

Film Formation from Polymer Dispersions

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Synopsis

The coalescence of a poly(vinylidene chloride/methyl acrylate/acrylic acid) latex was found to occur only above the T_g . The various theories of film formation from polymer dispersions attribute latex coalescence to three types of forces: the pressure due to the polymer-air interface, the pressure due to a polymer-water interface, and the pressure due to capillary action. Analysis of the forces indicates that none are sufficient to cause coalescence below T_g while any, or all, may cause coalescence above T_g .

INTRODUCTION

The formation of continuous films from polymer dispersions has continued to attract increasing interest because of its important role in latex paints, coating dispersions, and adhesives. Attempts to explain the general phenomenon have led to several theories of film formation.¹⁻⁶ These theories attribute latex coalescence to three types of forces: (1) $P_{p/a}$, the pressure due to the polymer-air interface; (2) $P_{p/w}$, the pressure due to a polymer-water interface; and (3) P_c , the pressure due to capillary action. We will show that rapid coalescence of poly(vinylidene chloride-methyl acrylate-acrylic acid) (80/20/5, wt.) latex occurs only above T_g . Analysis of the forces indicates that none are sufficient to cause coalescence below T_g , while any, or all, may cause coalescence above T_g .

EXPERIMENTAL RESULTS

Torsion Pendulum Analysis

To estimate the pressures necessary to coalesce a packed array of polymer particles, it was necessary to obtain shear modulus data for our polymer.² A compound torsion pendulum was employed for this purpose. The instrument used is similar to that described elsewhere⁷ and was fitted with a balance which permitted the changing of the inertia members while keeping a constant, low tension on the sample. Free oscillations were used exclusively (ca. 1 cycle/sec), and dry nitrogen was employed for thermostatic control.

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The test specimens were 0.25×2.00 in. strips cut from 10-20-mil films. In computing the shear modulus G , the appropriate form factor was used for our thin samples.⁸ Corrections were made for the slight tensile stress on the sample⁹ and also for the modulus component due to the torsion wire.

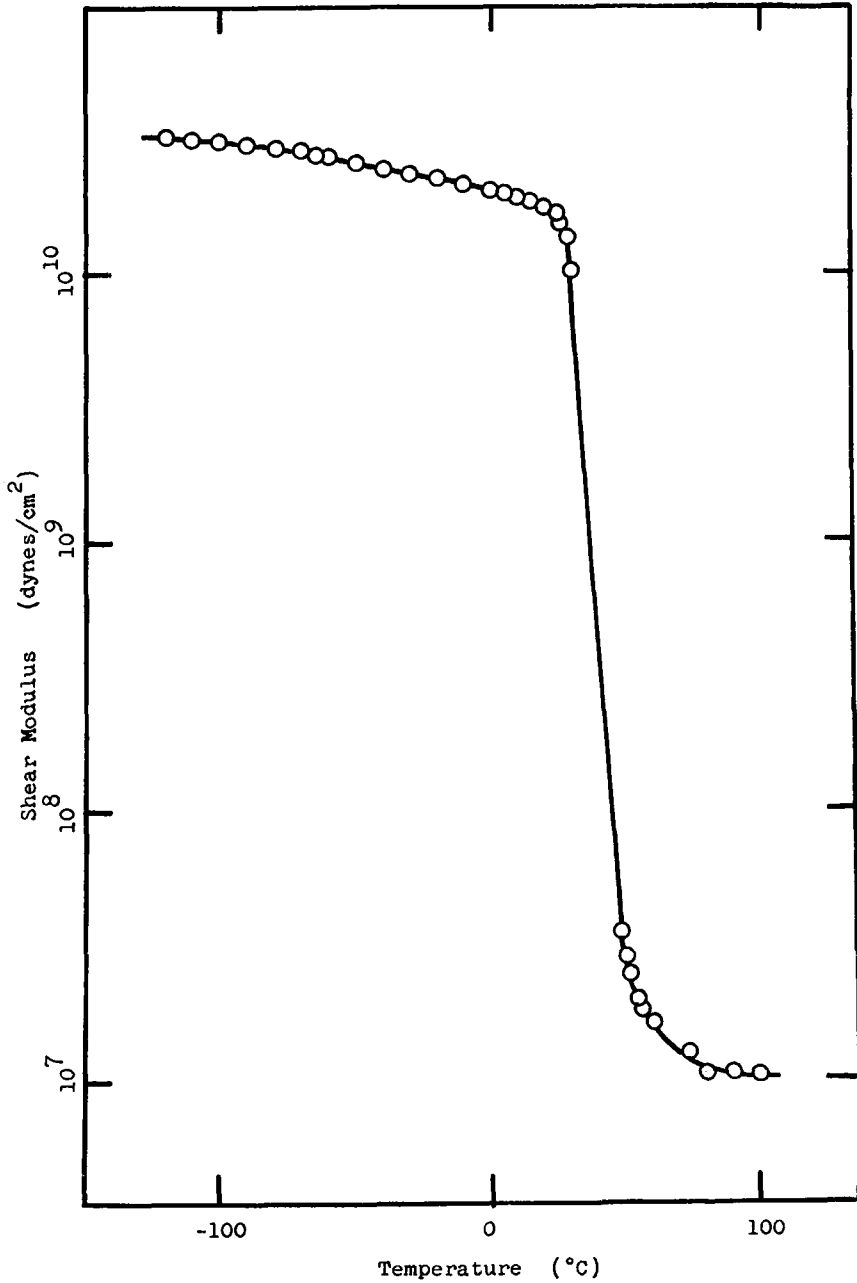


Fig. 1. Temperature dependence of shear modulus.

We estimate our accuracy to be on the order of 10–20%. This rather large uncertainty is mostly due to the imprecision of our thickness measurements.

In Figure 1, the shear modulus is plotted versus temperature for our amorphous vinylidene chloride terpolymer. Below 30°C, the material exhibits a glass-type modulus on the order of 2×10^{10} dynes/cm². Near the glass transition, there is a severe drop in modulus that is typical for an amorphous polymer. Above the T_g , from 50°–100°C, for example, the shear modulus is on the order of 2×10^7 dynes/cm².

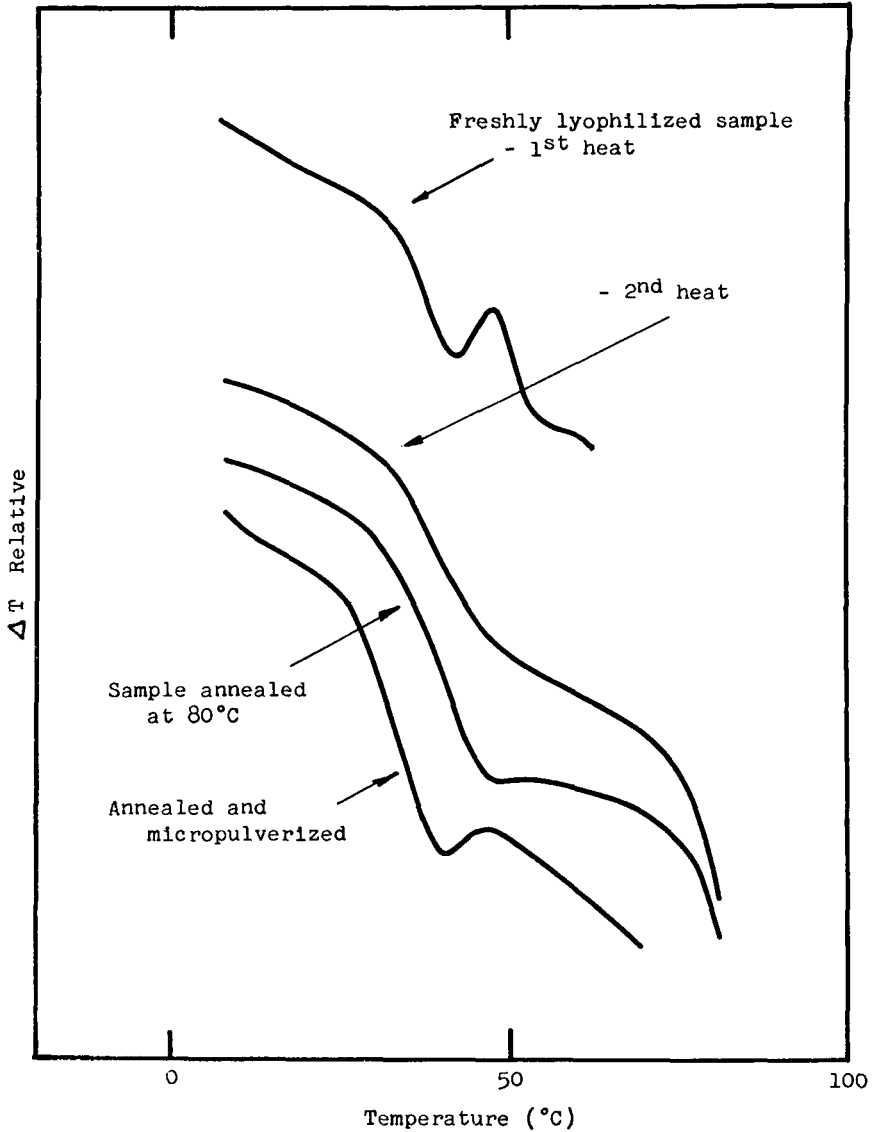


Fig. 2. Typical DSC thermograms.

Thermal Analysis

Dry latex was obtained through lyophilization in a Belco 4110 lyophilizer as described by Mahr.¹⁰ For thermal analysis we used a du Pont 900 differential thermal analyzer with the differential scanning calorimeter (DSC) cell. Latex samples, 20–25 mg, were used with a heating rate of 20°C/min.

Dry Coalescence. Mahr¹⁰ demonstrated that the loss of surface of a dry colloidal sample due to coalescence could be observed as an exotherm in DSC experiments. We were able to reproduce his irreversible exotherms on DSC thermograms (Fig. 2) using freshly lyophilized latices. Additional evidence linking the exotherms with particle coalescence was also obtained. A portion of freshly lyophilized latex was kept at 80°C for 15 min, cooled, and then micropulverized to particle sizes less than 1 micron in diameter. A DSC thermogram of the freshly lyophilized sample showed the irreversible exotherms mentioned above. The peak was absent in the sample kept at 80°C but reappeared after micropulverizing (Fig. 2).

Coalescence and T_g . Film formation (rapid coalescence) usually occurs slightly above T_g .¹⁰ Our dry vinylidene chloride terpolymer latices were no exception. With DSC we observed irreversible (rapid) coalescence only right above T_g . In other experiments, samples held 2°–3°C above T_g for 5 min were found to be coalesced, while those held 2°–3°C below T_g for 5 min were not. These observations also confine film formation to temperatures just slightly above T_g .

DISCUSSION

As stated in the introduction, the coalescence of latex particles has been attributed to three factors. The first is the pressure produced by the negative curvature of the polymer surface with air, $P_{p/a}$; the second is the pressure produced by the negative curvature of the polymer surface with the water, $P_{p/w}$; and the third is the capillary pressure, P_c , resulting from the presence of a water surface of negative curvature in the interstitial capillary system which is present during water loss. To evaluate these pressures, we considered a dispersion where the average diameter of the particles is 500 Å. For the closest packing of such spheres, the largest hole diameter would be approx. 130 Å. Since the pressure due to surface tension inside a spherical surface of radius R over that outside the surface is

$$P = \frac{2\gamma}{R}, \quad (1)$$

the pressures $P_{p/a}$ and $P_{p/w}$ can be calculated if the surface tensions, γ , are known. For vinylidene chloride polymers, the polymer–air interface tension can be taken as 40 dynes/cm.¹¹ Brown² estimated the polymer–water interface tension to be between 0 and 10 dynes/cm. From these values we calculated $P_{p/a}$ and $P_{p/w}$ as shown in Table I. For P_c , we found that the tensile strength of water has been reported to be between 7 and 300 atm. The high number was determined for pure degassed water. For our

TABLE I

Pressures available in our vinylidene chloride terpolymer dispersion, atm.			Pressures necessary to coalesce our vinylidene chloride terpolymer dispersion, atm.	
$P_{p/a}$	$P_{p/p}$	P_c	Below T_g	Above T_g
123	31	40	7300	7.3

purposes we have taken the P_c to be 40 atm, that determined for distilled water.^{4,12}

To estimate the pressures necessary to coalesce a packed array of polymer particles, we turn to an expression given by Brown²

$$P = 0.37G \quad (2)$$

where P is the pressure exerted on the particles toward their centers at coalescence and G is the shear modulus of the polymer particles. The general theories of elasticity were used in the derivation of this expression, and although rigorous application might be subject to a number of objections, we can comfortably use eq. (2) as a first-order approximation.

For the polymer latices described in this report, the torsion pendulum shear moduli were used with eq. (2) to compute the pressure needed to effect coalescence. Below T_g a shear modulus of 2×10^{10} dynes/cm² was found, and we calculate that 7300 atm are needed for coalescence. Above T_g , the modulus can be taken as 2×10^7 dynes/cm² and the coalescence pressure drops to 7.3 atm. In Table I, we compare these figures with those estimated for the three mechanisms. Below T_g , none of the assumed mechanisms appears capable of effecting coalescence—this is what we find experimentally. Above T_g , where we have observed coalescence, all of the mechanisms can coalesce our sample, and differentiation cannot be made among the different driving forces.

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