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Film formation of latices with crosslinked particles

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Summary

The mechanical strength of latex films is caused by the diffusion of chain segments across particle boundaries and the formation of entanglements. This process should be hindered when the film is formed from crosslinked particles with an average network chain length M_c smaller than the entanglement length M_e. This assumption is verified by tensile tests of films of polybutylmethacrylate latices with different degrees of crosslinking. In films of too highly crosslinked particles no mechanical strength is developed by annealing above the glass transition temperature.

1. Introduction

The film formation of latices can be regarded as a three stage process of (a)concentration, (b)deformation and coalescence, and (c)further gradual coalescence of the latex particles [1,2]. During the last stage of this process, mechanical film strength is developed by the diffusion of chain ends and segments across the particle boundaries and the formation of entanglements [3]. This interdiffusion in latex films has been studied by small angle neutron scattering (SANS) during the last years [4-7], partly in connection with measurements of film strength [7].

In many applications, polymer latices with crosslinked particles are used, and it is well known that films of too highly crosslinked particles show very poor mechanical strength. This offers another way to study the effect of interdiffusion and entanglement formation. Difficulties in developing sufficient film strength can be expected when the mean molecular mass between crosslinks, M_c, becomes smaller than the entanglement spacing, M_e, because in this case the formation of entanglements is hindered. In order to verify this, we have investigated a series of polymer latices with well defined degrees of crosslinking, covering the whole range from uncrosslinked to very highly crosslinked samples.

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2. Experimental

2.1 Samples

This study deals with model emulsion copolymers of n-butylmethacrylate (BMA) and the bifunctional monomer methallylmethacrylate (MAMA) with molar concentrations of MAMA betwen 0 and 5%. The latices were prepared by batchwise emulsion polymerization using a standard recipe [4] at 80°C and had typically a solid content of about 30% and a mean particle diameter of about 60 nm. The glass transition temperature of PBMA, determined by dynamic mechanical analysis with a frequency of 1 Hz, is 29°C. The latices, never-the-less, form clear, brittle films at 23°C. Due to the glass transition temperature it can be assumed that no significant interdiffusion occurs in the PBMA films.

2.2 Experimental methods

The BMA/MAMA copolymers have been characterized by dynamic mechanical measurements in a parallel plate geometry, by means of which the dynamic shear modulus (storage modulus G′ and loss modulus G″) is determined in dependence on angular frequency ω and temperature. Using the well-known frequency temperature superposition [8], master curves for G′ and G″ were obtained at a reference temperature of 100°C.

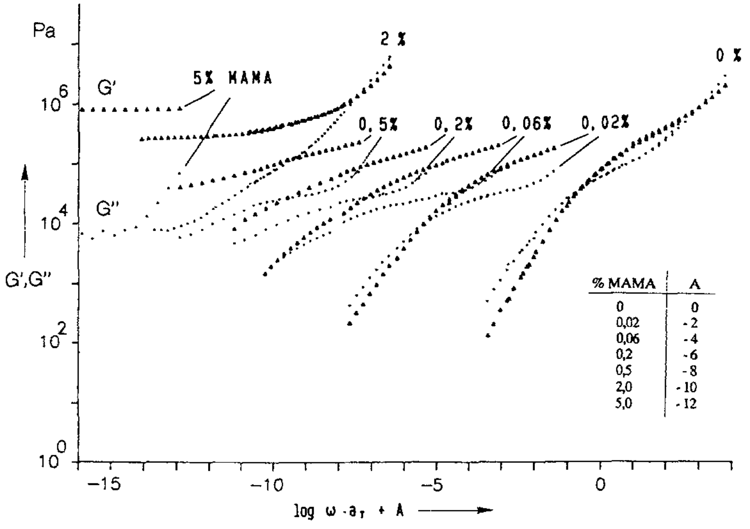

Fig.1 Storage and loss modulus as a function of frequency for poly-n-butylmethacrylate (PBMA) with various concentrations of methallylmethacrylate (MAMA), as indicated. T = 100°C

The mechanical strength has been determined by tensile tests at 23° C with dumbbell-shaped specimens of free films (elongation rate 0.33 mm/s). The fracture energy per unit of volume can be calculated by an integration of the resulting stress strain curves and is used as a measure of film strength.

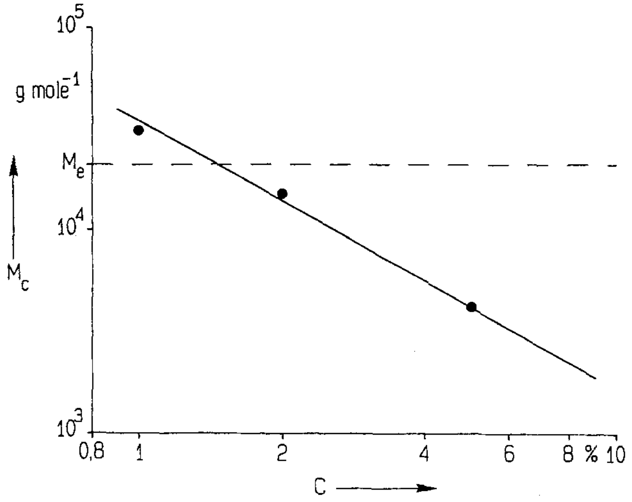

Fig.2 Mean molecular mass M_c between crosslinks, plotted vs. the molar concentration of MAMA, M_e = broken line

3. Results and discussion

In Fig.1, G′ and G″ are plotted versus frequency for the PBMA with various contents of MAMA, as indicated. In order to avoid too much overlap of the curves, the G′ and G″ plots for the different samples have been shifted horizontally what is indicated by the quantity A in the insert of Fig.1. The curves represent the complete transition from uncrosslinked behaviour (0 and 0.02% MAMA) to the behaviour of a crosslinked, rubber-like material at MAMA concentrations above 1% with a storage modulus independent of frequency and a loss modulus much smaller than G′. The gel point is found near a MAMA concentration of about 0.06%. If G′ is independent of ω, the mean molecular mass between crosslinks, M_c, can be calculated according to the well-known equation from the theory of rubber elasticity [9]

$$G' = \frac{\varrho}{M_c} \cdot RT \ ,$$

ϱ being the density of the polymer. The entanglement length M_e, on the other hand, can be calculated with a similar equation

$$G_{eN}^{0} = \frac{\rho}{M_e} \cdot RT \; [10]$$

which relates the pseudo equilibrium modulus of the entanglement network G_{eN}^{0} to M_e. G_{eN}^{0} has been determined from the modulus vs. frequency plots of the uncrosslinked and lightly crosslinked samples by means of various approximations, summarized in [10].

From Fig.2 where M_c is plotted versus the MAMA concentration and M_e is indicated as a broken line, it follows that $M_c = M_e$ is reached at about 1.5% MAMA. At concentrations above this critical point, accordingly, difficulties in obtaining films with good mechanical strength should be expected.

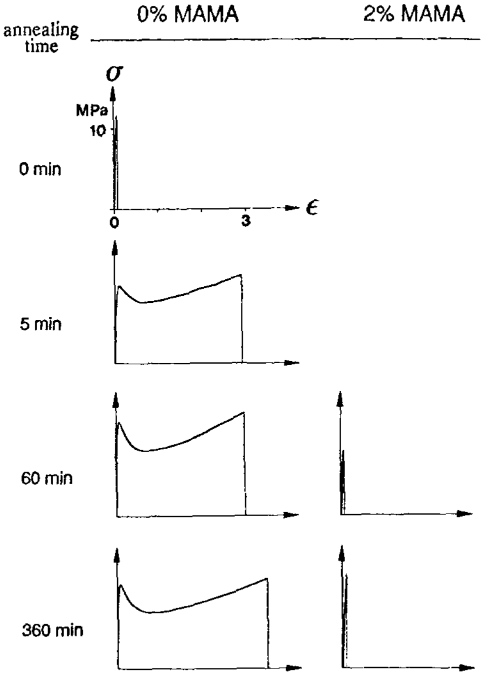

Fig.3 Stress strain curves for PBMA with 0 and 2% MAMA resp., determined at 23° C after different annealing times at 90° C

The films were annealed at 90° C, i.e. about 60° C above T_g, for different times and specimens were cut before the films cooled down to room temperature (RT). As the latex films are very brittle at RT, as already mentioned, the unannealed material had to be heated to about 50° C for a short time of 2 min in order to be able to cut a specimen. In Fig.3 some typical stress strain diagrams are shown for the "unnealed" specimen and samples with annealing times of 5, 60 and 360 min at 90°C. The uncrosslinked and not annealed material shows brittle fracture with a very low elongation at break. This fracture behaviour changes to yielding already after an annealing time of only 5 min. The PBMA with 2% MAMA could not be measured without annealing. Samples from this crosslinked material showed brittle fracture after annealing times of 60 and even 360 min.

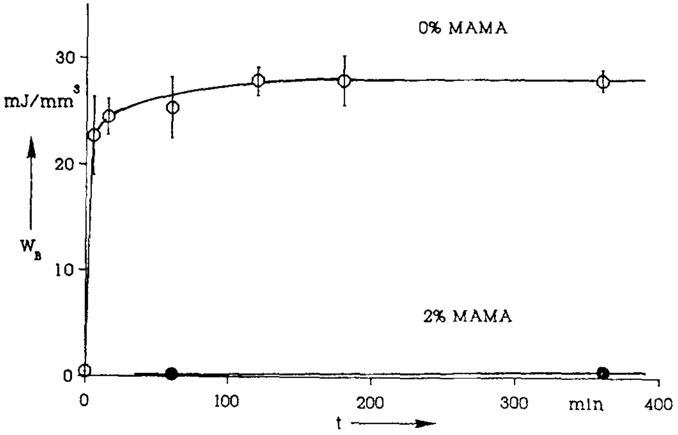

Fig.4 Fracture energy W_B per volume in dependence on the annealing time at 90°C for PBMA with 0 and 2% MAMA

Fig.4 shows the fracture W_B energy of both materials, which is proportional to the area under the stress strain curves in Fig.3, plotted versus the annealing time at 90°C. We can distinguish three time ranges with different behaviour for the uncrosslinked polymer:

- A rapid increase of W_B by nearly two orders of magnitude at short times.
- A further gradual increase up to an annaeling time of about 180 min. This is in good agreement with SANS investigations on the same samples which showed an increase of the radius of gyration of the particles by diffusion in this time range[4].
- Constant fracture energy at longer annealing times.

The PBMA with 2% MAMA does not show any significant increase of W_B with annealing time as already could be concluded from Fig.3.

The results can be interpreted as follows: During film formation at RT packing and deformation of the latex particles results in a film held together only by weak surface and van der Waals forces. No significant diffusion of segments across particle boundaries takes place, due to the T_g of 29°C. On annealing the films at 90°C the mechanical strength of the films increases gradually with the temper time. The origine of the rapid increase at short times is not yet clear. Two reasons can be envisaged: a dry sintering process which is connected with the disappearence of holes and voids between the particles due to incomplete film formation or the beginning of the diffusion process, leading to the formation of only few interparticular entanglements which possibly would be sufficient to increase the strength significantly.

The results of the stress strain measurements on the films of crosslinked latices which will be extended to other MAMA concentrations in a near future, clearly demonstrate that there exists a critical MAMA concentration below 2%, possibly near the "entanglement concentration" of 1.5%, above which films with significant mechanical strength cannot be formed. This is a strong argument for the assumption that interdiffusion of chain segments and the formation of entanglements across particle boundaries is decisive for the development of mechanical film strength.

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