Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. IV. Fusion Characteristics and Morphology Analyses

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SYNOPSIS

Poly(vinyl chloride) (PVC), PVC/chlorinated polyethylene (CPE), PVC/oxidized polyethylene (OPE), and PVC/CPE/OPE compounds were prepared in a Haake torque rheometer at various temperatures, rotor speeds, and totalized torques (TTQ). The fusion characteristics of these PVC compounds (fusion time, fusion torque, and fusion temperature) were studied. Longer fusion time results in higher fusion temperature. Higher fusion temperature results in lower fusion torque. The fusion time of PVC/OPE compounds is the longest among these PVC blends. However, the fusion time of PVC/CPE/OPE compounds is the shortest among these PVC blends. The fusion time of the PVC/CPE/OPE compound is significantly different from those of PVC, PVC/OPE, and PVC/CPE compounds at the medium starting temperature and the medium rotor speed. Scanning electron microscopy (SEM) analyses successfully revealed the surface morphological changes of the fusion of PVC, PVC/OPE, PVC/CPE, and PVC/CPE/OPE compounds. The lubrication mechanisms of these PVC compounds have also been postulated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) was first found and characterized more than 120 years ago, but, due to its poor thermal stability, making processing difficult, it was not until about 1930 that people began producing commercial PVC products.[1] To overcome its poor thermal stability and photochemical degradation, researchers developed suitable stabilizer systems,[2] heat stabilizers (e.g., lead compounds, organotin compounds, and other metal compounds), and light stabilizers (e.g., phenyl salicylate, oxalic anilide, and phenyl formamidine) to solve these problems and PVC is now one of the world's highest-volume synthetic polymers.

Chlorinated polyethylene (CPE) is commonly used as an impact modifier of PVC. The CPE used as impact modifiers in PVC are produced by chlorinating high-density polyethylene in aqueous slurry.[3] The chlorine distribution and chlorine 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. Due to 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.[4] In this study, the CPE (MW ≈ 160,000) with 36% chlorine was used.

Oxidized polyethylene (OPE) and calcium stearate are two important lubricants used in PVC processing. Oxidation reactions of polyethylenes occur at their molecular chain ends, at points of branching, or at infrequent sites of unsaturation. This oxidation creates polarity and compatibility with PVC at the point of oxidation. A typical OPE lubricant for PVC processing might be of medium density (MW 2000–4000) and slightly oxidized (acid number 6–20). In this study, an OPE with an acid number 6–8 was used; acid number is the number of carboxylic group per molecule. Carboxylic groups cause OPE to be polar. The melting temperature of OPE ranges from 100 to 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

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with C_{18} in the R—C linkage is the most popular lubrication 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 lubricants and external lubricants. Internal lubricants lower the intermolecular friction of PVC when the PVC composition is being hot-sheared 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 the fusion time or have very little effect on it. In actual applications, however, lubricants do not always abide by the rules, and some exceptions have been found and studied.

Several reports discussing the functions of lubricants for the processing of PVC blends are available.[5-13] Lindner[14] reported that the interaction between OPE and calcium stearate can be used to speed the fusion time of PVC blends significantly. Lubrication is the most important factor in influencing the fusion of PVC during processing, which, in turn, may determine the physical properties of final PVC products. In this research, we studied the influence of two lubricants, calcium stearate and OPE, on the fusion characteristics (fusion time, fusion temperature, and fusion torque) of PVC blends. Also, the surface morphological changes of these PVC blends were examined by SEM.

EXPERIMENTAL

Preparation of PVC Compounds

The materials used in this study are suspension PVC masterbatch powder, containing 100 parts PVC resin (MW $\approx$ 150,000), 1.5 parts process aid (acryloid, K120N), 1.0 part wax (intermediate lubricant, XL165), 1.0 part calcium stearate, and 1.5 parts heat stabilizer (tin thioglycolate, T-137). The other three samples are PVC masterbatch powder with 0.3 parts OPE, PVC masterbatch powder with 5 parts CPE, and PVC masterbatch powder with 0.3 parts OPE and 5 parts CPE. All samples were supplied by the Dow Chemical Co.

All PVC samples were prepared in a Haake torque rheometer, equipped with a three-sectioned mixing chamber and two non-interchangeable roller mixing rotors. The starting temperature, rotor speed, and totalized torque were chosen as the blending vari-

ables. Three levels, high, medium, and low, were also defined for each blending variable to enable statistical analysis of their effect. For starting temperatures, 190, 175, and 160°C were chosen as the high, medium, and low levels, respectively. For rotor speeds, 100, 60, and 20 rpm were chosen as the high, medium, and low levels, respectively. For totalized torques, 15, 8, and 1 kg-m-min were chosen as the high, medium, and low levels, respectively. The sample weight was 65 g for all runs. PVC samples were charged into the mixer at various starting temperatures and rotor speeds and removed when the predetermined totalized torque value was reached in the Haake torque rheometer.

The fusion characteristics—fusion time, fusion temperature, and fusion torque—were summarized and compared for different PVC blends prepared at high- and medium-level blending conditions. The low blending exclusion is discussed below. Also, the surface morphological differences were examined and compared for different PVC blends, especially those which were prepared at low totalized torque (1 kg-m-min) and low temperature (160°C).

SEM Analysis

PVC samples which were not well fused in the Haake torque rheometer were cut randomly, coated with 200 Å gold–palladium film, and examined on the Cambridge S-260 SEM. Well-fused PVC samples were immersed into liquid nitrogen for 45 s, fractured, coated with 200 Å gold–palladium film, and examined on a Cambridge S-260 SEM at the center of the fractured surfaces.

RESULTS AND DISCUSSION

Haake Torque Rheometer

Figure 1 shows fusion curves for the PVC/5 phr CPE melted in the Haake torque rheometer at a starting temperature of 190°C, a rotor speed of 60 rpm, and discharged when a 10 kg-m-min totalized torque was reached. These curves illustrate the changes of viscosity related to torque, temperature, and totalized torque vs. time. The viscosity-related torque curve shows two different peaks. The first peak, L, in the torque curve is due to loading, and the second peak, F, is due to compaction and onset of melting. 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; the torque then
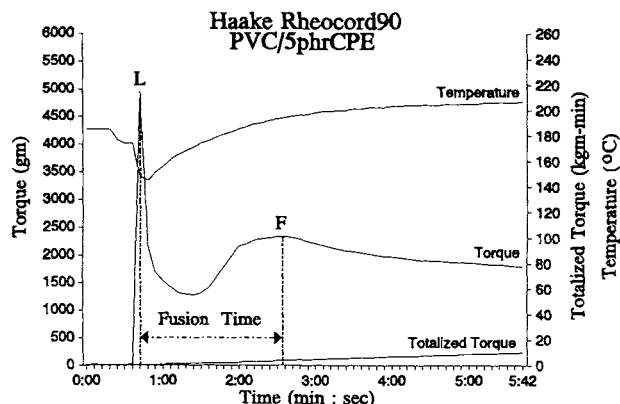
Figure 1 A typical temperature/torque/totalized torque curves of PVC/5 phr CPE blended in a Haake torque rheometer (starting temperature = 190°C, rotor speed = 60 rpm, TTQ = 10 kg-m-min).

begins to increase and generates the second peak. At this peak, F, the material reaches an effectively void-free state and starts to melt at the interface between the compacted material and the hot metal surface.[13] The temperature and torque with respect to this point, F, are defined as fusion temperature and fusion torque, respectively. Normally, the time between the loading point L and the fusion point F is defined as fusion time.

Fusion Characteristics and Lubrication Mechanisms

The fusion characteristics of PVC blends which were prepared at a low starting temperature or a low rotor speed are not discussed in this report, because of no apparent fusion peaks. They were included for other studies discussed in previous work.[15] Tables I–IV show the fusion characteristics of PVC blends which were prepared at high or medium starting temperatures and high or medium rotor speeds.

Rabinovitch et al.[11] studied the lubrication mechanism by considering haze, glass transition temperature, metal release, morphology, fusion, and extrusion characteristics of rigid PVC compounds. The effect of calcium stearate, paraffin wax, and

their synergistic combined lubricity was evolved, as shown in Figure 2. Figure 2 illustrates a model of PVC lubrication without CPE and OPE showing metal lubrication and lubrication between PVC microparticle flow units. The following discussion was also demonstrated by Rabinovitch et al.

Due to C — Cl groups in PVC polymer chains, PVC polymer chains are somewhat polar molecules. Because of this polarity, molten PVC is also attracted and sticks to the polar metal surface of processing equipment [Fig. 2(a)].

As mentioned before, calcium stearate is a salt containing a highly polar CaOOC group and a long, nonpolar hydrocarbon chain [(CH$_2$)$_{16}$CH$_3$]. If calcium stearate is added to PVC, the polar ends of its molecules adhere not only to the polar PVC but also to the polar metal surface, leaving the nonpolar tails to do the lubrication or, in other words, displacing the PVC melt from the metal surface, preventing it from sticking and providing limited slip between the metal and PVC melt surfaces. The polar groups in calcium stearate are also strongly attracted to each other and form a viscous layered structure which is very similar to a liquid crystal [Fig. 2(b)]. The OPE with acid number 6–8, which was used in this study, is polar also. Therefore, in the presence of only OPE, the carboxylic groups of OPE will attach to a metal surface, to the surface of a PVC particle, and to each other.

Because paraffin wax is a nonpolar, straight-chain hydrocarbon with a lower surface energy than that of PVC, it does not preferentially wet the metal surface and does not displace the more polar PVC microparticles. Therefore, in the presence of only paraffin wax, PVC sticks to the metal surface [Fig. 2(c)]. If the higher surface energy calcium stearate and paraffin wax are used together, interaction between the tails of adjacent calcium stearate molecules is hindered by the intervening presence of mobile nonpolar alkane paraffin wax molecules. These wax molecules are not attracted to the polar groups of calcium stearate, to PVC, or to the metal surface, but are weakly attracted to themselves and the nonpolar hydrocarbon tail of calcium stearate molecules

Table I   Fusion Characteristics of PVC Blends at Temperature = 190°C, Rotor Speed = 100 rpm

	PVC	PVC/OPE	PVC/CPE	PVC/CPE/OPE
Fusion temp (°C)	189.0	198.0	193.5	189.0
Fusion time (min)	0.80	1.30	1.05	0.70
Fusion torque (g m)	2946	2468	2645	2724

Table II Fusion Characteristics of PVC Blends at Temperature = 190°C,
Rotor Speed = 60 rpm

	PVC	PVC/OPE	PVC/CPE	PVC/CPE/OPE
Fusion temp (°C)	188.0	196.0	193.0	188.0
Fusion time (min)	1.25	2.30	1.80	1.20
Fusion torque (g m)	2701	2116	2339	2466

[Fig. 2(d)]. This mechanism demonstrates the formation of a mobile low-viscosity layer which increases the separation between the thin calcium stearate films on the metal surface and on the PVC melt surface. It also provides a more mobile interface between the calcium stearate molecules adhered to adjacent PVC microparticles due to the synergistic lubrication effect of the calcium stearate/paraffin wax system. Because a high starting temperature or a high rotor speed enhances the gummy property of calcium stearate,[5] the mobile layer has very little influence on delaying the fusion time. The fusion times of PVC compounds are very close to those of PVC/CPE/OPE compounds in Tables I–III. In this case, calcium stearate functions as a process aid. However, at a medium starting temperature and rotor speed, the calcium stearate is able to develop a more ordered structure and a mobile layer is formed [Fig. 2(d)]. This mobile layer results in a longer fusion time (Table IV) since less mechanical energy is converted to thermal energy.

If the fusion time of a PVC compound without OPE and CPE is considered as the normal fusion time, 0.3 phr OPE and 5 phr CPE delay the fusion time of PVC/OPE and PVC/CPE compounds, respectively. These tables illustrate that the fusion time of the PVC/OPE compound is the longest among these four PVC blends. Moreover, no fusion occurred when the medium starting temperature and high or low rotor speed were used. This may be due to a mobile layer, resulting from the synergistic combined lubricity between OPE and calcium stearate, which increases the separation and slipping among PVC particles [Fig. 3(e)]. At the high start-

ing temperature (190°C), this mobile layer can be destroyed, then PVC particles fuse together, but the fusion time is delayed already. At the medium starting temperature (175°C) and high (100 rpm) or medium (60 rpm) rotor speed, this mobile layer still exists; therefore, no fusion occurs.

These tables also illustrate that 5 phr CPE delays the fusion time of PVC/CPE compounds. This may be due to two factors: The first factor may be the less compatibility between the PVC resin and the CPE particles, and the second may be that the CPE particles may decrease the gummy property of calcium stearate, which can hold the PVC resin particles together and allow them to fuse together easily [Fig. 4(e)]. In this case, CPE acts as an external lubricant.

However, the fusion time of PVC/CPE/OPE compounds is the shortest among these PVC blends. This may be because 0.3 phr OPE and 5 phr CPE interact and form a powerful, viscous material which appears to act as a glue that allows the PVC resin particles to fuse together easily [Fig. 5(f)]. The fusion time of the PVC/CPE/OPE compound is significantly different than those of PVC, PVC/OPE, and PVC/CPE compounds at the medium starting temperature (175°C) and the medium rotor speed (60 rpm) (Table IV).

Since the fusion time of PVC/OPE compounds is the longest, it can be reasoned that more thermal energy is needed to be absorbed by PVC/OPE compounds in order for the PVC particles to fuse together. Thus, the fusion temperatures of PVC/OPE compounds are the highest (Tables I and II). Because a higher fusion temperature results in decreasing

Table III Fusion Characteristics of PVC Blends at Temperature = 175°C,
Rotor Speed = 100 rpm

	PVC	PVC/OPE	PVC/CPE	PVC/CPE/OPE
Fusion temp (°C)	186.5	NF[a]	192.5	187.5
Fusion time (min)	1.15	—	2.25	1.10
Fusion torque (g m)	3075	—	2768	2916

[a] No fusion.

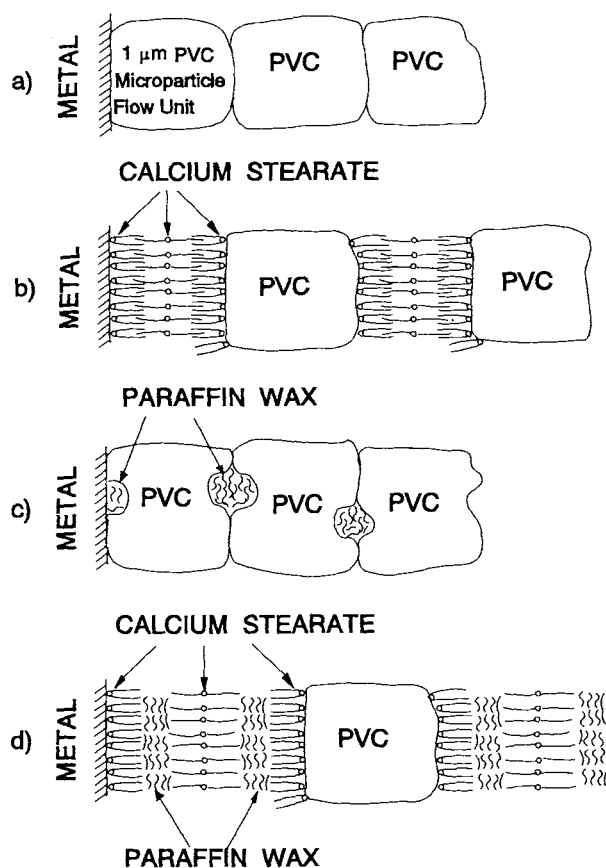**Table IV Fusion Characteristics of PVC Blends at Temperature = 175°C, Rotor Speed = 60 rpm**

	PVC	PVC/OPE	PVC/CPE	PVC/CPE/OPE
Fusion temp (°C)	186.5	NF[a]	189.0	185.0
Fusion time (min)	3.10	—	3.45	2.05
Fusion torque (g m)	2563	—	2547	2666

[a] No fusion.

the melt viscosity of samples in the Haake torque rheometer, the fusion torques of PVC/OPE compounds are the lowest (see Tables I and II). Applying the same reasoning used above, an explanation is provided for the fact that the fusion temperatures of PVC/CPE compounds are the highest and the fusion torques of these compounds are the lowest in Tables III and IV.

SEM Analysis

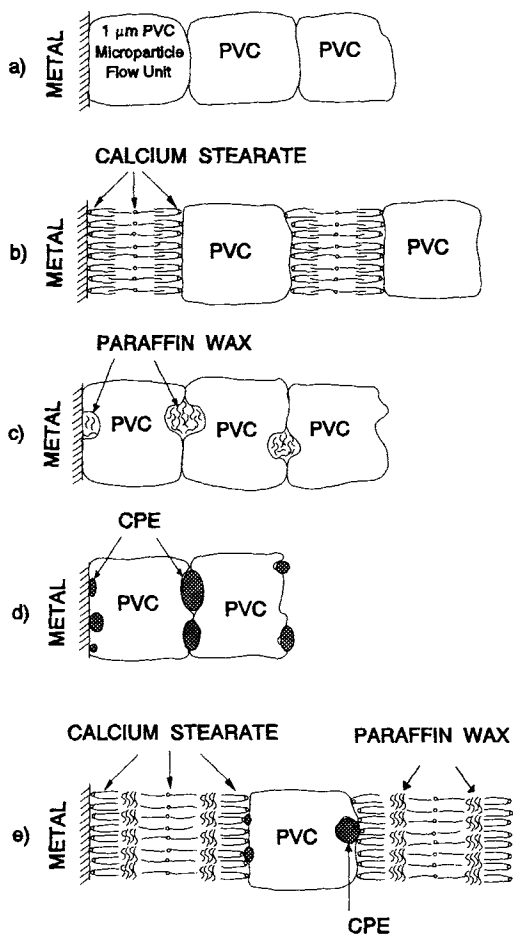Figure 6(a)–(d) shows the surface morphology of PVC, PVC/OPE, PVC/CPE, and PVC/CPE/OPE

compounds which were prepared in the Haake torque rheometer at temperature = 190°C, rotor speed = 60 rpm, and TTQ = 1 kg-m-min, respectively. There is not much difference between Figure 6(a) and (d). Figure 6(b) and (c), however, illustrate that more PVC resin particles remain intact. This phenomenon results in delaying the fusion times of PVC/OPE and PVC/CPE compounds (Table II). Similar morphological results were obtained for PVC blends which were prepared in the Haake torque

Figure 2 A model of PVC lubrication showing metal lubrication and lubrication between PVC microparticle flow units.
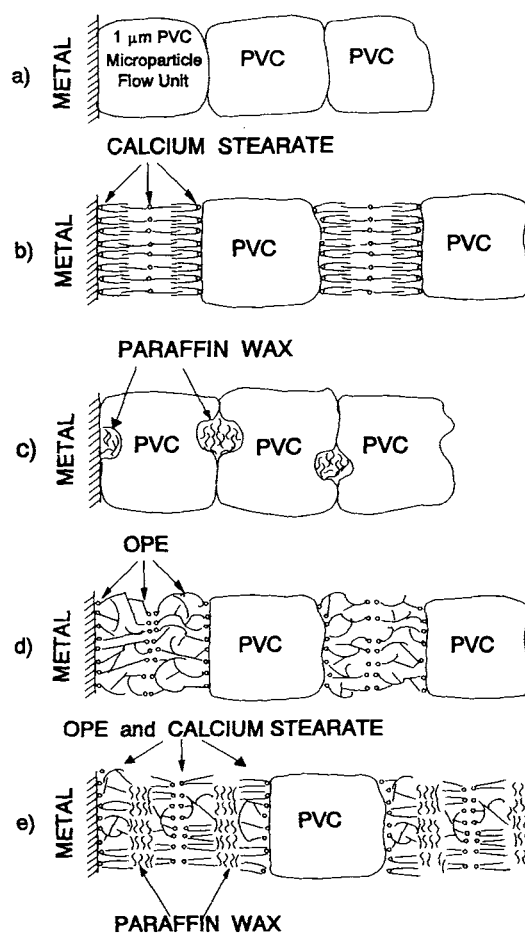
Figure 3 A postulated lubrication mechanism, showing metal lubrication and lubrication between PVC microparticle flow units, of PVC/OPE compounds.

Figure 4 A postulated lubrication mechanism, showing metal lubrication and lubrication between PVC microparticle flow units, of PVC/CPE compounds.

rheometer at temperature = 190°C, rotor speed = 100 rpm, and totalized torques (TTQ) = 1 kg-m-min or at temperature = 175°C, rotor speed = 100 rpm, and TTQ = 1 kg-m-min.

Figure 7(a) and (b) reveal the surface morphology of PVC/OPE compounds which were prepared in the Haake torque rheometer at temperature = 175°C and rotor speed = 60 rpm and 100 rpm, respectively. Even though the blending time was 15 min, no fusion occurred (Tables III and IV). This is due to the existence of one mobile layer which keeps PVC particles from fusing together.

Figure 8(a)–(d) reveal the surface morphology of PVC, PVC/OPE, PVC/CPE, and PVC/CPE/OPE compounds which were prepared in the Haake torque rheometer at temperature = 160°C, rotor speed = 20 rpm, and TTQ = 15 kg-m-min, respectively. These four figure parts illustrate the significantly different fusion phenomena among PVC, PVC/OPE, PVC/CPE, and PVC/CPE/OPE com-

pounds. In Figure 8(b) and (c), most of the PVC resin particles remain intact. In Figure 8(a), some of the PVC resin particles still remain intact. In Figure 8(d), however, the PVC resin particles were fused together and formed a 3-D network. These phenomena reveals that the interaction between CPE and OPE has a very significant influence upon fusion of PVC blends, especially those which were prepared at a low starting temperature and rotor speed. The fusion characteristics of PVC compounds are highly dependent upon their composition.

CONCLUSIONS

The concepts, similar to Rabinovitch's theory, of lubrication mechanisms of these four PVC blends have been postulated. Due to a mobile layer, resulting from the synergistic combined lubricity between
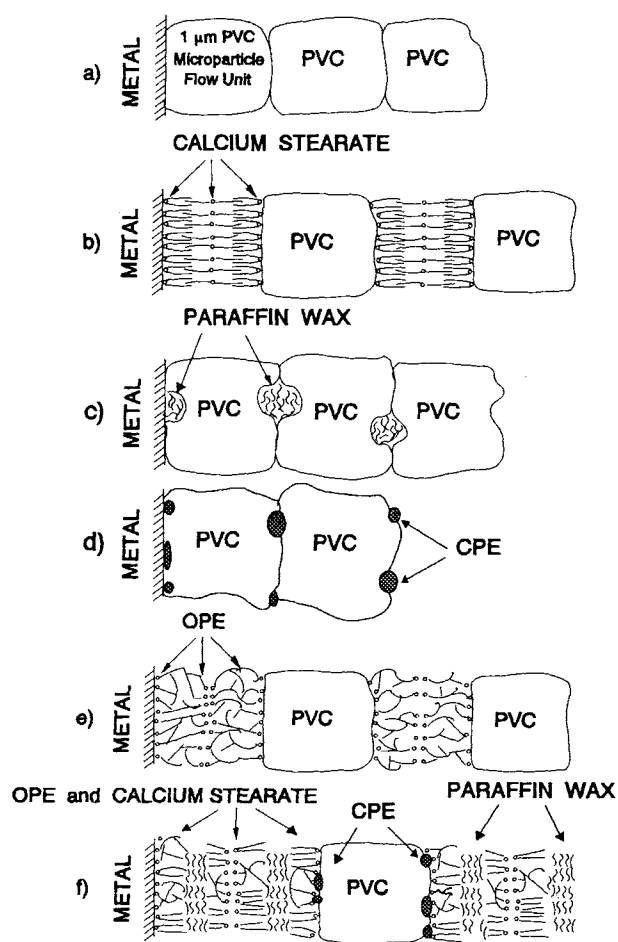
Figure 5 A postulated lubrication mechanism, showing metal lubrication and lubrication between PVC microparticle flow units, of PVC/CPE/OPE compounds.

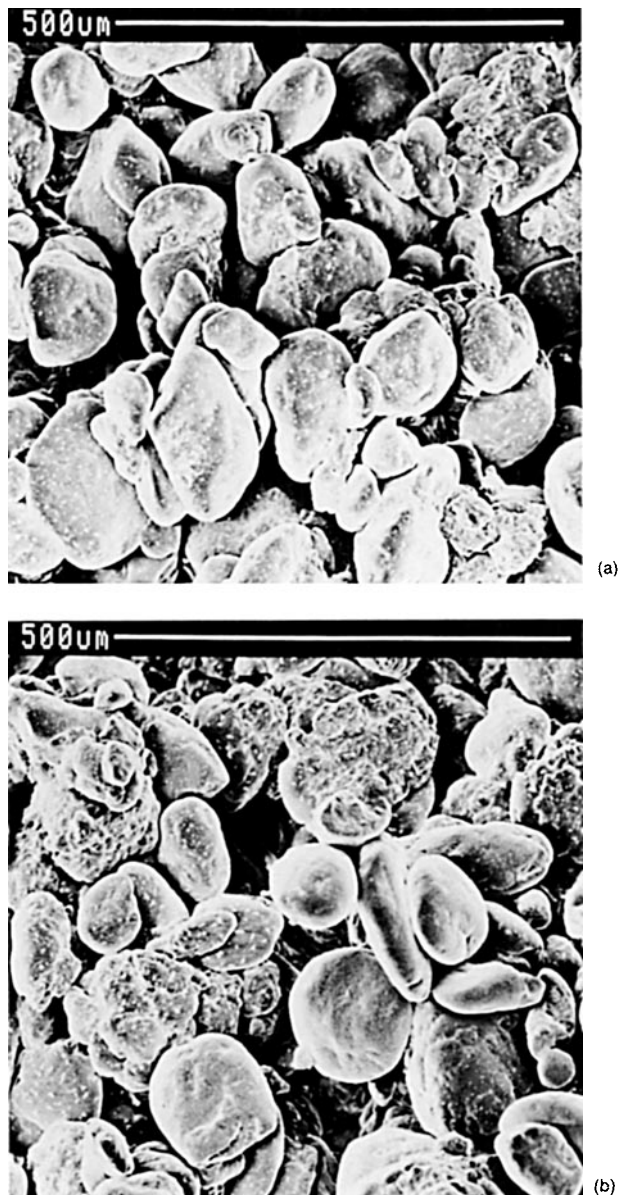However, the fusion time of PVC/CPE/OPE compounds is the shortest among these PVC blends. This may be because OPE and CPE interact and form a powerful, viscous material and appears to act as a glue, which enables the PVC particles to fuse together easily. The fusion time of the PVC/CPE/OPE compound is significantly different from those of PVC, PVC/OPE, and PVC/CPE compounds at the medium starting temperature and the medium rotor speed. Because a high starting temperature or a high rotor speed enhances the gummy property of calcium stearate,[5] the fusion times of PVC compounds are very close to those of PVC/CPE/OPE

Figure 6 (a) Surface morphology of PVC compound prepared in a Haake torque rheometer at temperature = 190°C, rotor speed = 60 rpm, and TTQ = 1 kg-m-min. (b) Surface morphology of PVC/OPE compound prepared in a Haake torque rheometer at temperature = 190°C, rotor speed = 60 rpm, and TTQ = 1 kg-m-min. (c) Surface morphology of PVC/CPE compound prepared in a Haake torque rheometer at temperature = 190°C, rotor speed = 60 rpm, and TTQ = 1 kg-m-min. (d) Surface morphology of PVC/CPE/OPE compound prepared in a Haake torque rheometer at temperature = 190°C, rotor speed = 60 rpm, and TTQ = 1 kg-m-min.

OPE and calcium stearate, which increases the separation and slipping among PVC particles, the fusion time of PVC/OPE compounds is the longest among these four PVC blends.

Figure 6 (*Continued*)

a higher fusion temperature results in decreasing the melt viscosity of samples in the Haake torque rheometer, the fusion torques of PVC/OPE compounds are the lowest. SEM analyses successfully
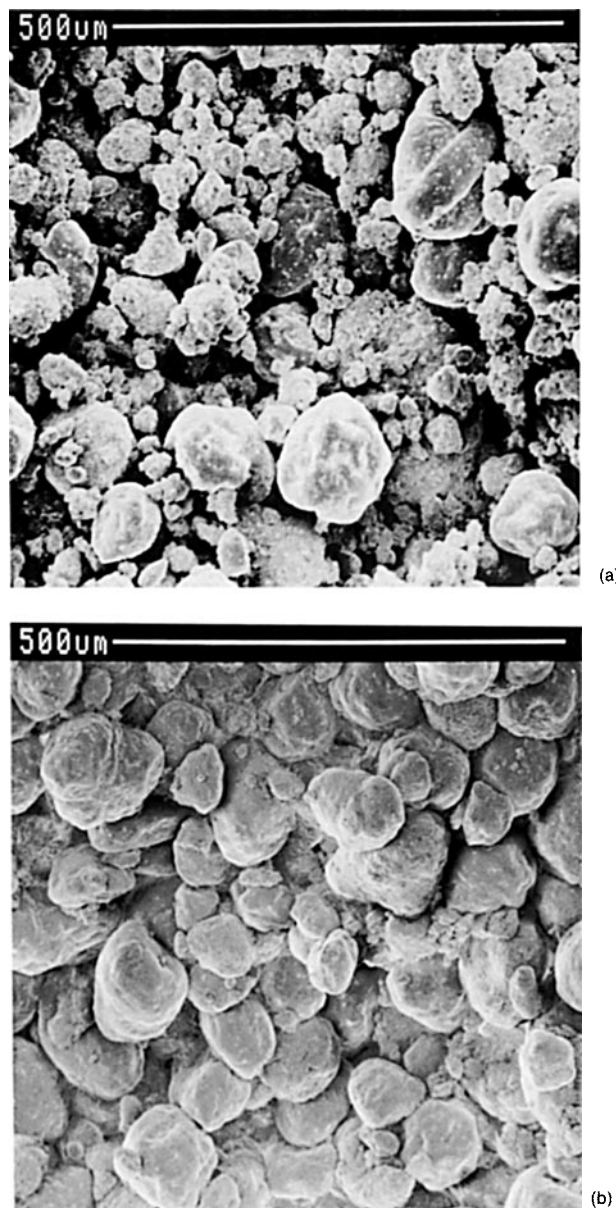

Figure 7   (a) Surface morphology of PVC/OPE compound prepared in a Haake torque rheometer at temperature = 175°C, blending time = 15 min, and rotor speed = 60 rpm. (b) Surface morphology of PVC/OPE compound prepared in a Haake torque rheometer at temperature = 175°C, blending time = 15 min, and rotor speed = 100 rpm.

compounds in Tables I–III. In this case, calcium stearate functions as a process aid.

Since the fusion time of PVC/OPE compounds is the longest, it can be concluded that more thermal or mechanical energy is needed to be absorbed by PVC/OPE compounds in order for the PVC particles to fuse together. Thus, the fusion temperatures of PVC/OPE compounds are the highest. Because
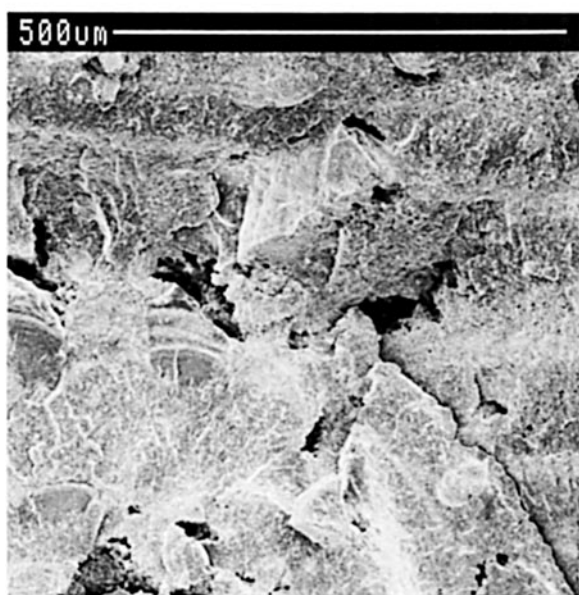
Figure 8   (a) Surface morphology of PVC compound prepared in a Haake torque rheometer at temperature = 160°C, rotor speed = 20 rpm, and TTQ = 15 kg-m-min. (b) Surface morphology of PVC/OPE compound prepared in a Haake torque rheometer at temperature = 160°C, rotor speed = 20 rpm, and TTQ = 15 kg-m-min. (c) Surface morphology of PVC/CPE compound prepared in a Haake torque rheometer at temperature = 160°C, rotor speed = 20 rpm, and TTQ = 15 kg-m-min. (d) Surface morphology of PVC/CPE/OPE compound prepared in a Haake torque rheometer at temperature = 160°C, rotor speed = 20 rpm, and TTQ = 15 kg-m-min.

(c)

(d)

Figure 8   *(Continued)*

revealed the surface morphological changes of the fusion of PVC, PVC/OPE, PVC/CPE, and PVC/CPE/OPE compounds, which were prepared at various conditions.

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