

The Distribution of Polymethyl Methacrylate Formed in Natural Rubber Latex: An Electron Microscopical Study

Interpolymer latices prepared by polymerization of methyl methacrylate in natural rubber latex have colloidal and film-forming properties which are intermediate between those of the parent latex and a simple emulsion of polymethyl methacrylate (PMM). These properties are influenced not only by the proportion of PMM but also by the method of preparation, and evidence has been presented by Cockbain, Pendle, and Turner that a controlling factor is whether the free radicals which initiate polymerization are formed in the aqueous phase or inside the particles themselves. This was interpreted to mean that colloidal and film-forming properties are influenced not just by the overall proportion of PMM, but specially by its concentration near the surface of the latex particles.¹ Supporting evidence was subsequently obtained by a study of the distribution of PMM among the various sizes of particles.² The purpose of this note is to present further evidence obtained by direct examination of the particles themselves using the electron microscope.

In the latices designated A and B, polymerization was initiated, respectively, with free radicals from benzoyl

peroxide plus dimethylaniline and from *tert*-butyl hydroperoxide plus tetraethylenepentamine. The former system is soluble in rubber but the latter is not. At this stage the latices contained about equal weights of rubber and PMM, but each was then mixed with unmodified natural rubber latex so that cast and dried sheets of polymer contained 30% PMM.

The sheets were torn across and the exposed surface replicated for electron microscopy using the two-stage replication technique (gelatin for the first stage and evaporated carbon for the second) described by Andrews and Walsh.³ The replicas were lightly shadowed with gold-palladium.

The results obtained for latices A and B are shown in Figures 1 and 2, respectively. Both micrographs show that the interpolymer latex particles retain their identity against a featureless background resulting from the subsequent addition of natural rubber latex. It is clear also that the material has torn in such a way as to expose the particle surfaces. This is in contrast to the effect produced by cutting the sheets with a razor blade (Fig. 3 shows this for latex A). Here the particles have evidently been sectioned and appear as circular regions lacking the smoothness of the surrounding matrix. In all micrographs the interpolymer particle diameter ranges from 1.5 μ to less than 0.2 μ , values typical for natural rubber latex.

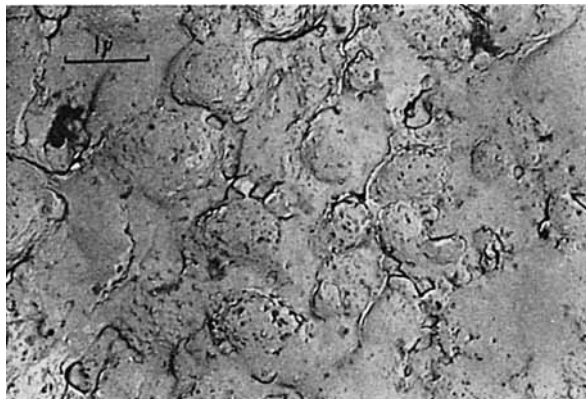


Fig. 1. From latex A.

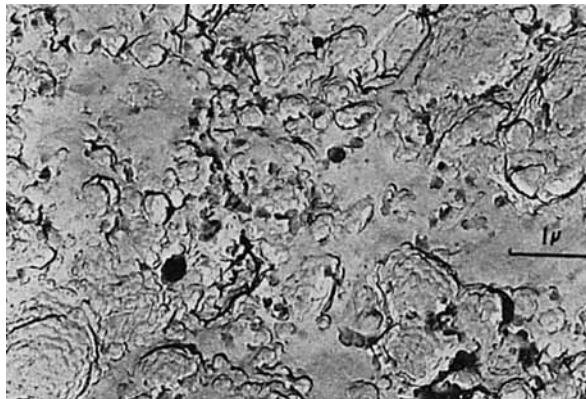


Fig. 2. From latex B.



Fig. 3. From latex A (cut surface).

The actual lower limit of particle size is obscured by the fine structure of the particle surfaces which we now consider. In latex A this consists of small pimples, spheres of roughly 500 A. diameter, spaced randomly over the interpolymer particle surfaces. In latex B a similar effect occurs, but now the pimples are larger (1000 to 1500 A.) and completely cover the particle surface which resembles the curd of a cauliflower.

It has been pointed out previously^{4,5} that microphase separation of PMM chains in the rubber interpolymer is likely. This has been confirmed directly by the authors by electron microscopical examination of one of these latices after mastication and recovery from solution. This treatment completely destroys the identity of the latex particles so that the heterogeneities now observed in a torn surface

(Fig. 4) can be due only to aggregates of PMM. The surface features of the interpolymer particles may thus be attributed to microphase separation of the PMM. The differences between latices A and B lie firstly in the size of the PMM aggregates and secondly in their distribution throughout the natural rubber latex particle. In case A a fairly uniform volume distribution of PMM is indicated while in latex B the PMM appears in much larger quantities on the particle surface.

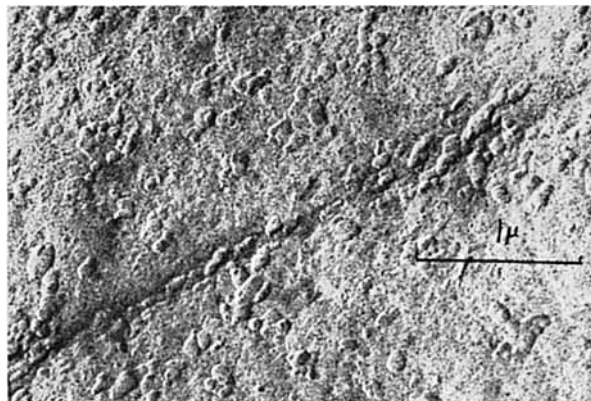


Fig. 4. From latex B after mastication and recovery from solution.

This conclusion is in complete harmony with the views previously held. Latex A has the better film-forming properties and more closely resembles natural rubber latex in its tendency to form a coherent coagulum on flocculation. As outlined above, the inferior performance of latex B may be attributed to reduction of particle to particle adhesion by a surface coating of PMM.

We hope in the near future to report the application of these techniques to a further study of interpolymers, having special regard to the variation of physical properties with the method of preparation.

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References

1. Cockbain, E. G., T. D. Pendle, and D. T. Turner, *J. Polymer Sci.*, **39**, 419 (1959).
2. Cockbain, E. G., and R. Mumford, unpublished work.
3. Andrews, E. H., and A. Walsh, *J. Polymer Sci.*, **33**, 39 (1958).
4. Cf. F. M. Merrett, *J. Polymer Sci.*, **24**, 467 (1957).
5. Allen, P. W., C. L. M. Bell, and E. G. Cockbain, International Rubber Conference, Washington, 1959.

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On Expansion of Capillary Jets of Viscoelastic Fluids

Several investigators¹⁻³ have reported the phenomenon of swelling of jets of viscoelastic fluids issuing from capillary tubes. This swelling is generally attributed to the recovery of elastic strain energy imparted to the fluid during its passage through the capillary. Some authors⁴⁻⁶ suggest that the recovery of such energy occurs through the action of positive radial stresses (pressures). These stresses are thought to be generated in viscoelastic fluids in capillary shear flow, and would be free to act unopposed by the capillary walls when the fluid is ejected.

Qualitatively, the same behavior would be expected if there were relaxing negative axial stresses (tensions) present in the jet. The existence of such axial tensions in jets of viscoelastic fluids issuing from capillary tubes has been demonstrated by the vibrating-jet experiments of Gavis and Gill.⁷⁻⁸ One may ask, therefore, to what extent the swelling may be accounted for by the axial stresses.

A relaxing axial tension in a jet of viscoelastic fluid would tend to diminish the jet's forward velocity, causing it to expand. The change in velocity and radius corresponding to a change in axial tension can be estimated by a simple stream tube analysis neglecting radial variations and viscous forces.

The equations of motion and continuity are:

$$\rho \frac{Du(x)}{Dt} = \rho u(x) \frac{du(x)}{dx} = \frac{dT(x)}{dx} \quad (1)$$

and

$$u(x)r^2(x) = \text{constant} \quad (2)$$

where ρ is the density of the fluid, $u(x)$ the average forward velocity of the jet, $r(x)$ its radius, $T(x)$ the average axial tension, and x the distance along the jet from the orifice of the capillary. The conditions at the orifice are:

$$u(0) = u_0; \quad r(0) = r_0; \quad T(0) = T_0 \quad (3)$$

where u_0 is the average ejection velocity, r_0 the radius, and T_0 the average axial tension in the jet at the orifice. With these the solution to eq. (1) is:

$$\left(\frac{u}{u_0}\right)^2 = \left(\frac{r_0}{r}\right)^4 = 1 - \frac{T_0 - T}{1/2 \rho u_0^2} \equiv 1 - G \quad (4)$$

Because the axial tension is relaxing, i.e., $dT/dx < 0$, the initial tension, T_0 , is always greater than any subsequent tension, T . Equation (4) therefore predicts an increase in jet radius, r , with distance, x . The actual rate and magnitude of growth of the jet radius depend on the group G . Where this group has a value small in comparison with unity, the jet radius increases only insensibly. For example, if the tension relaxes only very slowly, T will be close to T_0 for considerable distances along the jet. G will be small initially and increase only slowly so that one would expect only slow increase in radius. For short jets the increase may not be noticed.

If the tension relaxes rapidly, expansion close to the nozzle will occur, with a magnitude dependent upon the magnitude of the initial tension, unless the ejection velocity is large. Then both magnitude and rate of expansion will be small and the jet radius may appear constant over its entire length.