un-cross-linked, viscous materials at low MAMA or higher DMCT contents; (2) rather imperfect and loose networks just above the gel point; (3) cross-linked samples with a constant storage modulus and low internal losses at higher MAMA concentrations.

The modulus versus frequency plots for the latex films formed from cross-linked particles in Figures 5 and 6 are quite similar to corresponding curves for homogeneously cross-linked polymers.[13,15] Interparticular cross-linking during or after film formation seems, however, improbable for the latex films studied here. Accordingly, the coupling between adjacent particles should take place only by the diffusion of un-cross-linked polymer and chain ends across the interface and the formation of entanglements between particles.[16] That leads to the conclusion that mechanical measurements in the linear viscoelastic regime, i.e., at small strain, do not differentiate between homogeneous networks and the particular network structures supposed to be present in the PBMA and PBA latex films. Even in the swelling experiments, the samples behave like continuous networks insofar as they do not disintegrate into the original latex particles. A possible explanation is that such a disintegration would require the cooperative dissolution of all entanglements by which a particle is connected with its neighbors. This seems to be highly improbable.

If G' is independent of ω, the mean molecular mass between two cross-links, M_c, can be calculated according to eq 1. This M_c value and the corresponding cross-link density can be regarded as the network parameters of a hypothetical, homogeneously cross-linked polymer with the same storage modulus at low frequencies as the latex film. In Figure 7, M_c is plotted versus the molar concentration of MAMA for PBA as well as PBMA. It shows also the theoretical values of M_c which have been calculated under the assumption that all double bonds have reacted and that one molecule of the bifunctional MAMA gives rise to a tetrafunctional node. It follows from Figure 7 that the experimental values of M_c are a factor of 2 for PBA and 3.5 for PBMA higher than the theoretical; i.e., the films are less cross-linked than theoretically expected. This deviation is not surprising, considering the discussion of the preceding paragraph. Besides, there is no evidence that all double bonds of MAMA have reacted and contribute to the network.

5. Film Formation of Latices with Cross-Linked Particles

The film formation of latices can be regarded as a three-stage process of packing, deformation, and gradual coalescence of the particles.[17,18] During the last stage of this process, mechanical film strength is developed by the interdiffusion of chain ends and segments and the formation of entanglements across the particle boundaries.[16]

The development of film strength by interdiffusion and the formation of interparticular entanglements will be increasingly hindered in latices with cross-linked particles with a low fraction of nongelled polymer, especially when M_c becomes smaller than M_e. If one assumes that the chain length distribution of the dangling ends is similar

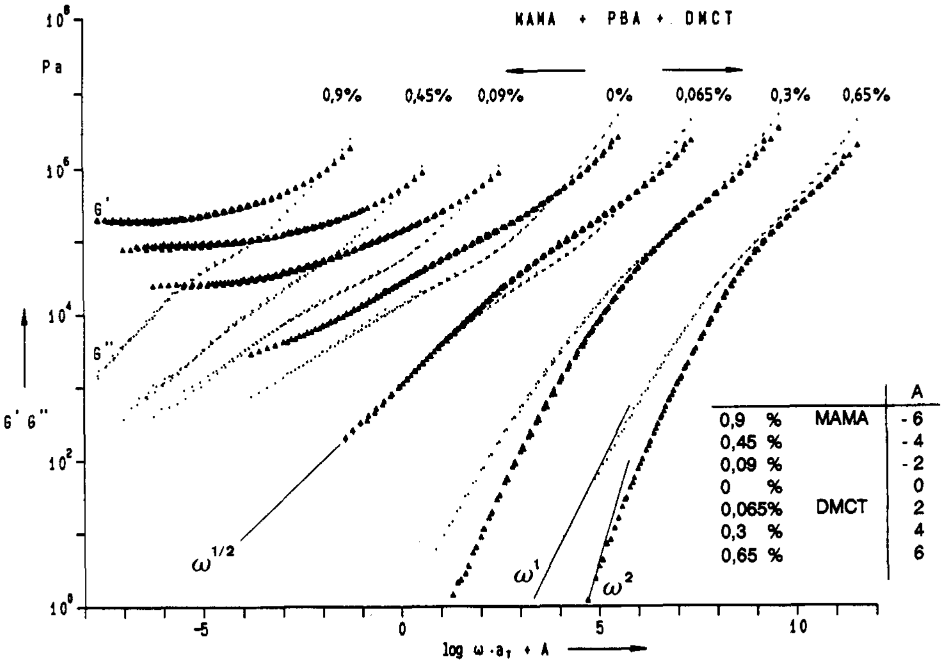

Figure 5. Storage modulus G' and loss modulus G'' as a function of frequency for PBA with various concentrations of MAMA or DMCT, respectively. The curves are shifted horizontally by a factor A, as indicated. T = 23 °C.

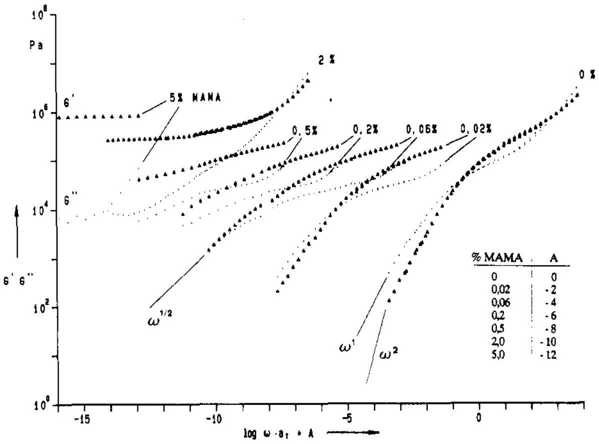

Figure 6. G' and G'' versus frequency for PBMA with various concentrations of MAMA. T = 100 °C.

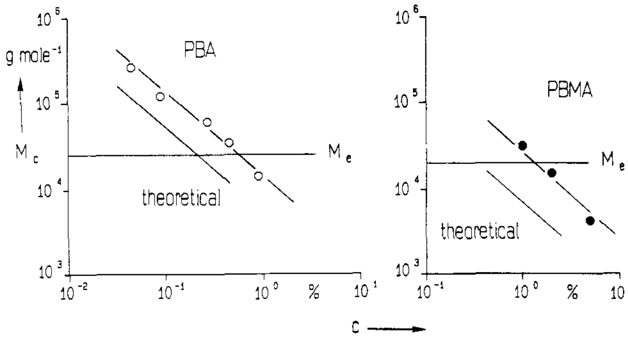

Figure 7. Mean molecular mass between cross-links, M_c, for PBA and PBMA versus the concentration of MAMA. M_e = mean molecular mass between entanglements.

to that of the chains between two nodes, the number of dangling ends with a length sufficient for entanglement formation decreases. Studying the development of mechanical strength in films with cross-linked particles, therefore, offers an access to the third state of film formation.

The entanglement length M_e can be calculated from the modulus vs frequency plots, as already mentioned. It is shown in Figure 7 for both polymers, indicating that the "critical" concentration of MAMA where M_c equals M_e is reached at about 0.7% MAMA for PBA and 1.5% for PBMA.

The PBMA latices are well suited for studies of interdiffusion as PBMA has a glass transition temperature of 29 °C but, nevertheless, forms coherent, brittle films at 23 °C, as already mentioned. As the polymer has a low segmental mobility at room temperature, it can be expected that no significant interdiffusion will take place. As has been shown earlier[7] interdiffusion processes start only on annealing or tempering the films at temperatures above T_g.

PBMA films formed at 23 °C were tempered at 50 and 90 °C for different times, and specimens were cut before the samples cooled down to room temperature. Due to the brittleness the unannealed films had to be heated to about 50 °C for a short time of less than 2 min in order to be able to cut specimens. Tensile tests were carried out at 23 °C. The energy per unit volume, W_B, which is necessary to break the sample, is calculated by integration of the stress–strain curve:

$$W_B = \int \sigma \, d\epsilon \tag{5}$$

It will be shown that the fracture energy or "toughness" W_B characterizes the mechanical strength of the films much better than the tensile strength, i.e., the tensile stress σ_B at break.

Some examples for stress–strain plots are given in Figure 8 for PBMA with 0 and 2% MAMA. The untempered film of un-cross-linked PBMA shows brittle fracture with a rapid increase of σ with increasing tensile strain ϵ and fracture at a low strain of about 4×10^{-2}. After an annealing time of 5 min already, this fracture behavior changes completely. A steep stress peak is observed at low strains too, but it is followed by yielding which gives rise to a high ultimate strain of about 3. A comparison of the stress–strain curves for 0 and 5 min clearly shows that the tensile strength is not suited to differentiate between the behavior at both annealing times, as σ_B is approximately equal. In the case of yielding, the area under the stress–strain plot is much higher than for brittle fracture, and that means that the fracture energy increases drastically. At an annealing time of 5 min or less, thus, a transition from brittle fracture to tough or yielding behavior is observed.

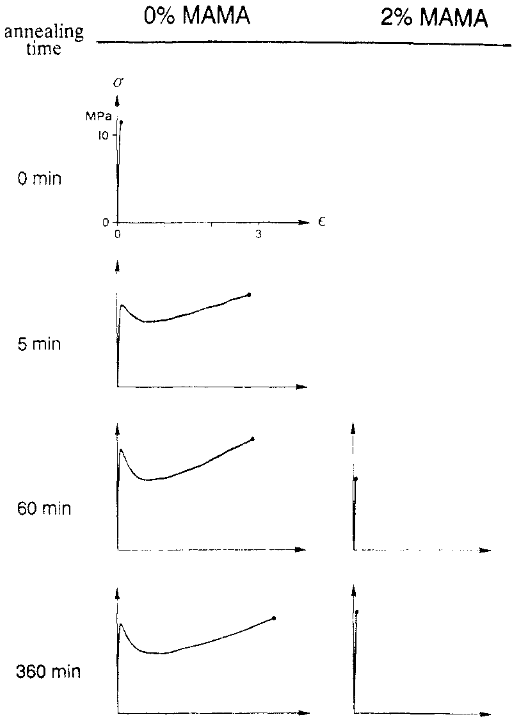

Figure 8. Stress-strain diagrams for PBMA with 0 and 2% MAMA. The parameter is the annealing time at 90 °C.

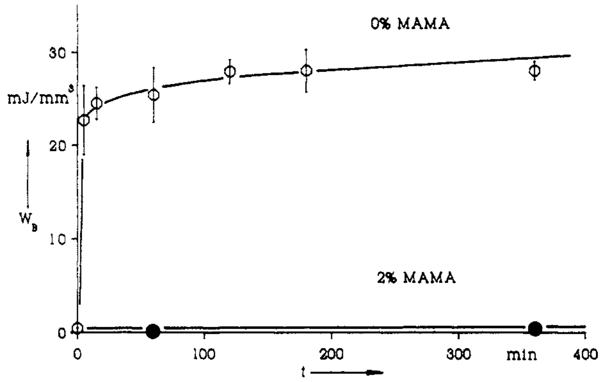

Figure 9. Fracture energy W_B per unit volume for PBMA with 0 and 2% MAMA as a function of the annealing time at 90 °C.

Longer annealing times only gradually change the shape of the stress–strain characteristics.

The PBMA with 2% MAMA, on the contrary, exhibits brittle fracture up to annealing times of 360 min without any significant change of the very low fracture energy. That indicates a significant difference between latex films made from cross-linked particles with cross-link densities below and above the critical concentration.

In Figure 9 the fracture energy W_B is plotted versus the temper time at 90 °C for PBMA with 0 and 2% MAMA. The fracture energy for the un-cross-linked polymer shows a strong increase by more than 2 orders of magnitude at annealing times below 5 min in correspondence with the transition from brittle to tough behavior. This transition is followed by a further gradual increase of W_B which is not finished in the time interval of 360 min, shown in Figure 9. The question if and at what annealing time a constant fracture energy is reached will be discussed later. For the films cross-linked with 2% MAMA, on the other hand, a fracture energy is determined up to an annealing time of 360 min, which is by nearly 3 orders of magnitude lower than in the case of tough behavior of the un-cross-linked PBMA.

Interesting results were obtained from measurements on the un-cross-linked PBMA, annealed at 50 °C (Figure 10). After an annealing time of 5 min the material still shows brittle fracture. At annealing times between 15 and 45 min brittle as well as yielding behavior can be found, as it is indicated in Figure 10 by two points at these times. Coalescence apparently is so low in this time range that the sample accidentally may behave brittle or tough, depending on the presence and size of defects for instance.

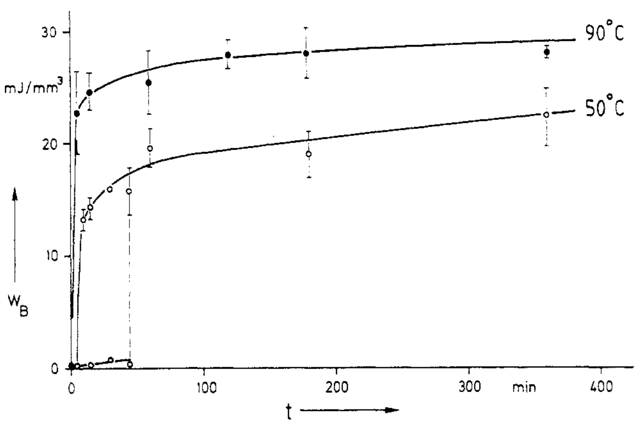

Figure 10. Fracture energy vs annealing time at 50 and 90 °C for PBMA with 0% MAMA.

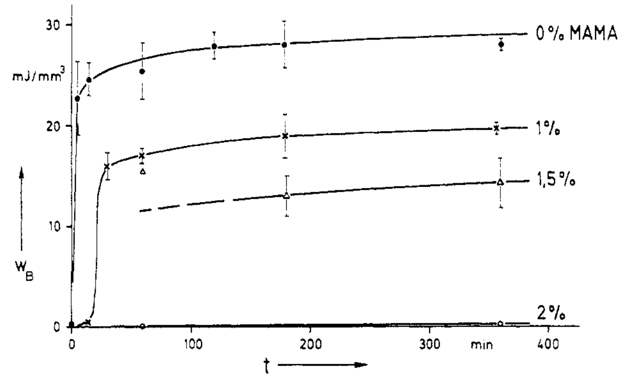

Figure 11. Fracture energy vs annealing time at 90 °C for PBMA with various concentrations of MAMA, as indicated.

A similar transition range is observed with films containing 1 or 1.5% MAMA. Figure 11 shows the fracture energy as a function of the temper time at 90 °C for both concentrations together with the results for 0 and 2% MAMA. The PBMA with 1% MAMA exhibits exclusively brittle fracture until 15 min, both fracture types at 30 min, and yielding at 60 min and longer times. For the samples with 1.5% MAMA brittle as well as tough fracture is observed between annealing times of 60 and 360 min. In the figure the data points are plotted for tough behavior only. Films with the MAMA concentration near the critical value, thus, show some kind of transition between the two fracture types.

6. Discussion

Interdiffusion during the film formation of polymer latices has to be discussed in the larger framework of healing and welding of polymer–polymer interfaces (e.g. refs 19–22). The various approaches, mainly based on the reptation model of de Gennes,[23] lead to the result that the diffusion or penetration depth increases proportional to the square root of the contact time. At present, there is no theory to relate the mechanical strength of the interface to the arrangement of chains in the interface. The models of de Gennes,[20] Prager and Tirrell,[22] and Kausch[21] agree that the fracture energy should increase proportional to $t^{1/2}$ too, which is verified by various experimental studies (see, e.g., ref 19).

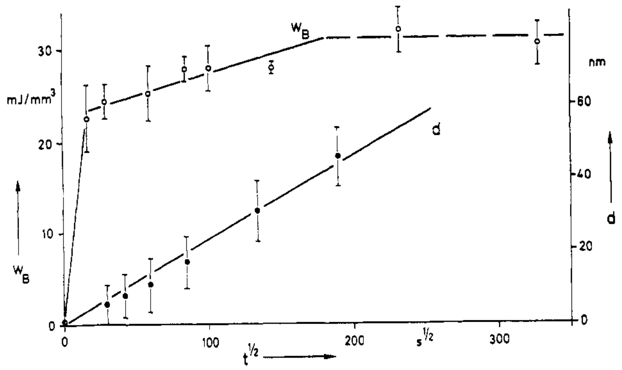

Figure 12. Fracture energy W_B and interpenetration depth *d*, determined by SANS experiments,[7] for PBMA with 0% MAMA, plotted versus the square root of the annealing time at 90 °C.

Interdiffusion in latex films has recently been studied by two groups, using small-angle neutron scattering (SANS): Hahn et al. at BASF[7,24] and Klein et al. at Lehigh University.[25,26] Besides SANS experiments the Lehigh group measured the tensile strength of latex films as a function of the annealing time and found a linear increase with $t^{1/4}$ and a leveling off at long annealing times. The BASF group studied films of the same PBMA latices with SANS as used for these measurements, so that a good comparison should be possible. In Figure 12 the fracture energy W_B and the interdiffusion depth *d*, the latter obtained from Table I of ref 7, are plotted versus the square root of the annealing time *t* at 90 °C. The penetration depth is proportional to $t^{1/2}$, as expected. W_B increases by about 2 orders of magnitude within the first 5 min, as already shown in Figure 10, then gradually increases linearly with $t^{1/2}$, and seems to level off with a constant value, as far as can be concluded from the relatively scarce data at long times.

If we assume that no considerable interdiffusion occurs during film formation below T_g, the untempered film is supposed to consist of a packing of the hard latex spheres, which has a certain mechanical strength, i.e., tensile stress at break, due to intermolecular forces such as van der Waals forces acting across the boundaries between the packed particles. However, it lacks a measurable toughness, i.e., the ability to store and to dissipate energy during deformation which is related to the slippage and the disentanglement of chain molecules. This toughness requires the interdiffusion of chain segments. That means that the first steep increase of W_B and the transition from brittle to tough fracture cannot be caused by further "dry" sintering but should be attributed to the beginning of the interdiffusion process, which gives rise to an interdiffusion depth of about 2 nm after 5 min at 90 °C, as estimated from the SANS data in Figure 12. This compares to about 3 nm for the length of an extended chain of M_c.

It has been shown by molecular modeling of polymer aggregates in solution[27] that chain ends and short chains are present in a surface layer of the aggregates with a higher concentration than in the "bulk" of the aggregates, forming a "hairy" surface layer of 2–4-nm thickness. As this material diffuses faster than the average weight molecules, it possibly is responsible for the fast rise of film toughness at short annealing times. The further slow increase of W_B is caused by the progressive interdiffusion and the formation of entanglements of the long molecules across the boundaries of the former particles. At least, the fracture energy levels off at an interpenetration depth of about 40 nm, which has the same order of magnitude as the radius of gyration of the PBMA molecules for which a weight-average molecular mass of about 5×10^5 g/mol has been found.

It follows from SANS experiments that the emulsifier sodium laurylsulfate is incompatible with PBMA and forms aggregates in the film which tend to cluster into larger domains upon tempering at higher temperature.[28] We, hence, assume that the emulsifier does not play any significant role in the development of mechanical film strength.

As a conclusion we propose the following three-stage model for the development of mechanical strength of the un-cross-linked latex film: (1) very quick formation of a continuous, though very brittle, film by sintering of the particles, increasing the area of close contact between the particles; (2) rapid transition from brittle to tough fracture by fast interdiffusion of chain ends and small chains in the interparticular boundaries; (3) slow development of the final mechanical strength by interdiffusion and entanglement of the long-chain molecules.

With increasing MAMA concentration these processes are more and more slowed down and hindered. Stages 2 and 3 of this model are absent in the formation of films from cross-linked particles with $M_c < M_e$, as can be concluded from the results shown in Figures 9 and 10. The films with 2% MAMA remain extremely brittle upon annealing, while the sample at the "critical" concentration of 1.5% MAMA shows some kind of transition insofar as brittle and tough behavior are observed. The highly cross-linked particles cannot perform any significant interdiffusion; they behave like "rubber balls" during film formation which are deformed under the action of external forces and recover immediately upon removal of the forces.

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