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Acrylic Latex Film Formation in the Critical Temperature Range

RAYMOND R. MYERS and RAY K. SCHULTZ,*
Lehigh University, Bethlehem, Pennsylvania

Synopsis

A shear wave of 15 megacycle frequency and four microsecond duration was made to impinge on the under-side of a series of ethyl acrylate-methyl methacrylate copolymer films on fused quartz. Reduction in the reflection coefficient of the pulse provided a direct measure of the increased viscosity and elasticity of the film as it dried, as well as the loss in adhesion which occurred in some cases. Upon reducing the minimum film-forming temperature (MFT) from 54 to 32°C. by increasing the ethyl acrylate content from 35 to 50%, the adhesion loss was reduced, eventually to zero, depending on the drying rate. Despite the fact that elasticity of the latex particles is the controlling parameter in film quality, a dependence on their viscosity was revealed by this work.

The properties of a surface coating made from a latex depend on the type of polymer comprising the dispersed phase. A minimum film-forming temperature (MFT) is established by the viscoelastic properties of the polymer spheres; the main factor which establishes the MFT is the elastic modulus G, a subordinate role being played by the viscosity η. These properties are combined in real materials to produce a composite property called shear mechanical impedance Z.

THEORY

The mechanism first proposed for the liquid-to-solid conversion in latex systems involved a sintering process[1,2] for the coalescence of two spheres under the driving influence of the polymer surface tension forces. In 1956, Brown[3] showed that the interfacial tension between the aqueous and dispersed phases was responsible for the loss of the integrity of the individual spheres. That is, the spheres merely deform into either polyhedra or ellipsoids. Although this advance sparked a general abandonment of the theory based on a sintering mechanism, it did not rule out the inclusion of viscosity as an important parameter.

The study reported here was designed to ascertain the combined roles played by G and η, using Brown's mechanism along with embellishments proposed in a subsequent paper.[4] The method involved the following of

* Paint Research Institute Fellow in Rheology.

the drying rate using an ultrasonic pulse echo instrument[5] described earlier in this series.[6,7] In this technique, the shear mechanical impedance of the film is measured during the drying process, and the results are interpreted in terms of the percentage area of the substrate which is covered by the spheres as they undergo deformation.

ULTRASONIC STUDIES OF FILMS

Method

A shear wave of 15 megacycle/sec. frequency and 4 μsec. duration was made to impinge on an optically flat surface of a fused quartz bar at an angle of incidence of 11°. The wave was polarized so that a transverse displacement of the quartz occurred in a direction parallel to the optically flat surface of the bar. An exponential decrease occurred in the intensity of successive echoes of the mechanical pulse back and forth along the bar; the change in the decrement was followed as each latex was cured on the bar.

The absorption of ultrasonic energy occurred at the film–substrate interface, and resulted in a decrease in the reflection coefficient at the fused quartz surface. This feature distinguishes the ultrasonic pulse echo method of monitoring drying from conventional drying time device.

With no film on the bar, the attenuation (intensity decreases due to reflection losses, and to absorption by the quartz) was 3 db./echo, and as many as twenty echoes could be displayed on an oscilloscope. When a latex was placed on the bar, a nearly imperceptible increase in attenuation (Δ) occurred, owing to the faint absorption of the ultrasonic energy by liquids. As the latex dried, generally after a certain induction time, the attenuation became progressively larger, ultimately rising to over 24 db./echo ($\Delta = 24$) in favorable cases.

Four acrylic latex emulsions were made from ethyl acrylate (EA) and methyl methacrylate (MMA) by the Rohm and Haas Company. Their MFT's varied according to the EA–MMA ratio of the copolymer as shown in Table I.

TABLE I
Polymer Compositions and Properties

Latex no.	Composition, EA/MMA	MFT, °C.	Solids, %
1	35/65	54	47.3
2	40/60	47	47.3
3	45/55	37	46.8
4	50/50	32	47.0

Results

At or above the MFT, the S-shaped curve characteristic of an adherent film was observed; however, below the MFT the attenuation reached a

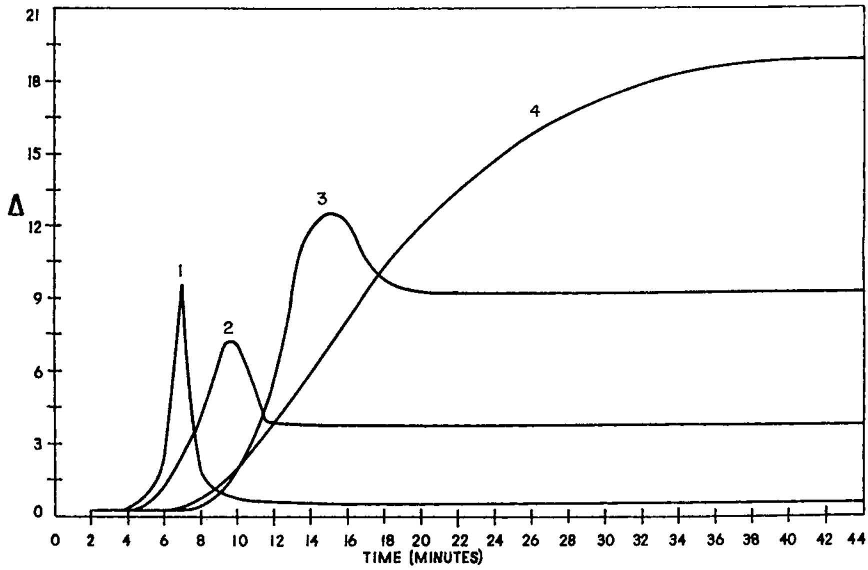

Fig. 1. Drying curves for acrylic latices listed in Table I. Curing was done rapidly at 35°C. and low humidity.

maximum value and then declined to a value characteristic of the area of contact between the film and the surface. These results suggested that a systematic study be made of the influence of the temperature and drying rate on the properties of the cured films.

The four latices produced the drying curves shown in Figure 1. All data were taken at a temperature of 35°C. and a relative humidity of less than 20%. Only latex 4 was cured above its MFT, and only this latex produced a continuous film. The number of cracks and the lack of adhesion on drying increased as MFT increased.

When the evaporation rate was decreased by an increase in the relative humidity to 55%, latex 3 began to take on the characteristics of an acceptable film, as shown by Figure 2 and by the difficulty experienced in removing the dried film. Note the increase in the time required for attainment of the peak, as well as the broadening of the peak between Figures 1 and 2.

Further reduction in drying rate at a temperature 2°C. below the MFT was studied by increasing the relative humidity to 80%. Only latex 3 was used at this stage. Table II reveals that at 35°C. a critical drying rate was found below which no drop in attenuation was suffered by the film. This rate,[7] in the arbitrary units of decibels per echo per minute lay somewhere between 0.079 and 0.155 Δ/min. The means of attaining the information is discussed.

Temperature, also, influenced the shape of the drying curve. Inasmuch as the trend occurred in the predictable manner, no figure is given; as the drying temperature approached the MFT, the attenuation peak

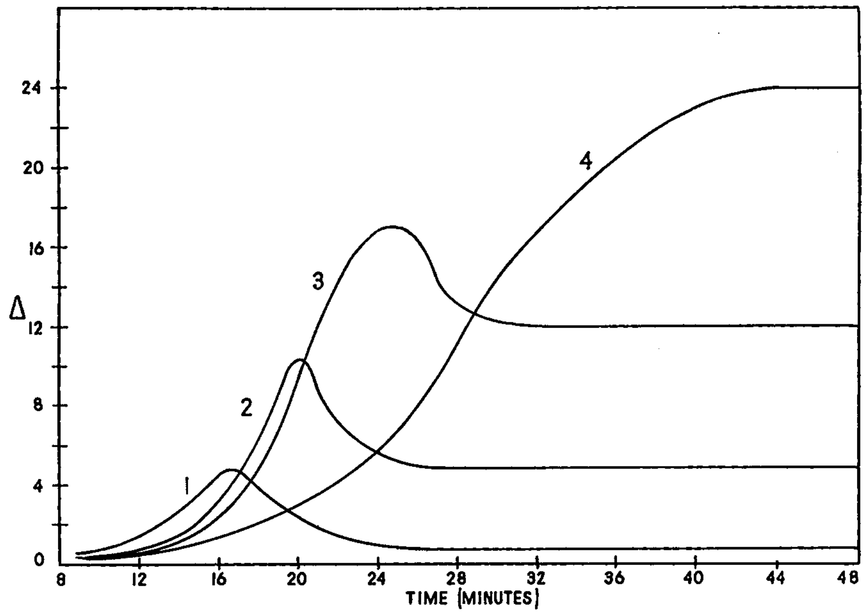

Fig. 2. Drying curves for acrylic latices listed in Table II. Curing was done slowly at 35°C. and high humidity.

TABLE II
Effect of Drying Rate on Attenuation Pattern

Key (Fig. 3)	Approximate relative humidity, %	Rate, Δ/min.	Attenuation per echo (Δ)		
			Peak	Dry film	% Decrease
A	15	0.286	12.5	9.5	24
B	35	0.238	15.5	10.0	23
C	55	0.155	17.0	12.0	29
D	80	0.079	18.0	18.0	0

became more blunt and disappeared in the vicinity of the MFT. The exact temperature at which the peak disappeared depended on the drying rate in a manner consistent with Figures 1 and 2.

Within the rate limits imposed by this study, the stresses which accumulated on drying are reduced by lowering the drying rate. The reduction eventually reaches a value low enough to permit a continuous film to be formed.

KINETIC ANALYSIS OF DRYING DATA

General Discussion

Figures 1 and 2 reveal that loss of adhesion is detected at an early stage in the drying of a latex. The acrylic latices used in this study provided confirmation of a phenomenon observed repeatedly with other types of latices, with certain lacquer films, and with salt solutions. In every case in which the dried material failed to remain in intimate contact with the entire substrate, an attenuation peak was reached, followed by a more or less drastic decline to a final value.

A tentative interpretation of this behavior is offered on the basis of adhesion. Residual stresses in the film cause it to lose not only its continuity but also a certain percentage of its contact with the substrate. Detection of the incipient withdrawal of the film from the surface is provided by ultrasonic impedance measurements, long before any other recognized means of detecting adhesive failure.

Calculation of Drying Rates

Figure 3 augments this argument by delineating the role of the drying rate as a determinant of film quality. When log Δ is plotted against time, an extensive linear portion of the drying curve is evident in virtually every

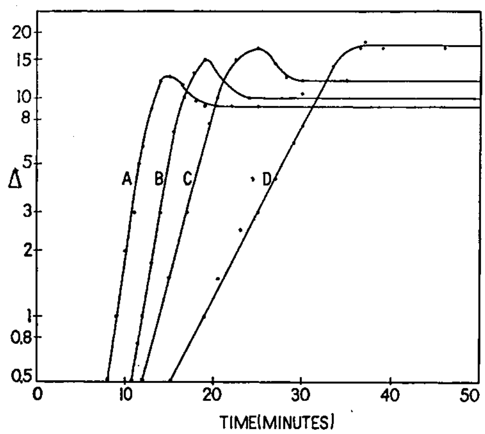

Fig. 3. Linearized drying curves for latex 3 under conditions listed in Table II. Rates are determined by the slopes of the lines.

instance of drying. The use of a logarithmic plot is conventional whenever population increases are expressed graphically;[8] from the slope of the linear portion a quantitative evaluation can be made of the drying rate in arbitrary terms.[7] The problem at hand is to interpret these rates in terms of the physical process involved.

A photomicrographic study of the dried films revealed that in the cases in which bad checking had occurred, the area of contact represented only a fraction of the total area, as suggested by the ultrasonic data. Figure 4 is a typical phase contrast photomicrograph at about 100× magnification, and shows that contact with the substrate was effected only through a circle located near the center of the individual chips of polymer. Reference to Figure 4 reveals that some of the chips evidently failed com-

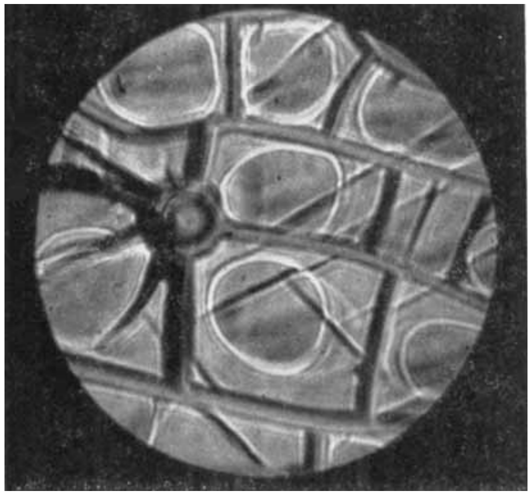

Fig. 4. Phase-contrast photomicrograph of latex 2. Dried 20°C. below MFT. Circles represent areas of contact of the chips whose outlines are more or less rectangular. ×100.

pletely. The MFT of the latex in question was 10°C. above the drying temperature.

Drying rates, computed from the slopes of numerous plots similar to Figure 3, are recorded in Table III. Remarks pertain generally to experimental findings other than the two main attenuation readings from which impedances Z were calculated.

TABLE III
Summary of Impedance Results

Latex no.	Drying temp., °C.	Degrees below MFT, °C.	Drying rate, logΔ/min.	Δ Maximum	Δ Dry film	Remarks
1	47	7	0.22	12.5	7.5	
	35	19	0.13	4.5	0.8	Complete failure
	35	19	0.50	9.5	0.5	
2	47	0	0.64	17.5	13.5	
	40	7	0.19	14.5	7.5	Earlier (in Δ) adhesive failure at low rate
			0.17	12.8	7.3	
			0.10	13.5	7.0	
			0.09	11.2	7.0	
	35	12	0.32	7.2	3.7	
3	35	2	0.29	12.5	9.3	Later (and less) adhesive failure at low rate
			0.28	15.5	10.0	
			0.08	18.0	16.5	
			0.06	20.0	17.5	
4	35	—	0.17	19.0	19.0	No failure

It is difficult to make generalizations based on the trends in Table III because of the apparent operation of two competing factors: (*1*) slow drying allows the film to achieve greater continuity than does rapid drying; (*2*) slow drying, by virtue of creating larger chips, allows larger residual stresses to remain in the film.

Now, when drying is effected on the low side of the MFT, three possibilities are in evidence, depending on the rate of drying and on the proximity of the drying temperature to the MFT. At the slowest rate, as long as the temperature lies above some critical value which appears to be within 6°C. of the MFT, a certain amount of creep can occur; this creep lessens the stress which exists in and among the polyhedra, and permits a completely continuous and adherent film to form. Undoubtedly, this film still contains residual stresses, but they remain below the threshhold necessary to break the film. When the drying rate is increased, the time allowed for operation of the creep mechanism is insufficient to keep the accumulated stresses below the threshhold value, and some of the film integrity is lost. At first, a pattern of large patches develops in the dried film, but at higher drying rates the outlines become distinct cracks; at this point, the patches become chips which undergo significant shrinkage in response to the residual stresses. Further increases in drying rate produce progressively smaller chips with progressively smaller shrinkage per chip (and consequently lower residual stress). The three possibilities, therefore, are (*1*) continuum; (*2*) adherent patches containing large residual stresses; and (*3*) chips in which the stresses have been alleviated extensively by curling or separation from the substrate.

The ultimate reduction in residual stress would occur with latex particles of such high rigidity that a continuum could not form at all. This case is a trivial one from the viewpoint of the coatings chemist. Under these conditions no residual stresses would build up, nor would the impedometer detect any adhesion to the substrate during any stage of the drying. This situation is responsible for the enormous sensitivity of peak height to drying rate in the case of latex 1 (compare Figs. 1 and 2).

The break in the exponential progression of Δ, as shown acutely by the linearized plot of Figure 3, signifies an approach to maturity, or to a limiting capacity.[9] This limit, naturally, is set by the area of the impedometer; but two important considerations must be added to account for the case at hand.

First, the approach to saturation in the case of latex drying is characterized by two phases: an early accelerating phase wherein spheres are squashed into circular contact with the surface, and a later decelerating phase wherein the circles contact each other in a close-packed array and begin to deform into the shape of hexagons.

Second, a catastrophe occurs at about the same time as the approach to saturation in three-quarters of the cases under study. This catastrophe has been interpreted as a sudden reduction in the area of intimate contact between film and substrate.

The first consideration suggests that the logarithmic function which expresses the increase in Z on drying might be substituted on equally strong theoretical grounds by a function representing the area of contact. This possibility was not investigated further at this time. The second consideration is discussed in more detail.

The coincidence involving the decrease in chip area and decrease in final impedance values demands that viscosity be given some stature as a determinant of film quality. Furthermore, the attainment of a plateau in Z rather than a peak in Figure 3*D* reveals beyond doubt that the MFT was actually lowered by operating at a drastically reduced rate. Evidently, the distorted spheres needed 10 min. or longer for the stresses to relax to less than the threshold level. Not only does η represent a time-dependent phenomenon, but it also couples with G in viscoelastic systems to produce a characteristic parameter referred to as relaxation time or retardation time, depending upon how η and G are coupled. A certain amount of relaxation of stress is needed during the drying process in order to obtain a continuous film.

The rate effect can be explained in a different manner. Scofield[10] has advanced the explanation that evaporation of water from a latex on an insulator such as quartz is likely to be adiabatic, and that the more rapid drying produced a more drastic lowering of temperature. Recent studies[11] on the rapid evaporation of water show that the surface temperature can be reduced as much as six degrees below that of the bulk liquid. Coincidentally, the critical temperature range found in this work was approximately 6°C.

Calculations

Inasmuch as only one quantity is measured with the present ultrasonic impedometer, a clear-cut direct evaluation of G and η cannot be made. Impedance, of course, follows directly from the attenuation data, and can be evaluated from the equation,

$$Z = Z_q \cos \theta[(1 - r)/(1 + r)]$$

where Z_q ($=8.29 \times 10^5$ g./sec. cm.^{2}) is the impedance of the fused quartz bar; $\cos \theta$ ($=\cos 79°$) is 0.191; and r, the complex reflection coefficient, is expressed in terms of the intensity ψ of the reflected and incident waves by

$$r = (\psi_r/\psi_i)e^{-i\delta}$$

where intensity is related to the measured Δ by

$$\log (\psi_r/\psi_i) = -\Delta/40$$

Here the assumption is made that the phase angle δ between the incident and reflected wave is so small that the imaginary term can be neglected ($e^0 = 1.0$). When the surface sites are completely populated by polymer, a typical value of Δ is 25 db./echo. Under these conditions, $\psi_r/\psi_i = 0.237$, and

$$Z = 8.29 \times 10^5 \times 0.191 \times (0.763/1.237)$$
$$= 9.8 \times 10^4 \text{ g./sec. cm.}^2 \text{ (mechanical ohms)}$$

This computation was checked against the value obtained for the shear modulus G obtained in a separate experiment in which the velocity of propagation of a 10 kilocycle compression wave was measured along a strip of the free film. A commercial device called a Pulse Propagation Meter (manufactured by the KLH Instrument Co.) was used for this check. A velocity of 1.467×10^5 cm./sec. was found and was converted into Young's modulus Y by the relation,

$$Y = v^2\rho$$

assuming 1.15 g./cm.³ for the density ρ. Then assuming that $3G = Y$ (this assumes, reasonably, that Poisson's ratio is 0.5),

$$G = (1.467 \times 10^5 \times 1.15)^2/3 = 0.82 \times 10^{10}$$

and

$$Z = G^{1/2}\rho^{1/2} = 9.7 \times 10^4 \text{ ohms}$$

One would not expect the agreement to be even this close in comparing a modulus at kilocycle frequencies with one at megacycle frequencies.[7] The order-of-magnitude agreement is sufficient, and allows one to represent the ordinates in Figures 1–3 by shear mechanical impedance.

CONCLUSIONS

(*1*) The rate of drying of acrylic latices affected film quality when the temperature lay in a narrow region immediately below the minimum film-forming temperature (MFT).

(*2*) A plateau was reached in the shear mechanical impedance of MMA–EA latices under conditions of drying which produced coherent, adherent films (i.e., at or above the MFT).

(*3*) Films cured below the MFT displayed maxima in the trend of impedance with time whose heights depended inversely upon the drying rate. Final impedance levels depended directly upon the temperature.

(*4*) A correlation was established between final impedance levels and the area of contact of the chips of dried film.

(*5*) Development of impedance during drying followed a mathematical relation suggestive of population increases. This behavior was interpreted as a steady growth of the contact area between polymer spheres and the substrate.

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Résumé

Une onde de cisaillement d'une fréquence de 15 mégacycles et d'une durée de 4 microsecondes a été appliquée à une série de copolymères acrylate d'éthyleméthacrylate de méthyle sous forme de film sur quartz fondu en vue de recouvrir leur face inférieure. La réduction du coefficient de réflexion de l'impulsion a fourni une méthode de mesure directe de la viscosité intrinsèque et de l'élasticité du film lorsqu'il sèchait, aussi bien que la diminution d'adhésion qui a eu lieu dans certains cas. Par réduction de la température minimum de formation du film (MFT) de 54° à 32°C en augmentant la teneur en acrylate d'éthyle de 35 à 50%, la perte d'adhésion a diminué, éventuellement jusqu' à zéro, tout en dépendant de la vitesse de séchage. En dépit du fait que l'élasticité des particules de latex est le paramètre contrôlant la qualité du film, ce travail a révélé une dépendance vis-à-vis de leur viscosité.

Zusammenfassung

Man hat eine Scherungswelle mit einer Frequenz von 15 Megahertz und einer Dauer von 4 Mikrosekunden auf die Unterseite einer Reihe auf Quarzgut aufgrebrachter Äthylacrylat-Methylmethacrylat-Copolymer-filme einwirken lassen. Die Verminderung des Reflexionskoeffizienten der Schwingung gibt direktes Mass für das Ansteigen von Viskosität und Elastizität des Filmes beim Trocknen sowie für die in manchen Fällen auftretende Adhäsionsabnahme. Bei der Erniedrigung des Filmbildungstemperaturminimums (MFT) von 54° auf 32°C durch Erhöhung des Äthylacrylatgehaltes von 35 auf 50% wurde die Adhäsionsabnahme je nach der Trocknungsgeschwindigkeit verringert, u.zw. in manchen Fällen bis auf den Wert Null. Die Filmqualität ist zwar in erster Linie durch die Elastizität der Latexteilchen bestimmt, hängt aber, wie in der vorliegenden Arbeit gozeigt wird, auch von deren Viskosität ab.

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