

Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. I. Morphological Characteristics of Poly(vinyl chloride)/Chlorinated Polyethylene (PVC/CPE) Blends

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SYNOPSIS

Chlorinated polyethylene (CPE) is a commonly used impact modifier of poly(vinyl chloride) (PVC). The major goal of this research was to understand the fundamental morphological aspects of PVC/CPE blends. Scanning electron microscopy (SEM) was used to image the surface structure of these blends, and both transmission electron microscopy (TEM) and scanning-transmission electron microscopy (S-TEM) were used to image the morphological boundaries of the blends. TEM imaging distinguishes the boundaries between PVC and CPE more clearly or better than does S-TEM, but it is time-consuming. However, some CPE particles are not observed in TEM because of inefficient staining. S-TEM imaging is much faster and does not depend on staining for the imaging of the CPE phase. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The morphology of an immiscible polymer blend has a significant effect on the impact behavior of the material. Based on compounding conditions, Siegmann and Hiltner¹ reported that at concentrations less than 13 wt % chlorinated polyethylene (CPE) poly(vinyl chloride) (PVC) was in the continuous phase, while the CPE was in the noncontinuous phase. The CPE particles ranged between 100 and 400 nm in size. Increasing the CPE concentration above 13 wt % reversed the phase distribution. A significant increase in impact properties was also observed for CPE levels above 13 wt %.

Several variables may effect the observed morphology and thus the effectiveness of PVC/CPE blends. The resulting blend morphology depends upon the mixing conditions used during the blending process. The molecular weight, crystallinity, chlorine content, and chlorine distribution of the CPE, as well as the ultimate CPE loading in the PVC, have a significant effect on the mixing requirements and the resulting blend morphology. To facilitate study-

ing each of these effects individually, a method should be available which illustrates the morphology of the blend.

Earlier researchers used a staining procedure and transmission electron microscopy (TEM). This method requires time-consuming chemical-staining reactions. A less time-consuming method has been developed for PVC/CPE blends. This newer method does not require sample staining and also provides contrast through the use of scanning-transmission electron microscopy (S-TEM). In this article, the results of scanning electron microscopy (SEM), TEM, and S-TEM are discussed.

EXPERIMENTAL

Preparation of PVC/CPE Blends

The materials used in this study were suspension PVC masterbatch powder (containing 5% additive and stabilizers) with or without fillers (TiO₂ and CaCO₃) and CPE (containing 36% chlorine). All samples were supplied and preblended by The Dow Chemical Co.

Three blends of PVC/CPE, 0, 10, and 20 parts per hundred resin (phr) of CPE, were prepared by

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dry mixing the components and then melt blending at 180°C until 10 kg-m-min totalized torque was reached in a Haake Rheomix 600 batch mixer with a Haake Rheocord 90 drive. The samples discharged from the Haake Rheometer were compression-molded with a ram force of 20 tons for 2 min at 200°C and cooled for 5 min at room temperature at the same pressure. These compression-molded samples were used for morphological examination.

SEM Analysis

Samples were immersed into liquid nitrogen for 45 s, fractured, and coated with 200 Å gold-palladium film. They were then examined only at the center of the fractured surfaces using a Cambridge S-260 SEM.

TEM Analysis

Specimens were prepared by the procedure of Fleischer et al.,³ as discussed below. Selective staining of the CPE phase was accomplished by a two-stage procedure involving selective dehydrochlorination of the CPE to form double bonds, followed by reaction with OsO₄.⁴

Small rectangular blocks about 0.5 by 1 by 10 mm were cut from the moldings and immersed in 1,8-diazabicyclo-(5,4,0)-undecene-7 for 2 days at 0°C, then rinsed with 2*N* HCl and stained 14 days in 1% OsO₄ aqueous solution. Ultrathin sections (approximately 80 nm) were cut from the stained blocks by an ultramicrotome, mounted on grids with carbon coating, and examined under 80 kV accelerating voltage in a JEOL 100CXII TEMSCAN.

S-TEM Analysis

Specimens were not subjected to staining or any other further chemical treatments. Small rectangular blocks about 0.5 by 1 by 10 mm were cut from the moldings. Ultrathin sections (approximately 80 nm) were cut from the rectangular blocks by an ultramicrotome, mounted on grids with carbon coating, and examined under 100 kV accelerating voltage in the JEOL 100CXII TEMSCAN. To avoid charging of the ultrathin sections in the S-TEM, it is necessary to focus on one area of the sample and then move to another area of the sample and take a picture quickly.

RESULTS AND DISCUSSION

SEM Analysis

Figure 1 (a)–(c) show the SEM images of 0, 10, and 20 phr PVC/CPE blends, respectively. No CPE particles were found in the SEM micrographs. The small white particles in this figure are fillers or unfused PVC primary particles.⁵

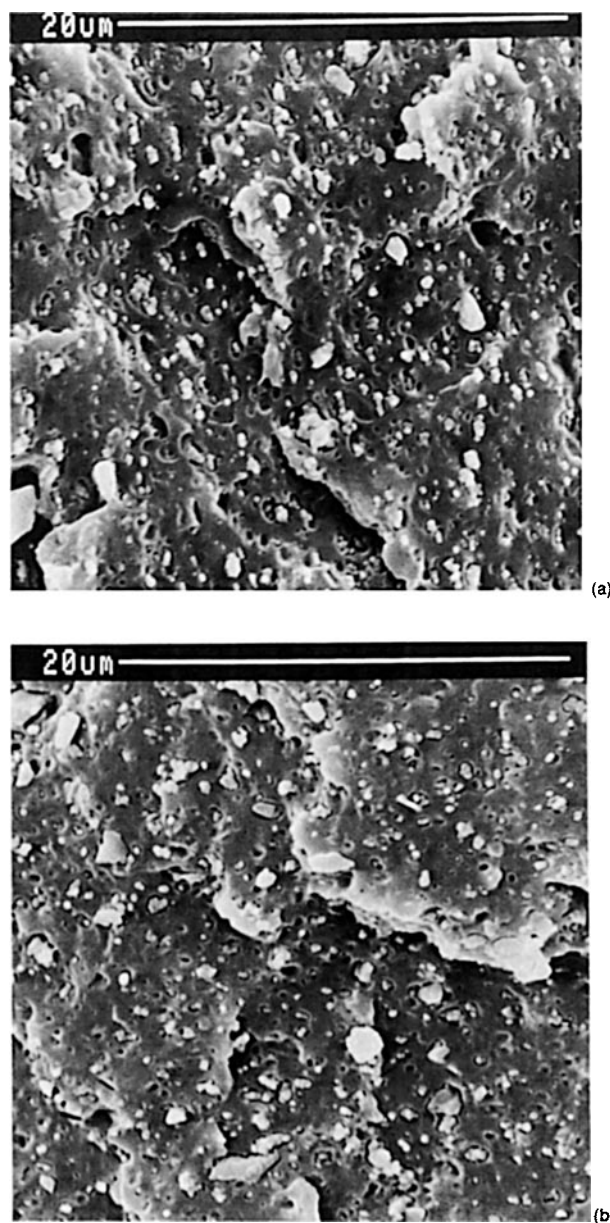


Figure 1 (a) 0 phr CPE in PVC/CPE blend coated with 200 Å of gold-palladium and examined by SEM. (b) 10 phr CPE in PVC/CPE blend coated with 200 Å of gold-palladium and examined by SEM. (c) 20 phr CPE in PVC/CPE blend coated with 200 Å of gold-palladium and examined by SEM.

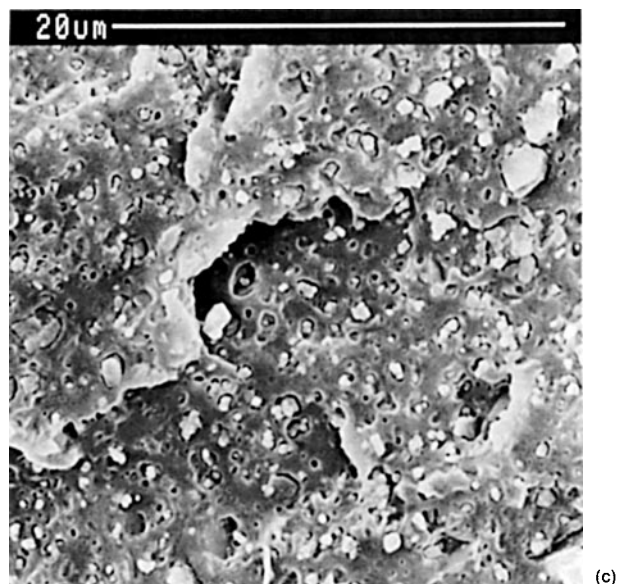


Figure 1 (Continued)

TEM Analysis

The TEM imaging of PVC treated by the selective staining procedure without the impact modifier, CPE, is shown in Figure 2(a). No staining effects are observed. The dark particles are fillers and additives, and the dark lines are knife marks from the microtome.

Using the selective staining procedure, 10 and 20 phr blends exhibit gray particles of stained CPE dispersed in an unstained PVC matrix [Fig. 2(b) and (c)]. In some areas of the 20 phr blends, the appearance of the CPE particles is similar to that in the 10 phr PVC/CPE blends except that the particles are more numerous and larger in size. In other areas, the CPE particles are observed in elongated forms that are sometimes aggregates of discrete particles and sometimes continuous structures probably formed by fusion of particles during processing.¹ The size of individual CPE particles and CPE clusters range between 100 and 500 nm. Without the two-stage chemical-staining procedure, no CPE particles are observed in the TEM imaging [Fig. 2(d)].

S-TEM Analysis

Figure 3(a)–(c) shows the micrographs of 0, 10, and 20 phr PVC/CPE blends without staining in S-TEM, respectively. No CPE particles are observed in Figure 3(a). The dark particles are fillers and additives similar to those in Figure 2(a).

Figures 2(d) and 3(b) are images of the same area of the same sample. However, many gray par-

ticles (CPE particles) are observed in Figure 3(b) even though no chemical-staining procedure is required. Blackson and Liou² reported that the reduced beam flux per area present in S-TEM coupled with the ability to electronically increase gain is largely responsible for the success of this technique in contrasting the two phases. This statement leads to the conclusion that S-TEM is better than TEM

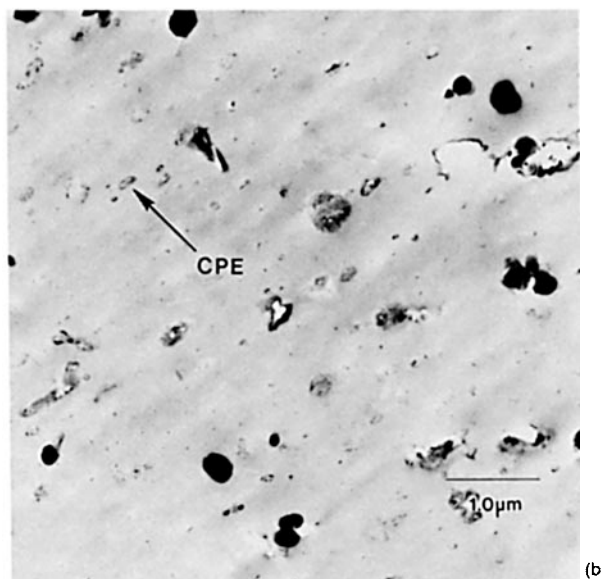
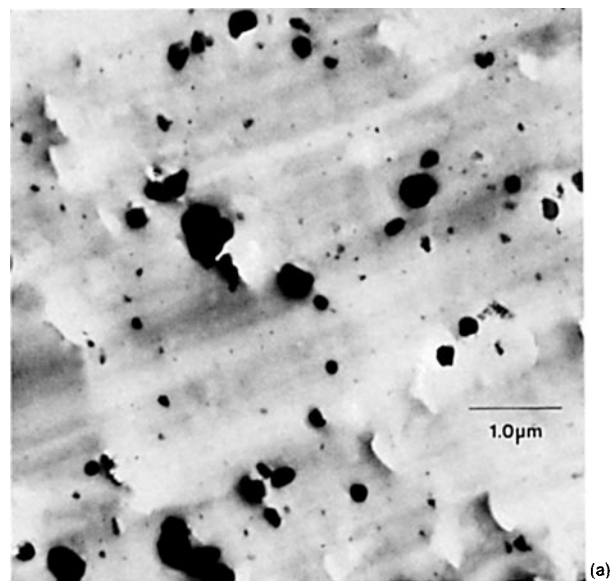


Figure 2 (a) 0 phr CPE in PVC/CPE blend treated by chemical-staining procedure and examined by TEM. (b) 10 phr CPE in PVC/CPE blend treated by chemical-staining procedure and examined by TEM. (c) 20 phr CPE in PVC/CPE blend treated by chemical-staining procedure and examined by TEM. (d) 10 phr CPE in PVC/CPE blend without any chemical treatment examined by TEM.

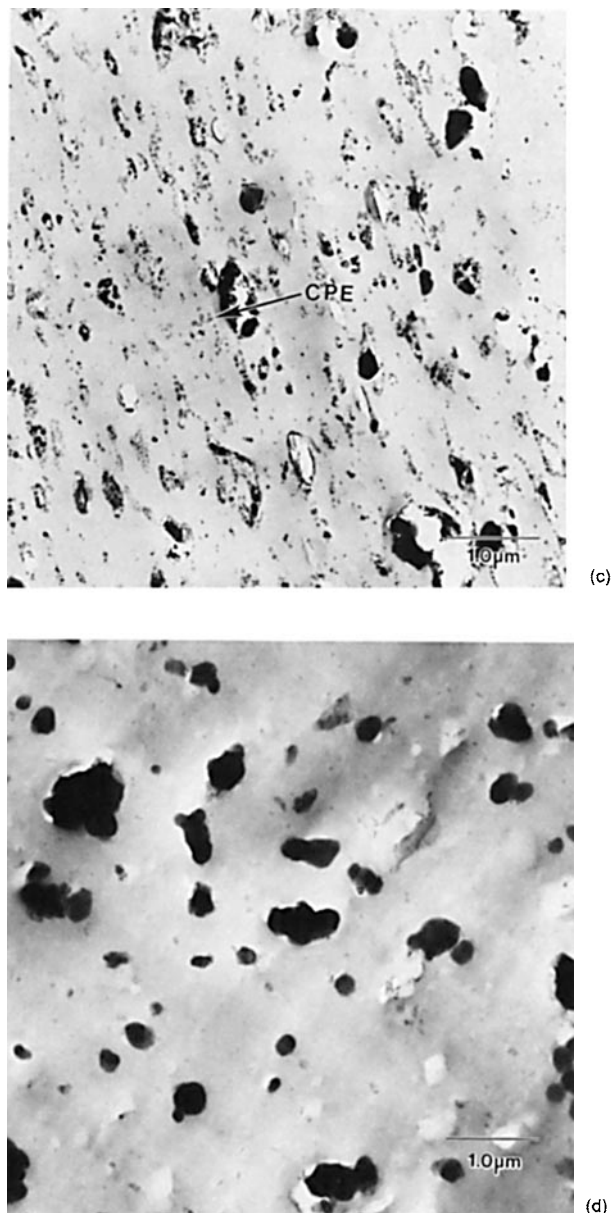


Figure 2 (Continued)

for discriminating between samples containing small density differences.

When comparing Figure 2(b) with Figure 3(b), and Figure 2(c) with Figure 3(c), two important observations were made: One observation is that a large amount of CPE particles in PVC/CPE blends may not have been stained during the chemical-staining treatment due to very slow diffusivity. Not all the CPE particles may be on the surface of the sample and therefore are not easily stained. Three procedures—increasing reaction temperature of dehydrochlorination, increasing OsO_4 concentration, or extending staining time more than 2 weeks—may be able to improve the staining effect.

The other observation is that the phase boundaries between PVC and CPE are clearer in the TEM analysis than are those in the S-TEM analysis. This may be due to slow OsO_4 diffusivity, thereby causing enhanced CPE particle surface staining.

In some regions, the micrographs of the CPE particles in Figure 3(c) (20 phr) are similar to those in Figure 3(b) (10 phr) except that the particles are more numerous and larger in size. In other re-

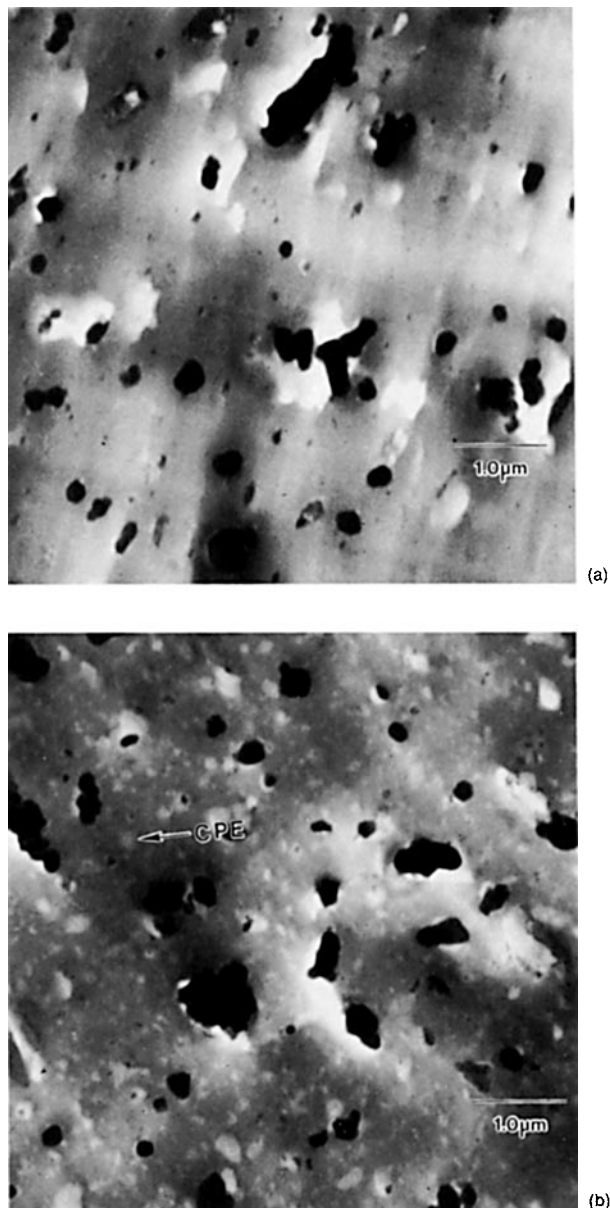


Figure 3 (a) 0 phr CPE in PVC/CPE blend without any chemical treatment and examined by S-TEM. (b) 10 phr CPE in PVC/CPE blend without any chemical treatment and examined by S-TEM. (c) 20 phr CPE in PVC/CPE blend without any chemical treatment and examined by S-TEM.

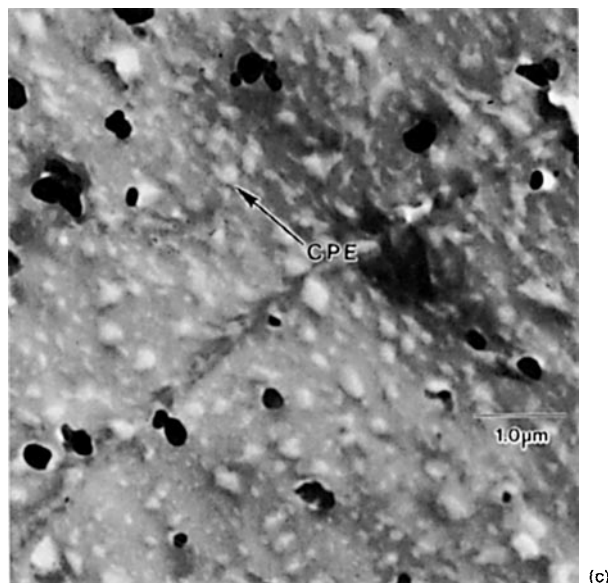


Figure 3 (Continued)

gions of Figure 3(c), the CPE domains are interconnected and almost form a network between the PVC phases. These phenomena are more obvious in S-TEM than in TEM imaging.

CONCLUSIONS

The morphology of a series of various concentrations of CPE in PVC/CPE blends have been examined in SEM, TEM, and S-TEM. Using SEM, the CPE particles in PVC/CPE blends cannot be discerned even though this technique does reveal similar surface morphologies in all PVC/CPE blends. Although the TEM technique allows clearer determination of phase boundaries, this technique is time-consuming because of the required sample staining. Furthermore, the TEM staining process does not stain all

the CPE phase and this procedure may alter the CPE phase and the interfacial region. Incomplete staining could result for CPE particles and portions of CPE particles that are not on the surface. Therefore, the apparent size and density of CPE particles as determined by TEM may not be comparable to the S-TEM appearance. Three approaches may improve the staining effect: increasing reaction temperature of dehydrochlorination, increasing OsO_4 concentration, or extending the staining time more than 2 weeks.

The S-TEM technique is fast and does not require staining and may allow observation of CPE particles that are not on the surface of the samples. In addition, this technique does not alter the CPE phase. One disadvantage of this method is that it does not provide as clear a phase discrimination of the boundaries between PVC and CPE compared to TEM analysis. The S-TEM technique can be also used for observing the other modifiers if the density of these modifiers is quite different from that of PVC.

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