

A Study on PVC/LLDPE Blends with Solid-State-Chlorinated Polyethylene as Compatibilizer

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ABSTRACT: Chlorinated polyethylene (CPE) prepared by solid-state chlorination was used as a compatibilizer for poly(vinyl chloride) (PVC)/linear low-density polyethylene (LLDPE) blends. Effects of CPE molecular structure on stress-strain behaviors, dynamic mechanical properties, and morphologies of PVC/LLDPE blends were studied by using SEM, TEM, DMA, and testing mechanical properties. The results showed that the compatibility of PVC/LLDPE blends was improved with the addition of CPE. Also, adhesion strength between the two phases and mechanical properties of the blends were increased. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2535–2541, 1997

INTRODUCTION

Polymer blends are an important route for extending the uses of polymeric materials. Polymer modification through blending has undergone a rapid development in recent years.^{1,2} Since, however, there exist only a limited or no compatibility between most of the simple blend systems, it is difficult to obtain desirable properties for simple blends. It has been demonstrated that the incorporation of a compatibilizer is an effective method to improve the compatibility of blend systems.^{3,4} Poly(vinyl chloride) (PVC) is one of a kind of common plastics with high strength, good friction resistance, fine comprehensive properties, and low price. But it has some shortcomings such as brittleness and poor thermal stability and is difficult to process. It is important to blend PVC with LLDPE, whose thermal stability and melt fluidity are fine. But due to different structures and poor compatibility, the processibility and product properties of noncompatible PVC/linear low-density polyethylene (LLDPE) blends are not desirable. Paul et al.,⁵ Ghaffer et al.,⁶ and Xu et al.⁷ im-

proved the compatibility of PVC/PE (high-density polyethylene [HDPE] and LDPE) blends by incorporation of compatibilizers or crosslinking. We had synthesized chlorinated polyethylene (CPE) with various chlorine contents and molecular structure by a solid-state chlorination process.⁸ In this article, this CPE was used as a compatibilizer for PVC/LLDPE blends, and a series of PVC/LLDPE blends were produced. The mechanical properties and morphologies of the blends were studied. Until now, there has been no report on PVC/LLDPE blends with CPE prepared by solid-state chlorination as the compatibilizer.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC, XJ-4, Tianjin Chemical Works), linear low-density polyethylene (LLDPE, LL1001, MI = 0.8, Exxon Chemical Co.), lead stearate, barium stearate (Wuhan General Plant of Auxiliaries), and tribasic lead sulfate (Hubei Huangshi Auxiliaries Works) were used.

Compatibilizer

The preparation of CPE with various chlorine contents, crystallinity, and segment structure were prepared as described elsewhere.⁸

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Preparation of Blends

A mixture of CPE and LLDPE with stabilizers, tribasic lead sulfate, lead stearate, and barium stearate (the amounts used were 5, 0.5, and 1.2 phr to that of PVC), was prepared by melt pre-mixing for 5 min with a twin-roll masticator at 160–165°C. Then, PVC was added. Also, a blend specimen was obtained after melt-mixing for 10 min. This specimen was preheated for 5 min with a compression-molding machine at 165°C, then pressed with a pressure of 20 MPa. The laminates of specified thickness were taken as the test specimens.

Measurements

The notch impact strength was measured according to GB1043-79; the tensile strength and elongation at break were measured according to GB1040-79 with a speed of 10 mm/min at 23°C, using a DL-250A electron tensile tester (Changchun No. 2 Material Testers Works). The melt index (MI) was measured according to GB-3682-83 at 190°C (sample weight, 5000 g), using an XRL-400B melt index tester (Scientific and Educational Apparatus Works of Jilin University).

Dynamic Mechanical Analysis (DMA)

DMA was done with a Japan Rheovibron-DDV-II-EA full-automatic dynamic viscoelastomer at a frequency of about 110 Hz over the temperature range of -150 to +150°C; heating rate was 2°C/min. The film specimens produced by thermal pressing were 5 cm in length, 3 mm in width, and about 0.1 mm in thickness.

Scanning Electron Microscopy (SEM)

The impact-fractured surfaces were sputtered with gold and observed through a Japan JSM-35 CF scanning electron microscope; accelerating voltage was 15 kV.

Transmission Electron Microscopy (TEM)

The specimens were stained according to Ref. 9 and observed through a JEM-100C transmission electron microscope; accelerating voltage was 80 kV.

Infrared Spectroscopy (IR)

IR was done with an America PE-580B infrared spectroscope.

RESULTS AND DISCUSSION

The Structure of Solid-State-Chlorinated Polyethylene

High-density polyethylene (HDPE) is a crystalline polymer. When chlorinated, the structures of CPE obtained will be different depending on the chlorination processes (solution, suspension, and solid state) or different reaction conditions.

Figure 1 shows the IR spectra of CPE with various chlorine content produced in different conditions by the solid-state chlorination process. We can see that for CPE chlorinated at low temperature the peak intensities of 720 and 730 cm^{-1} , which are the characteristic spectra of a long-chain structure, $-(\text{CH}_2)_n$ ($n \geq 4$), decrease gradually with increase of the chlorine content, i.e.,

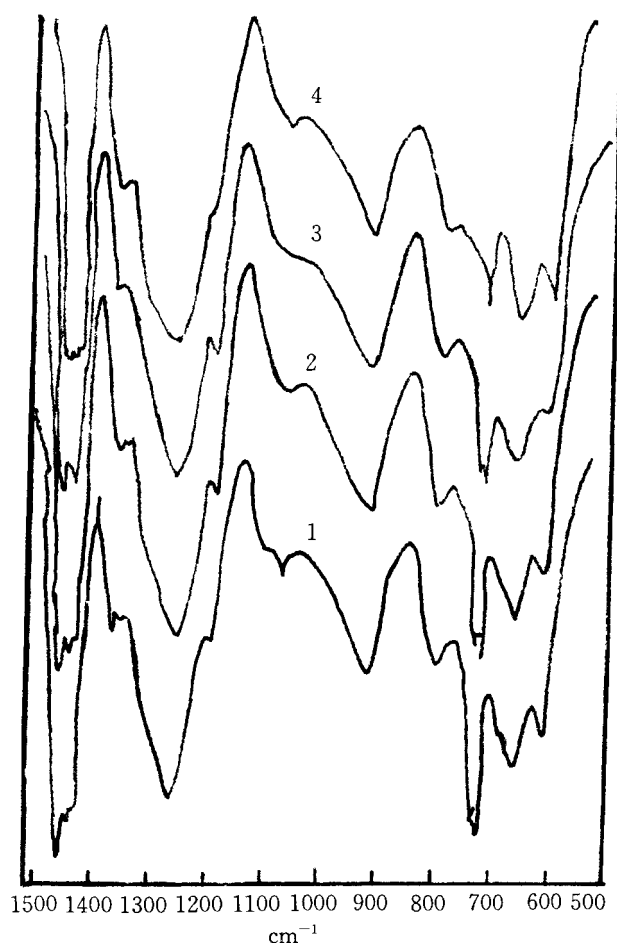


Figure 1 IR spectra of CPEs: (1) CPE₁ (Cl—28.9%), (2) CPE₂ (Cl—32.8%), (3) CPE₃ (Cl—36.5%) (1–3 are chlorinated at low temperature); (4) CPE₄ (Cl—36%, two-step chlorination at low-high temperature).

the crystallinity of CPE decreases slightly. However, there still exists a strong double peak when the chlorine content reaches 36.5%. But, for CPE chlorinated at a certain extent of high-temperature with 36% chlorine content, the peak of 730 cm^{-1} (the orthorhombic system of PE) disappears, and the peak intensity of 720 cm^{-1} was much weaker than that of CPE prepared at low-temperature. In Figure 1, $605\text{--}615$ and $660\text{--}685\text{ cm}^{-1}$ are the characteristic peak regions of -(CHCl)- in PVC and $740\text{--}750$, $785\text{--}800$, and $1195\text{--}1200\text{ cm}^{-1}$ are the characteristic peak regions of -(CHCl)- in $\text{-(CH}_2\text{CHCl-CHCl)-}$ and -(CHClCHCl-CHCl)- .¹⁰ Obviously, the CPE synthesized at low-temperature, a structure like PVC decreases after a certain chlorine content, but intensively chlorinated structures increase slightly with increasing chlorine content. In comparing band 3 with 4 in Figure 1, we can clearly find that their structures are different even though their chlorine content is close to each other: For the CPE prepared at low-temperature, the structure like PVC is less and the content of the unchlorinated long-chain $\text{-(CH}_2\text{)}_n$ ($n \geq 4$) is higher. In addition, the difference of the bending vibration peak of $\text{-CH}_2\text{-}$ in the range of $1400\text{--}1500\text{ cm}^{-1}$ is also obvious, and the peak intensity of the former at 1460 cm^{-1} is much stronger than that of the latter. This means that low-temperature chlorination results in a very heterogeneously CPE.

The Stress-Strain Behaviors of PVC/LLDPE Blends Compatibilized by Various CPE

It can be seen from Figure 2 that the tensile strength of a simple PVC/LLDPE blend is poor and the elongation at break is only 10%. After addition of the CPE compatibilizer, tensile strengths of the blends are improved remarkably, and a long tensile platform appears in every sample. Especially, the compatibilizing effect of CPE_2 (chlorine content, 32.8%; produced by chlorination at low temperature) to PVC/LLDPE blends is the most remarkable [curve (4) in Fig. 2]. This is because CPE_2 not only contains some extent of unchlorinated PE segments, but also contains many more segments similar to PVC than does CPE_3 . Comparing the compatibilizing effect of CPE_3 with that of CPE_4 [curves (5) and (6)], we can see that the result of CPE_3 produced by chlorination at low temperature is better than that of CPE_4 produced by two-step chlorination at a low-

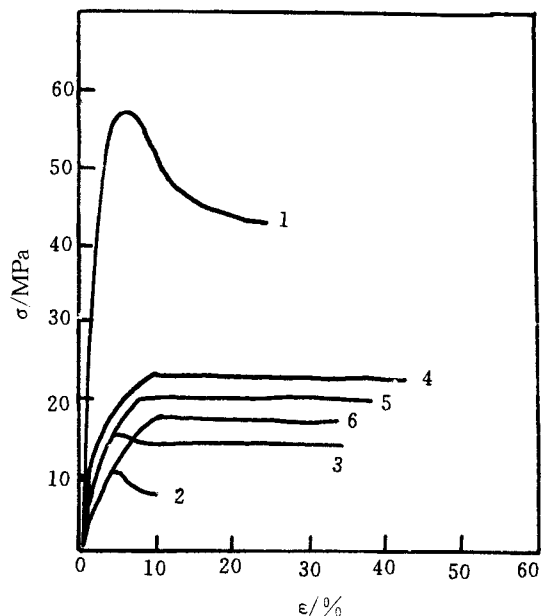


Figure 2 Stress-strain curves for the blend systems: (1) PVC; (2) PVC/LLDPE (100/20); (3) PVC/ CPE_1 /LLDPE (100/5/20); (4) PVC/ CPE_2 /LLDPE (100/5/20); (5) PVC/ CPE_3 /LLDPE (100/5/20); (6) PVC/ CPE_4 /LLDPE (100/5/20).

high temperature. A double structure of chlorinated and unchlorinated regions in solid-state CPE is the key factor of controlling the properties of CPE. The variation of double-structure is the reason why CPE has various compatibilizing effects. The CPE, with suitable chlorine content and chlorine distribution, containing some unchlorinated segments, is a fine compatibilizer of PVC/LLDPE blends. More unchlorinated PE segments are kept on the CPE molecular chain produced by low-temperature chlorination than that produced by two-step chlorination at a low-high temperature. It is closer to the structure of LLDPE and easier to permeate into the LLDPE phase of the blends. Those segments similar to PVC have better affinity to the PVC phase of the blends and are easier to diffuse and permeate into the PVC phase. So, CPE acts as an anchor chain or an adhesive. In addition, a function of CPE similar to an emulsifier makes diffusion and the entanglement extent between PVC and LLDPE macromolecules increase. The above actions improve the combining strength of interfaces and mechanical properties of the blends remarkably.

Effect of Composition on Properties of the Blends

The mechanical properties of the PVC/LLDPE blends (with 3 parts of CPE_2) are listed in Table I

Table I Mechanical Properties of PVC/LLDPE Blends^a with Various LLDPE Content

| Weight Ratio of PVC/LLDPE | Tensile Strength at Break (MPa) | Ultimate Elongation (%) | Notch Impact Strength (kJ/m ²) | Melt Flow Index (g/10 min) |
|---------------------------|---------------------------------|-------------------------|--|----------------------------|
| 100/0 | 55.6 | 24 | 3.9 | — |
| 100/10 | 26.5 | 42 | 6.7 | 0.543 |
| 100/20 | 19.7 | 38 | 5.4 | 1.051 |
| 100/30 | 16.4 | 34 | 4.8 | 1.644 |
| 100/40 | 10.5 | 30 | 3.3 | 2.231 |
| 100/50 | 9.2 | 22 | 3.1 | 2.547 |

^a With 3 parts of CPE₂.

as a function of the blend composition. The tensile strength and elongation at break decrease with increasing LLDPE content. At low LLDPE content, impact strength is improved. With increase of the LLDPE content, the impact strength decreased and the fluidity of the blend melts is improved. The higher the LLDPE content, the better the fluidity of the blend melts.

The effects of the compatibilizer amount on the mechanical properties of PVC/LLDPE blends are shown in Figures 3 and 4. We can find that CPE does play a compatibilizing role in PVC/LLDPE blends. The tensile strength of the blends increase with increasing CPE amount. Also, they reach the maximum when CPE is 5 parts. When the amount of CPE is more than 5 parts, tensile strength decreases with increase of the CPE amount. Elongation at break of the blends increases continuously with increasing CPE amount.

There exists an optimum compatibilizer amount in the blends⁴ and dispersion reaches a critical state at this condition. An increasing dispersant amount more will not increase dispersion. An excessive compatibilizer will reduce the mechanical properties of the materials. When the amount of compatibilizer is less than the critical amount, increasing its amount will assist the dispersion. The results in this study show that the optimum amount of the CPE compatibilizer for PVC/LLDPE blends is 5 parts.

It also can be seen from Figures 3 and 4 that the compatibilizing effect of CPE with a lower molecular weight is better than that with a higher molecular weight. This is because, in the range of a certain molecular weight and mechanical strength, the lower the molecular weight, the larger the free movement extent of the molecular chain and the higher probability of the compati-

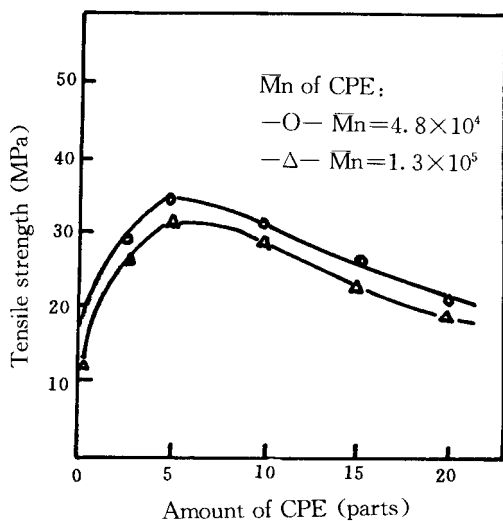


Figure 3 Effect of CPE amount on the tensile strength at break of PVC/LLDPE (100/10) blends.

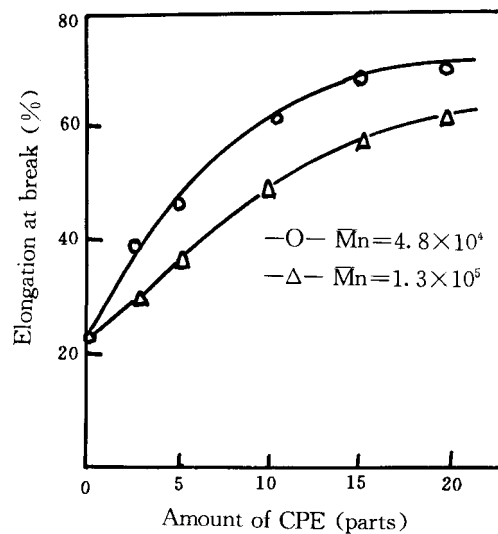


Figure 4 Effect of CPE amount on elongation at break of PVC/LLDPE (100/10) blends.

lizer diffusing and permeating into corresponding phases in the blends.

Effects of CPE on Dynamic Mechanical Properties of PVC/LLDPE Blends

Miscibility between polymers is a primary factor dominating the mechanical properties of blend systems. Dynamic mechanical analysis (DMA) is one of the best methods at present of characterizing compatibility. Figures 5 and 6 show the dynamic viscoelastic spectra of PVC, LLDPE, PVC/LLDPE (100/10), and PVC/LLDPE/CPE (100/10/5). It can be seen that the $\tan \delta$ of PVC goes through a maximum at 102.7°C, which is related to the relaxation associated with the glass transition. Two maxima in the $\tan \delta$ curve of LLDPE occur at approximately -105 and -20°C. On the $\tan \delta$ - T curve of PVC/LLDPE blends, two distinct T_g s are observed (102.7 and -105°C), which are the same as that of the two components of the blend. It demonstrates that PVC is incompatible with LLDPE completely. For PVC/LLDPE/CPE (100/10/5) blends, the $\tan \delta$ peak of LLDPE drifts from -105 to -80°C nearby, while the T_g of PVC does not move, only showing peak broadening. This is because the amount of the LLDPE dispers-

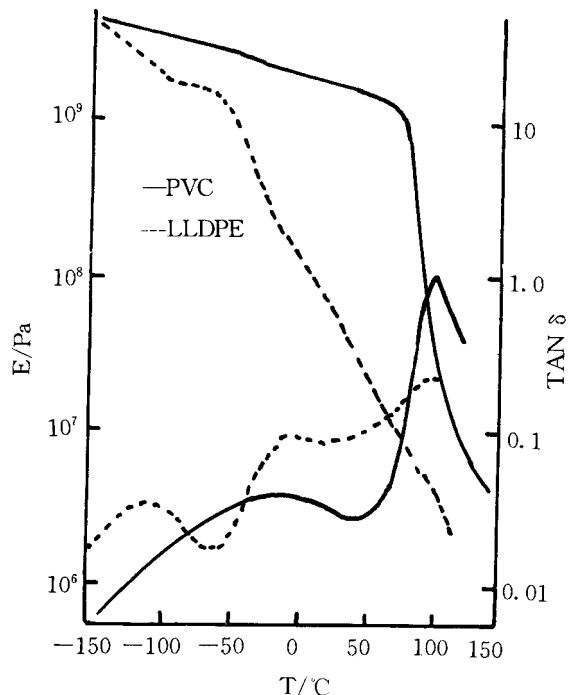


Figure 5 Dynamic mechanical behavior of PVC and LLDPE.

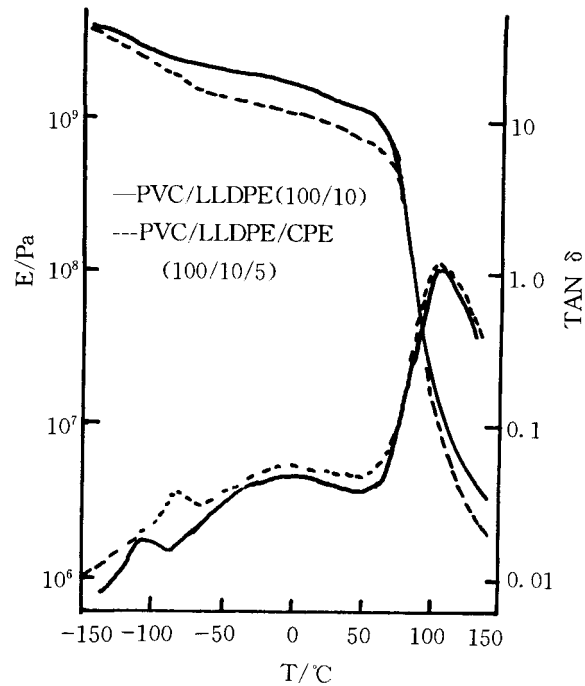


Figure 6 Dynamic mechanical behavior of PVC/LLDPE (100/10) and PVC/LLDPE/CPE (100/10/5) blends.

ing phase is much less than that of the PVC continuous phase. So, the effect of the compatibilizer CPE on the T_g transition behavior of LLDPE is much more than that of PVC. But it is not enough to change the latter remarkably, just to broaden it somewhat due to the heterogeneity of the PVC phase. All the above results indicate that the addition of CPE makes the incompatible PVC/LLDPE blend system to be a partially compatible one, i.e., the distribution of CPE on the interface of PVC/LLDPE blends reduces the interfacial tension, improves the dispersing of LLDPE, and enhances the adhesion strength between PVC and LLDPE. CPE is an effective compatibilizer for the PVC/LLDPE blend system.

Morphologies of the Polyblends

Figure 7 shows scanning electron micrographs of impact-fractured surfaces of PVC/LLDPE blends with and without the CPE compatibilizer.

Obviously, due to thermodynamic incompatibility, the impact-fractured surface of PVC/LLDPE blends without the CPE compatibilizer is smooth, indicating a brittle fracture mode [Fig. 7(a)]. So, their mechanical properties are worse

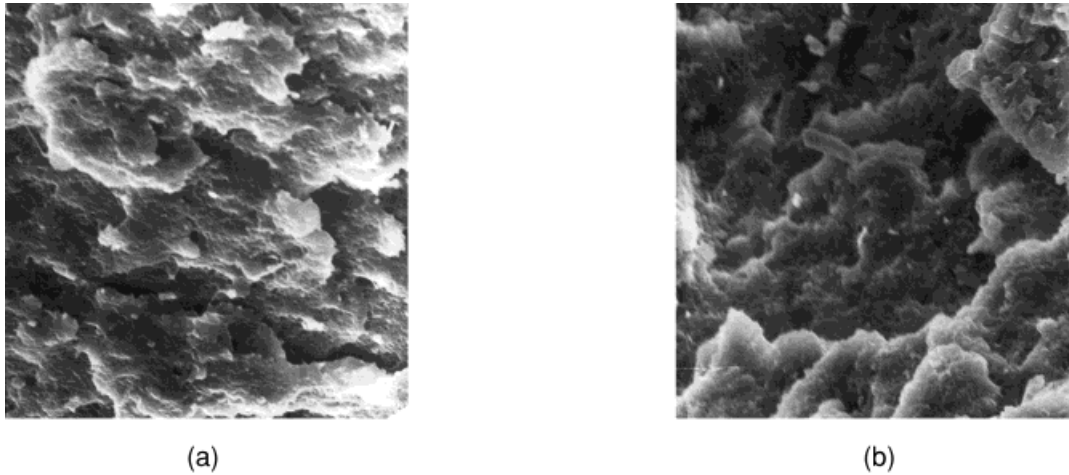


Figure 7 SEM micrographs of impact-fractured surface of (a) PVC/LLDPE (100/20) and (b) PVC/LLDPE/CPE (100/20/5) blends (magnification $\times 2000$).

(Figs. 2–4). As shown in Figure 7(b), with 5 parts of CPE, the fracture surface of PVC/LLDPE blends is highly deformed in a manner characteristic of ductile fracture. Numerous fibril broken ends and concave and convex morphologies are observed. The transition from the brittle to the ductile fracture mode clearly coincides with the increase in impact strength.

Figure 8 shows transmission electron micro-

graphs of PVC/LLDPE (100/10) and PVC/LLDPE/CPE (100/10/5) blends. For PVC/LLDPE blends, due to the incompatibility between the two phases, the wetting situation on the interface is poor and the interaction between two phases is small. So, the interface is clear [Fig. 8(a)] and some small voids (those small white particles) appear in it. Addition of the CPE compatibilizer improves the interaction and reduces

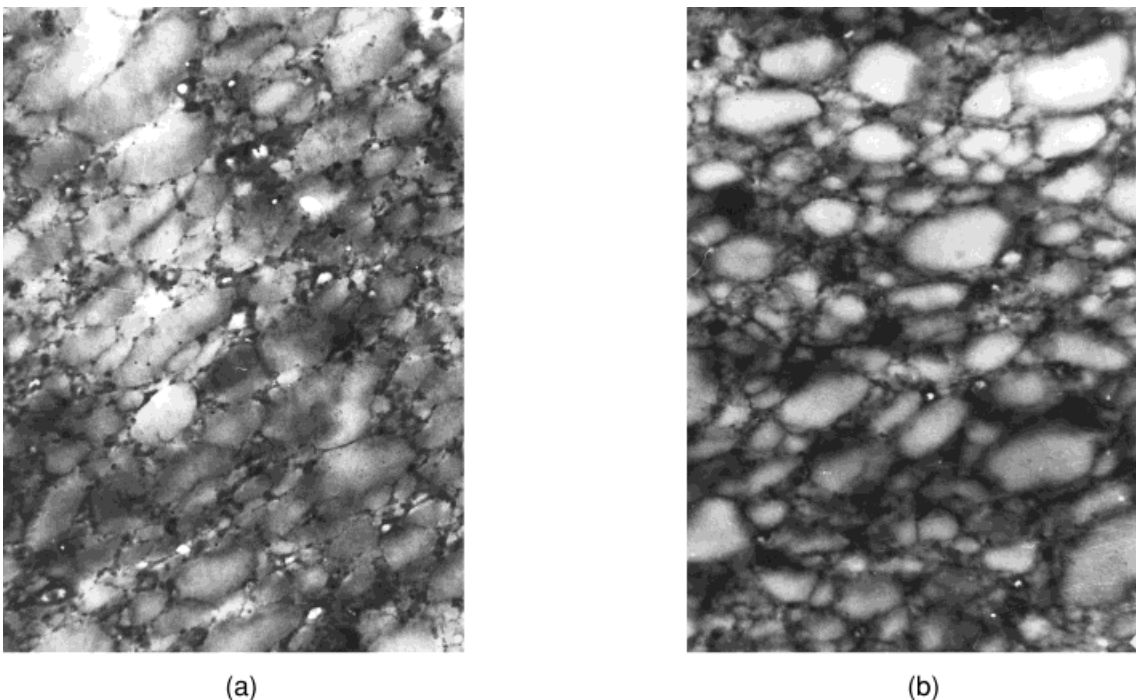


Figure 8 TEM micrographs of (a) PVC/LLDPE (100/10) and (b) PVC/LLDPE/CPE (100/10/5) (magnification $\times 13,250$). Dark area, LLDPE and CPE; white area, PVC.

the interfacial tension between two phases due to the function of CPE similar to the emulsifier (interfacial activator). So, the interface between PVC (white areas) and LLDPE (black areas) in PVC/LLDPE/CPE blends is much rougher. A network structure is formed.

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