## NOTES

# The Water Penetration of Emulsion Polymer Films

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Many studies[1-4] have been made of the mechanism of polymer film formation from emulsions, but little attention has been paid to the mechanism of water penetration into emulsion films.[5] The properties of the films deposited from polymer emulsions may be said to be essentially different from those of solution-cast or milled polymer films, considering the fact that the emulsion films more easily undergo several changes when exposed to water or water vapor a swelling and whitening of the films, accompanied by a deterioration of the mechanical properties and a decrease in adhesion to the substrate.

The present study was made in order to clearly establish the mechanism of water penetration into emulsion films. For this purpose vinyl acetate (VAc)-butyl acrylate (BA) copolymer emulsions were selected as samples because of their enormous consumption in the paint industry and in other fields.

## Experiments

**Materials.**—Emulsions were prepared by the usual method. They were prepared by using 2% of sodium polyoxyethylene nonylphenyl sulfate as an emulsifier and 0.3% of ammonium persulfate (based on the monomer) as an initiator.

Solid polymers free from water-soluble substances were obtained as follows: an emulsion state was destroyed by freezing; small masses of the polymer so obtained were then washed with water for 7 days and dried at 50°C for 4 days.

The films used in the study were prepared by drying the chosen emulsion or solution on a leveled glass plate. The films so obtained then were left to stand at 20°C under 65% R. H. for more than 4 days.

**Methods.**—The weight of the water absorbed ($Q$) was determined as follows. Samples (4×5 cm.) were cut from the film and weighed on a direct reading balance. They were then immersed in water at 20°C, taken out at appropriate intervals, blotted quickly with a hard filter paper, and weighed. Five samples were used for each measurement, and the values obtained were averaged. The films 70±10 micron thick were used for the measurements. The film thickness was measured by a thickness gauge.

## Results and Discussion

**The Water-Absorption Behavior of Emulsion Film in Aqueous Solutions.**—When an emulsion is dried, its particles approach each other and eventually touch, thus forming a continuous polymer network. The spherical particles deform, flow together and interpenetrate, leaving small deposits of water which contain the water-soluble substances originally present in the emulsion. As the last water evaporates through the polymer network and the spaces between the fused particles (channels), small clots of the water-soluble substances remain behind.[5,6]

Water penetrates into the clots through the polymer network and channels when the emulsion film is immersed in water. Simultaneously, the polymer network absorbs water to attain an equilibrium. Therefore, it is reasonable to consider that the driving force for the water penetration is given by the difference between the vapor pressure inside the film and that of the external phase to which the film is exposed.

To check this assumption, the films deposited from the VAc-BA (75 : 25) copolymer emulsion were immersed in aqueous solutions of various concentrations of ammonium chloride, sucrose and glucose. The value of $Q$ is plotted against the square root of the time in Fig. 1.

The diagram shows that $Q$ initially increases linearly as a whole with the square root of the time, and that it then gradually approaches an equilibrium value. Although $Q$ soon reaches the equilibrium in a rather concentrated solution, it continues to increase slowly in water or in a diluted

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[1] R. E. Dillon, L. A. Matheson and E. B. Bradford, *J. Colloid Sci.*, **6**, 108 (1951).

[2] W. A. Henson, D. A. Taber and E. B. Bradford, *Ind. Eng. Chem.*, **45**, 735 (1953).

[3] G. L. Brown, *J. Polymer Sci.*, **22**, 423 (1956).

[4] S. S. Voyutskii, "Autohesion and Adhesion of High Polymer," Interscience Pub., New York (1963), p. 63.

[5] G. L. Brown and J. P. Scullin, *Ind. Eng. Chem.*, **45**, 743 (1953).

[6] H. Fikentscher, H. Gerrens and H. Schuller, *Angew. Chem.*, **72**, 856 (1960).

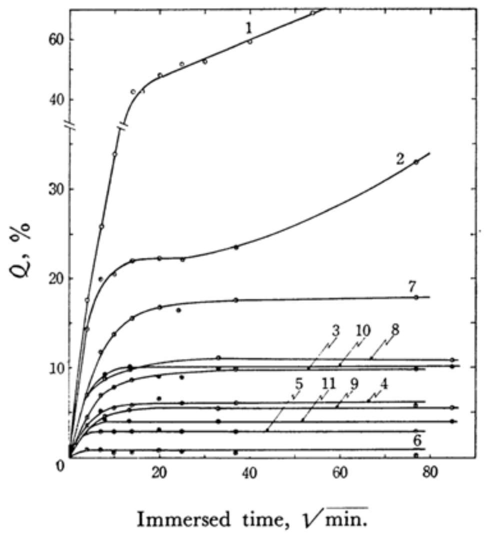

Fig. 1. Effect of concentration of aqueous solutions on water absorption behaviors of emulsion films. (1) water, (2) 0.1 N ammonium chloride, (3) 0.5 N ammonium chloride, (4) 1 N. ammonium chloride, (5) 2 N ammonium chloride, (6) 5 N ammonium chloride, (7) 0.5 N sucrose, (8) 1 N sucrose, (9) 2 N sucrose, (10) 1 N glucose, (11) 2 N glucose

solution, even after an extended time of immersion. The values of Q after a sufficient time of immersion decrease with an increase in the concentration of the solutions, approaching zero as the concentration of the solutions approaches saturation.

The results obtained here suggest that, as expected, the force for water penetration decreases with a reduction in the activity of the external phase (the vapor pressure of the external phase). This may be seen distinctly in Fig. 2, which gives the relationship between the activity of water in the external phase and the value of Q after 100 min. The activity was determined by calculation. Figure 2 shows that Q begins to increase rapidly beyond the activity value of 0.9, almost regardless of the solute nature. This may show that the water-soluble substances contain some water and that, consequently, the activity of water inside the film is rather high.

Another experiment determined the Q of the film deposited from an emulsion which had been dialyzed in a cellophane dialysis tube for 7 days. The dialysis of the emulsion was conducted under such conditions that the emulsifier in the emulsion was not removed; the resulting emulsion was stable. The value of Q for the film after immersion for 7 days ($\sqrt{\text{min.}} \fallingdotseq 100$) was only 18%, against 87% for the untreated emulsion film (it must be noted that these values involve the weight of the water absorbed by the copolymer itself 6.8% as is seen in Table I). On the basis of the results obtained here, it can be said that even a small amount of the salts present in the film, salts which are derived from the initiator and the impurities contained in the emulsifier, may play a leading role for water penetration, whereas the emulsifier may have rather less effect. This may be attributed to the difference in their solubilities in the copolymer.

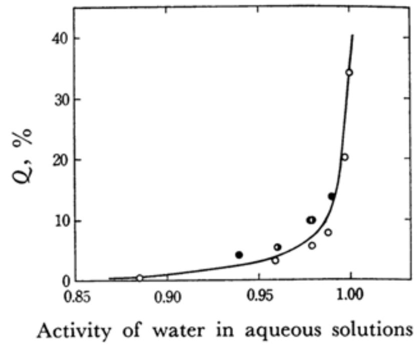

Fig. 2. Relationship between activity of water in aqueous solutions and Q after 100 min. ○: ammonium chloride solution, ●: sucrose solution, ◑: glucose solution.

In a subsequent experiment, films which had been 60% pre-swollen by immersing in water for about 48 hr. ($\sqrt{\text{min.}} \fallingdotseq 54$) were dehydrated by immersing them in aqueous solutions of different concentrations. The dehydration rates of the pre-swollen films are much higher than their water absorption rates, as is shown in Fig. 3. For example, it takes about 48 hr. for the original emulsion film to absorb 60% of the water, as has been mentioned above, while the pre-swollen film is almost completely dehydrated in about 36 min. in 5 N aqueous ammonium chloride. This fact indicates that, in water absorption, water must penetrate into a film against the resistance of the polymer

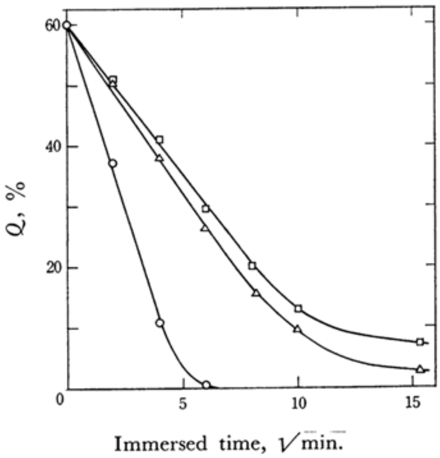

Fig. 3. Dehydration of pre-swollen emulsion films in aqueous ammonium chloride at different concentrations.
○: 5 N, △: 0.5 N, □: 0.1 N

network, while in dehydration there is no such resistance.

**The Effect of the Modulus of the Polymer Network on Water-Absorption Behavior.**—The water-absorption behavior of the films with different moduli, prepared from the emulsions of VAc with BA in different copolymerization compositions, was determined over extremely extended immersion periods. The results are shown in Fig. 4. The moduli of the copolymers are expressed in terms of Young's moduli of solution-cast films, which have the copolymerization compositions corresponding to those of the respective emulsion films and are free from water-soluble substances, as Table I shows.

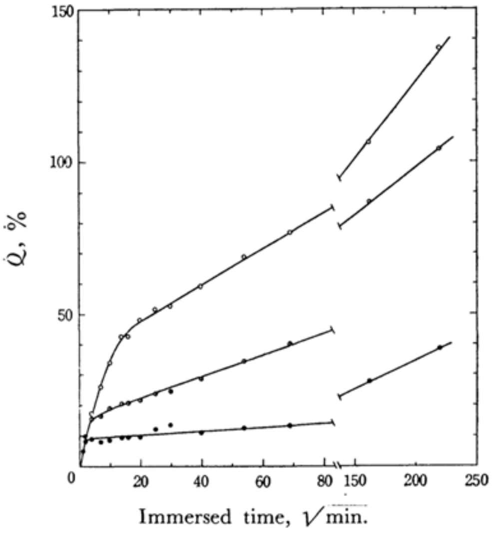

Fig. 4. Effect of modulus of polymer network on water absorption behavior.
●: PVAc, ◑: VAc/BA 90/10, ○: VAc/BA 75/25

TABLE I. YOUNG'S MODULUS AND WATER ABSORPTIVITY OF SOLUTION-CAST FILMS FREE FROM WATER SOLUBLE SUBSTANCES

| VAc : BA | Young's modulus (dyne/cm$^2$)$10^9$ | Q after 7 days, % |
|---|---|---|
| 100 : 0 | 9.6 | 13.7 |
| 90 : 10 | 4.2 | 9.9 |
| 75 : 25 | 1.4 | 6.8 |

The values of $Q$ for all emulsion films initially increase at the same rate linearly against the square root of the time, but the rate sharply decreases at a certain $Q$, in correspondence with the modulus of the film (polymer network). The values of the breaks increase with a decrease in the modulus of the polymer network. The water absorptivity of the film increases with the reduction in its modulus, that is, with the increase in the BA component in the copolymer. On the other hand, the solution-cast film free from water-soluble substances, contrary to the tendency of the emulsion film, shows a small decrease in $Q$ (after 7 days' immersion) with an increase in the BA component, as Table I shows.

It is evident from the results obtained here that the resistance to water penetration is due to the resistance of a polymer network to deformation. On the other hand, it is of great interest to note that $Q$ did not attain an equilibrium but continued to increase slowly, even after one month ($\sqrt{\text{min.}} \fallingdotseq 208$).

**The Water-Absorption Behavior of Solution-Cast Film Prepared from Emulsion Film.**—The water-absorption behavior of the emulsion film and the solution-cast film, which have exactly the same composition, is compared in Fig. 5. The cast film was deposited from the solution which had been prepared by dissolving the VAc-BA (75 : 25) copolymer emulsion film in ethyl acetate.

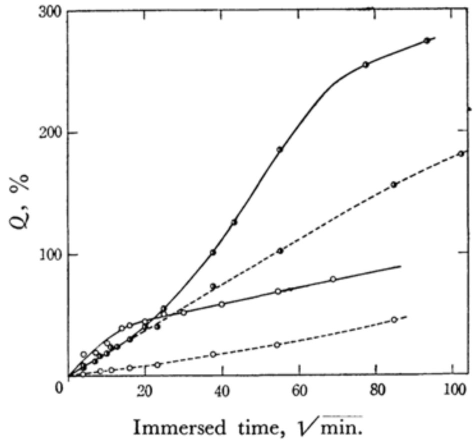

Fig. 5. A comparison between water absorption behavior of emulsion film and that of solution-cast film prepared from the emulsion film.
——: original film, ----: film after a water absorption-redrying cycle, ○: emulsion film, ◑: solution-cast film

The water absorption rate in the initial stage is more rapid for the emulsion film than for the cast film, but in the later stage the $Q$ of the cast film is a few times of that of the emulsion film.

The cast film may show such high water absorptivity because the clots of the water-soluble substances originally present in the emulsion film are kept undissolved in ethyl acetate and, consequently, the film prepared from this solution has the same structure as that of the original emulsion film. In addition, less water-soluble substances might be extracted from the cast film than from the emulsion film because the former has fewer channels. For such reasons, the cast film would ultimately absorb much more water than the emulsion film.

In order to verify this assumption, the weight of the film before and after immersion-redrying were ascertained. The films were immersed in water until the water absorption rates broke. It took about 400 hr. to reach that stage for the cast film, and 24 hr. for the emulsion film. Then they were redried at 20°C under 65% R. H. for 4 days. The weight reductions of the films, based on the original weight, were 0.6% for the cast film and 1.9% for the emulsion film.

The water-absorption behavior of the redried films was then again ascertained. The water absorptivities of the films are markedly lowered, as is shown by the dotted lines in Fig. 5. Obviously, this results from the decrease in the water-soluble substances in the films.

In a subsequent experiment, the water absorptivities of solution-cast films prepared from solutions of the VAc-BA (75 : 25) copolymer emulsion films in various solvents were determined. The results are shown in Table II.

TABLE II. EFFECT OF SOLVENTS USED FOR DISSOLUTION OF EMULSION FILM ON WATER ABSORPTIVITY OF RESULTING CAST FILM

| Solvent | $Q$ after 7 days, % |
|---|---|
| Carbon tetrachloride | 110 |
| Toluene | 137 |
| Acetone | 140 |
| Methanol | 58 |
| Formic acid | 63 |

According to the values of $Q$ in Table II, they may be classified into two groups; the first group showing higher values, and the second, lower values, than that of the emulsion film. The former films are prepared by those solvents which dissolve salts only with difficulty, while the latter are prepared by those solvents which dissolve salts to some extent.

It seems that in the film of the lower-$Q$ value group the water-soluble substances are dispersed unimolecularly, while in the film of the higher-$Q$ value group, they are dispersed as clots, as has been mentioned above. This difference in film structure may affect the water absorptivity. It is not known, however, how the difference in film structure can be related to that in water absorptivity.

## Conclusion

From the results obtained so far, it can be understood that there is no essential difference between the water absorption behavior of emulsion films and that of solution-cast films. Emulsifiers and salts are necessarily attendant on emulsion films, and, consequently, they absorb extremely much water. Furthermore, emulsion films are obliged to have a rather low modulus because of their forming mechanism. On the other hand, solution-cast or milled films have no limitation on their formation, and films of a rather high modulus are often used. Emulsion films may generally be regarded to absorb water much more easily than solution-cast or milled films because of the difference in the factors mentioned above.

As far as the present study has so far discovered, the water-resistance of PVAc emulsion film can not be improved by the copolymerization of a higher acrylic ester.

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