

Gelation and Fusion Profiles of PVC Dispersion Resins in Plastisols

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Synopsis

Poly(vinyl chloride) (PVC) plastisols are used for coatings, films, sheets, foams, and rotational castings. In order to satisfy the requirements for the different applications, a variety of PVC dispersion resins are manufactured. The requirements for the plastisols are many: for example, good air release, viscosity stability, fine particle size, foamability, and good heat stability. Processability is another important requirement, which emphasizes the rheological behavior at room temperature and the gelation–fusion behavior. This paper documents research to fingerprint the gelation and fusion profiles of various PVC dispersion resins. The viscoelastic measurements were used to continuously monitor the changes of moduli during gelation and fusion under a heating rate which simulates the temperature profile of the processes. The effects of molecular weight, resin type, and copolymer on the gelation–fusion behavior are discussed.

INTRODUCTION

In 1926, the plasticization of poly(vinyl chloride) (PVC) was achieved, thus giving birth to the flexible vinyl plastics industry.¹ In 1947, the first vinyl resin designed for stir-in plastisol compounding was developed; this development facilitated the wide use of PVC plastisols.¹ Today, the commercial applications of PVC plastisols are coatings, films, sheets, foams, and rotational castings as well as extrusion and injection molding. Vinyl dispersion resins are used to produce a variety of formulations, including those for automotive applications, coated fabrics, and resilient flooring.

Requirements for the plastisols are many: for example, good air release, viscosity stability, fine particle size, foamability, and good heat stability. In general, the processability requirements emphasize the rheological behavior at room temperature and the gelation–fusion behavior. The former has been the subject of our previous study.² This paper documents research to fingerprint the gelation and fusion profiles of various vinyl dispersion resins.¹

When a PVC plastisol is heated, the plasticizer diffuses into the resin particles. Consequently, the system becomes a dry, coherent mass; at this point, the material has not attained its ultimate strength. This stage is called gelation. Upon continued heating to a higher temperature, for example, 175°C or higher, the microcrystallites of PVC melt and the polymer molecules fuse together more uniformly. Upon cooling, the material exhibits the intrinsic strength of a plasticized PVC. The rate of gelation and fusion are important and are often critical aspects of the processing of the plastisol. For example, the rate of gelation controls the residence time needed to build the wall thickness desired in slush-molded boots or hot dipmolded pieces. Gel rate also affects the uniformity of rotocast parts and the penetration of plastisol into fabric in cast coating opera-

tions. Fusion rate and the rate of decrease in melt viscosity after fusion affect uniformity of cells in chemically blown foams. Therefore, many commercial grades of vinyl dispersion resins are offered, each having a different rate of gelation and fusion.

The most commonly used methods for characterizing gelation behavior are the determination of the "gelation point," which is a temperature where a significant change is brought about by heating. One such temperature is, for example, about 75°C, where the plastisol film loses tackiness of the surface. At this temperature, all the plasticizer molecules have been absorbed by the PVC particles.³

Whereas the gelation point supplies practical information, the actual gelation process takes place over a range of temperatures; and so it is with fusion. Therefore, it is important to monitor the process of gelation and fusion continuously over the temperature range of interest. For this purpose, a torque rheometer was used to observe the development and changes of torque with the increase of the stock temperature. The gelation and fusion characteristics were fingerprinted this way for the plastisols made with commercial dispersion resin.⁴ Whereas, this method provides a good fingerprint, there are two shortcomings: one is that mechanical work is exerted on the material during gelation and fusion; this does not happen in many of the plastisol processes. Another problem is that from the torque values alone, one cannot tell whether the material is in the rubbery state or in the more fluid state. The viscoelastic measurements eliminate these problems. Such a method has been developed previously,⁵ and the present work is its application for fingerprinting the gelation and fusion profiles of commercial vinyl dispersion resins.

EXPERIMENTAL

Samples

Eleven samples of commercial dispersion resins were characterized. Their molecular weight expressed as inherent viscosity (IV) in cyclohexanone at 30°C⁶ and the gelation point³ are listed in Table I. The plastisol formulation used for this fingerprinting is given in Table II.

TABLE I
PVC Dispersion Resins¹

Product name ^a	Sample designation	Molecular weight, expressed as IV (dL/g)	Gelation point (°C)
Geon 121	A1	1.20	77
Geon 123 (120 × 251)	A2	1.00	75
Geon 124	A3	0.89	75
Geon 125 (120 × 241)	A4	0.73	74
Geon 184 (124F-1)	A5	0.92	77
Geon 186 (120 × 276)	A6	1.00	74
Geon 178 (128)	B1	1.10	96
Geon 171 (120 × 271)	B2	1.40	107
Geon 179 (120 × 279)	B3	1.00	83
Geon 135	C1	1.12	66
Geon 137 (130 × 17)	C2	1.12	71

^a All are products of the BFGoodrich Chemical Group.

TABLE II
Plastisol Formulation

Component	Parts by weight
Resin	100
Plasticizer	60
Epoxidized soybean oil	5
Barium, cadmium, zinc stabilizer	3

Method

The Rheometrics Mechanical Spectrometer was used in the dynamic oscillatory mode with a programmed increase in temperature. The 50-mm-diameter parallel plates were used with a gap setting of 1 mm. The strain was imposed at 0.1 V, which corresponded to a maximum strain amplitude of 0.35 at the periphery of the plates.

The frequency of oscillation was chosen to be 1 Hz. A lower frequency was desirable for process simulation, because, in most cases, the gelation and fusion in practice take place either under no mechanical stress or under very low shear rates. However, the lower frequency measurements require a heating rate much slower than these occurring in actual commercial practice. This is necessary because the temperature of the specimen must remain approximately constant while the instrument is completing a minimum number of cycles for data acquisition. Therefore, 1 Hz is an arbitrary choice and a compromise between stimulation of the processing shear rate and that of the heating rate.

The heating was started from room temperature with a stepwise increase in temperature of 20°C for every minute, eventually equilibrating at 200°C. The temperature profile is shown in Figure 1, where the upper curve is the usual way of indicating temperature which was monitored at the upper surface of the top plate. The lower curve is the actual material temperature which was measured in a special run by inserting a thermocouple in the sample between the plates with the plates separated by 2 mm. The actual heating profile was found to be quite different from that indicated by the temperature of the top plate. Not

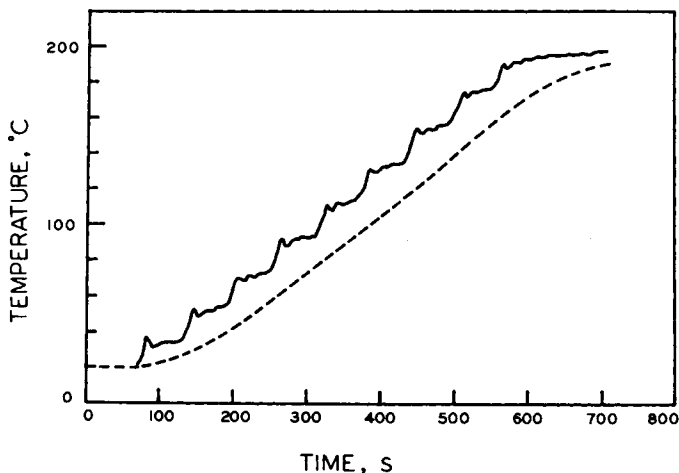


Fig. 1. Temperature profile with 20°C/min heating rate.

only was the material temperature about 20°C lower than that indicated at the top plate, but also the profile was approximately linear instead of stepwise as induced.

The elastic modulus G' , loss modulus G'' , and the complex viscosity $|\eta^*|$ were recorded as functions of temperature.

RESULTS

Gelation and Fusion Profile

Figure 2 is the gelation and fusion profile of sample A1, where G' , G'' , and $|\eta^*|$ are shown as functions of time. The sample temperature, corresponding to the lower curve of Figure 1, is also given to indicate the heating rate. With the increase in temperature, the viscosity and moduli initially decrease, indicating that the system remains a suspension of PVC solids in DOP. The values of G' , G'' , and $|\eta^*|$ of the ungelled suspension vary from sample-to-sample. This variation is related to the size, size distribution, and shape of PVC particles, and it was the subject of a previous publication.² At temperatures slightly above 50°C, the gelation begins and the viscoelastic properties increase very rapidly with temperature.

The plasticizer, DOP, is absorbed into the resin particles until the material appears dry at 77°C. Therefore, the increase in moduli and viscosity at the earlier stage of the gelation is attributable to the rapid depletion of the low vis-

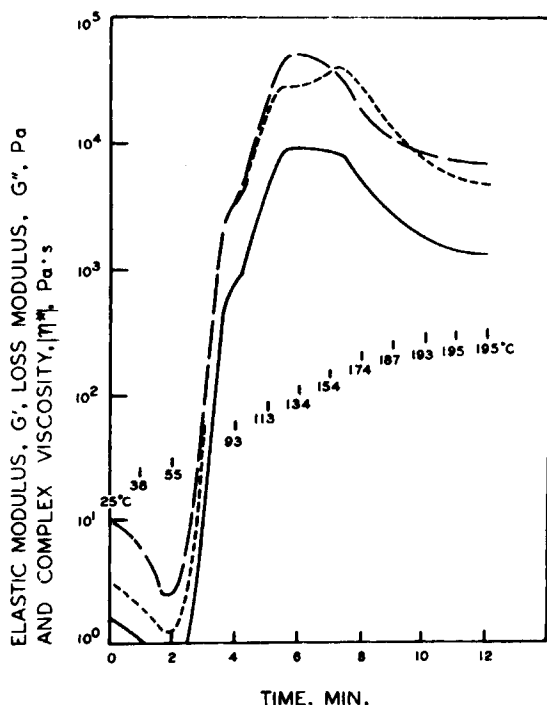


Fig. 2. Elastic modulus G' (---), loss modulus G'' (-·-·-), and complex viscosity $|\eta^*|$ (—) during gelation and fusion of plastisol with sample A1.

cosity phase. In the latter part of the gelation at above 77°C, the viscoelastic properties keep increasing by 2 orders of magnitude. The polymer chains from different particles may progressively entangle with each other, and the interparticle boundary may be disappearing. The maximum values are reached between 130°C and 170°C, indicating the end of gelation. The elastic modulus G' value at this point is of the magnitude of a lightly crosslinked, unfilled rubber. This implies that the plasticizer is uniformly distributed and the microcrystallites are acting as the crosslinks. Above this temperature, at which gelation is complete, the viscoelasticity of the material decreases for two reasons: one is the normal temperature dependence primarily attributable to the thermal expansion, and the other is caused by the melting of microcrystallites. Finally, the data are seen to approach their equilibrium values at 195°C.

The curve of complex viscosity $|\eta^*|$ is displaced approximately by 2π below the curves of G' and G'' because

$$|\eta^*| = (G'^2 + G''^2)^{1/2}/\omega \quad (1)$$

where ω is the angular frequency, which is related to the frequency of oscillation, ν , by

$$\omega = 2\pi\nu \quad (2)$$

ν is 1 Hz in this experiment. Because there are only two independent parameters, only G' and G'' will be shown for the remaining samples. Once the gelation begins, the values of G' and G'' are practically identical with each other. However, at their maxima and thereafter, some difference is seen between G' and G'' .

A Series Resins

Figures 3(a) and 3(b) are the gelation and fusion profiles expressed as G' and G'' , respectively, of four resins, A1, A2, A3, and A4, where the material variable is the molecular weight. Although the gelation rates appear similar among these resins, the steepness of the slopes is masking the real differences. Actually, the lower molecular weight resins tend to gel faster. If certain processes require a faster attainment of the maximum modulus, for example, the maximum value of G' , there can be significant difference in the time and temperature required. These data are listed in Table III.

A very similar trend is observed with G'' maxima. The G' and G'' values at the fusion stage are significantly dependent on the molecular weight,⁷ as may be expected, because the system is becoming more amorphous as the crystallites melt.

TABLE III
Time and Temperature Required to Reach G' Maximum

Resin	G' maximum	
	Time required (min)	Temperature (°C)
A1	7.1	156
A2	6.0	134
A3	6.1	136
A4	3.7	87

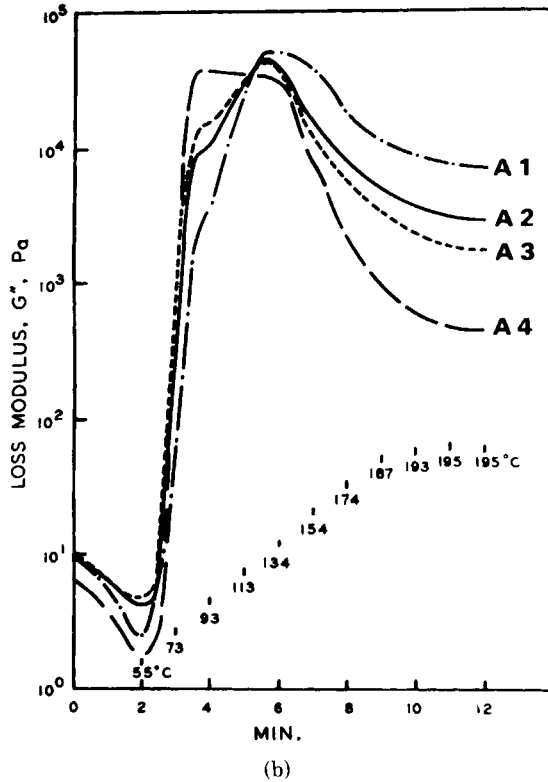
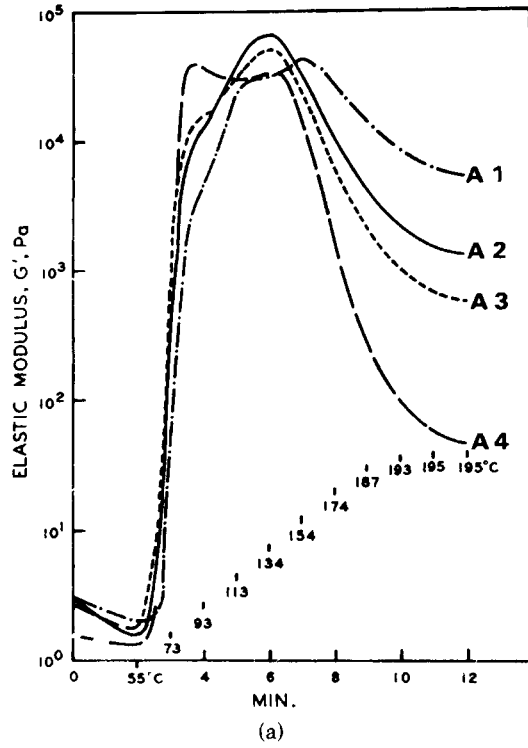
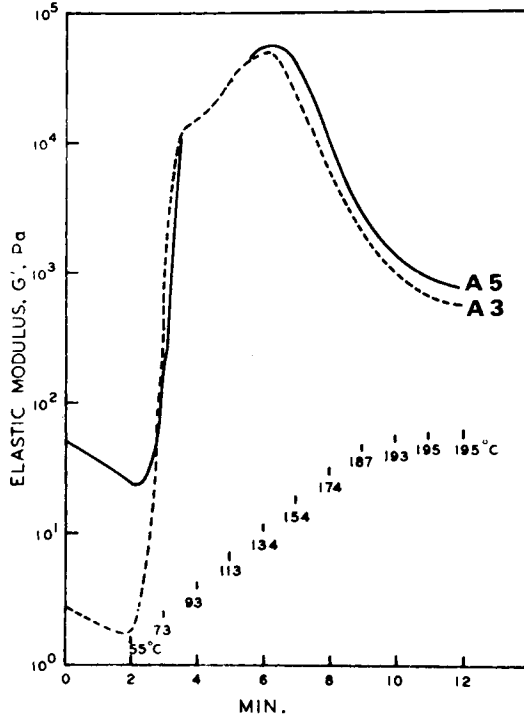
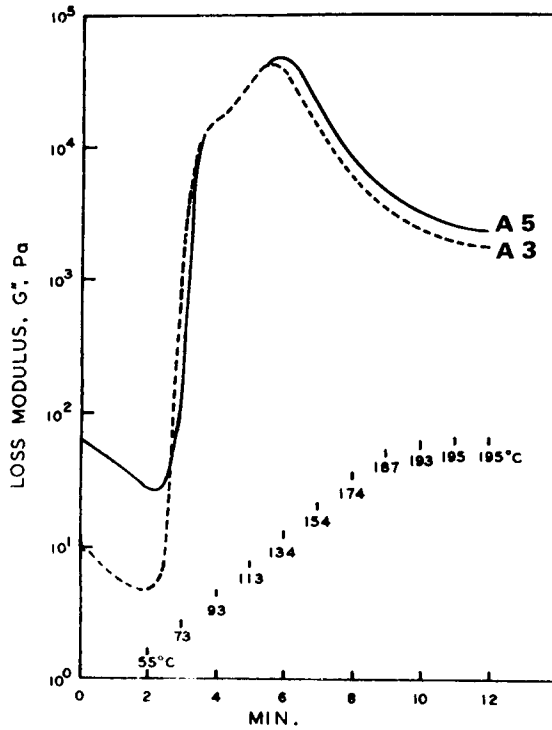


Fig. 3. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples A1, A2, A3, and A4.



(a)



(b)

Fig. 4. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples A3 and A5.

In Figures 4(a) and 4(b), the profiles of samples A3 and A5 are compared. The gelation and fusion behavior of these two resins are very similar, except that the moduli at the fusion stage is somewhat different, reflecting the difference of the molecular weights, IV of 0.89 and 0.92 (Table I). The moduli at temperatures below the starting of gelation are significantly different, because samples A5 is designed to have a high Brookfield viscosity.¹

Figures 5(a) and 5(b) are comparisons of samples A2 and A6, the latter being the high Brookfield viscosity resin. The ungelled suspension of the latter resin gave a higher moduli than those of the former as expected, but the differences are not as large as those seen in examples of Figures 4(a) and 4(b). Although the gelation curves are parallel, the curve of A6 is at a few degrees lower than that of A2. Once the moduli pass the maxima, the fusion curves of these resins are exactly the same, because they have the same molecular weight, $IV = 1.0$ (Table I).

B Series Resins, "Low Extractables" Resins

Comparison of samples A1 and B1 is given in Figures 6(a) and 6(b). They were chosen to represent two types of the resin series. The major difference exhibited in these profiles is that the initial gelation of B1 is about 10°C higher than that of A1. The same temperature difference is required to attain comparable values of the moduli during the progress of gelation. There is no significant difference in fusion behavior between the two types of resins; the observed difference is attributable to the difference of molecular weight (Table I), but not to the resin type.

Overall characteristics of gelation and fusion behavior are very similar among samples B1, B2, and B3, except for two systematic differences [Figs. 7(a) and 7(b)]. One is that the gelation rate is faster for the lower molecular weight resin (Table I), the trend which was also observed with A series resins [Figs. 3(a) and 3(b)]. Another difference is the fusion curves, where the magnitude of the moduli again reflects the molecular weight difference.

Low Fusion Resins

Figures 8(a) and 8(b) are comparisons of sample A1, homopolymer, and sample C1, vinyl acetate copolymer. The latter is designed as a low fusion resin. As it is seen in the decrease of G' from the maximum value, the fusion of C1 starts about 20°C below that of A1, i.e., 134°C and 154°C, respectively. The moduli at the fusion stage is lowered by the presence of vinyl acetate comonomer, because the magnitude of difference is too large to be attributable solely to the molecular weight difference implied by the difference of $IV = 1.12$ and 1.20 (Table I). Actually, the inherent viscosity is also somewhat dependent on the vinyl acetate content, but the precise data are not available at present.

In addition to the low fusion characteristics, C1 gives a lower gelation temperature and a faster gelation rate; the difference of the gelation behavior between A1 and C1 are at least as significant as the difference of the fusion behavior.

Specialty Resins

Figures 9(a) and 9(b) are comparisons of sample C2 specialty copolymer and C1, vinyl acetate copolymer. There is no large difference in the gelation and

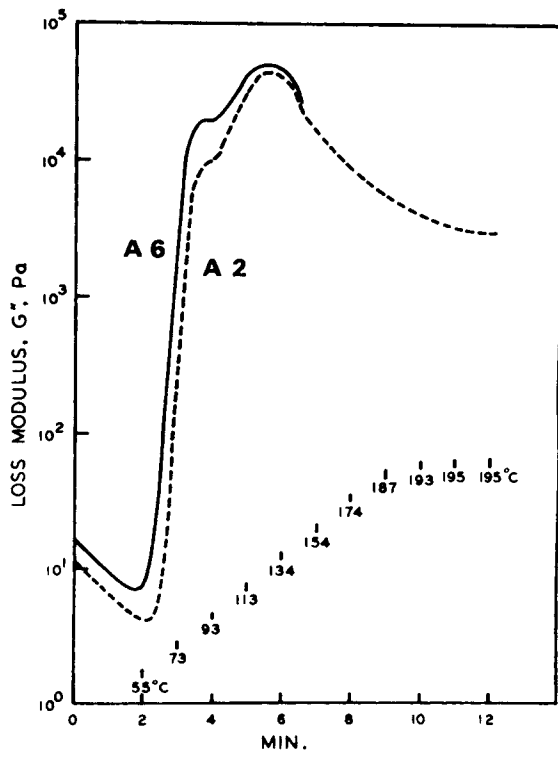
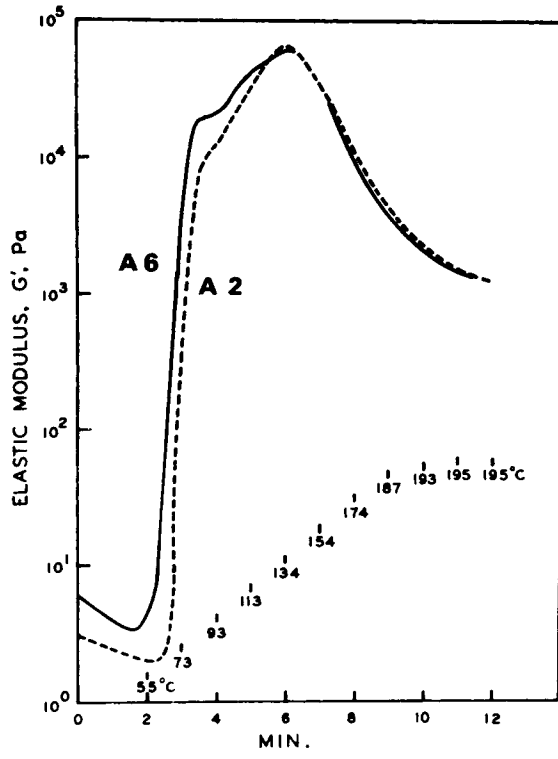


Fig. 5. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples A2 and A6.

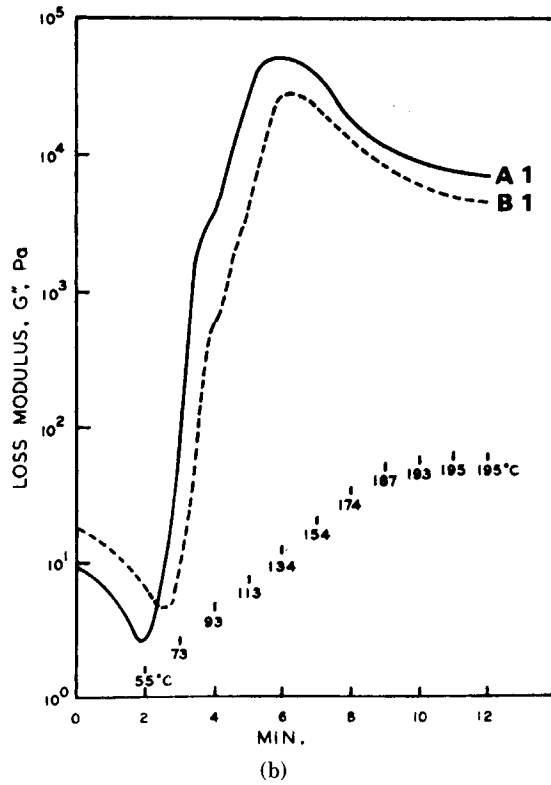
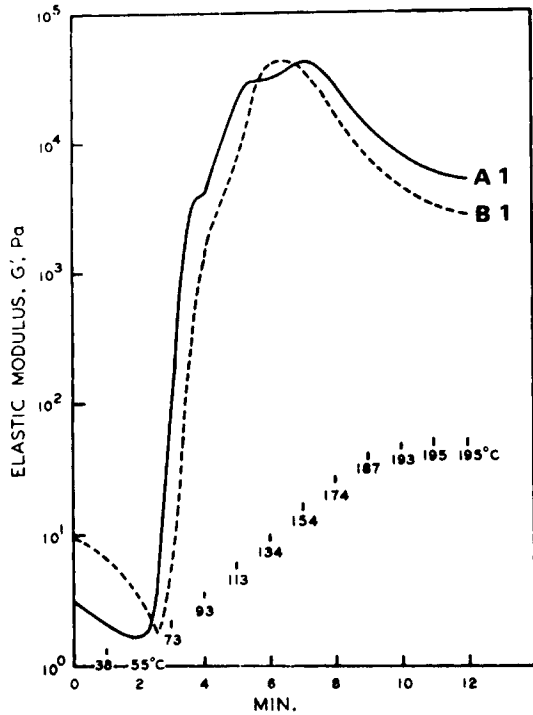


Fig. 6. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples A1 and B1.

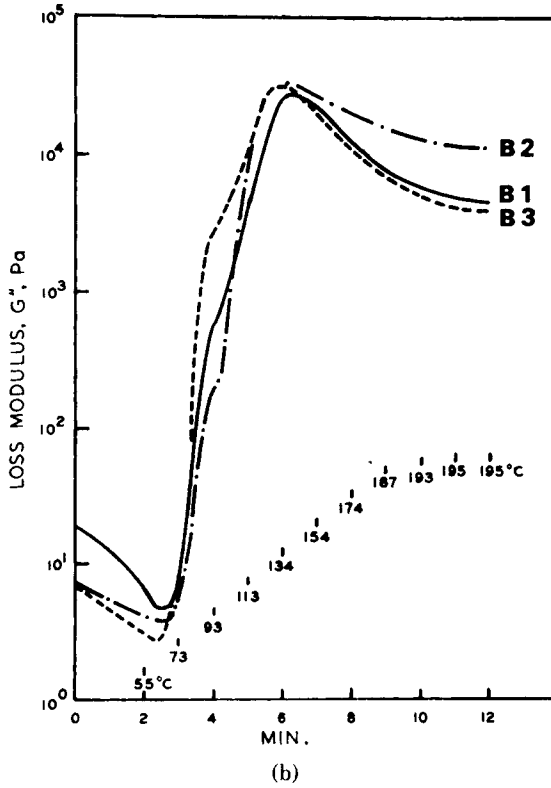
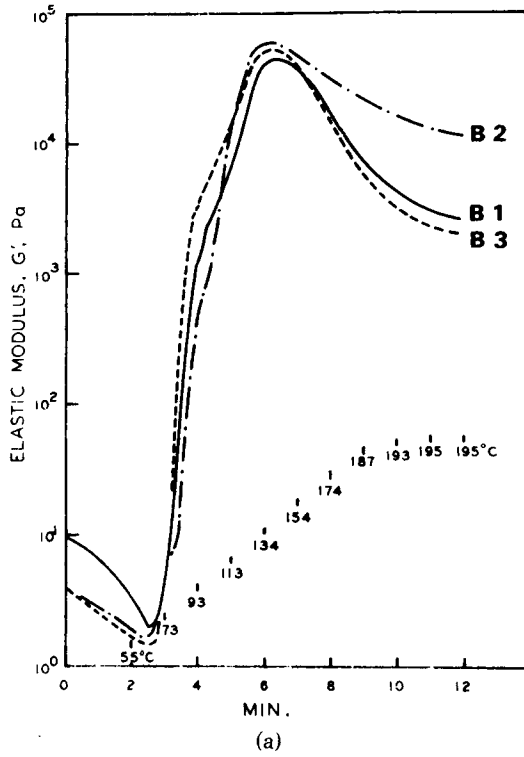
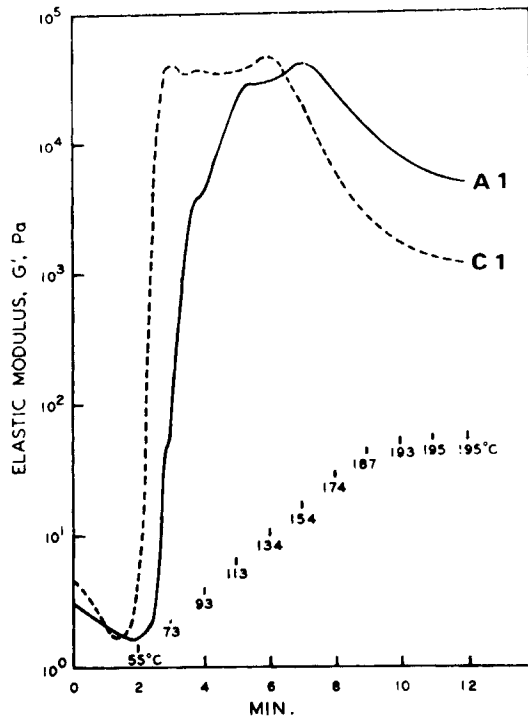
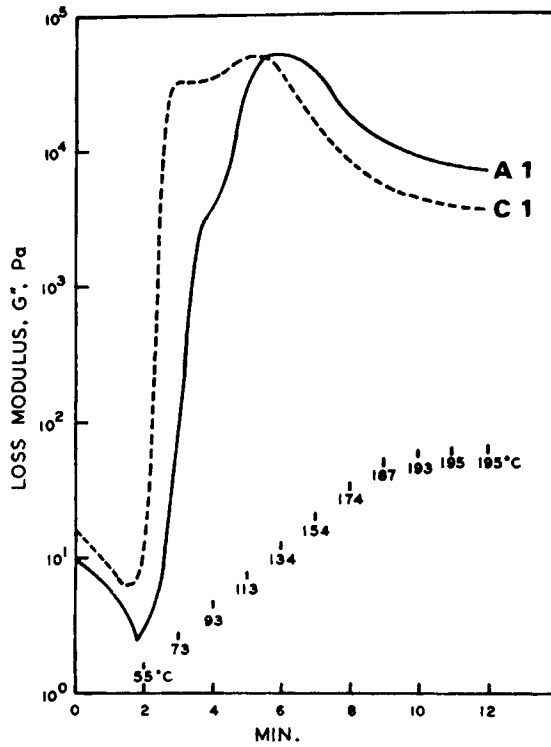


Fig. 7. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples B1, B2, and B3.



(a)



(b)

Fig. 8. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples A1 and C1.

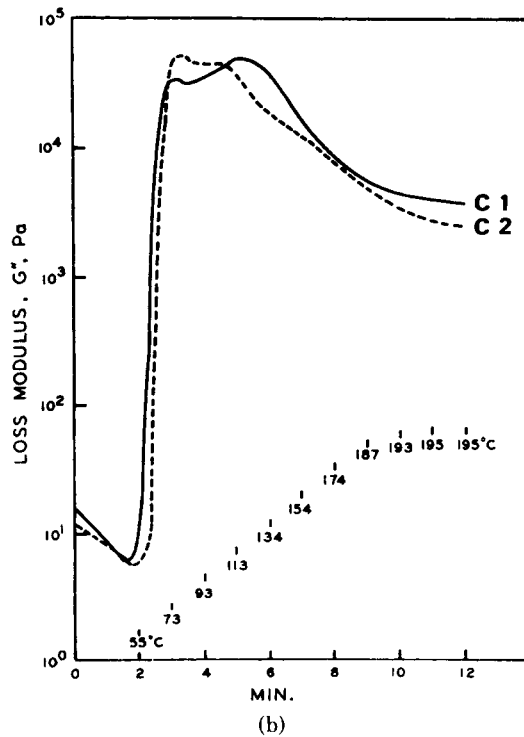
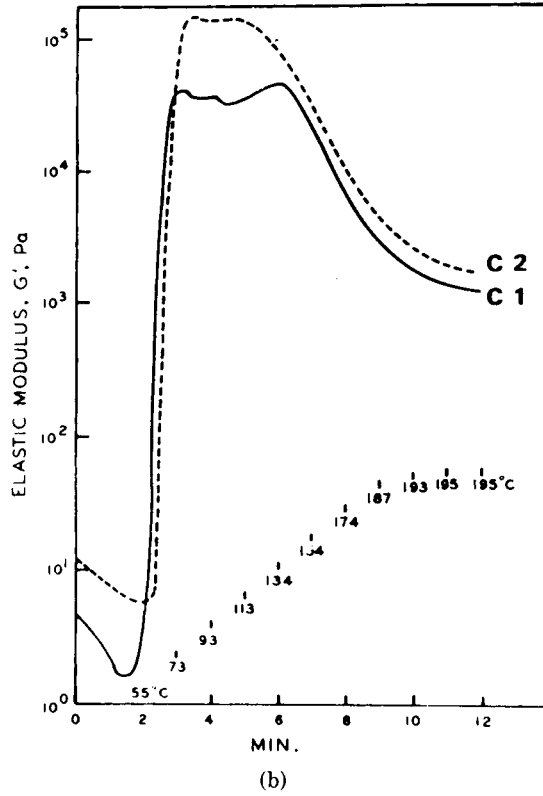


Fig. 9. (a) Elastic modulus and (b) loss modulus during gelation and fusion of plastisols with samples C1 and C2.

fusion profiles of these two copolymers, because the design feature C2 over that of C1 is not in the gelation and fusion. C2 contains a carboxyl group to improve its adhesion to otherwise difficult substrates, such as nylon, polyester, fiberglass, aluminum, steel, galvanized metal, and ABS.¹

One significant observation in the gelation and fusion profile is that G' maximum of C2 is very high, higher than 10^5 Pa, whereas, in all other resins examined in this study, the maximum G' is about 5×10^4 Pa. The carboxyl group of this copolymer may be associated with each other, contributing to an addition stiffness to the material at the gelled state. Once the fusion starts, the moduli levels of these two resins become very similar. Because the molecular weight of these resins are about the same, again assuming that IV represents the molecular weight (see Table I), we can conclude that the difference of the comonomer type has relatively small effect on the fusion profile.

DISCUSSION

Gelation Profile

The start of gelation is when the plasticizer begins to penetrate into solid PVC. This can happen only when there is a significant increase in free volume and an increase in the segmental mobility of the polymer chain so that the plasticizer molecule can diffuse into the polymer matrix. That is, the glass-rubber transition must start at this temperature. Normally, the glass transition temperature T_g of PVC homopolymer is considered to be in the range of 80–100°C, which depends upon the molecular weight and polymerization temperature.⁸ However, the gelation started for these samples at the lowest of about 45°C for sample C1, the highest of about 65°C for B series resins, and at about 50–60°C for most other resins. The dynamic mechanical properties reported in the literature^{9,10} show that the glass transition actually starts at about 40–60°C, the exact temperature depending upon the sample history. Our unpublished data with a standard suspension polymerized PVC also confirms this. It is reflected especially in the temperature at which $\tan \delta$ begins to increase.

At more than halfway up the gelation curve, a shoulder appears in the curve, implying there might be a transition. For sample A4 and for copolymers, the first peaks are seen at temperatures where the shoulder appears for other resins. The temperature of the transition is about 73°C, the lowest, with C1, about 96°C, the highest, with B2, and the temperature between these with other resins. These temperatures approximately correspond to the glass transition temperature T_g observed with the differential scanning calorimeter (DSC). A Perkin-Elmer DSC2 was used and the temperature at the inflection point of the DSC trace was read as T_g .

When the plastisol with sample A1 in the present formulation was characterized with the DSC at a heating rate of 20°C/min (the heating rate corresponding to that of the viscoelastic measurements), the T_g was essentially unaffected by the presence of DOP. This means that at least until the temperature of the resin reaches T_g , a substantial portion of the resin is not penetrated by the plasticizer. However, T_g is above 10°C above the gel point (Table I), where all the plasticizer is absorbed by the resin. Therefore, at the shoulder of the gelation curve, the plasticizer is concentrated in the outer shell of the resin particles and the inner core of the particle remains 100% PVC.

The modulus level at the T_g is significantly dependent upon the sample; the lower molecular weight resin and copolymers have the higher modulus, a fact which indicates more uniform distribution of plasticizer, i.e., a more advanced state of gelation. This is also indicative of relative ease by which the plasticizer diffuse into the resin. The lower crystallinity of the lower molecular weight resins and copolymers may be facilitating the diffusion.

After passing T_g , the plasticizer seems to diffuse more uniformly inside of the polymer particle, but the precise temperature ending the diffusion has not been determined yet. In the DSC measurement, the sample was heated past T_g up to 100°C and subsequently cooled very rapidly at about 320°C/min. In the subsequent reheating at 20°C/min, the T_g of the resin phase almost completely disappeared, indicating that the system is now almost one phase. The T_g of plasticized PVC with the present composition is observed to be about -30°C.

The viscoelastic behavior above T_g up to the moduli maxima indicates not only the increase uniformity of the plasticizer distribution, but also partial melting of microcrystallites. This aspect will be discussed under the heading of fusion profile. In reality, there is a temperature region where gelation (diffusion of plasticizer) and fusion (melting of crystallite) are occurring simultaneously.

Fusion Profile

In the fusion stage, two significant events take place: one is the melting of crystallites, and the other is a development of the mechanical strength (upon cooling) which results from the disappearance of the particulate structure. In the latter process, polymer chains presumably develop a better "knitting" at the interparticle interface.

The melting of PVC crystallites occurs in the temperature range of 120–210°C.¹¹ However, the crystallites of PVC dissolve in a good solvent such as cyclohexanone at 37°C and a somewhat poorer solvent, acetophenone, at 84°C.¹² Therefore, it is not difficult to assume that the melting range is lowered by the presence of DOP. With a microscopic observation, a *relative* measure of the melting point has decreased from 174°C for the pure polymer (extrapolated value) to 116–118°C in the presence of DOP.¹³ Therefore, it is quite possible that in the presence of DOP, the partial melting starts at some temperature about T_g and it may be completed at 150–180°C. This also implies that reforming of more stable crystallites may take place at these temperatures. These will be the subject of the future investigation.

A development of significant tensile strength requires heating to at least 163°C. For most of the homopolymers, the highest value is attained after heating to 177°C or higher.¹ No specific feature has been observed in the fusion profile at the temperature range corresponding to the full development of tensile strength. The development of "knitting" of polymer chains must be a gradual process. However, in general, the lower the temperature of gelation and fusion, the lower the temperature for full development of tensile strength.¹

A morphological examination of the fracture surface indicated that the particulate structure disappeared by heating up to 160°C or above. This temperature is somewhat lower than the threshold temperature required for the full development of the tensile strength.¹⁴

CONCLUSION

The viscoelastic properties have been shown to be a very effective means of characterizing the gelation of fusion behavior of PVC resins formulated as plastisols. The profiles serve not only as the fingerprints of different types of resins, but also provide means of interpreting the mechanisms of gelation and fusion. The interpretation was aided by the T_g measurements with DSC and by the measurements of tensile strength, after the plastisol was heated to different temperatures.

The users of the plastisols may select a particular resin for a particular application on the basis of the gelation and fusion profile. However, each resin is designed not only for the specific behavior of gelation and fusion, but also for other features.¹ Therefore, the selection of the resin should take into consideration all the important features.

It is well known that the viscoelastic properties depend upon the condition of measurements. Although the condition selected in this work is a reasonable one and the profiles thus obtained are reliable, it does not guarantee the prediction of the gelation and fusion behavior in practice, if the processing condition is much different from that for the present viscoelastic measurements.

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