# Influences of Chlorinated Polyethylene and Oxidized Polyethylene on the Fusion of Rigid Poly(vinyl chloride) Compounds

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ABSTRACT: Fusion time, fusion temperature, and fusion torque of poly(vinyl chloride) (PVC) compounds with various components were studied in this article. Influences of chlorinated polyethylene (CPE), oxidized polyethylene (OPE), and calcium stearate on fusion characteristics of PVC compounds were illustrated. The synergistic reaction among CPE, OPE, and calcium stearate forms a powerful and effective processing aid that allows the PVC particles to fuse more quickly and uniformly. In PVC/CPE compounds, a higher concentration of CPE can function like a processing aid and help PVC particles to fuse together easily. Meanwhile, the interaction between a higher concentration of OPE and calcium stearate in PVC/OPE compounds can promote the PVC particles to fuse together easily in the beginning of the fusion process. However, the external lubricant property of OPE still exists and results in more intact PVC microparticles not fused. The fusion temperature of the PVC in a Haake mixing bowl increases as the fusion time increases. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 699–705, 1999

**Key words:** poly(vinyl chloride); chlorinated polyethylene; oxidized polyethylene; fusion time; fusion torque

## INTRODUCTION

Currently, poly(vinyl chloride) (PVC) products are widely used in automobile parts, components for houses and buildings, and packaging for everything from food to electronic parts. To perform such diverse functions, various additives for the PVC have been found and used.

Chlorinated polyethylene (CPE) is commonly used commercially as an impact modifier of PVC. According to the results reported by Chang et al.,<sup>1</sup> chlorination in solution gives the greatest uniformity of distribution of chlorine atoms in HDPE

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polymer chains. The chlorine distribution and content of CPE are major factors in the mixing of CPE with PVC, which may influence the mechanical properties of the final product. The melting temperature of CPE ranges from 110 to 130°C. Because of better elasticity and less compatibility with PVC, the CPE with 36% chlorine is usually used as an impact modifier for PVC and is the optimum composition for impact, processing, and strength.<sup>2</sup> Therefore, CPE ( $M_w \approx 160,000$ ) with 36% chlorine was used in this study.

Oxidized polyethylene (OPE) and calcium stearate are two important lubricants used in PVC processing. OPE can be made by oxidizing polyethylene at the ends of the chain, at sites of unsaturation, or at points of branching. This oxidization creates slight polarity and compatibility

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**Figure 1** Surface morphological micrograph of a suspension PVC particle.

at the point of oxidation. A typical OPE lubricant for PVC processing is a medium density polyethylene ( $M_w = 2000-4000$ ) with slightly oxidized characterization (acid number, 6–20). In this study, the OPE with acid number 6–10 was used. Because of the carboxylic groups, OPE is polar and has a melting temperature between 100 and 130°C.

Calcium stearate is a salt containing a highly polar CaOOC group and a long, nonpolar hydrocarbon chain  $-(CH_2)_{16}CH_3$ . Calcium stearate with  $C_{18}$  in the R-C linkage is the most popular lubricating material for PVC processing and has a melting temperature between 145 and 160°C.

Depending on the lubricating action and effects, lubricants may be divided into two categories, internal and external lubricants. Internal lubricants lower the intermolecular friction of PVC when the PVC composition is being hotsheared or fused into a melt. External lubricants reduce the friction and sticking between the hot PVC composition and the working surfaces of processing machinery. Generally speaking, external lubricants (e.g., OPE) delay the fusion time of a PVC compound, and internal lubricants (e.g., esters) speed up the fusion time or have very little effect on it. In actual applications, however, lubricants do not always abide by the rules. Some exceptions have been found and studied. Bower<sup>3</sup> reported that an internal/external classification is inadequate, particularly for a rigid PVC lubrication mechanism.

Several reports discussing the functions of lubricants for the processing of PVC blends are available.<sup>4–12</sup> Lindner<sup>13</sup> reported that the interaction between OPE and calcium stearate can be used to speed up significantly the fusion time of

PVC blends. Therefore, lubrication is the most important factor in influencing the fusion of PVC during processing which may determine the physical properties of final PVC products.

The fusion characteristics of PVC blends are highly dependent on their composition. In this study, the influences of CPE and two lubricants, calcium stearate and OPE, on the fusion characteristics of PVC compounds were studied.

## **EXPERIMENTAL**

#### Preparation of PVC Compounds

Materials used in this study are suspension PVC masterbatch powder, containing 100 parts PVC resin particle ( $M_w \approx 150,000$ ), 1.5 parts process aid (acryloid, K120N), 1.0 part paraffin wax (intermediate lubricant, XL165), 1.0 part calcium stearate, and 1.5 parts heat stabilizer (tin thioglycolate, T-137). The other four samples are PVC masterbatch powder with various parts CPE (0, 1, 3, 5, 10, and 15), PVC masterbatch powder with various parts CPE (0, 1, 3, 5, 10, and 15), and 0.3 parts OPE (external lubricant), PVC masterbatch powder with various parts OPE (0, 0.1, 0.3, 0.5, 0.5)1.0, and 1.5), PVC masterbatch powder with various parts OPE (0, 0.1, 0.3, 0.5, 1.0, and 1.5), and 5 parts CPE. All materials were supplied by the Dow Chemical Company, Louisiana, USA.

All PVC samples were prepared in a Haake torque rheometer, Haake Rheocord 90, equipped with a three-sectioned mixing chamber and two



**Figure 2** A typical torque curve of PVC compound melted in a Haake torque rheometer at temperature  $= 190^{\circ}$ C and rotor speed = 60 rpm.

Characteristic	0 phr	1 phr	3 phr	5 phr	10 phr	15 phr
Fusion temperature (°C) Fusion time (min) Fusion torque (g m)	$188 \\ 1.25 \\ 2701$	$196 \\ 2.5 \\ 2244$	$195 \\ 2.2 \\ 2223$	193 1.8 2339	$187 \\ 1.1 \\ 2415$	184 0.9 2559

Table I Fusion Characteristics of PVC/CPE Compounds with Various phr of CPE at Temperature = 190°C, Rotor Speed = 60 rpm

noninterchangeable roller mixing rotors. The sample weight was 65 g for all runs. PVC powder samples with various compositions were charged into the mixer at a starting temperature of 190°C and a rotor speed of 60 rpm, and removed when a total torque of 8 kg m min was reached in the Haake torque rheometer. The fusion characteristics, fusion time, fusion temperature, and fusion torque have been summarized and compared for PVC samples of varying compositions.

## **SEM Morphological Analyses**

PVC samples were immersed in liquid nitrogen for 45 s. Then, samples were fractured and coated with 20-nm gold-palladium film. Finally, they were examined in a Cambridge S-260 SEM.

## **RESULTS AND DISCUSSION**

The surface morphological micrograph of a suspension PVC powder particle is shown on Figure 1.<sup>14</sup> This particle is known as a grain, is irregular in shape, and is approximately 100–150  $\mu$ m in diameter. Each grain consists of many microparticles that are approximately 1–2  $\mu$ m in diameter. These microparticles are loosely packed together causing the grain to be porous. Each microparticle is made up of still smaller structures known as submicroparticles that are approximately 100–300 Å in diameter. These submicroparticles are reported to be about 5–10% crystallinity. To get the PVC products with good mechanical and physical properties, heat and shear must be applied. The grains have to be broken down and the

microparticles must be altered and compacted together. After significant interdiffusion, the boundaries of submicroparticles disappear and a three-dimensional network of polymer chains is formed. This is referred to as the PVC fusion or gelation.<sup>15</sup>

Figure 2 shows typical fusion curves when PVC was melted in a Haake torque rheometer at a starting temperature of 190°C and a rotor speed of 60 rpm and removed when a total torque of 10 kg m min was reached.<sup>16</sup> These curves illustrate the changes of viscosity related to torque, temperature, and total torque versus time. The viscosityrelated torque curve shows two different peaks. The first peak, L, in the torque curve is due to loading. The second peak, F, is due to compaction and onset of fusion. When the PVC sample is loaded into the system, the initial peak is generated. Then, the torque begins to decrease sharply because of free material flow before it begins to compact. After that, the torque begins to increase and generates the second peak. At this peak, F, the material reaches a void-free state and starts to melt at the interface between the compacted material and the hot metal surface.<sup>4</sup> If the sample is melted and fused for a long time in the mixer, the temperature increases slightly because more thermal energy is absorbed by this sample. A higher temperature results in decreasing the melt viscosity of the sample; therefore, the torque decreases as time slowly increases.

Usually, the time between the loading point L and the fusion point F is defined as fusion time. Here we consider that the fusion time of the PVC sample without CPE and OPE is a normal fusion

Table II Fusion Characteristics of PVC/CPE/0.3phrOPE Compounds with Various phr of CPE at Temperature = 190°C, Rotor Speed = 60 rpm

Characteristic	0 phr	1 phr	3 phr	5 phr	10 phr	15 phr
Fusion temperature (°C)	196	194	193	188	179	174
Fusion torque (g m)	2116	2256	2368	2466	2619	2773



**Figure 3** Fusion time curves, varying with the phr of CPE, PVC/CPE, and PVC/CPE/0.3phrOPE compounds.

time. The temperature, with respect to the fusion point F, is defined as fusion temperature. Similarly, the torque, with respect to the fusion point F, is defined as fusion torque. The processing time is defined as the time between the loading point L and the stopping point.

Tables I and II summarize the influence of varying phr of CPE on the fusion characteristics of PVC/CPE and PVC/CPE/0.3phrOPE compounds prepared at a temperature of 190°C and a rotor speed of 60 rpm. Figure 3 shows the fusion time curves of PVC/CPE and PVC/CPE/0.3phrOPE compounds varying with the phr of CPE. It illustrates that the fusion times of PVC/CPE/ 0.3phrOPE compounds decrease as the phr of



**Figure 5** Surface morphological micrograph of PVC/ 15phrCPE/0.3phrOPE compound.

CPE increase. It also shows that the fusion time curve of PVC/CPE compounds has a plateau (between 0 and 3 phr CPE). Normally, the fusion times of PVC/CPE compounds decrease as the phr of CPE increases.

For PVC/CPE compounds, a lower phr of CPE (<10 phr) may function like an external lubricant that decreases the gummy property of calcium stearate and forms a mobile layer among PVC particles. Therefore, it delays the fusion time. On the other hand, if the phr of CPE in PVC/CPE compounds is increased, sufficient CPE melt can act as a processing aid that promotes fusion process and increases the transfer of heat and shear throughout the PVC grains. This processing aid also promotes friction in the system and allows



**Figure 4** Surface morphological micrograph of PVC/ 10phrCPE/0.3phrOPE compound.



**Figure 6** Changes of fusion temperature and fusion torque of PVC/CPE/0.3phrOPE compounds various with the phr of CPE.

Characteristic	0 phr	0.1 phr	0.3 phr	0.5 phr	1.0 phr	1.5 phr
Fusion temperature (°C)	188	195	196	194	188	187
Fusion time (min)	1.5	2.2	2.3	1.8	1.2	1.0
Fusion torque (g m)	2701	2079	2116	2223	2351	2404

Table III Fusion Characteristics of PVC/OPE Compounds with Various phr of OPE at Temperature = 190°C, Rotor Speed = 60 rpm

the fusion process to occur more quickly and uniformly.

For PVC/CPE/0.3phrOPE compounds, a higher phr of CPE may result in a more effective and powerful processing aid that resulted from the synergistic reaction among CPE particles, OPE wax, and calcium stearate. This powerful processing aid can easily break down the boundaries of PVC grains, increase the friction, and improve the fusion process to occur at a shorter time and more uniformly. Chen et al. postulated a fusion mechanism explaining this synergistic reaction.<sup>16</sup> Figures 4 and 5 show the surface morphological micrographs of PVC/10phrCPE/0.3phrOPE and PVC/15phrCPE/0.3phrOPE compounds, respectively. It indicates that only a few intact PVC microparticles in these two micrographs exist. There is no significant difference between these two micrographs.

Figure 6 illustrates the fusion temperature and torque of PVC/CPE/0.3phrOPE compounds varying with the phr of CPE. It shows that the fusion temperature increases as the fusion time increases. On the other hand, the fusion torque decreases as the fusion time increases. This is because a higher thermal energy is necessary to be absorbed by a PVC compound in order for the PVC to fuse together, and this event causes a longer fusion time. It is also believed that a higher thermal energy results in higher fusion temperature. Moreover, a higher fusion temperature results in a decrease in the melt viscosity of a PVC sample in a Haake torque rheometer. Therefore, the fusion torque decreases as the fusion temperature increases.

Tables III and IV illustrate the influence of varying phr of OPE on the fusion characteristics of PVC/OPE and PVC/5phrCPE/OPE compounds prepared at a temperature of 190°C and a rotor speed of 60 rpm. Figure 7 illustrates the fusion time curves of PVC/OPE and PVC/5phrCPE/OPE compounds varying with the phr of OPE. It shows that the fusion times of PVC/5phrCPE/OPE compounds decrease with the phr of increasing OPE. It also shows that the fusion time curve of the PVC/OPE compounds passes a plateau (between 0.1 and 0.3 phr OPE), then decreases as the phr of OPE increases.

For PVC/OPE compounds, a lower phr of OPE (<1.0 phr) may function like an external lubricant and result in a mobile layer that increases the separation and slipping among PVC particles and therefore, delays the fusion times.<sup>16</sup> When increasing the phr of OPE in PVC/OPE compounds, the synergistic reaction between OPE and calcium stearate may function like a processing aid which allows the PVC grain particles to fuse together quickly.<sup>13</sup> Figure 8, 9, and 10 show the surface morphological micrographs of PVC/0.3phrOPE, PVC/1.0phrOPE, and PVC/1.5phrOPE compounds, respectively. There is no significant difference between Figures 9 and 10. Comparing Figure 8 with Figure 9 or with Figure 10, one can notice that although a higher phr of OPE results in shorter fusion time, more PVC microparticles are not fused. This event may be due to the influence of the external lubricant property of OPE. The synergistic reaction between OPE and calcium stearate promotes the PVC fusion process in the beginning, but the external lubricant property of OPE still exists and

Table IV Fusion Characteristics of PVC/5phrCPE/OPE Compounds with Various phr of OPE at Temperature = 190°C, Rotor Speed = 60 rpm

Characteristic	0 phr	0.1 phr	0.3 phr	0.5 phr	1.0 phr	1.5 phr
Fusion temperature (°C)	193	194	188	185	184	174
Fusion time (min)	1.8	1.7	1.2	0.9	0.8	0.5
Fusion torque (g m)	2339	2367	2466	2447	2527	2692



**Figure 7** Fusion time curves of PVC/OPE and PVC/ 5phrCPE/OPE compounds various with the phr of OPE.

results in more PVC microparticles nonfused. This result is interesting. We believe that the fusion process of a PVC compound is complex and highly dependent on the compositions.

Figure 11 shows the surface morphological micrographs of PVC/5phrCPE/1.0phrOPE compound. Comparing Figure 9 with Figure 11, one can observe that less intact PVC microparticles are found in Figure 11 than in Figure 9. The difference is due to the synergistic reaction among CPE, OPE, and calcium stearate in PVC/5phrCPE/OPE compounds. Generally speaking, a



**Figure 8** Surface morphological micrograph of PVC/ 0.3phrOPE compound.



Figure 9 Surface morphological micrograph of PVC/ 1.0phrOPE compound.

higher phr of OPE can result in an effective and powerful processing aid and allow the fusion process to occur more quickly and uniformly. This material, similar to glue, can easily destroy the boundary of a PVC particle, increase the friction, and improve the fusion at a shorter time (similar result as mentioned above). Figure 12 illustrates the changes of fusion temperature and fusion torque of PVC/5phrCPE/OPE compounds varying with the phr of OPE. It shows that the fusion temperature increases with fusion time and the fusion torque decreases with fusion time (same reason as mentioned for Fig. 4).

## **CONCLUSIONS**

Influences of CPE and OPE on the fusion characteristics and surface morphological changes of



**Figure 10** Surface morphological micrograph of PVC/ 1.5phrOPE compound.

PVC compounds are illustrated in this article. The fusion time of the PVC/CPE/OPE compound is the shortest among these PVC compounds. This may be due to the synergistic reaction among CPE, OPE, and calcium stearate that forms an effective and powerful processing aid. Meanwhile, it allows the fusion process to occur more quickly and uniformly. For PVC/CPE compounds, a lower phr of CPE may be due to less compatibility with PVC and a decrease in the gummy property of calcium stearate, and therefore, the longer fusion times. When increasing the concentration of CPE in PVC/CPE compound, sufficient CPE melt can function as a processing aid that helps PVC grain particles to fuse together easily.

For PVC/OPE compounds, a lower phr of OPE (<1.0 phr) may function as an external lubricant and result in a mobile layer that increases the separation and slipping among PVC particles and delays the fusion times. When increasing the phr of OPE in PVC/OPE compounds, the interaction between OPE and calcium stearate may function as an effective processing aid in the beginning of the fusion process, but the external lubricant property of OPE still exists and results in more PVC microparticles nonfused. It is believed that the fusion process of a PVC compound is very complex and highly dependent on the compositions. The fusion temperature increases as the fusion time increases. On the other hand, the



**Figure 11** Surface morphological micrograph of PVC/ 5phrCPE/1.0phrOPE compound.



**Figure 12** Changes of fusion temperature and fusion torque of PVC/5phrCPE/OPE compounds various with the phr of OPE.

fusion torque decreases as the fusion time increases.

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