

The Glass Transition and Gelation of PVC Resins in Plastisol

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INTRODUCTION

Poly(vinyl chloride) (PVC) plastisol is a suspension of small particles of PVC resin in plasticizer. The particle size range may, for example, be from about 15 to 0.2 μm and smaller.¹ Since commercial plastisol resins are spray dried and ground, the size range includes agglomerates as well as the primary particles produced by polymerization.

The applications of plastisols are coatings, films, sheets, foams, and rotational castings, where the plastisol is first spread on substrates, and then heated to gel and fuse.¹ When a PVC plastisol is heated, the resin particles are penetrated by the plasticizer and become swollen. Consequently, the system becomes a dry, coherent mass; at this temperature the material has not attained its ultimate strength. This stage is called gelation. Upon continued heating to a higher temperature, for example 195°C, the microcrystallites of the PVC melt and the polymer molecules fuse together uniformly. Upon cooling the material exhibits the intrinsic strength of a plasticized PVC. The gelation and fusion behavior are important and often critical aspects of the processing of plastisols. For example, the rate of gelation controls the residence time needed to build the wall thickness desired in slush-molded boots on hot-dip molded pieces. It also affects the uniformity of rotocast parts and the penetration of plastisol into fabric in cast-coating operations. Fusion rate and the rate of decrease in melt viscosity affect uniformity of cells in chemically blown foams.

Gelation and fusion behavior have been subjects of our extensive studies. Viscoelastic measurements have been made to characterize the progress of gelation and fusion.^{2,3} The present work examines the role of the glass transition (T_g), of PVC resin in gelation behavior, since the T_g occurs in the temperature range where the gelation takes place. The differential scanning calorimeter (DSC), was used, first, to characterize the T_g of resins in the absence of a plasticizer. Secondly, the progress of gelation of the plastisol was followed via DSC.

Finally, the viscoelastic data³ and the DSC data were used to analyze the disappearance of the pure PVC phase and the formation of the plasticized PVC phase during gelation.

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EXPERIMENTAL

Samples

Eleven samples of commercial PVC resins were examined in this work. Their molecular weights expressed as inherent viscosity (IV) in cyclohexanone at 30°C⁴ are listed in Table I. The plastisol formulation is given in Table II.

TABLE I
PVC Dispersion Resins⁵

Product name ^a	Sample designation	Molecular weight, expressed as IV (dL/g)	Resin T_g by DSC (°C)	Gel point of plastisol (°C)
Geon 121	A1	1.20	80.0	77
Geon 123 ^b (120 × 251)	A2	1.00	84.3	75
Geon 124	A3	0.89	82.2	75
Geon 125 (120 × 241)	A4	0.73	83.4	74
Geon 184 (124F-1)	A5	0.92	83.1	77
Geon 186 (120 × 276)	A6	1.00	83.1	74
Geon 178 (128)	B1	1.10	91.0	96
Geon 171 (120 × 271)	B2	1.40	95.7	107
Geon 179 (120 × 279)	B3	1.00	91.0	83
Geon 135	C1	1.12	73.1	66
Geon 137 (130 × 17)	C2	1.12	75.6	71

^a All are products of the B.F. Goodrich Chemical Group.

^b The numbers in parentheses are older designations.

TABLE II
Plastisol Formulation

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

METHODS

"Gel Point" Determination

The most commonly used methods for characterizing gelation behavior include the determination of the "gel point," which is a temperature where a significant change is brought about by heating. One such temperature is where the surface of a plastisol film becomes dry and loses tackiness. The measurements were made by casting a film on a hot plate with a programmed heating.

Viscoelastic Measurement³

The Rheometrics Mechanical Spectrometer was used in the oscillatory mode with a programmed increase in temperature. Parallel plates of 50 mm diameter were used with a gap setting of 1 mm. The maximum strain amplitude was 0.35 at the periphery of the plates and the frequency of oscillation was 1 Hz. Heating was started from room temperature to 200°C with a 20°C/min heating rate. The elastic modulus, G' , and loss modulus, G'' , were recorded as functions of temperature.

DSC Measurements

A Perkin-Elmer DSC-2 was used with heating and cooling rates of 40°C/min. The glass transition temperature(s) was defined as the inflection point(s) in the DSC trace as will be shown within later sections.

RESULTS

Onset of Gelation Observed in Viscoelastic Measurements and the Glass Transition of PVC Resins

Figure 1 is a viscoelastic profile of the gelation and fusion behavior of a plastisol with resin A1. The onset of gelation is indicated at about 55°C, where the moduli begin to increase with increasing temperature. Evidently, the plasticizer begins to penetrate into the resin particles at this temperature, implying that the glass transition begins at approximately 55°C. Independent studies^{6,7} had shown that the glass-rubber transition measured dynamic mechanically starts at about 45–55°C, and that the exact temperature depends upon sample history.

The onset of the glass transition as observed viscoelastically varied from 45 to 65°C for the 11 resins of this study. Figure 2 shows DSC scans with resin A1 for the temperature range of 30–105°C. Whereas the onset of gelation observed in the viscoelastic behavior is a very distinct point (i.e., a minimum) in the curves, no such transition can be observed by DSC. Apparently, the mechanical method is more sensitive than the thermal method for characterizing the onset of this transition. A question is whether a mechanical method can be used to determine this temperature with a resin alone in the absence of plasticizer. However, the samples are fine powders,

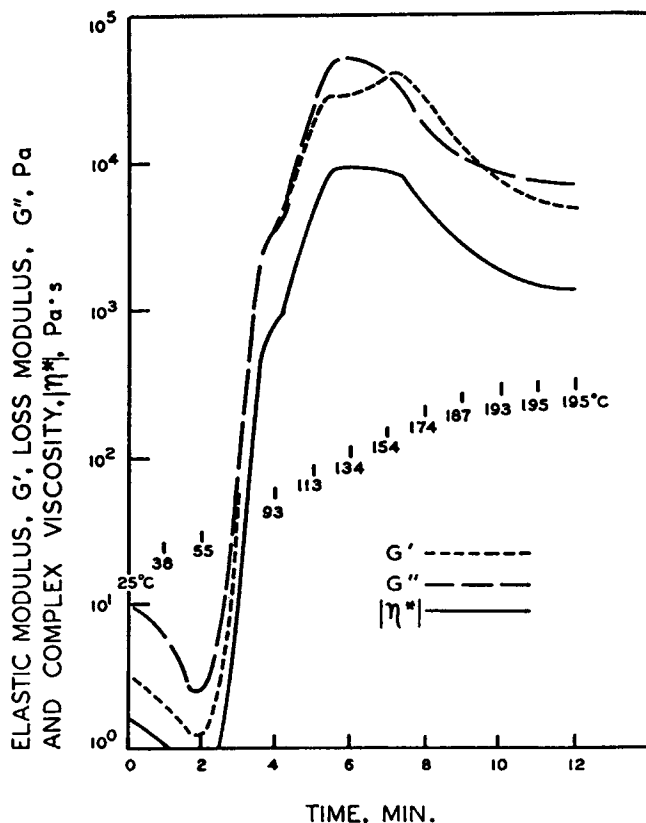


Fig. 1. Viscoelastic profile of gelation and fusion of a plastisol made with resin A1.

which make an accurate and reproducible measurement rather difficult. If the powder is molded to make a test specimen, the molding process destroys the morphology which we wish to examine. As it stands now, placing powder in plasticizer and performing the viscoelastic measurements described in this work may be the best way to determine the onset of the glass-rubber transition of the resin.

PROGRESS OF GELATION IN THE VICINITY OF THE T_g OF PVC RESINS

The viscoelastic profiles of gelation in Figures 3 and 4 show a peak or a shoulder at a temperature approximately corresponding to the T_g of the resin (indicated with arrows). The temperature at which the shoulder occurs for the plastisol was estimated from G' and G'' profiles and plotted against the T_g measured via the DSC (Table I) in Figures 5 and 6, respectively. Good correlations were found in both figures. This implies that when the temperature of the plastisol passes the T_g of the resin a significant part of the resin particle is still untouched by the plasticizer. However, the increasing moduli indicate that the diffusion of plasticizer into the resin particles and the concurrent depletion of the plasticizer, the continuous liquid phase,

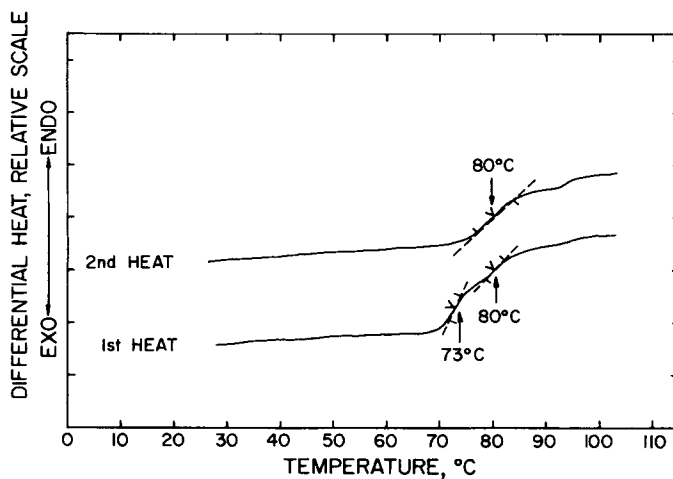


Fig. 2. The glass transition temperature of resin A1 observed with the DSC.

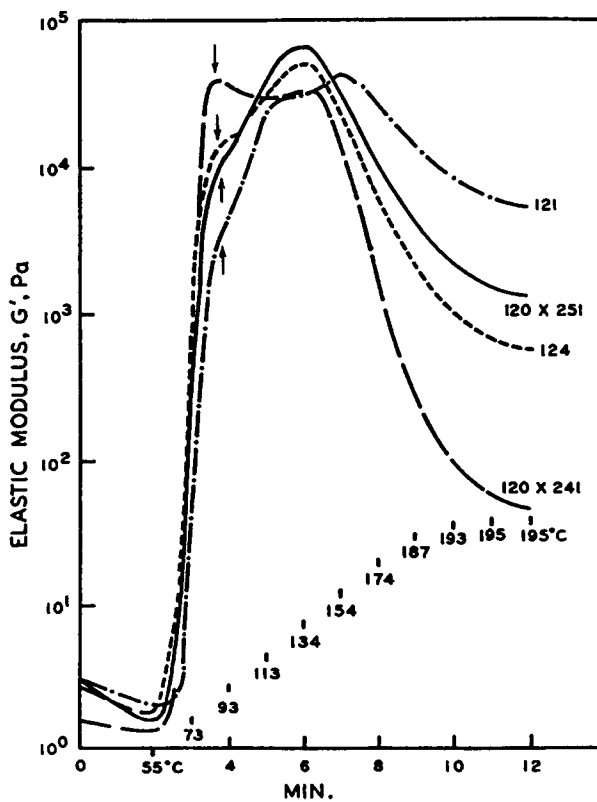


Fig. 3. Change of the elastic modulus during gelation and fusion of plastisols made with resins A1, A2, A3, and A4.

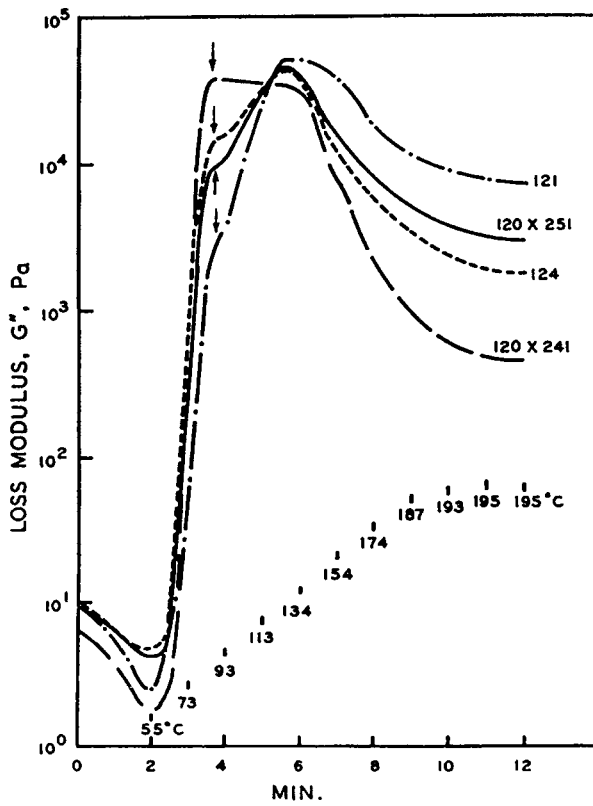


Fig. 4. Change of the loss modulus during gelation and fusion of plastisols made with resins A1, A2, A3, and A4.

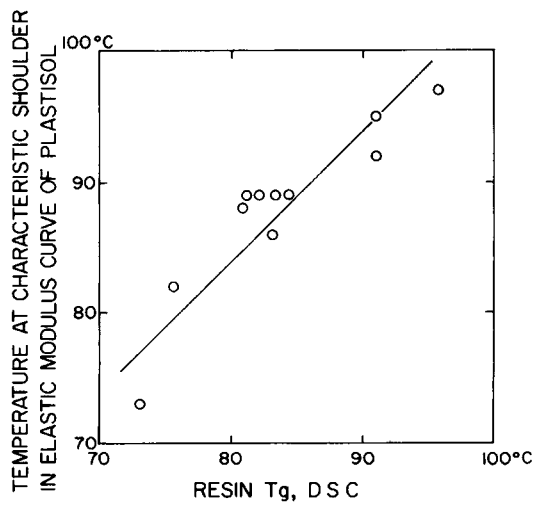


Fig. 5. Relation between resin T_g and characteristic shoulder in the elastic modulus curve of plastisol.

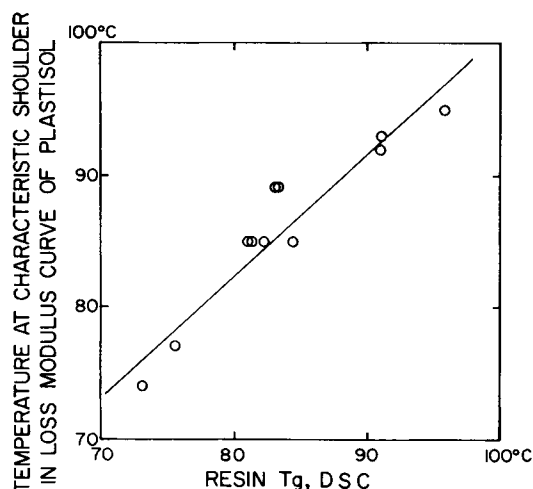


Fig. 6. Relation between resin T_g and characteristic shoulder in the loss modulus curves of plastisol.

have already started. Therefore, the plasticizer must be concentrated in the small particles and in the outer shell of the large particles. It may also be absorbed in the interstitial pores of the agglomerated particles. Our previous morphological study⁸ showed that in this temperature range the original particle boundaries are preserved, even though the particles are swollen with the plasticizer.

Gel Point and T_g of PVC Resins

A general correlation was found between gel points (Table I) and the T_g 's of PVC resin determined with the DSC (Fig. 7). The loss of tack and the dry appearance can arise from not only the diffusion of plasticizer into resin particles but also the filling of the interstitial pores of the agglomerated particles. The difference in the porosity may account for the somewhat larger scattering of the data in the correlation.

Plasticizer Diffusion and Gelation

During gelation, at least three separate phases are present: (i) plasticizer or plasticizer containing dissolved polymer, (ii) regions of the PVC particles swollen with the plasticizer, and (iii) PVC untouched by plasticizer. The proportion of these three phases as well as the concentration within phases (i) and (ii) depend upon the progress of gelation. Phases (i) and (iii) decrease and eventually disappear before gelation is completed.

The presence and the compositions of these phases may be characterized by observing the glass transition of each phase. The sample was first cooled down at 40°C/min to -130°C , which is below the T_g of DOP. Then, it was scanned at a heating rate of 40°C/min up to a prescribed temperature. Next, the sample was cooled down again to below the T_g of DOP and the second scan was made. The second scan was to characterize the phases which existed

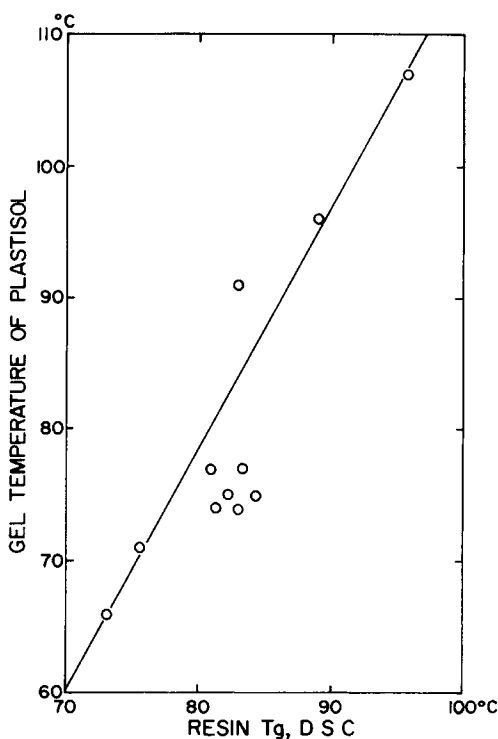


Fig. 7. Relation between resin T_g and gel temperature of plastisol.

at the highest temperature reached previously in the first scan. An example of this series of the experiment is shown in Figure 8 for a plastisol made with resin A1. The lower curve is the first scan, in which the T_g 's of DOP and PVC are very clearly seen. In this example, the first scan was terminated at 100°C. In the second scan, three or four small transitions are indicated. Also, the overall shape of the curve implies that there is a nearly continuous distribution of concentrations, corresponding to the transitions which extend over the temperature range of -80 to 50°C.

In the first scan, the T_g 's of the DOP and PVC phase were $-77.9 \pm 0.4^\circ\text{C}$ and $81.1 \pm 0.2^\circ\text{C}$, respectively, in the total of five runs. These values are in good agreement with the values observed in the previous series. In addition, the T_g 's of samples of pure DOP and DOP containing the stabilizers were measured as -78.2 and -78.0°C , respectively. These T_g values indicate that the plastisol as prepared, but not aged, contains an essentially pure DOP phase and a pure PVC phase. However, a small additional transition seen at $-37.8 \pm 0.3^\circ\text{C}$ implies that a small portion of PVC may be already plasticized (Fig. 8).

Figure 9 shows all the second scans of this series of experiments and one of the first scans, which was terminated at 85°C. Other first scans are not shown, because they are the same, showing only the T_g 's of PVC and DOP. When the first scan was terminated at 85°C, the T_g of DOP in the second scan is still -74°C , but is decreased in magnitude. When the first scan was

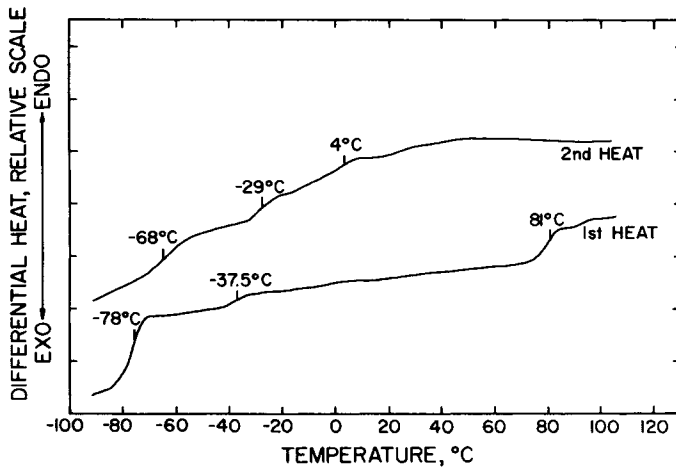


Fig. 8. The DSC scans of a PVC plastisol with resin A1. The bottom curve is the first scan which was carried to 100°C and the top is the second scan.

carried to 100°C, the DOP T_g shifted up to -68°C in the second scan with the magnitude further reduced. In both cases, a small transition is seen at -32°C and -29°C , respectively. For the latter case an additional small transition appeared at 4°C . There seem to be two plasticized PVC phases of different concentrations. In these two examples the transition may be extended over the approximate temperature range of -70 – 50°C , as indicated by a gradual increase of the differential heat input over these temperatures. Assuming that the DOP is in the process of diffusing into the resin particles and that there is a continuous change in the concentration of the plasticized resin phase, the broad range for the transition temperature is expected.

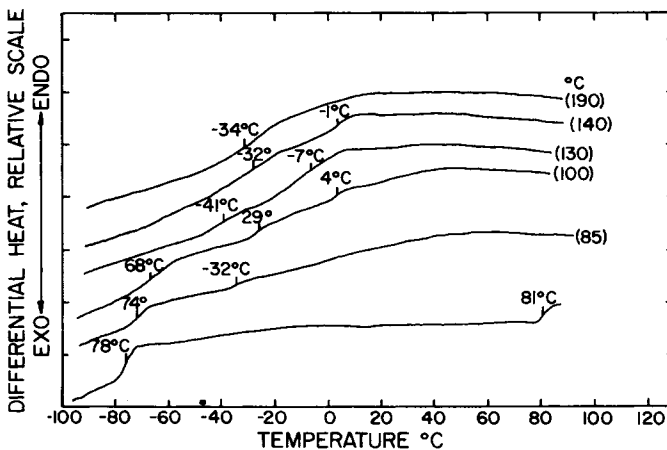


Fig. 9. The DSC scans of PVC plastisol with resin A1. The bottom curve is the first scan which was carried to 85°C, and the one above is the second scan. All other curves are the second scans for which the curves of the first scans are not shown. The highest temperature of the first scan is identified by the temperature in parentheses.

When the first scan is carried up to 130 or 140°C the transition range of the plasticized PVC phase becomes narrower, approximately -55 – 5 °C.

Small transition-like temperatures (i.e., inflection points), indicated by the arrows may indicate the presence of relatively large domains of fixed concentrations. This suggests that the diffusion of DOP into PVC particle may be, by and large, complete at these temperatures, but some domains contain more plasticizer than others, simply because the swelling of polymer started earlier in the former domains, thus containing more plasticizer. When the first scan is terminated at 190°C, only one major T_g is observed in the second scan at -34 °C, which is the T_g of the completely plasticized material of the present plastisol formulation. The redistribution of the plasticizers among the different domains must have taken place in some temperature between 140 and 190°C.

These observations may also suggest that the redistribution of plasticizer in the PVC phase, characteristics of the gelation process, ultimately requires the melting of the residual PVC crystalline domains. Thus at temperatures above the T_g of the PVC phase, the progress of gelation is closely related to the progress of the fusion process, both of which are nearly complete at approximately 190°C for this system.⁸

DISCUSSION

Gelation is a process in which the plasticizer diffuses into resin particles; therefore, the process is completed when the plasticizer is uniformly distributed inside the resin particle. The gelation of PVC plastisol is effected by heating. It occurs over the temperature range where the glass-rubber transition takes place for the resin phase. At room temperature the resin particle is little affected by DOP. Perhaps only the polymer segments on the surfaces of the particles are solvated.⁹ When the glass-rubber transition begins at about 45–65°C, DOP is able to penetrate into the resin particles. This is observed with the increase of the storage modulus and the loss modulus. A variation of T_g 's observed with DSC is approximately related to the variation in the starting temperature of gelation.

The T_g values determined with the DSC is also related to the gel point, a temperature where the plastisol becomes "dry" on a hot plate. The gel point defined this way is perhaps also affected by the porosity of the agglomerated particles.

The most illuminating observation of this investigation is the manner in which the T_g 's of the DOP phase, the pure polymer phase, and the plasticized polymer phase change with the progress of gelation. DSC has proved to be very useful in this study. Until the plastisol is heated to slightly above T_g (i.e., 85°C), a pure DOP phase is present. However, the amount of this phase is somewhat decreased when the temperature goes above T_g . The pure DOP phase must be in the pores of the agglomerated particles, when the temperature reaches 77°C, which is the gel temperature of this resin.

When the temperature is raised to above T_g , the T_g of the resin phase disappears. The transition of the plasticized PVC phase is spread over a wide range of temperatures, which becomes narrower with the progress of gelation. The final stages of the gelation process are concurrent with those

of the fusion process, since the uniform distribution of the plasticizer occurs only after residual crystalline domains melt. When the gelation is complete, the T_g of this composition is approximately -34°C .

SUMMARY

This work explores an effective means of characterizing gelation behavior of PVC plastisol with differential scanning calorimetry and viscoelastic measurements. The plastisol samples were made from 11 commercial PVC resins with a standard formulation.

The gelation temperature determined by a hot-plate method is shown to be quantitatively related to the T_g measured by DSC. Also, characteristic gelation behavior observed in the viscoelastic measurements were identified with the T_g of the resin phase.

Subsequently the sample was heated to various temperatures, which corresponded to various degrees of gelation, and then quenched by cooling. The quenched samples were examined with respect to the presence or absence of the T_g 's of pure resin phase and the pure plasticizer phase. The development of the plasticized PVC phase was also characterized by the change of T_g of this phase. An extremely complex picture of the plasticizer diffusion into resin particles and the microheterogeneity of the plasticizer concentration in the resin have been observed by the DSC method.

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