

# Study of Fusion Percolation Thresholds of Rigid PVC Compounds

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**ABSTRACT:** Rigid poly(vinyl chloride) (PVC), PVC/chlorinated polyethylene (CPE), and PVC/CPE/oxidized polyethylene (OPE) compounds were prepared in a Haake torque rheometer. The fusion percolation thresholds (FPTs) of these compounds were defined and compared. Moreover, the fusion curves of these compounds were illustrated and compared. A higher processing temperature resulted in a shorter fusion time and a lower FPT. For PVC/CPE compounds, a higher concentration of CPE could decrease the FPT and promote PVC particles to fuse together easily. Meanwhile, in the beginning of the fusion process, the interaction between a higher concentration of OPE and calcium stearate in PVC/OPE compounds could also promote an easy fusion of the PVC particles. For PVC/CPE/OPE compounds, the synergistic interaction among CPE, OPE, and calcium stearate resulted in the shortest fusion time and the lowest FPT. The FPTs of rigid PVC samples were strongly dependent on not only the processing conditions but also the formulations of the samples. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3022–3029, 2001

**Key words:** poly(vinyl chloride) (PVC); chlorinated polyethylene (CPE); oxidized polyethylene (OPE); fusion percolation threshold; fusion time

## INTRODUCTION

Poly(vinyl chloride) (PVC) is a very common and important commodity plastic. PVC products are widely used in automobile parts, components of houses and buildings, and packaging for everything from food to electronic parts. For such diverse functions, various additives for PVC have been used. The suspension polymerization process is the principal commercial route to producing PVC resins in industry today. Various levels of morphology exist in suspension PVC powder,

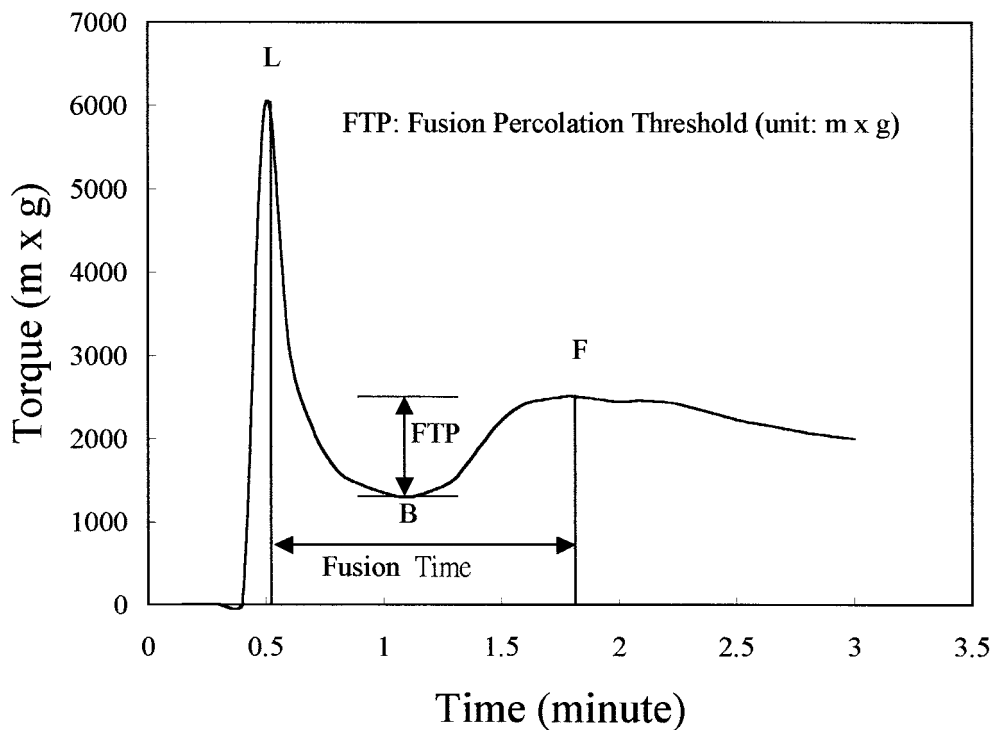
and these were illustrated by Butters.<sup>1</sup> Powder particles, which are stage-III particles and are visible to the naked eye, are known as *grains*. These are irregular in shape and about 100–150  $\mu\text{m}$  in diameter. Each grain consists of many microparticles, stage-II particles, which are about 1–2  $\mu\text{m}$  in diameter. The microparticles are loosely packed together, causing the grains to be porous. Each microparticle is made up of still smaller structures, known as stage-I particles (submicroparticles), approximately 100–300  $\text{\AA}$  in diameter. These stage I particles are reported to have about 5–10% crystallinity.

For good mechanical properties, grain boundaries must be eliminated, and the microparticles must be altered and compacted together. After

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**Figure 1** Typical fusion curve of a rigid PVC compound melted in a Haake torque rheometer at a temperature of 190°C, a rotor speed of 60 rpm, and a processing time of 3 min.

significant interdiffusion, the boundaries of sub-microparticles disappear, and a melt state of the polymer is formed. This is called the *fusion*, or *gelation*, of PVC.<sup>2,3</sup> Normally, the fusion mechanism of PVC particles, processed in either an extruder or a batch mixer, is a combination of these three patterns. Optimum values of impact ductility and modulus occur prior to 100% fusion. Benjamin<sup>4</sup> suggested that although the strength of the material increases monotonically with an increase in the degree of fusion, the material reaches optimum ductility and then becomes increasingly brittle because of the higher entanglement of the three-dimensional network.

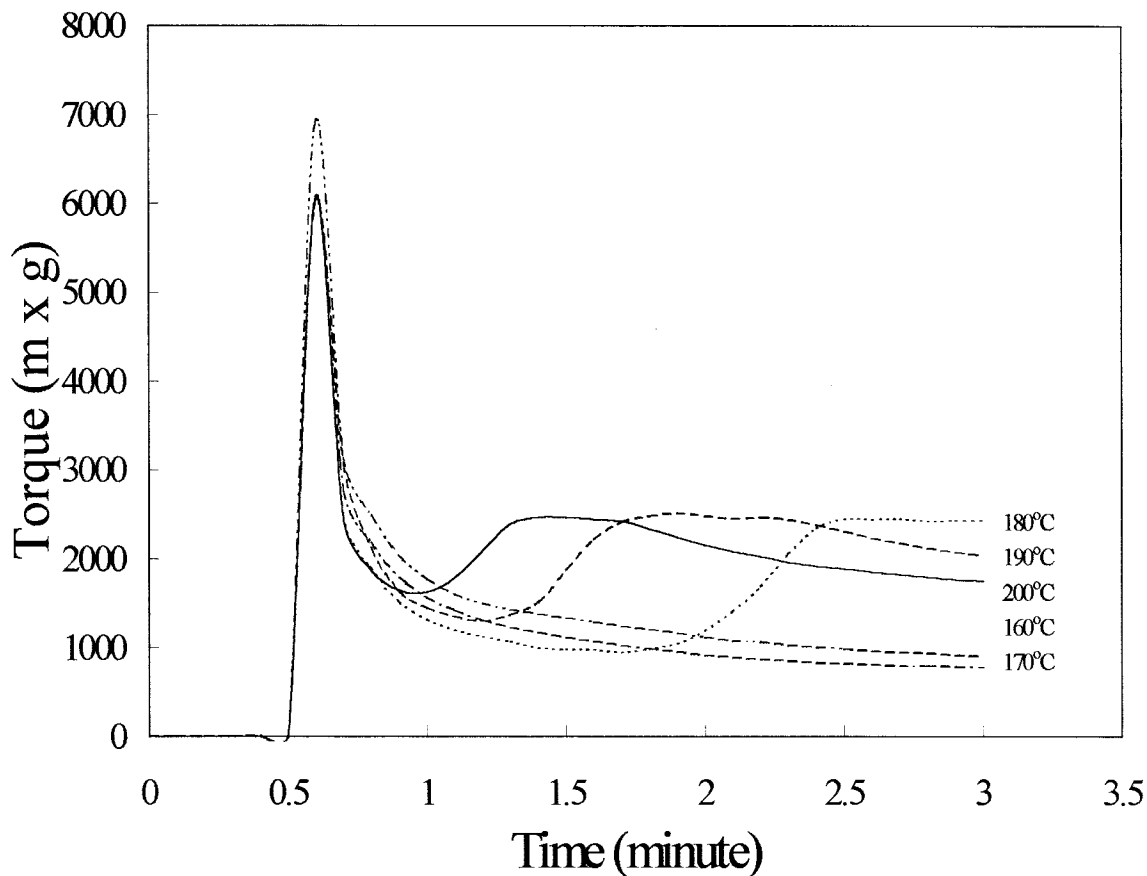
In our previous studies,<sup>5-9</sup> the morphological characteristics and fusion mechanism of rigid PVC compounds were investigated. The influences of additives on the fusion of rigid PVC compounds were also illustrated. In this article, an interesting observation, called the *fusion percolation threshold* (FPT), is defined and discussed. The fusion of rigid PVC compounds prepared in a Haake torque rheometer equipped with a three-sectioned mixing chamber and two noninterchangeable rotors at various temperatures is illustrated. Also, the influences of chlorinated poly-

ethylene (CPE) and oxidized polyethylene (OPE) on the fusion of rigid PVC compounds are discussed.

## EXPERIMENTAL

The materials used in this study were suspension PVC masterbatch powders without any plasticizers, with 100 parts of PVC resin particle [weight-average molecular weight ( $M_w$ ) = 150,000], 1.5 parts of processing aid (K120N), 1.0 part of wax (XL165), 1.0 part of calcium stearate, and 1.5 parts of heat stabilizer (T-137). All PVC compounds were prepared in a Haake torque rheometer (Rheocord 90) equipped with an electrically heated mixing head and two noninterchangeable rotors. These PVC compounds were prepared at various processing temperatures (160, 170, 180, 190, and 200°C) and removed when the processing time reached 3 min.

The suspension PVC masterbatch powders were blended with various phr's (per hundred resin) of CPE (impact modifier  $M_w$  = 160,000 with 36% chlorine): 5, 10, and 15. The processing tem-



**Figure 2** Fusion curves of rigid PVC compounds melted in a Haake torque rheometer at a rotor speed of 60 rpm, a processing time of 3 min, and various temperatures (160, 170, 180, 190, and 200°C).

perature, rotor speed, and processing time were set at 190°C, 60 rpm, and 3 min, respectively.

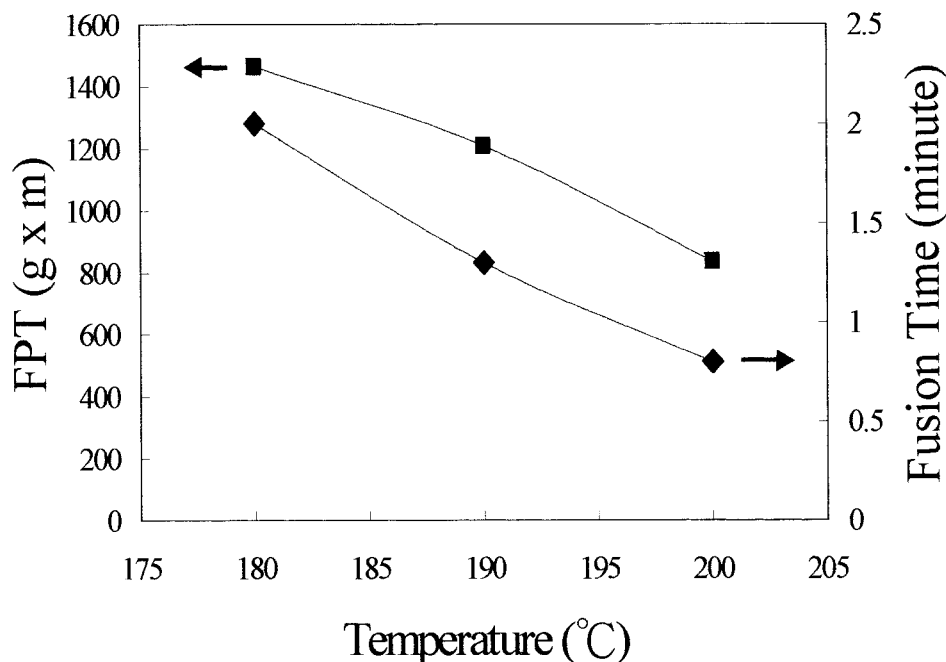
The suspension PVC masterbatch powders were blended with various phr's of OPE ( $M_w \approx 3000$ ): 0.5, 1.0, and 1.5. The processing temperature, rotor speed, and processing time were set at 190°C, 60 rpm, and 3 min, respectively.

The suspension PVC masterbatch powders were blended with 5 phr's of CPE and 0.5, 1.0, and 1.5 phr's of OPE. The processing temperature, rotor speed, and totalized torque were set at 190°C, 60 rpm, and 10 kg m min, respectively. All PVC samples were supplied by Dow Chemical Co., Louisiana, USA.

## RESULTS AND DISCUSSION

Figure 1 shows a typical fusion curve for a PVC compound when it was melted in a Haake torque rheometer at a starting temperature of 190°C and

a rotor speed of 60 rpm and was removed when a processing time of 3 min was reached. This curve illustrates the changes of viscosity related to torque, temperature, and totalized torque versus time. The viscosity-related torque curve shows three different points. The first point, *L*, in the torque curve was caused by loading. The second point, *B*, was caused by free material flow. The third point, *F*, was caused by compaction and the onset of fusion. When the PVC compound was loaded into the system, the first point was generated. Then, the torque began to decrease sharply, and this generated the second point because of free material flow before it began to compact. After that, the torque began to increase, and this generated the third point. At this point, *F*, the material reached a void-free state and started to melt at the interface between the compacted material and the hot metal surface. When the sample was melted and fused for a long time in the mixer, the temperature increased slightly because of

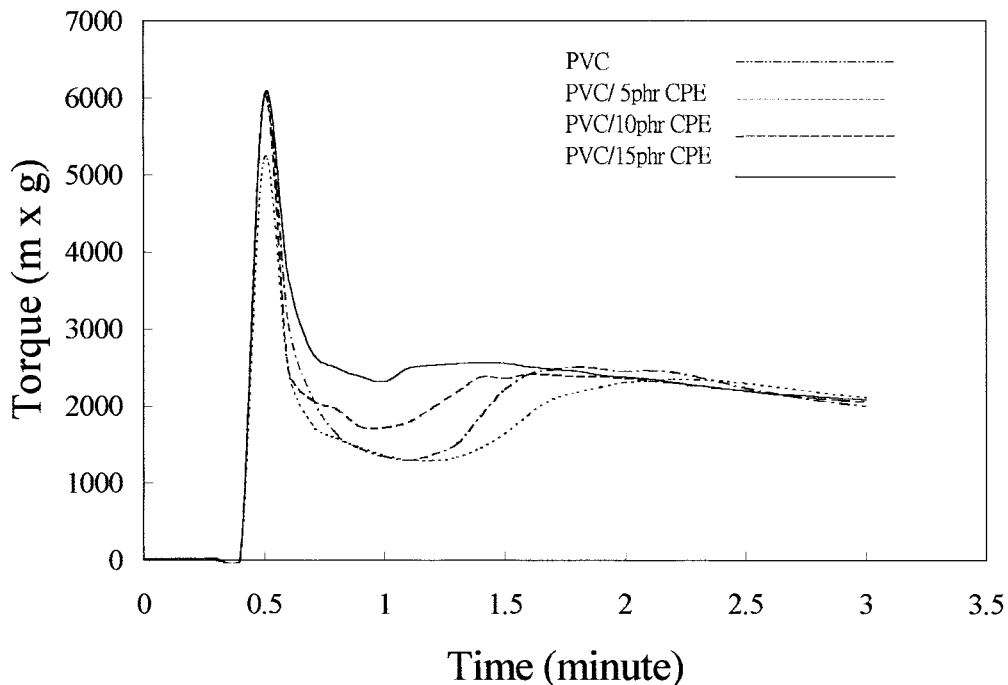


**Figure 3** Changes in the FPT and fusion time for PVC compounds varying with the blending temperature.

more thermal energy absorbed by this sample. The higher temperature resulted in a decrease in the melt viscosity of the sample; therefore, the torque decreased as time slowly increased. Usually, the time between  $L$  and  $F$  is defined as fusion time. The processing time is defined as the time between  $L$  and the stopping point.<sup>10</sup> In this study, the torque difference between  $B$  and  $F$  was defined as the FPT of this PVC sample. This is not only an interesting observation but also a new definition in the PVC fusion mechanism.

Figure 2 shows the influence of various temperatures on the fusion curves of rigid PVC compounds. Figure 3 illustrates the changes in the FPT and the fusion time of PVC compounds varying with the processing temperature. Figure 3 shows that a higher processing temperature resulted in a lower FPT. Moreover, the fusion time decreased as the FPT decreased. This is because the higher processing temperature provided a higher thermal energy to PVC compounds and let PVC compounds more easily reach the FPT. At low processing temperatures, 160 and 170°C, PVC compounds were not fused. This is because a lower processing temperature resulted in lower thermal energy. If the thermal energy was not high enough to pass the FPT, PVC compounds could not be fused.

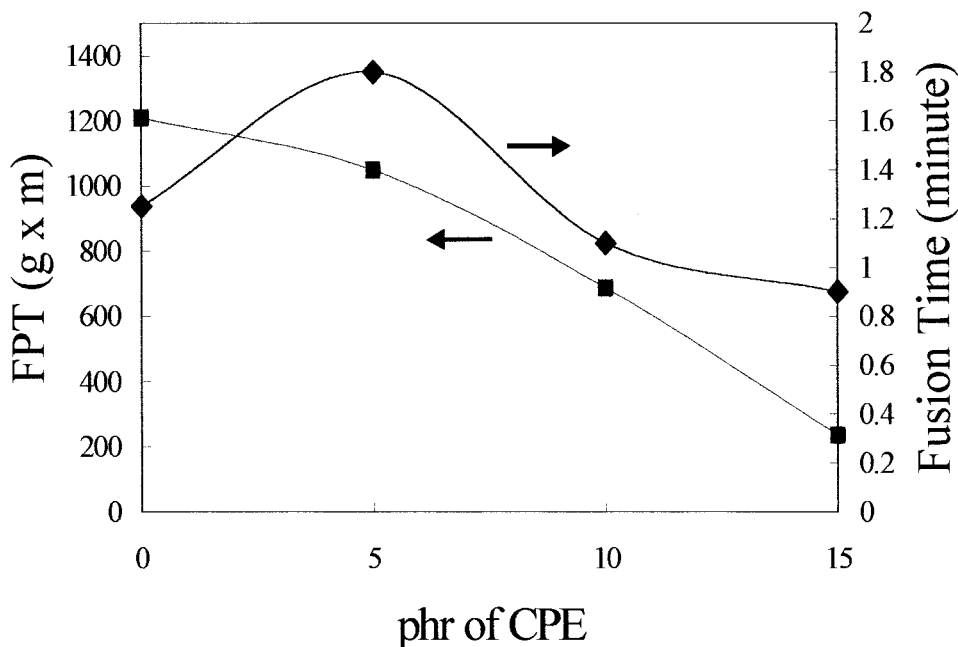
Figure 4 shows the influence of various concentrations of CPE on the fusion curves of rigid PVC/CPE compounds. Figure 5 shows the changes in the FPT and fusion time of PVC/CPE compounds varying with the phr of CPE. Figure 5 shows that the FPT of PVC/CPE compounds decreased as the phr of CPE increased. Although the FPT of the PVC/5-phr CPE compound was lower than that of the PVC compound, the fusion time of the PVC/5phr CPE compound was longer than that of the PVC compound. This was because a lower phr of CPE (5 phr) might have functioned as an external lubricant that decreased the gummy property of calcium stearate and formed a mobile layer among PVC particles. Therefore, it delayed the fusion time. However, if the phr of CPE in PVC/CPE compounds was increased, sufficient CPE ( $\geq 10$  phr) melt could act as a processing aid that promoted the fusion process, increased the transfer of heat and shear throughout the PVC grains, and decreased the FPT of PVC/CPE compounds. This processing aid also promoted friction in the system and allowed the fusion process to occur more quickly and uniformly.<sup>9</sup> The higher concentration of CPE could function as a processing aid and promote PVC particles to fuse together easily.



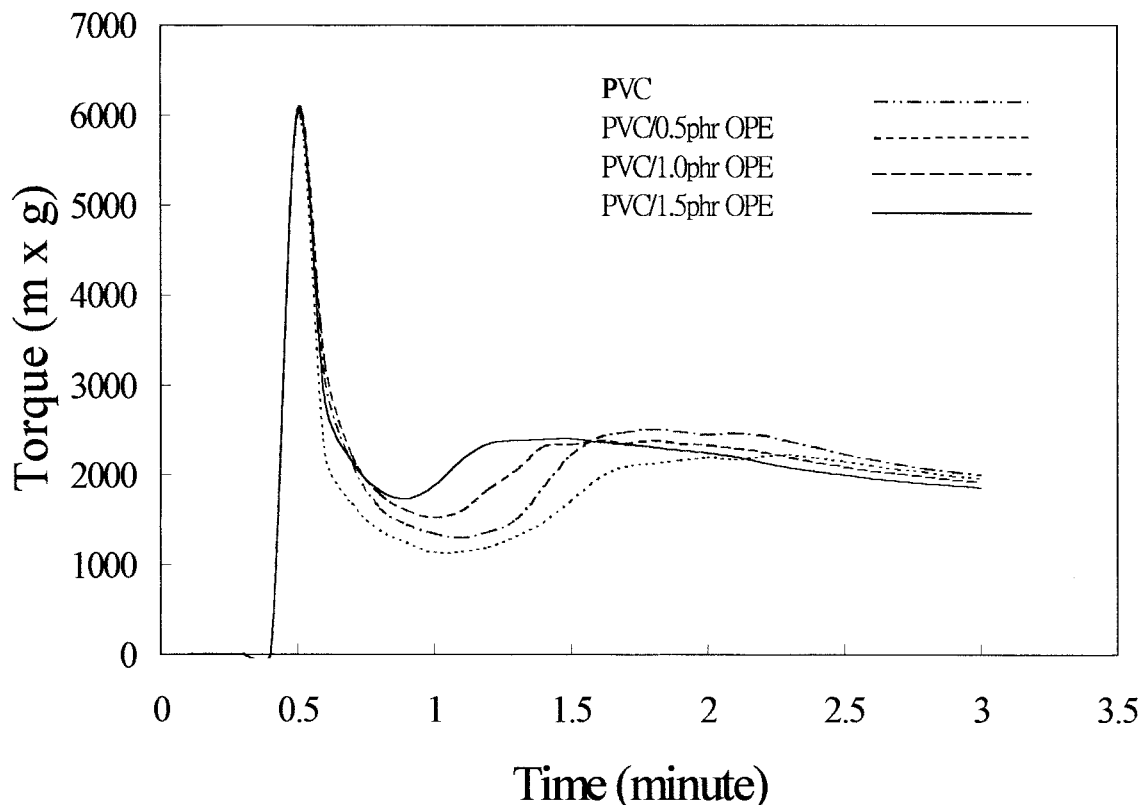
**Figure 4** Fusion curves of rigid PVC/CPE compounds with various phr's of CPE (0, 5, 10, and 15) melted in a Haake torque rheometer at a rotor speed of 60 rpm, a processing time of 3 min, and a temperature of 190°C.

Figure 6 shows the influences of various concentrations of OPE on the fusion curves of rigid PVC/OPE compounds. Figure 7 illustrates the

changes in the FPT and fusion time of PVC/OPE compounds varying with the phr of OPE. Figure 7 shows that the FPT of PVC/OPE compounds de-



**Figure 5** Changes in the FPT and fusion time of PVC/CPE compounds varying with the phr of CPE.



**Figure 6** Fusion curves of rigid PVC/OPE compounds with phr's of OPE (0, 0.5, 1.0, and 1.5) melted in a Haake torque rheometer at a rotor speed of 60 rpm, a processing time of 3 min, and a temperature of 190°C.

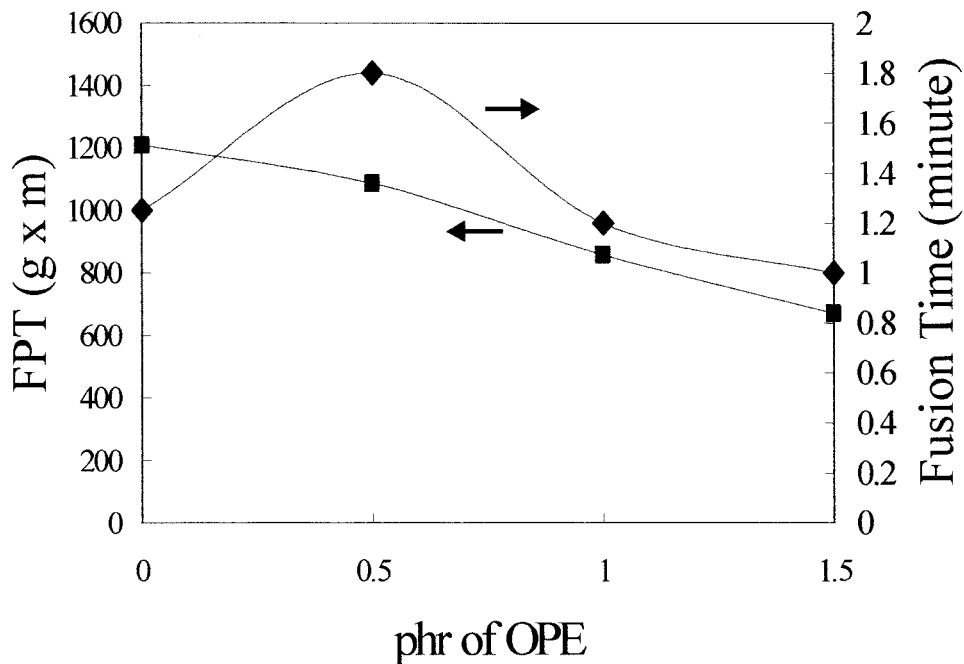
creased as the phr of OPE increased. Although the FPT of the PVC/0.5-phr OPE compound was lower than that of the PVC compound, the fusion time of the PVC/0.5-phr OPE compound was longer than that of the PVC compound. This was because a lower phr of OPE (< 1.0 phr) may have functioned as an external lubricant and resulted in a mobile layer that increased the separation and slipping among PVC particles and, therefore, delayed the fusion times.<sup>8</sup> When the phr of OPE in PVC/OPE compounds was increased, the synergistic reaction between OPE and calcium stearate may have functioned as a processing aid that could decrease the FPT and allow the PVC grain particles to fuse together quickly.<sup>11</sup> The interaction between a higher concentration of OPE and calcium stearate in PVC/OPE compounds could also promote the easy fusion of the PVC particles in the beginning of the fusion process.

Figure 8 shows the influences of various concentrations of OPE on the fusion curves of rigid PVC/CPE/OPE compounds. Figure 9 shows the changes in the FPT and fusion time of rigid PVC/5-phr CPE/OPE compounds varying with the phr

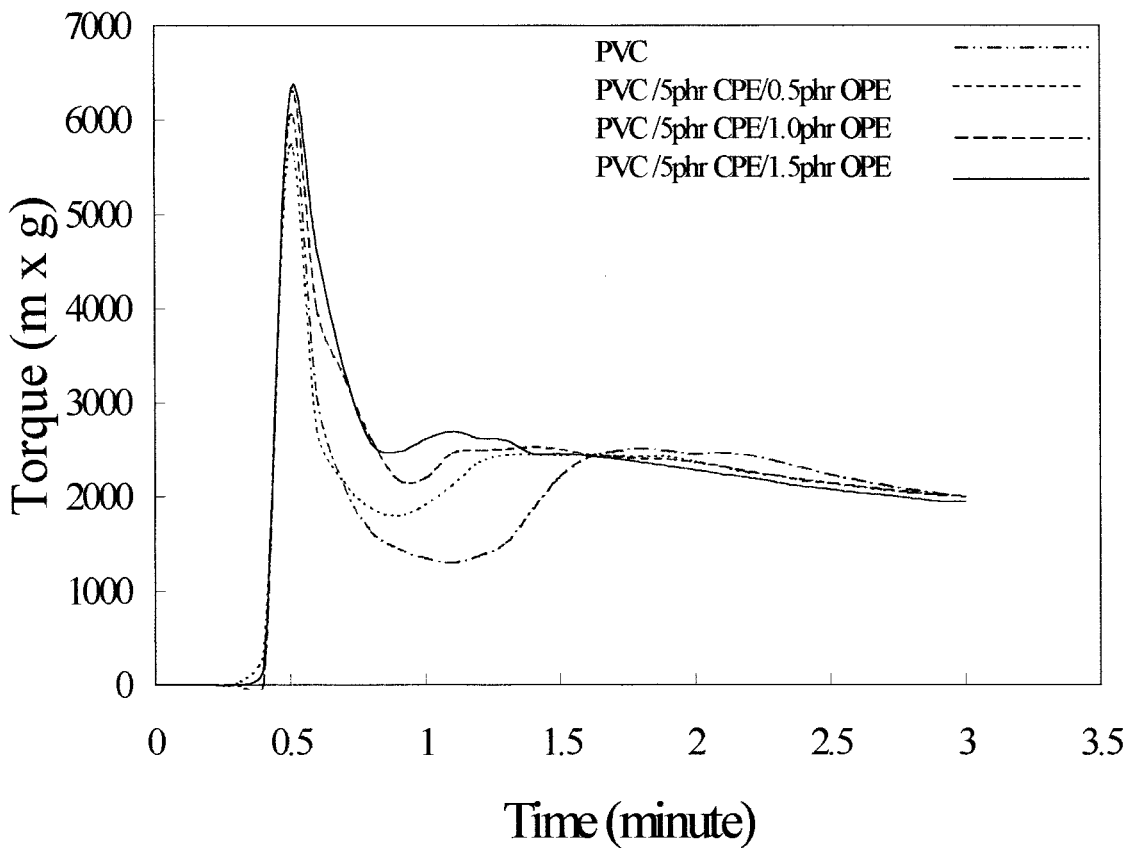
of OPE. Figure 9 shows that the FPT of PVC/5-phr CPE/OPE compounds decreased as the phr of OPE increased. Not only was the FPT of the PVC/5-phr CPE compound lower than that of the PVC compound, but the fusion time of the PVC/5-phr CPE compound was also shorter than that of the PVC compound. For PVC/5-phr CPE/OPE compounds, a higher phr of OPE may have resulted 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 could easily break down the boundaries of PVC grains, increase the friction, decrease the FPT of this compound, and improve the fusion process to occur in a shorter time and more uniformly. Chen et al.<sup>8</sup> postulated a fusion mechanism to explain this synergistic reaction. The synergistic interaction among CPE, OPE, and calcium stearate resulted in the shortest fusion time.<sup>9</sup>

## CONCLUSIONS

A novel definition, FPT, has been illustrated. Generally speaking, the fusion times of PVC,

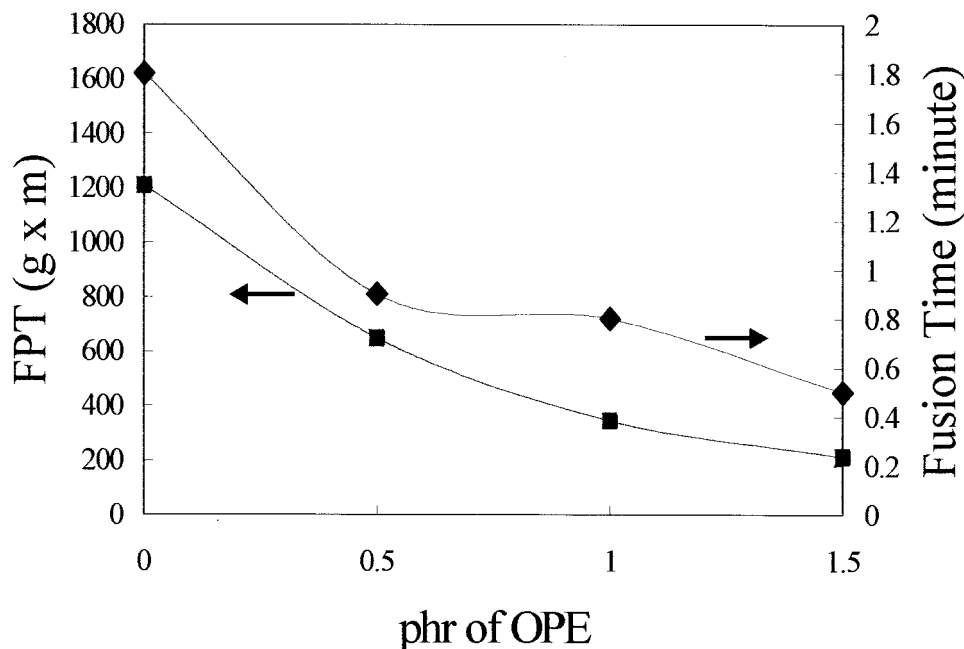


**Figure 7** Changes in the FPT and fusion time of PVC/OPE compounds varying with the phr of OPE.



**Figure 8** Fusion curves of rigid PVC/5-phr CPE/OPE compounds with phr's of OPE (0, 0.5, 1.0, and 1.5) melted in a Haake torque rheometer at a rotor speed of 60 rpm, a processing time of 3 min, and a temperature of 190°C.





**Figure 9** Changes in the FPT and fusion time of PVC/5-phr CPE/OPE compounds varying with the phr of OPE.

PVC/CPE, PVC/OPE, and PVC/5-phr CPE/OPE compounds decreased as the FPT decreased. The FPTs of rigid PVC samples were strongly dependent on not only the processing conditions but also on the formulations of these samples. Higher processing temperatures resulted in not only lower FPTs but also shorter fusion times. For PVC/CPE compounds, a higher concentration of CPE could promote the easy fusion of PVC particles. Also, the FPT of PVC/CPE compounds decreased as the phr of CPE increased. In this study, we found that the interaction between a higher concentration of OPE and calcium stearate in PVC/OPE compounds could also promote the easy fusion of PVC particles in the beginning of the fusion process. Also, the FPT of PVC/OPE compounds decreased as the phr of OPE increased. For PVC/5-phr CPE/OPE compounds, the synergistic interaction among CPE, OPE, and calcium stearate resulted in the shortest fusion time. Meanwhile, the FPT of PVC/5-phr CPE/OPE compounds decreased significantly as the phr of OPE increased.

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