Gelation and Fusion of Vinyl Plastisols

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Synopsis

The gelation of vinyl plastisols at constant temperature has been found to follow the equation $\ln [(C - C_e)/(U - C_e)] = (-\pi^2/a^2)D\tau + \ln (8/\pi^2)$, where C is the resin phase concentration, C_e the equilibrium resin phase concentration, U the critical resin phase concentration, a the average particle size, D the diffusion constant, and τ the time required for the onset of gelation. A light reflectance apparatus capable of measuring the gelation process is described. The effect that various resin–plasticizer parameters have on the gelation and fusion process is discussed. The light-reflectance apparatus is also useful for estimating various resin and formulating parameters.

INTRODUCTION

A plastisol is a pourable dispersion of a finely divided poly(vinyl chloride) polymer in a nonvolatile liquid plasticizer. When a plastisol is gradually heated, its viscosity at first decreases because of the viscosity dependence of the plasticizer on temperature. At higher temperatures the polymer rapidly swells by imbibing the plasticizer and the viscosity of the plastisol increases until the whole mass becomes immobile or gelled. The temperature at which the plastisol first gels is designated as the gel temperature G_t. The gelled plastisol is still weak and opaque at this stage. During the gelation process the wet, glossy plastisol surface becomes very dull. This change in gloss is explained by the fact that the resin has swollen to the point where the particles are exposed on the surface. The surface is now quite rough on a microscopic scale and scatters the incident light, which gives the surface a dull appearance. Heating the material to even higher temperatures causes the resin particles to fuse together and become quite clear, and the entire composition upon cooling to become tough and flexible. The temperature at which the resin just begins to fuse and become clear is called the "clear" point C_p[1] or "fusion" point f_p.[2] The conversion of the liquid dispersion to a tough semisolid is a physical process and does not involve a chemical change in the usual sense.

Poly(vinyl chloride) and its copolymers are the only polymeric materials which have so far been used in plastisol-type applications to any important extent. Attempts to utilize other polymers have usually failed, mainly because of the poor shelf stability of the liquid dispersion, i.e., the liquid plasticizer rapidly swells or dissolves the resin at room temperature, and this in turn gels the dispersion, making it useless for plastisol application

methods. This suggests that poly(vinyl chloride) has some singular property which readily adapts it to the plastisol and organosol techniques. Even though poly(vinyl chloride) plastisols have been studied extensively, little is known concerning the actual process of gelation and fusion. For this reason a comprehensive study of the gelation and fusion process was made.

THEORY OF PLASTISOL GELATION

The total volume of a simple plastisol V_t is composed of the volume of the resin phase V_r and the volume of the plasticizer phase V_p [eq. (1)].

$$V_r + V_p = V_t \tag{1}$$

When a plastisol is heated at a temperature near the gel temperature, the resin imbibes plasticizer and swells. Since the overall volume change of the plastisol during the gelation process is negligible, the volume of plasticizer absorbed is equal to the volume change in the resin phase due to swelling or

$$\Delta V_r - \Delta V_p = 0 \tag{2}$$

During the swelling process it must be remembered that there is not only plasticizer surrounding the resin phase but also plasticizer bound in the resin phase as absorbed plasticizer. The plasticizer which is outside the resin phase will be termed "free" plasticizer, and that which is absorbed or imbibed will be termed "bound" plasticizer. As a consequence of this fact it is necessary to distinguish between two resin concentrations: that of the resin phase in the "free" plasticizer, and that of pure resin in the swollen resin phase. The former resin concentration C is expressed as the volume of the resin phase V_r divided by the total volume of the plastisol V_t [eq. (3)]. The latter resin concentration v'_2 is expressed as the volume of the pure resin R_v divided by the volume of the swollen resin phase V_r (swollen) [eq. (4)].

$$C = V_r/V_t \tag{3}$$

$$v'_2 = R_v/V_r \text{ (swollen)} \tag{4}$$

The immediate effect of this combination of resin swelling and simultaneous decrease in "free" plasticizer volume is an increase in plastisol viscosity, since the net result of the swelling process is equivalent to an effective increase in the resin phase concentration C. Continuation of the swelling process ultimately leads to gelation of the plastisol.

Consider now a particle of resin of volume αa^3, where a is the average radius of the particle and α a geometrical shape constant, surrounded by an element of volume βL^3, where L is the average length of the volume element and β another geometrical shape constant. The resin-phase concentration C of the plastisol is then

$$C = \alpha a^3/\beta L^3 \tag{5}$$

As the resin-phase concentration C is increased, it approaches as a limit $\alpha/8\beta$ as the radius of the particle approaches $L/2$. The ratio of $\alpha/8\beta$ is the critical resin-phase concentration U, that is, where the particles just touch. U, the "packing" constant, is a function of the probable packing of the resin, as well as the particle size distribution.

Consider again a particle of resin surrounded by an element of volume in which L is greater than $2a$. If the resin particle is caused to swell, its effective particle size is increased, and the resin-phase concentration C is increased also. As the resin particle swells its radius a approaches $L/2$ and the resin-phase concentration U, and incipient gelation ensues (Fig. 1).

Differentiating eq. (3) yields eq. (6):
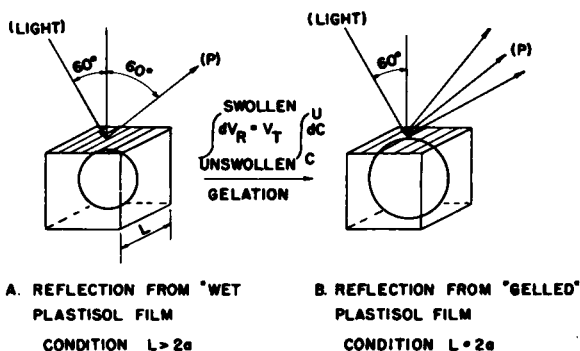
$$dC = dV_r/V_t \tag{6}$$

Fig. 1. Idealized model of a plastisol during the gelation process, showing the relationship of reflectance of the unswollen plastisol to that of the gelled plastisol.

Integration of eq. (6) between the limits of C to U and between V_r (unswollen) to V_r (swollen) gives the volume change of the resin phase that takes place during the gelation process [eq. (7)].

$$\Delta V_r = [V_r \text{ (swollen)}] - [V_r \text{ (unswollen)}] = V_t(U - C) \tag{7}$$

There is evidence to show that plastisol resins have a limited swellability at temperatures below the fusion temperatures. This means that there is some minimum resin-phase concentration C_e below which the conditions for gelation, namely, $a = L/2$, cannot be met. In other words, at a given temperature below the fusion temperature, the initial resin-phase concentration is such that even at maximum swelling, the resin-phase concentration is just able to reach the critical resin-phase concentration U. Integrating eq. (6) over the limits C_e to U and V_r (swollen) to V_r (unswollen) gives the maximum volume change in the resin phase during the gelation process [eq. (8)]:

$$\Delta V_{r \text{ max}} = [V_r \text{ (swollen)}] - [V_r \text{ (unswollen)}] = V_t(U - C_e) \tag{8}$$

If it is assumed that the diffusion of the plasticizer into the resin follows Fick's law and the resin particles are spherical, eq. (9) can be written:[3a]

$$\frac{\Delta V_p}{\Delta V_{p\infty}} = \left(1 - \frac{8}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \exp\left\{\frac{n^2\pi^2 D\tau}{a^2}\right\}\right) \tag{9}$$

where ΔV_p is the volume of plasticizer absorbed in time τ, $(\Delta V_{p\infty})$ is the volume of plasticizer absorbed in an infinite period of time, D is the specific diffusion constant of the resin–plasticizer system, and n is the number of terms in the series. Since $\Delta V_r = \Delta V_p$, substitution of eqs. (7) and (8) into eq. (9) and expanding the series gives

$$\frac{C - C_e}{U - C_e} = \frac{8}{\pi^2} e^{-\theta} + \frac{1}{4} e^{-4\theta} + \frac{1}{9} e^{-9\theta} + \ldots + \frac{1}{n^2} e^{-n^2\theta} \tag{10}$$

where $\theta = \pi^2 D\tau/a^2$. Since the higher terms of the series become diminishingly small, all but the first term may be neglected, and we obtain

$$\frac{C - C_e}{U - C_e} = \frac{8}{\pi^2} \exp\left\{-\frac{\pi^2 D\tau}{a^2}\right\} \tag{11}$$

which by converting into log forms becomes

$$\ln \frac{C - C_e}{U - C_e} = -\frac{\pi^2}{a^2} D\tau + \ln \frac{8}{\pi^2} \tag{12}$$

Equation (12) predicts that a plot of $\ln (C - C_e)$ against τ should yield a straight line whose slope is $\pi^2 D/a^2$ and whose intercept is $\ln (8/\pi^2)(U - C_e)$.

The diffusion constant D is temperature-dependent according to equation (13):[3b]

$$D = D_0 e^{-E/RT} \tag{13}$$

where R is the gas constant, T absolute temperature, D_0 a parameter which is a function of the entropy of activation, and E the energy of activation for the process. Substitution of eq. (13) into eq. (12) leads to eq. (14):

$$\ln \tau = \frac{E}{RT} - \ln \frac{\pi^2}{a^2} D_0 + \ln\ln \left[\frac{8(U - C_e)}{\pi^2(C - C_e)}\right] \tag{14}$$

From eq. (14) it follows that the plot of the log of the time required for gelation to ensue against reciprocal absolute gel temperature $1/G_t$ should approach a straight line whose slope is E/R and whose intercept is

$$\ln \frac{\pi^2}{a^2} D_0 + \ln\ln \left[\frac{8}{\pi^2} \frac{(U - C_e)}{(C - C_e)}\right]$$

The picture is complicated further by the fact that both E and D_0 change at the glass transition temperature of the polymer,[4] that is, there is a definite break in the curve of log D versus $1/t$ at the glass transition temperature, and at this temperature the diffusion constant increases

rapidly with increasing temperature. This phenomenon has been observed by Alter[5] in his viscosity–temperature studies on plastisols.

Equations (12) and (14) form a basis for a test of the theory. All that need be determined is the time τ required for gelation to ensue at various resin volume concentrations C. The previously noted changes in gloss of a plastisol film during gelation suggests a method for determining the required gel times. When a plastisol film is heated and the gloss observed, the incident light is at first reflected from the smooth uniform surface (Fig. 1A). However, as the resin particles swell beyond a certain point, the condition that exists at the onset of gelation, or $2a$ just exceeds L in Figure 1B, the incident light is scattered, and the reflection value decreases. Therefore, the time required then for the onset of decrease in gloss is the time required for onset gelation.

EXPERIMENTAL

Apparatus

An instrument capable of measuring the gloss level of a plastisol film during the gelation and fusion process was devised. A schematic diagram of the apparatus is given in Figure 2. In essence, the apparatus consists of a stable light source (L) placed at a 60° angle from the normal to the surface of the film and a phototube (P) placed at the specular angle equal to but opposite that of the incident light beam. A small bright metal panel, on which a 20-mil film of the plastisol to be tested has been applied, is held in place on an aluminum heating block by means of a vacuum hold-down system. The aluminum heating block has a thermocouple well just beneath the metal panel. The heating block is heated with a 300-w. heater which is controlled by means of a variable transformer. Both temperature and reflectance are recorded on a multipoint recorder against time.
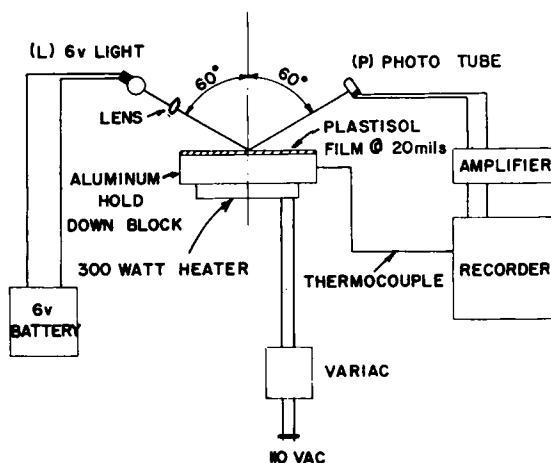

Fig. 2. Schematic diagram of the reflectance temperature method (RTM).

Constant-Temperature Studies

In order to test the mathematical analysis, presented in eq. (12), the time required for gelation to take place at a constant temperature and for several resin volume concentrations C was determined on PVC–di(2-ethylhexyl) phthalate (DOP) plastisols. These data are summarized in Table I and graphically represented in Figure 3.
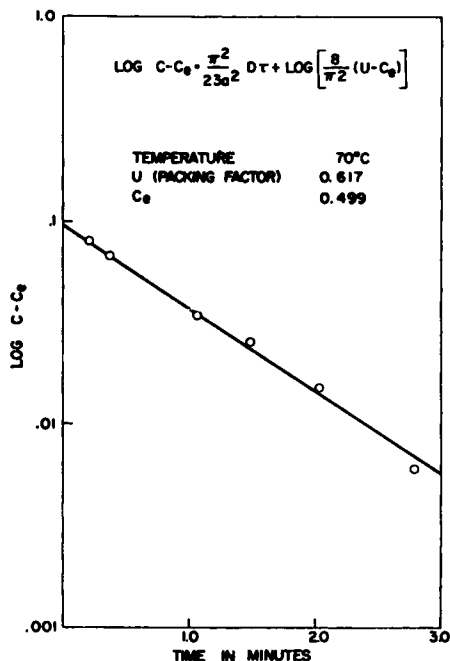

Fig. 3. Mathematical test of eq. (12).

TABLE I
Gelation of PVC–DOP Plastisols at 70°C.

Plasticizer content, phr by wt.	Vol. fraction of resin C	Time τ, min.	$C - C_e$
50	0.578	0.22	0.079
55	0.566	0.38	0.067
60	0.533	1.18	0.034
62	0.524	1.50	0.025
65	0.514	2.04	0.015
68	0.505	2.80	0.006
70	0.493	—	—

The value of C_e was obtained by plotting C against $1/\tau$ and extrapolating to infinite time τ; i.e., as $1/\tau$ approaches zero, C approaches C_e (see Fig. 4). A test of eq. (14) is represented in Figure 5, which shows the results of
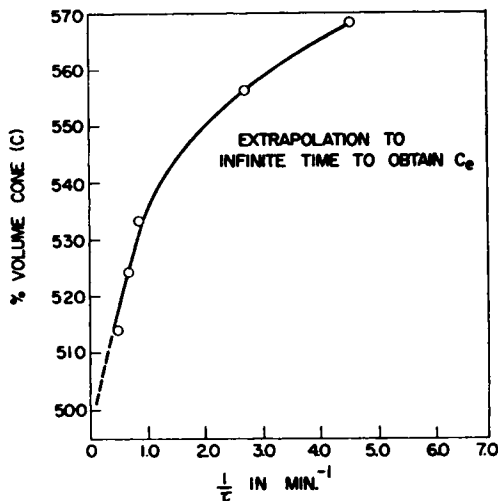
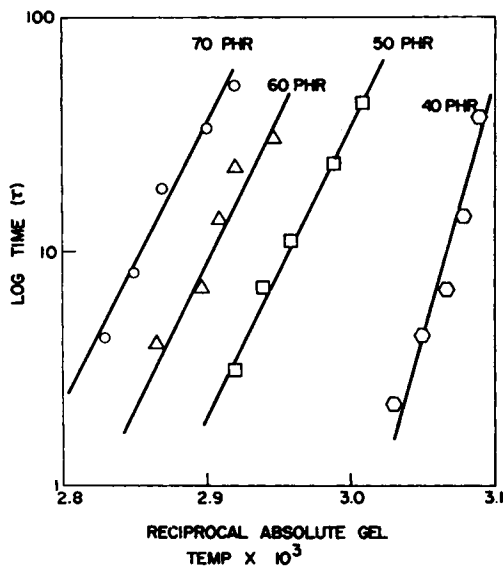Fig. 4. Method of determining the equilibrium swelling concentration C_e.

Fig. 5. Mathematical test of eq. (14).

plotting the log of the time required for gelation to ensue against the reciprocal absolute gel temperature.

DISCUSSION

In general, the observed data fit the derived equations well. Of particular interest is the observed limited swellability of poly(vinyl chloride), particularly at lower temperatures. It is believed that the partial crystallin

character of the resin is a unique property which accounts for the apparent network structure of the virgin polymer. It must be realized that the ratio of crystalline to amorphous polymer must be just right in order that gelation may take place at a reasonable temperature. Further, the interaction of plasticizer with resin must be such that after the film has been fused extensive recrystallization of the polymer is retarded,* otherwise the fused plastisol would tend to be incompatible and the liquid plasticizer would separate or sweat out.

The fusion temperature of the resin (clear point) has been found to be nearly independent of concentration. Fusion can be considered as the melting out of the crystallites or, more properly, the solution of the crystalline polymer in the plasticizer. This, of course, destroys the network structure and allows the particles of resin to flow together.

Since the resin-phase concentration which will just gel at a constant temperature is C_e and the resin-phase concentration of this gelled plastisol is U, and since the volume of the resin phase V_r (unswollen) is equal to the volume of the resin R_v before swelling, the ratio of C_e to U is the volume fraction of the resin in the swollen phase at equilibrium [eq. (15)].

$$\frac{C_e}{U} = \frac{V_r \text{ (unswollen)}/V_t}{V_r \text{ (swollen)}/V_t} = \frac{R_v}{V_r \text{ (swollen)}} = v'_2 \tag{15}$$

Through eq. (15) it is possible to relate the swelling of the plastisol to the resin–plasticizer interaction constant χ_1 [eq. (16)][3,8,9]:

$$\chi_1 v_2{}^2 = -\ln (1 - v_2) - v_2[1 - (2/fZ)] - (v_2{}^{1/3}/Z) \tag{16}$$

where Z is defined as the number of segments per chain, the size of the segment being taken as equal in volume to one plasticizer molecule, and f is defined as the functionality of the junctions between chains. It must be remembered that the theory of swelling of network systems as developed by Flory[9,10] was for amorphous polymers and not partially crystalline polymers like PVC. In the amorphous network, the crosslink is assumed to occupy no volume, but is represented as a point of junction between polymer chains. In PVC it is apparent that the pseudo-crystalline crosslinks occupy a real volume and, therefore, a correction of the measured value of v'_2 in the present experiment is suggested. If it is assumed in the initial swelling of the plastisol only the amorphous polymer is affected, then eq. (17) may be written:

$$v_2 = (v'_2 - v_c)/(1 - v_c) \tag{17}$$

where v_c is the volume of crystalline polymer. Substitution of eq. (17) into eq. (16) yields

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* There is evidence which indicates that at room temperature small quantities of plasticizer (up to 10–15 phr) actually increases the crystalline character of poly(vinyl chloride); however, at higher plasticizer concentrations the apparent network structure of the fused compositions is reduced.[6,7]

$$\chi_1 \left(\frac{v'_2 - v_c}{1 - v_c} \right) = -\ln \left(\frac{1 - v'_2}{1 - v_c} \right)$$
$$- \left(\frac{v'_2 - v_c}{1 - v_c} \right) \left(1 - \frac{2}{fZ} \right) - \frac{1}{Z} \left(\frac{v'_2 - v_c}{1 - v_c} \right)^{1/3} \quad (18)$$

The interaction parameter (χ_1) is related to temperature by eq. (19).[11]

$$\chi_1 = \chi_s + (A_{12} \bar{V}_1 / RT) \quad (19)$$

where χ_s is related to the entropy of mixing and A_{12} to the heat of mixing. Substitution of eq. (18) into eq. (19) yields a relation of swelling to temperature [eq. (20)].

$$x_s + \frac{A_{12} \bar{V}_1}{RT} = \frac{-\ln (1 - v_2)}{v_2{}^2} - \frac{1}{v_2} \left(1 - \frac{2}{fZ} \right) - \frac{\bar{V}_2{}^{-5/3}}{Z} \quad (20)$$

It is apparent that if one reduces the crystalline character of the resin by copolymerization to obtain a lower-fusing resin one would also expect to have greater swellability (decreases v'_2) and hence reduced shelf stability of the plastisol.   On the other hand, if the crystallinity of the resin is increased to improve shelf stability the gelation and fusion temperature would be expected to increase.   The theory also explains why completely amorphous polymers such as poly(methyl methacrylate) and polystyrene do not make good plastisol resins, since they tend to swell infinitely even at room temperature and thus have relatively little plastisol stability.   On the other hand, highly crystalline polymers do not make good plastisol resins, since the tendency to recrystallize is so great that the plasticizer sweats out and the films become incompatible.

The effect that average particle size and distribution has on the gelation process is clearly indicated by the parameters C_e, U, and a.   Thus, from
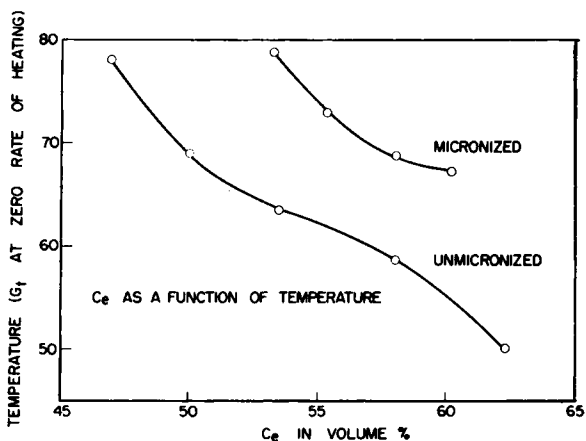

Fig. 6. Effect of grinding resin (micronization) on the equilibrium swelling concentration C_e.

eq. (12) one would expect an 0.1 μ particle to swell 100 times faster than a 1 μ particle. Further, it explains why milling or grinding a plastisol affects its gel properties markedly. If the parameter U is increased (decreased viscosity) by milling then the gel temperature is raised, since the resin must swell more to reach the gel point. If the parameter U is decreased (increased viscosity) then the gel temperature is reduced. U and C_e are related to each other by eq. (15). Figure 6 shows the effect that micronizing a poly(vinyl chloride) dispersion resin has on the value of C_e.

Differential Temperature Studies

In the first part of this paper, consideration was given to gelation of plastisols at a constant temperature. In the following, consideration will be given to the more practical aspects of gelation and fusion of plastisols, that is, what happens under conditions more like those in practice.

When a plastisol film is heated at a specified rate and the reflectance is measured, the gloss level initially decreases in the manner expected from earlier considerations. The temperature at which the gloss level just begins to decrease is defined here as the gel temperature G_t. As the film is heated to higher temperatures, the resin fuses and becomes transparent. Since the film is applied to a mirrorlike surface, the reflectance increases as the film fuses. The temperature at which the reflectance level just begins to increase is the clear point C_p. Figure 7 shows a typical reflectance-temperature measurement (RTM) result for a 60 phr DOP plastisol, and the method of determining the gel temperature G_t and clear point C_p.
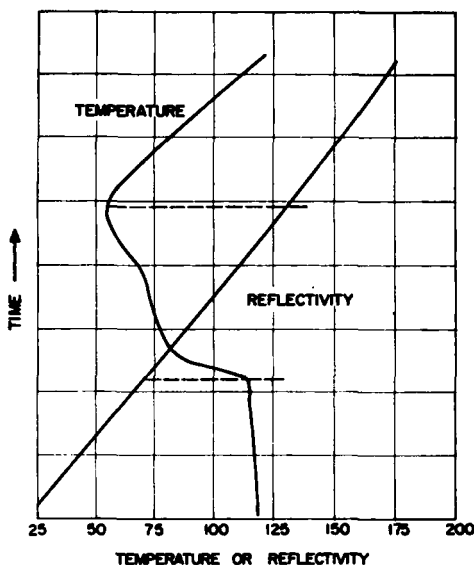

Fig. 7. Typical RTM curve obtained from a plastisol during the gelation process.
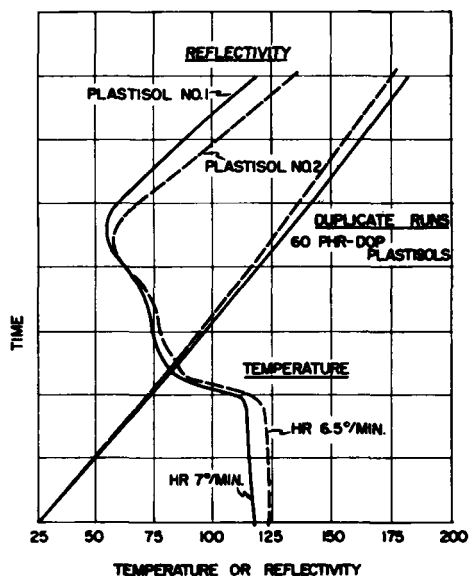
Fig. 8. Duplicate determination on two different plastisols prepared from the same resin and plasticizer, superimposed to illustrate reproducibility of the RTM method.

Time is on the vertical axis running from right to left, while temperature (Centigrade) reflectivity in terms of arbitrary units are on the horizontal axis.

The reproducibility of the method is indicated in Figure 8 which shows duplicate determinations on two different samples of 60 phr DOP plastisols. The curves do not coincide exactly, because of the slightly different heating rates and initial reflectivities. The determination of gel temperature G_t and fusion temperature C_p by this method requires only 15–20 min. and as little as 2 g. of sample is required.

Others have studied the temperature–viscosity relationships during the gelation process.[12–14] A comparison of the data obtained by viscosity measurements with the data obtained by the RTM method is shown in Table II.

TABLE II
Gelation and Fusion Properties of Various Poly(vinyl Chloride)
Plastisol Resins (60 phr in DOP)

Resin sample	G_t, °C.[a]	C_p, °C.[a]	Temp. of gelation, °C.[b]
B	76	124	69–70[c]
C	64	125	62
D	76	133	76
E	72	119	—
F	75	127	—

[a] Data on 60 phr DOP plastisols from present study.
[b] Determined after the method of Newton and Cronin.[14]
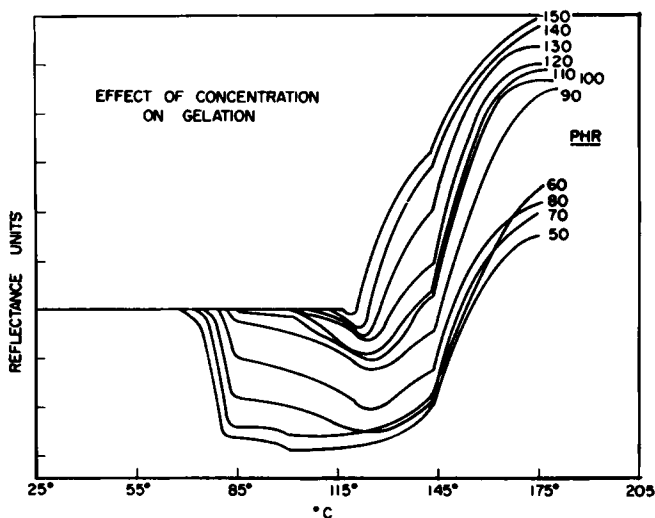[c] Value depends on sample.

Fig. 9. Effect of resin concentration on the RTM curve.

As expected from the theoretical considerations, the resin concentration can affect markedly the gel temperature, whereas the clear point is nearly independent of the resin concentration. Figure 9 illustrates the relationship of concentration to both the gel temperature and clear point.

A comparison of data taken for selected plasticizers is given in Table III,

TABLE III
Effect of Plasticizer on Gelation and Fusion Properties

Plasticizer trade name	Chemical name	Gel temp. G_t, °C.[a]	Clear point, C_p, °C.[a]	Clear point (lit.), °C.[b]	Fusion temp., °C.[c]
Santicizer 141	2-Ethylhexyl diphenyl phosphate	62	108	105	69
Santicizer 160	Butyl benzyl phthalate	56	128	126	76
Flexol 77G	Dipropylene glycol dibenzoate	66	98	—	82
Kronitex AA	Tricresyl phosphate	60	131	85	73
Flexol 426	Mixed phthalates	73	123	—	—
Flexol DOP	Di(2-ethylhexyl) phthalate	76	124	132	110
Flexol CC-55	Di(2-ethylhexyl) hexa-hydrophthalate	91	135	144	125
Flexol TOF	Tri(2-ethylhexyl) phosphate	82	142	130	123
Flexol 10-10	Didecyl phthalate	103	141	146	—
Flexol 10-A	Didecyl adipate	128	156	156	156

[a] Data from RTM method, 60 phr plastisols
[b] Data of Severs and Smitmans.[1]
[c] Data of McKenna.[2]

and compared to literature values for these same plasticizers. The clear points[1] were determined by noting the temperature at which a dilute suspension of the resin in plasticizer became clear. The fusion[2] temperatures were measured on a thermal gradient bar.

It is interesting to note that the gel curve between the gel temperature and clear point has a different but characteristic shape for each of the resins tested. In some cases the curve appears to have a "steplike" shape; in others the "step" is seemingly not apparent. This peculiar phenomenon is illustrated in Figure 10, which shows characteristic gelation curves for a number of commercially available plastisol resins. It is also found that although the gelation curves can and do vary between different lots of resin from the same supplier, yet each plastisol resin sample has a characteristic gel curve which is quite reproducible from the same sample of resin.

In order to gain a better understanding of this phenomenon, electron micrographs were made of surface replicates of a plastisol film during the gelation process. The gel curve of the particular resin chosen is shown in Figure 11. The corresponding electron micrographs are shown in Figures 12–15. In Figure 12, point A on Figure 11 is just after the onset of gelation; the larger particles and some smaller particles are now exposed. Figures 13, 14, and 15 correspond to the progressive changes in the surface character as indicated by points B, D, and C in Figure 11. In Figure 15, all the free plasticizer has been imbibed, and all the surface particles are now visible.

Figure 16 is taken after the onset of fusion and shows the melting and flow of the system as it forms a continuous film.

A careful examination of the electron micrographs indicates that the larger particles and agglomerates tend to be exposed first; while the smaller particles, which can lie embedded between the larger particles or agglomerates, are not exposed until the later stages of gelation. This means that the shape of the gel curve is dependent upon the "effective" particle size distribution of a particular resin blend. If this supposition is valid, then it should be possible to alter the gel curve by grinding a given resin to "break up" any agglomerates which might be present. It should be pointed out that it is not suggested that grinding can alter the ultimate particle size of the resin.

Accordingly, a sample of resin, whose gel curve is illustrated in Figure 17, was ground by micronization. The shape of the gel curve of the resulting resin is quite different from that of the parent resin. Figure 18 illustrates the marked changes which occur in the shape of the gel curve. Further, it is found that if the ground resin is blended with resin which does not exist a curve with a pronounced steplike shape (Fig. 19) the resultant curve, (Fig. 20), appears to be the summation of the two parent curves.

Since the data as generated are based on somewhat arbitrary reflectance units and since the gel temperature upon the critical resin-phase concentra-
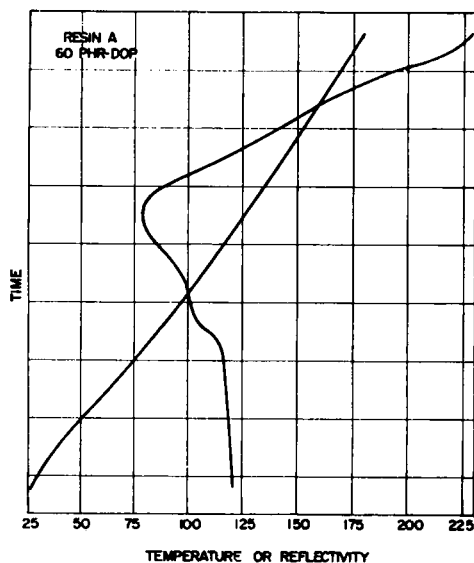
(a)
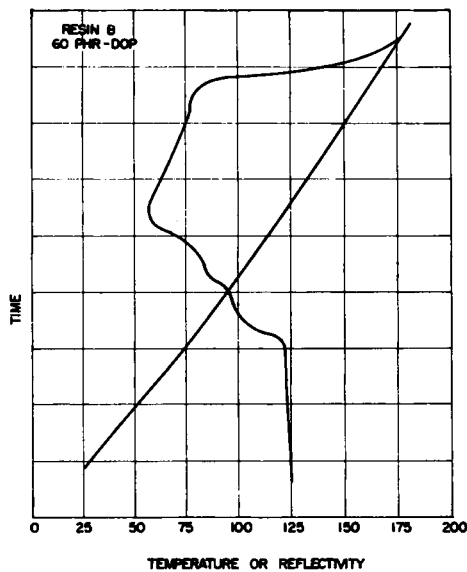
(b)

Figure 10. See caption, p. 1185.

tion [U factor in eq. (12)] it is necessary to reduce the data to the same relative scales. When this mathematical procedure is taken into account, then the resultant curve is indeed the algebraic sum of the two parent curves, i.e., any point on the resultant curve is defined by eqs. (21) and (22).

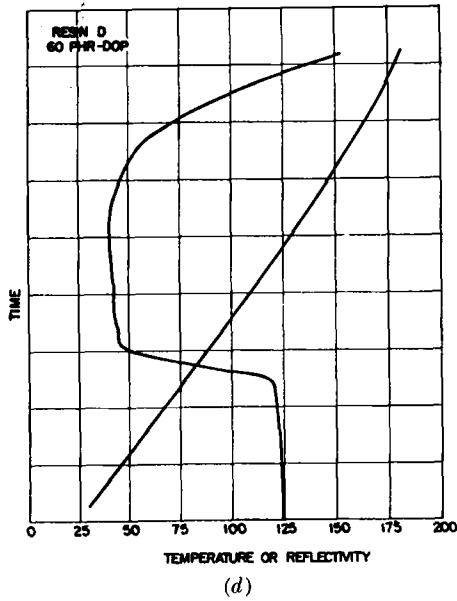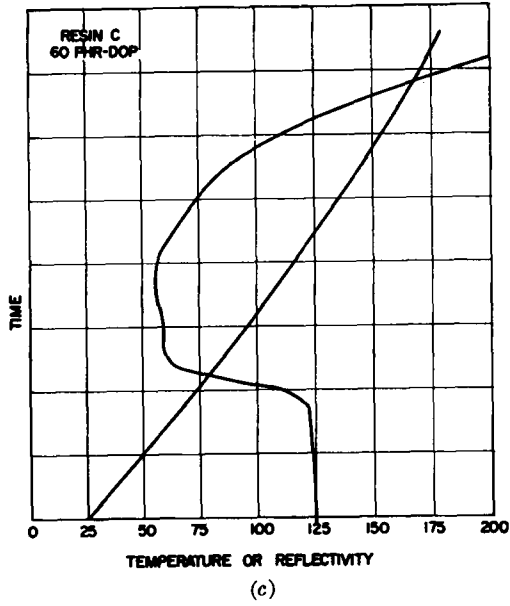$$P_i = w'[(I_0' - I_i')/(I_0' - I_f')] + w''[(I_0'' - I_i'')/(I_0'' - I_f'')] \quad (21)$$

(c)

(d)

Fig. 10. Characteristic RTM curves obtained from different 60 phr plastisols of commercial resins: (a) resin A, 60 phr DOP; (b) resin B, 60 phr DOP; (c) resin C, 60 phr DOP; (d) resin D, 60 phr DOP.

$$P_i = w'[(T_i' - T_0')/(T_f' - T_0')] + w''[(T_i - T_0'')/(T_f'' - T_0'')] \quad (22)$$

where P_i is relative reflectance at point i,t; w is weight fraction of resin; I_0 is reflectance at gelation; I_f is reflectance at fusion; I_i is reflectance at
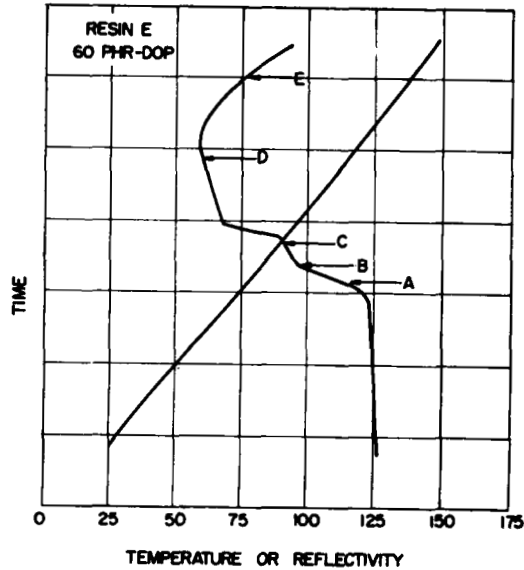
Fig. 11. RTM curve obtained from resin E. Letters refer to the points at which electron micrographs were taken of surface. See Figs. 12–16.
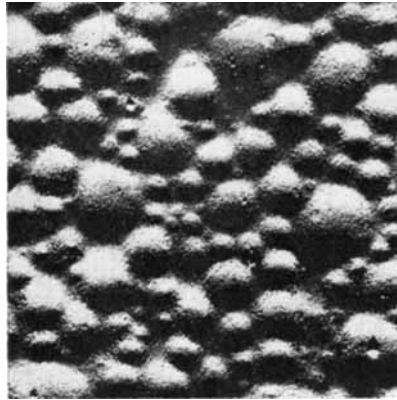
Fig. 12. Electron micrograph of surface at point A in Fig. 11.

point i,t; P_t is relative temperature at point i,t; T_0 is gel temperature G_t; T_f is fusion temperature or clearpoint; T_t is temperature at point i,t; the prime and double prime indicate first and second resin, respectively.

The validity of these equations is illustrated in Figures 21 and 22. Figure 21 shows the normalized curves for a sample of micronized resin, a sample of the same resin unground, and a 50–50 blend of these two resins. Figure 22 illustrates a comparison of the results obtained with the curves calculated from eqs. (18) and (19). The fit of the data is remarkable, and shows that the RTM method is capable of yielding a measure of "effective" particle size distribution for plastisol resins. Practically, the RTM method

Fig. 13. Electron micrograph of surface at point B in Fig. 11.
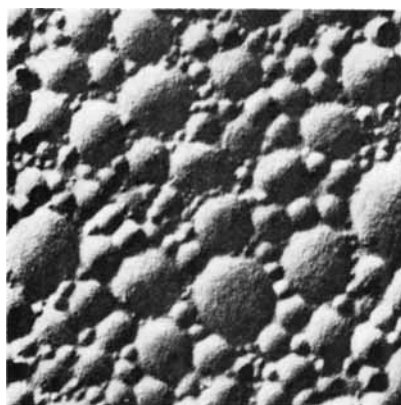

Fig. 14. Electron micrograph of surface at point C in Fig. 11.
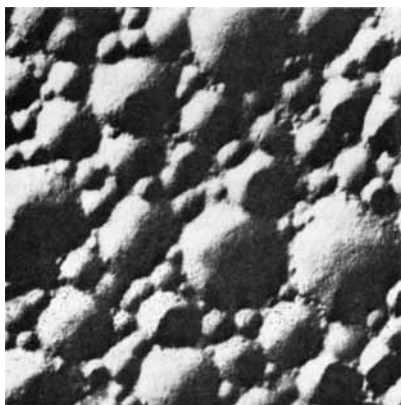

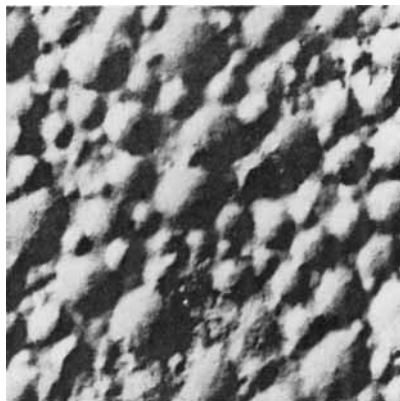Fig. 15. Electron micrograph of surface at point D in Fig. 11.

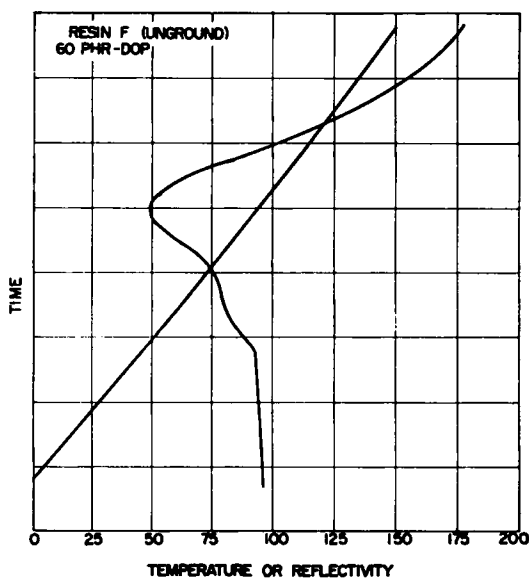Fig. 16. Electron micrograph of surface at point E in Fig. 11.

Fig. 17. RTM curve obtained on ground resin F.   Compare with Fig. 18.

allows the formulator to measure the effects that formulation variables and techniques will have on the application characteristics of plastisol systems. Further, the theory as developed can provide a basis by which the formulator can alter his formulation to produce the desired application characteristics.

CONCLUSIONS

(1) The reflectance-temperature method of analysis has been found to give a basic insight into the gelation and fusion process of plastisols.   A
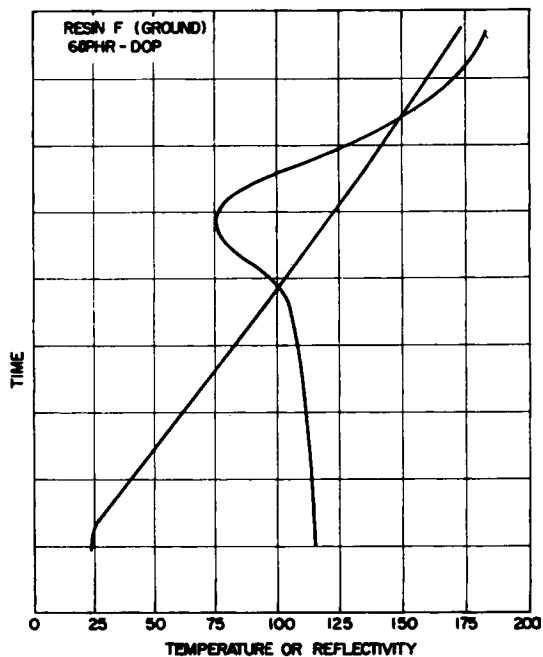
Fig, 18. RTM curve obtained from ground resin F. Compare with Fig. 17.
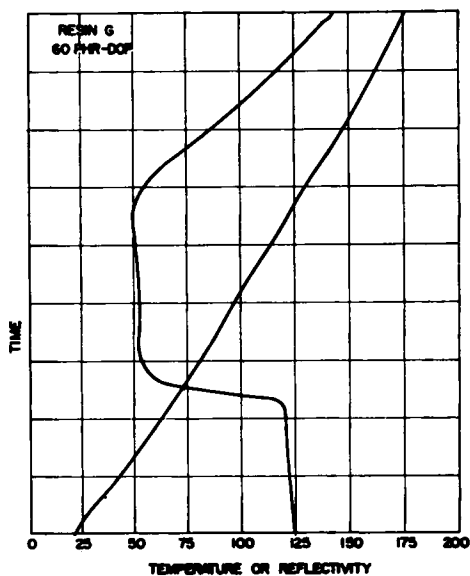

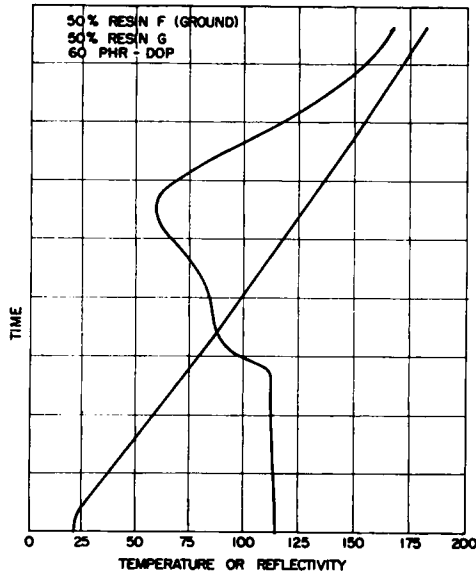Fig. 19. RTM curve of resin G. Notice the absence of characteristic step in gel curve.

Fig. 20. Resultant RTM curve at a 50–50 blend of resin F (ground) and resin G.
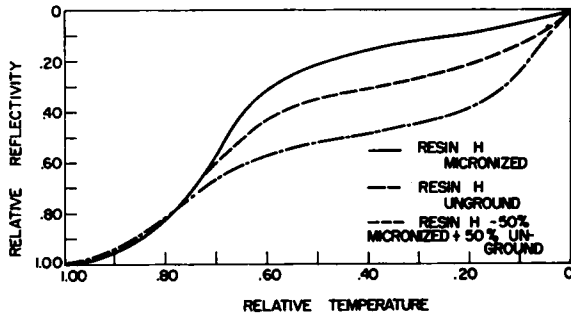

Fig. 21. Normalized RTM curves of resin H (ground, unground, and a 50–50 blend of ground and unground).
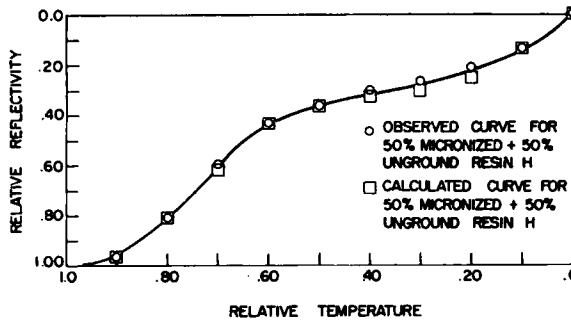

Fig. 22. Mathematical test of eqs. (21) and (22) for resin H.

mathematical analysis of the process has been derived and data to support the basic theory are presented.

(2) The RTM analysis can be of significant value in the characterization of resins for fusion gelation and particle size distribution.

(3) The RTM analysis can be of significant value in the characterization of plasticizers as well as resin.

(4) The RTM analysis should be of value in the quality control of formulations.

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Résumé

La formation de gel de plastisols vinyliques à température constante suit l'équation ln $(C - C_e/(U - C_e) = -(\pi^2/a^2)D\tau + \ln (8/\pi^2)$, où (C) est la concentration de la phase résineuse, (C_e) la concentration de la phase résineuse à l'équilibre, (U) la concentration de la phase résineuse critique, (a) la grandeur moyenne des particules, (D) la constante de diffusion et (τ) le temps nécéssaire à la gélification. Un appareil à réflexion lumineuse, capable de mesurer le processus de gélification est décrit. On discute l'influence des divers paramètres plastifiants des résines sur les processus de gélification et de fusion. Le même appareil à réflexion lumineuse peut aussi servir à l'évaluation de diverses résines et de diverses formules.

Zusammenfassung

Die Gelierung von Vinylplastisolen bei konstanter Temperatur gehorcht der Beziehung ln $(C - C_e)/(U - C_e) = -(\pi^2/a^2)D\tau + \ln (8/\pi^2)$, wobei (C) die Konzentration der Harzphase, (C_e) die Gleichgewichtskonzentration der Harzphase, (U) die kritische Konzentration der Harzphase, (a) die mittlere Teilchengrösse, (D) die Diffusionskonstante und (τ) die Zeit bis zum Beginn der Gelbildung bedeutet. Ein zur Messung des Gelierungsprozesses geeigneter Lichtreflexionsapparat wird beschrieben. Der Einfluss der verschiedenen Harz-Weichmacher-Parameter auf den Gelierungs-und Schmelzprozess wird diskutiert. Der Lichtreflexionsapparat ist auch zur Bestimmung verschiedener Harz- und Rezeptparameter brauchbar.