Effect of Plasticizer Type on Gelation and Fusion of PVC Plastisol, Dialkyl Phthalate Series*

N. NAKAJIMA and S-Y. KWAK

Institute of Polymer Engineering
The University of Akron
Akron, Ohio 44325-0301

Different grades of PVC resins and a variety of plasticizers are used to adjust processability and properties of plastisol. The plastisol, which is a dispersion of fine particles of PVC in plasticizer, is coated on a substrate and heated in an oven to gel and fuse. In the gelation stage the resin particles become swollen with plasticizer and then, in the fusion stage the entire system fuses to become one homogeneous phase. The finished products are flexible PVC such as coated fabrics and surgical globes. Different plasticizers, because of the difference in solvent power, affect the process of gelation and fusion, and hence, processability. This paper examines such an effect systematically by employing a homologous series of plasticizers, dialkyl phthalates. The progress of gelation and fusion are followed by the measurements of dynamic moduli and by the observation with a scanning electron microscope. As it may be expected, the shorter the alkyl chain, the higher the solvent power of the plasticizer.

INTRODUCTION

Flexible PVC (polyvinyl chloride) products may be made through two distinctly different routes. One is to use resins made through suspension polymerization (1). The resin is a porous powder of approximately 100μm size (2). The powder may absorb a large quantity of liquid plasticizer and yet remain free-flowing; or the resin-plasticizer mixture may be compounded and pelletized. The other route uses resins made through emulsion polymerization. The resulting emulsion of PVC is spray-dried; the dried powder contains the primary particles of about 1μm and smaller as well as the agglomerated particles, which are ground to the size smaller than 20μm. The proportion of the primary particles and the agglomerated particles may be for example 85 to 15. The powder is mixed with a plasticizer in approximately equal volume to prepare a paste called "plastisol" (3, 4).

The compound made with the suspension resins may be melt-processed with plastics-processing equipment such as an extruder, injection molding machine, compression molding, and calendaring. Although plastisol may also be processed through these equipments, its real advantage is the much lower viscosity of the paste compared to the melt, rendering unique fabrication techniques. The plastisol may be coated on a substrate with high speeds, such as fabric coating; it may be made into films and sheets; dip coating may be used to make complex shapes like boots and surgical gloves; the rotational molding and slush-molding may be used to make hollow objects. Uses of relatively inexpensive equipment, particularly inexpensive mold are another advantage of plastisol.

After plastisol is coated on the substrate, it is heated in an oven to gel and fuse. In the gelation stage the resin particles become swollen with plasticizer and in fusion stage they fuse to become a uniform mass. In this process the system changes from a pasty liquid to viscoelastic melt. The development of modulus is important in some processes, e.g. foaming, where the generation of the desired cell structure is intimately related to the viscoelastic properties of the system (5).

Rheological property is one of the most important criterion for selecting the resin grade and plasticizer type for a given formulation. The rheological requirements may be divided into two areas; one is the rheology at room temperature, where the coating operation is performed (6). The other area is the development of modulus during gelation and fusion (7) as mentioned already. This study and many preceding studies concern the latter area. In one paper the viscoelastic finger-printing typical commercial grade of resins (dispersion resins) were presented (8). In another, the viscoelastic profile was related to the morphological changes accompanying gelation.
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Among the available material variables the plasticizer type makes a most significant effect on the development of modulus (10). Apparently the difference of solvent power of the plasticizer plays the key-role.

From the morphological observation with a scanning electron microscope, SEM, the following four steps were identified as the gelation and fusion proceed: (i) a portion of polymer dissolves into plasticizer; the dissolution of polymer may come from the surface of some particles. However, there appears to be the particle-particle differences in solubility that some particles dissolve earlier and others remain long after most have dissolved. (ii) The plasticizer containing the dissolves polymer looks like it is glueing particles together. As more polymer dissolves, this phase becomes the matrix with relatively minor amount of particles dispersed in it. (iii) Simultaneously with the step (i), the polymer particles become swollen with plasticizer. (iv) As the swelling continues the particles form clusters and eventually coalesce to form a uniform mass. For a given PVC-plasticizer system all four steps may be occurring at some stage of gelation and fusion. However, in the examples seen by SEM, steps (i) and (ii) dominate in some system and (iii) and (iv) dominate in others. The former example is the tricresylphosphate (TCP) system at above 100°C. The latter example is the dioctylsebacate (DOS) system. With the di-2-ethylhexyl phthalate (DOP) system it is not clear as to which step dominates. With the dibenzylsebacate (DBS) system the coalescence of the swollen particles appears to be the dominant reaction.

The difference in the solvent power of the above plasticizer comes from very different chemical structure. In order to examine more detail of the effect of solvent power, we have chosen a homologous series of dialkylphthalates, dimethyl-(DMP), di-(iso)hexyl-(DHP), di-2-ethylhexyl-(DOP) and di-isooctyl-(DIOP). As before both viscoelastic measurements and morphological observation have been performed.

EXPERIMENTAL

Materials

The PVC resin in this study in one of the representative dispersion resins, Geon 121, a product of the B. F. Goodrich Company.

The homologous series of plasticizers are di-methyl phthalate (DMP), di-(iso)hexyl phthalate (DHP), di-2-ethylhexyl phthalate (DOP) and di-isooctyl phthalate (DIOP). As before both viscoelastic measurements and morphological observation have been performed.

Table 1. Chemical Structures of Plasticizers.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-methyl phthalate</td>
<td>((\text{C}<em>{10}\text{H}</em>{10}\text{O}_4))</td>
</tr>
<tr>
<td>di-(iso)hexyl phthalate</td>
<td>((\text{C}<em>{20}\text{H}</em>{30}\text{O}_4))</td>
</tr>
<tr>
<td>di-2-ethylhexyl phthalate</td>
<td>((\text{C}<em>{24}\text{H}</em>{38}\text{O}_4))</td>
</tr>
<tr>
<td>di-isooctyl phthalate</td>
<td>((\text{C}<em>{24}\text{H}</em>{38}\text{O}_4))</td>
</tr>
</tbody>
</table>

Table 2. Physical Properties of Plasticizers.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Weight (g/mole)</th>
<th>Specific Gravity ((^\circ\text{C}/^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>194</td>
<td>1.190</td>
</tr>
<tr>
<td>DHP</td>
<td>334</td>
<td>1.008</td>
</tr>
<tr>
<td>DOP</td>
<td>390</td>
<td>0.982</td>
</tr>
<tr>
<td>DIOP</td>
<td>390</td>
<td>0.982</td>
</tr>
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</table>

*Ref. 11

Table 3. Plastisol Formulation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC resin</td>
<td>100</td>
</tr>
<tr>
<td>(I.V. 1.20 dl/g)* Plasticizer</td>
<td>57</td>
</tr>
<tr>
<td>Epoxidized soybean oil</td>
<td>3</td>
</tr>
<tr>
<td>Barium, cadmium, zinc stabilizer</td>
<td>2</td>
</tr>
</tbody>
</table>

*I.V. = Inherent viscosity in cyclohexanone at 30°C (12).

Plastisol Preparation

Plastisols were prepared by mixing the dry PVC powder with liquid plasticizer containing epoxidized soybean oil and stabilizer. A small amount of the plasticizer was slowly added to the dry PVC powder while stirring manually with a stainless steel spatula.

The manual stirring was continued until all plasticizer was added and the mixture changed to a viscous fluid. Then, a mechanical stirrer
with a two-blade propeller was used for a further homogenization.

After mixing was completed, air bubbles in plastisols were removed by applying vacuum, but slowly in order to prevent foaming. Then, the plastisols were aged for two weeks before their use. The aging is necessary because viscosity increases initially primarily because of deagglomeration but it stabilizes after two weeks (13).

Viscoelastic Measurements

A Rheometrics Mechanical Spectrometer (RMS), model RMS-605, was used in the dynamic oscillatory mode with a controlled heating rate. The 25 mm-diameter parallel discs were used with a gap setting of 2 mm. In this study, the cone and plate assembly can not be used because, during the heating cycle, the gap change, which, although very slight, can have a significant effect on the accuracy of the results. The frequency of oscillation was maintained to be 1 Hz.

Heating was started from room temperature to 190°C with a programmed increase rate of 5°C/min. After allowing a few minutes for equilibrating to the desired temperature, the measurements were made. The shear strain amplitude was 25% in the range from room temperature to about 60°C where gelation started. After this temperature, the strain amplitude was reduced to 2.5%. The 25% was large enough to obtain accurate torque signals when the moduli were low in the beginning of measurement, i.e., in the fluid state. The 2.5% was small enough not to disturb the system at the later stage of the measurement. At this strain amplitude, the system did not indicate non-linearity.

Morphological Observations

A Scanning Electron Microscope (SEM), ISI model SX-40 was used to observe the morphological changes of PVC plastisol during gelation and fusion.

The samples for SEM were made by using Rheometrics Mechanical Spectrometer. The plastisols were loaded between upper and lower plate of RMS and then heated up to a desired temperature without imposing shear strain to the system. The sampling temperatures were selected with reference to the viscoelastic data and the stepwise increase of temperature of about 5°C for every minute was used. The samples were immersed in liquid nitrogen and then freeze-fractured.

RESULTS

Viscoelastic Measurements

Figures 1 to 4 are changes of elastic modulus, G', and loss modulus, G", during gelation and fusion as a function of temperature. For the first three systems, PVC-DOP, -DIOP, and -DHP, with the increase of temperature, the moduli decrease initially. At slightly above 60°C, the gelation process begins and the elastic and the loss moduli increase very steeply with temperature by three orders of magnitude. A first peak or a shoulder appears in the curves and then the moduli increase more gradually (DOP and DIOP) or level off (DHP). The maximum values of the moduli are between 125°C and 135°C for DOP and DIOP systems. The second maxima appear for DHP system between 110 and 125°C. With further increase in temperature the moduli decrease indicating the end of gelation and dominance of fusion, melting of microcrystallites (14). Figure 4 shows the viscoelastic profile of PVC-DMP system, which is quite different from that of other three systems. When the PVC-DMP plastisol was aged for two weeks, the system turned into a solid cake, which is no longer paste-like. The solid-like state of the PVC-DMP system at the lower temperature ranges is indicated by the magnitude of the elastic modulus. At 55°C, the magnitude of the elastic modulus is approaching 10^5 Pa, which is comparable in magnitude to those of the shoulder or the first peak of other three systems. The fact indicates that the gelation already started at room temperature. With further increase in temperature, the moduli increase slightly and remain constant up to 120°C and then decrease gradually, indicating the dominance of the fusion step. In all four systems the maximum of the elastic modulus occurs at a higher temperature than that of the loss modulus. The reason for this is not known yet.

Fig. 1. Viscoelastic profile of gelation and fusion of a plastisol made with PVC-DOP.
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PVCl/DIOP

![Graph showing viscoelastic profile of gelation and fusion of a plastisol made with PVC-DIOP.]

Fig. 2. Viscoelastic profile of gelation and fusion of a plastisol made with PVC-DIOP.

PVCl/DMP

![Graph showing viscoelastic profile of gelation and fusion of a plastisol made with PVC-DMP.]

Fig. 4. Viscoelastic profile of gelation and fusion of a plastisol made with PVC-DMP.

Morphological Observation

Table 4 lists sampling temperatures which were chosen on the basis of characteristic features of the viscoelastic curves. The sampling temperatures of the PVC-DMP system are somewhat arbitrary because no clear feature is observed in the moduli.

The SEM micrographs of the fracture surfaces of the PVC-DIOP system are shown in Figs. 5 through 8 at two magnifications of 2000x and 5000x. At 90°C individual particles are still identifiable and the presence of agglomerates is also apparent. But some particles may be swollen somewhat with the plasticizer. At 130°C, which is the second maximum in loss modulus, changes in morphology are obvious such that only a limited number of particles are identifiable and that the interparticle boundaries are obscured. The texture of the fracture surface looks like a ghost of particles. At 159°C the fusion has taken over and the particulate morphology has disappeared. At 193°C, the fusion seems to be completed, because the fracture surfaces are very similar at 159 and 193°C.

The SEM observations of the PVC-DOP system are very similar to those reported before (14). They are also similar to PVC-DIOP system. Therefore, they are not shown here.

Figures 9 through 13 are the SEM photographs of the PVC-DHP system. At 83°C the particles of PVC are clearly identifiable. At 104°C the original parti-
Table 4. Sampling Temperature for Morphological Observation.

<table>
<thead>
<tr>
<th>Characteristic Behavior</th>
<th>Temperature (°C)</th>
<th>PVC-DIOP</th>
<th>PVC-DHP</th>
<th>PVC-DMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>First peak (or shoulder)</td>
<td>90</td>
<td>83</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Valley after first peak</td>
<td></td>
<td>104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second peak in G&quot;</td>
<td>130</td>
<td>126</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Dominance of fusion</td>
<td>159</td>
<td>159</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>Completion of fusion</td>
<td>193</td>
<td>193</td>
<td>190</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Scanning electron micrographs of PVC-DIOP plastisol at 90°C.

Fig. 6. Scanning electron micrographs of PVC-DIOP plastisol at 130°C.

Figures 14 through 17 are the SEM photographs of the PVC-DMP system. At 25°C the original particles are clearly visible but some degree of swelling has already started. In general, the plasticizers such as DOP and DIOP are rather a poor solvent which has little effect on the PVC resin at room temperature. From the fact that swollen particles exist at 25°C, DMP is considered to be the best solvent of the four plasticizers in this study. At 90°C PVC particles are on the verge of losing their boundaries. The disappearance of interparticle boundaries is much more progressed compared to that of PVC-DIOP system at the same temperature. At 130 and 160°C the interparticle boundaries disappeared almost completely. At 190°C, there is no indication of particle boundaries.

DISCUSSION

Viscoelastic Measurements

In Figs. 18 and 19 the elastic moduli and loss moduli are plotted separately for four PVC-plasticizer systems. With the increase of temperature, the elastic and the loss moduli of three systems except for the PVC-DMP decrease initially below 60°C. This
indicates that they remain a suspension of PVC solids in a plasticizer. At slightly above 60°C, the gelation process begins. The temperature, where the first peak or the shoulder appears at 83–90°C corresponds approximately to the glass transition temperature of the PVC (15). In the PVC-DHP system, the temperature where the first peak appears is somewhat lower and the magnitude of modulus in the first peak is higher compared to the PVC-DOP and the PVC-DIOP system. This indicates the better solvent power of DHP.

Concerning the PVC-DMP system, the plasticizer appears to have penetrated into some of the PVC particles and swelled or even dissolved them at room temperature, Fig. 14. This system has gelled at room temperature similar to other three systems at the higher temperature where the first peak (or shoulders) appear. The moduli of the PVC-DMP system at 50°C (and probably even at room temperature) are as high as those of other three systems at the higher temperatures.

After passing the second maxima, the elastic and the loss moduli decrease for two reasons. One is the normal temperature dependence, primarily attributable to the thermal expansion. The other is caused by the loss of the network junctions by melting of the PVC microcrystallites.

The gelation and fusion profiles presented in Figs. 18 and 19 show an apparent effect of solvent power of plasticizers. There are apparent differences in gelation and fusion behavior, particularly at the temperature range from 60°C to 120°C. One of the most obvious and systematic differences is the first peak (or shoulder) in the elastic and the loss moduli, indicating that the solvent power plays a significant role while the gelation is progressing. A quantitative comparison for three systems except for PVC-DMP is made by taking the temperature of the first peak (or shoulder) and the magnitude of moduli at the same temperature, Table 5. From the viscoelastic data, the lower the peak temperature and the higher the magnitude of moduli indicate the better solvent.
Because the PVC-DMP system has high moduli at room temperature, obviously DMP is the best solvent. The order of solvent power is DMP, DHP, DOP/DIOP. It is well known that polar (ester) groups in the homologous series of dialkyl phthalates are the main functional groups responsible for plasticization (11).

During gelation and fusion process, PVC plastisol changes from a suspension of PVC particles in a liquid plasticizer to a uniform mass. The morphological study with SEM provides direct and unique information which is not obtainable from other measurements.

As before (10) a large variation in solubility of particles is observed: some particles have swollen, while others appear to be least affected. The cause of the variation was explained on the basis of difference in the heat history during drying. Those particles that become agglomerated may be slower to be touched by the plasticizer, while the decrease in crystallinity by partial melting may facilitate swelling. Although speculative, differences in syndiotacticity or in the surface coverage with emulsifier may also occur among the particles.

In the beginning of gelation (i) a portion of PVC dissolves into plasticizer, (ii) some particles become swollen with plasticizer and (iii) other particles appear unaffected. Because the solvent power, i.e. polymer-solvent interaction, is concentration dependent, the following mechanism was postulated; if a given plasticizer is a relatively better solvent at dilute regions but poorer at high concentrations, the above process (i) should dominate over the process (ii). If the converse is the case, the swelling should be the dominant reaction but not the dissolution. In the previous study TCP seem to give the former, and DOS the latter. However, with DOP it was not clear whether one process dominates over the other or not. In the present study of the alkylphthalate series, again we cannot tell which process dominates.
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Fig. 11. Scanning electron micrographs of PVC-DHP plastisol at 126°C.

Fig. 12. Scanning electron micrographs of PVC-DHP plastisol at 159°C.

Fig. 13. Scanning electron micrographs of PVC-DHP plastisol at 193°C.
Fig. 14. Scanning electron micrographs of PVC-DMP plastisol at 25°C.

Fig. 15. Scanning electron micrographs of PVC-DMP plastisol at 90°C.

Fig. 16. Scanning electron micrographs of PVC-DMP at 130°C (left) and 160°C (right).
Although the SEM photographs provide direct viewing of the morphological changes, the differences in the solvent power are shown to be relative and qualitative. In this regard viscoelastic method is superior in that the difference is clearly demonstrated quantitatively in Figs. 18 and 19. The extent of differences in the temperature dependence of moduli are important in processing (8).

CONCLUSIONS

Solvent power of a dialkyl phthalate series, DOP, DIOP, DHP, and DMP, in PVC plastisol was examined as they affect progress of gelation and fusion. The viscoelastic measurements and morphological observations were performed. As demonstrated by the development of elastic and loss modulus the solvent power is in the order of better to poorer, DMP, DHP, and DOP/DIOP. The DOP and DIOP systems gave an identical behavior.

In the morphological observation significant differences in solubility were observed among the par-
Table 5. Viscoelastic Data at the First Peak, Peak Temperature, and Interaction Parameter.

<table>
<thead>
<tr>
<th>Data</th>
<th>DOP</th>
<th>DIOP</th>
<th>DHP</th>
<th>DMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G'(\text{dyne/cm}^2)$</td>
<td>$3.43 \times 10^5$</td>
<td>$2.48 \times 10^5$</td>
<td>$2.90 \times 10^6$</td>
<td>$(8.65 \times 10^5)^a$</td>
</tr>
<tr>
<td>$G''(\text{dyne/cm}^2)$</td>
<td>$3.40 \times 10^5$</td>
<td>$2.40 \times 10^5$</td>
<td>$1.36 \times 10^6$</td>
<td>$(5.82 \times 10^5)^a$</td>
</tr>
<tr>
<td>$T(\text{C})$</td>
<td>90</td>
<td>90</td>
<td>83</td>
<td></td>
</tr>
</tbody>
</table>

* Moduli at 50°C.

particles; some became swollen while others appear unaffected. In the SEM photographs the solvent power of DMP, DHP, DOP, and DIOP were shown to be in agreement with the results of the viscoelastic measurements.

REFERENCES