(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 Cockbain, E. G., and R. Mumford, unpublished work.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 investigators[1-3] 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 authors[4-6] 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:

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

and

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

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:

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

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:

$$\left(\frac{u}{u_0}\right)^2 = \left(\frac{r_0}{r}\right)^4 = 1 - \frac{T_0 - T}{{}^1/_2\,\rho u_0{}^2} \equiv 1 - G \qquad (4)$$

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.

In the experiments of Gavis and Gill, no appreciable change of velocity or radius along the jet was observed; in all of their experiments, however, G was always negligible with respect to unity, and so eq. (4) is concordant with their observations but cannot be quantitatively tested thereby.

For other reports where expansion has been described no data are available for axial tensions. Further experiments in the region where G is comparable with unity are presently being pursued.

References

1. Merrington, A. C., *Nature*, **152**, 663 (1943).

2. Clegg, P. L., *The Rheology of Elastomers*, Pergamon, New York, 1958, p. 174.

3. Mooney, M., *Rheology, Theory and Applications*, Academic Press, New York, 1958, Vol. 2, p. 181.

4. Lodge, A. S., *The Rheology of Elastomers*, Pergamon, New York, 1958, p. 70.

5. Truesdell, C., *J. Rational Mech. Anal.*, **1**, 173 (1952).

6. Braun, I., and M. Reiner, *Quart. J. Mech. Appl. Math.*, **5**, 42 (1952).

7. Gill, S. J., and J. Gavis, *J. Polymer Sci.*, **20**, 287 (1956).

8. Gavis, J., and S. J. Gill, *J. Polymer Sci.*, **21**, 353 (1956).

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Ion Exchange Properties of Nitrocellulose-Coated Cellophane Membranes

It has been observed that nitrocellulose-coated cellophane membranes (M.S.A.T. 400) exhibit cation selective properties. These properties were first observed indirectly when cellophane membranes were used in conjunction with Permaplex permselective membranes in a three-compartment electrodialysis cell for the simultaneous electrodialysis and electrodecantation of ammoniated skim rubber latex.[1] Experiments with pure ammonia solutions were also carried out (see Fig. 1) and are reported below.

Figure 2 shows the current at constant voltage flowing across the cell plotted against time for three combinations of membranes;

(1) Permaplex C.20 (cation-selective)–Permaplex A.20 (anion-selective), (no cellophane).

(2) Permaplex C.20–(Permaplex A.20 together with cellophane M.S.A.T. 400) (Fig. 1).

(3) (Permaplex C.20 together with cellophane M.S.A.T. 400)–Permaplex A.20.
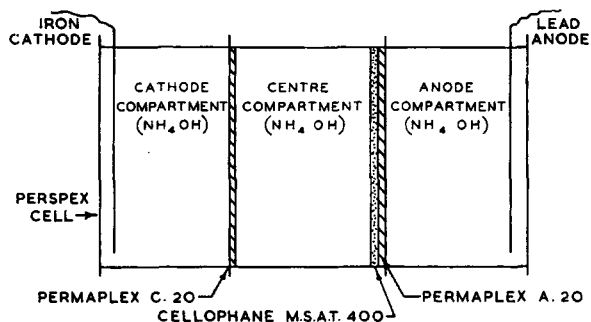
The electrolytes used were identical in all cases.

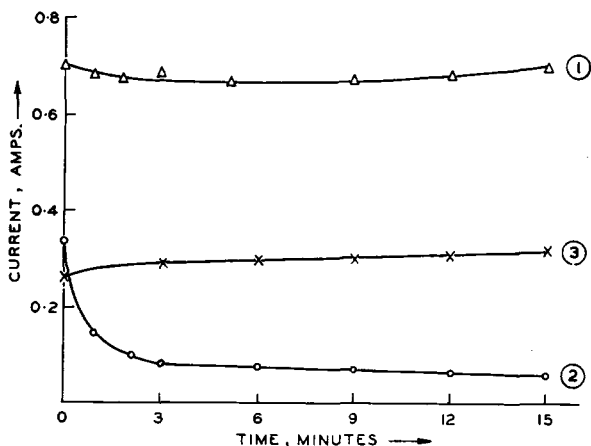Fig. 1. A schematic representation of a three-compartment electrodialysis cell.

Fig. 2. The variation with time of current at constant voltage for three different combinations of membranes.

Curve 1 shows that without cellophane the current remains almost constant. If cellophane is used together with the anion-selective membrane (A.20), the current falls rapidly to a low level (Curve 2), but if the cellophane is used together with cation-selective membrane (C.20) the current, although lower than when no cellophane is used, again remains constant (Curve 3). A possible explanation is that the cellophane acts as a cation-selective membrane so that the film of liquid between the cellophane and Permaplex A.20 (condition *2*) is deionized and the resistance rises. But in the case of condition *3* where the cellophane membrane is combined with the cation-selective membrane, C.20, the film of liquid between them is supplied with cations, and therefore no increased resistance results. In the case of condition *1*, no such film is present. In all the experiments the cellophane membranes used were presoaked in the electrolytes used.

When the experiments were repeated with plain transparent cellophane (uncoated), P.T. 300, no increased resistance was found with time for the combination of Permaplex A.20 and cellophane, thus indicating no cation selectivity.

In order to find the degree of cation selectivity of the nitrocellulose-coated cellophane membrane, a few quantitative experiments were conducted in a two-compartment electrodialysis cell, using only a cellophane membrane. The transport number of the cations, which is directly related to