

Morphology Evolution of Immiscible LDPE/PVC Blends in the Presence of Compatibilizer and Phase Dispersant

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ABSTRACT: Phase dispersion and coalescence in low-density polyethylene (LDPE)/polyvinyl chloride (PVC) (70/30) blends influenced by compatibilizer and phase dispersant was studied. It was found that the morphology evolution of blends is sensitive to not only processing conditions (shear strength and mixing time) but also the added compatibilizer or phase dispersant. In our conditions, the stable phase morphology of each blend is obtained after mixing 15–25 min. In addition, the dispersed PVC phase in blends is easy to aggregate when the mixing rotor speed changed

from high to low for the binary blends. As a compatibilizer, chlorided polyethylene (CPE) or nitrile rubber (NBR) can stabilize the morphology and hinder the coalescence of the dispersed PVC phase when added to the blends. However, the phase dispersant butadiene rubber (BR) or styrene butadiene rubber (SBR) could not stabilize the phase structure, although it could accelerate phase dispersion. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 763–772, 2004

Key words: morphology; polyethylene; polyvinyl chloride

INTRODUCTION

The morphology of polymer blends is of essential importance to their properties. As a result of the deformable nature of the minor phase in immiscible blends, a wide range of sizes and shapes can be generated during processing. Since the size and the shapes of the minor phase can influence a multiplicity of physical properties, including impact strength,¹ tensile properties,² and permeability characteristics,^{3,4} it is of great value to know how these complicated morphologies are formed in situ and controlled during compounding. In general, during the processing of polymer blends, several factors are especially important in determining the final size and shapes of the minor phase: composition,^{4,5} viscosity ratio,⁶ interfacial tension,⁷ shear rate/shear stress,⁸ and processing conditions,^{9–13} such as time of mixing, rate of rotation of rotor or screw, and type of mixer.

Scott and Macosko¹⁴ found that the time of mixing plays an important role in determining the morphology and related properties of polymer blends. It was observed that as the time of mixing increased, the dispersed domain size decreased in the case of ethylene-propylene-diene monomer (EPDM)/nylon and EPDM/polystyrene (PS) blends. Moreover, having compared the development of morphology in nonre-

active and reactive polymer blends, they found the interfacial chemical reaction between the phases reduced the dispersed phase size and narrowed the size distribution. Ha¹⁵ studied the effects of shear intensity of mixing on the morphology of EPDM/polypropylene (PP)/high-density polyethylene (HDPE) ternary blends and found that the domain size of the dispersed PP decreased as the mixer speed increased. Plochocki et al.¹⁶ studied the effect of the mixing process on the interface of binary mixtures containing a corresponding block copolymer. It was found that the dispersed domain size decreased with increased mixing energy. Li¹⁷ and Moon¹⁸ found that the size of the dispersed phase would reduce when the compatibilizer was added to the blends.

In our laboratory we have undertaken a series of studies aimed at understanding how the morphology of immiscible polymer blends is controlled during processing. It was found that the phase structures and mechanical properties of immiscible polyvinyl chloride (PVC)/low-density polyethylene (LDPE) blends were strongly influenced by the viscosity ratio of the components.⁸ Addition of a compatibilizer (chlorided polyethylene (CPE) or nitrile rubber (NBR)) could improve the dispersion of the blends and promote the tensile properties.^{19–21} A solid phase dispersant, such as butadiene rubber (BR) or styrene butadiene rubber (SBR), could also modify the morphology but has a negative effect on the mechanical properties.^{22,23}

However, the difference between the effects of compatibilizer and phase dispersant on morphology evolution during the mixing process has not been investigated. In this study, we intended to gain knowledge

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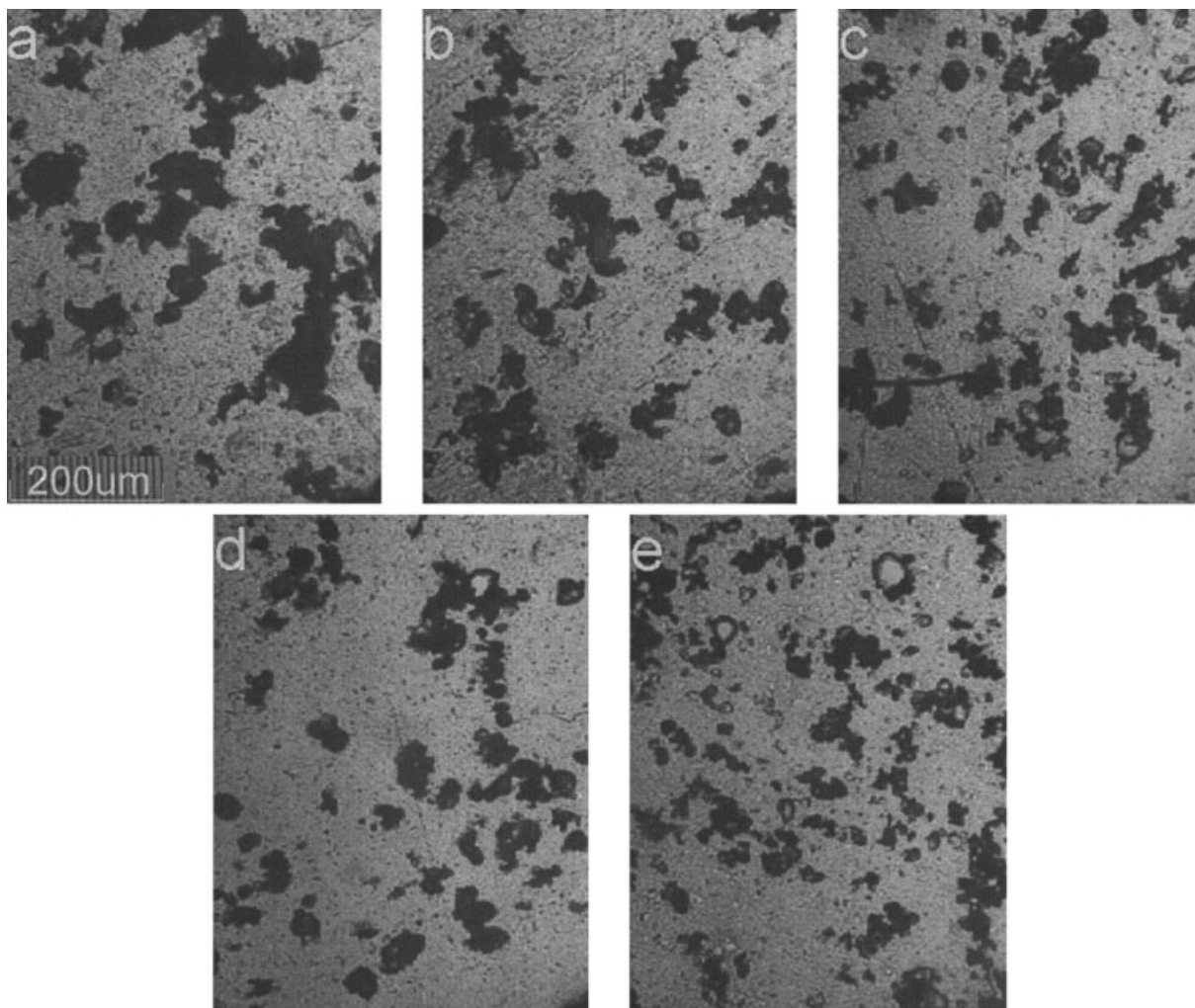


Figure 1 Optical micrographs of LDPE/PVC (70/30) blends for different mixing times (in minutes) at 50 rpm during melting mixing. (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

of the different functions of compatibilizer and phase dispersant in the process of phase dispersion and coalescence of immiscible PVC/LDPE blends. An additional goal of this work is to compare the effects of mixing time and rotor speed on the morphology evolution of immiscible polymer blends.

EXPERIMENTAL

A plasticized PVC material was compounded according to the following composition: PVC/dioctyl phthalate/tribasic lead sulphate/dibasic lead phosphite/stearic acid (100/32/3/3/1), where PVC (WS-800S, its average polymerization degree is between 750 and 850) is a product of Shanghai Chloralkali Chemicals (Shanghai, China). Low-density polyethylene (LDPE, 2F2B) with a melt flow rate of 2.0 g/10 min and a density of 0.922 g/cm³ is a product of Shanghai Petrochemical General Works (Shanghai, China). Wuhu Chemical and Engineering Co. (Wuhu, China) sup-

plied CPE (36.4 wt % Cl). NBR (N240S, 24.0–28.0 wt % AN) was supplied by Japan Synthetic Rubber Co. (Japan) BR (9000) was obtained from Yanshan Petrochemical Co. (Beijing, China), while SBR (1500) was obtained from Jilin Chemical Industry Stock Co., Ltd. (Jilin, China).

LDPE/PVC (mass ratio 70/30) and LDPE/PVC/CPE (NBR, BR, or SBR) (mass ratio 70/30/7.5) samples were mixed in the chamber of a HBI 90 Hakke Rheocord, in which the temperature was set at 160 °C. The rotation speed of the rotors was changed so as to change the shear stress that the material bore. The torque was recorded during the mixing process. After the specified mixing time (5, 15, 25, 35, and 40 min), the roller blades were stopped and the sample was cut from the large gap region of the roller blades. The sample was then transferred to the mould and the films (about 50 μm in thickness) were formed at the same temperature. An optical microscope (Nikon B10phot) was also used to observe the phase morphol-

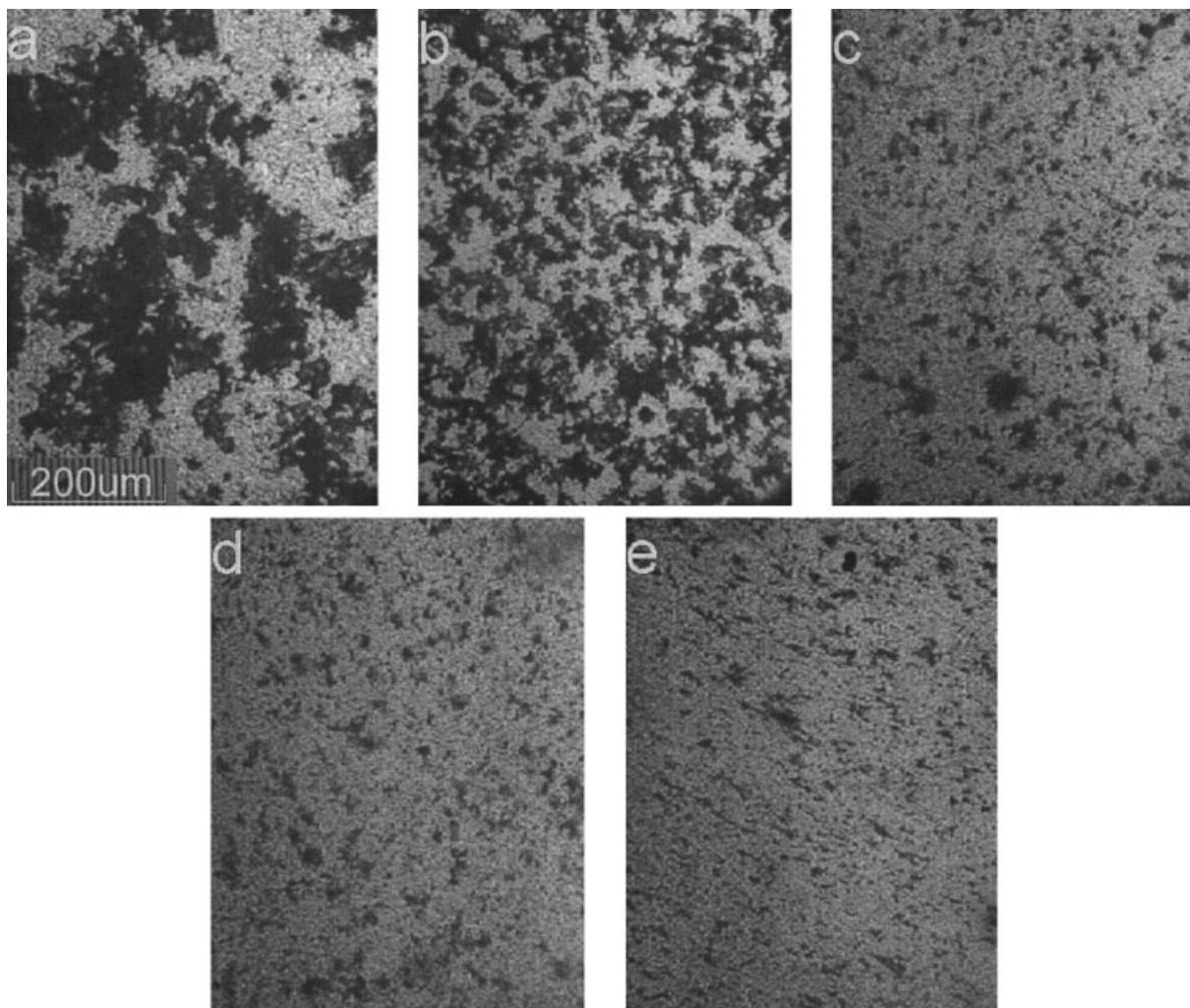


Figure 2 Optical micrographs of LDPE/PVC (70/30) blends for different mixing times (in minutes) at 150 rpm during melting mixing: (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

ogy of the blends. For enhancing the phase contrast between PVC and LDPE phases, the film of the sample was treated with a θ -like solvent²⁴ before observation.

RESULTS AND DISCUSSION

Influence of mixing time and rotor speed on morphology of immiscible blends

The binary blends of PVC and polyethylene (PE) are typically immiscible with the poor phase structure, and the morphology of LDPE/PVC (70/30) blends exhibits dispersed PVC particle in a continuous LDPE matrix in our conditions. When the film of the blends is treated with a θ -like solvent, the black PVC domain and white LDPE matrix is presented.^{8,24}

The final morphology obtained by melt mixing is always the result of a dynamic equilibrium between droplet breakup and coalescence, the collision and subsequent merging of droplets of the small size, which is a function of the impact forces and times of

collision as droplets hit each other. After a certain mixing time, both processes will be in equilibrium, leading to the stable phase morphology.²⁵ With our conditions, the stable phase morphology of blends is obtained after mixing 15–25 min with a rotor speed of 50 or 150 rpm (see Figs. 1 and 2). The major effect of additional mixing time is to reduce the size of the largest particles in the distribution, especially after 5 min of additional mixing. Therefore, a mixing time of 25 min was used for all samples in order to ensure the largest particles break up.

The result obtained in our experiment is consistent with that of other researchers.^{12,26} Increasing the rotor speed resulted in a finer and more uniform PVC distribution. It is necessary to indicate that such a phase structure is not a stable state. When the shear strength is decreased or eliminated, the two phases will aggregate via thermofluctuation of the corresponding polymer chains. This can produce a coarsening of the dispersed phase when the rotor speed changes from

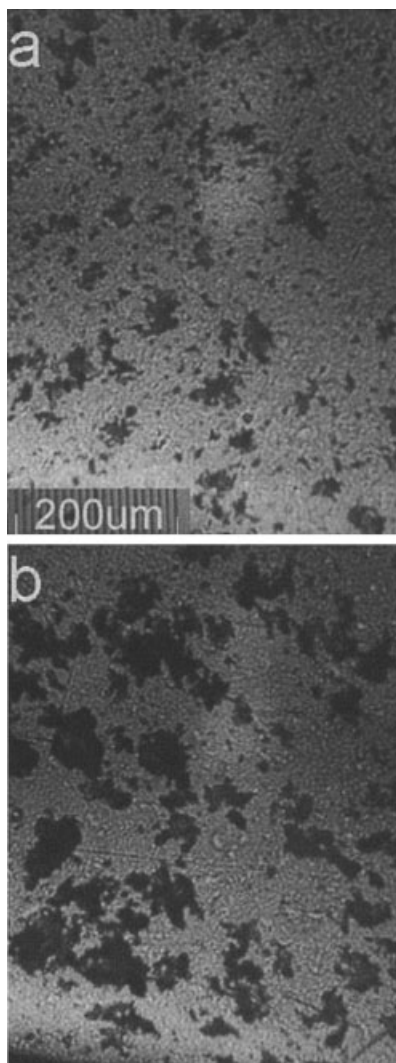


Figure 3 Morphology evolution of LDPE/PVC (70/30) blends: (a) optical micrograph of the blends after mixing 25 min at 150 rpm; (b) optical micrograph of (a) after mixing another 25 min at 50 rpm, showing the coalescence of the dispersed phase.

150 to 50 rpm, as shown in Figure 3. The coalescence of the PVC dispersed phase is due to the immiscibility of PVC and LDPE. Comparing Figure 3(b) and Figure 1(c), we also found that the morphology of blends can return to the metastable morphology of 50 rpm whether or not they endure the mixing process at 150 rpm.

Differing effects of compatibilizer and phase dispersant on morphology

The same experiment is done to get the metastable morphology of LDPE/PVC/CPE (70/30/7.5) blends and LDPE/PVC/BR (70/30/7.5) blends. The morphology evolution processes are recorded in Figures 4–7. Comparing Figures 4 and 5 with Figures 1 and 2, it is found that the phase structure of LDPE/PVC/

CPE blends is finer than that of LDPE/PVC blends, no matter what the rotor speed and mixing time are. The interface seems more blurred, inferring that CPE plays the role of interfacial emulsifier.

The phase structure of the blends with BR is finer than that of the corresponding binary blends at the first stage of mixing, after 5 min. of mixing (see Figs. 6 and 7). However, the interface is as clear as that of LDPE/PVC blends, and the phase structure for a longer mixing time is not as fine as that of the blends containing CPE. As indicated in the former article,²⁷ the melt viscosity of LDPE will increase when it is mixed with BR. Thus, addition of BR to LDPE/PVC blends could accelerate the phase dispersion of LDPE/PVC blends by reducing the viscosity ratio of the two phases and increasing the shear force. Because of the limited activity of polymer chains, the dispersed phase structure will be maintained after the sample is cooled, though it is not thermodynamically stable.

Differing effects of compatibilizer and phase dispersant on coalescence

Figures 8, 9, 10, and 11 show the different effects of compatibilizer CPE (or NBR) and phase dispersant BR (or SBR) on the morphology evolution of the blends. It is easy to discover that the blends containing CPE have a stable phase structure. The fine phase structure does not change when the rotor speed decreases from 150 to 50 rpm (see Fig. 8), whereas the dispersed phase in LDPE/PVC/BR blends is aggregated much more easily than that of LDPE/PVC/CPE blends (see Fig. 9). The same result was obtained for compatibilizer NBR (Fig. 10) and phase dispersant SBR (Fig. 11) in the blends.

It is well known that CPE or NBR can act as the compatibilizer of LDPE/PVC blends.²⁸ The function of the compatibilizer is to increase the interfacial adhesion between the two phases and keep the finer morphology during processing. BR or SBR, which is suggested to be phase dispersant, can accelerate the phase dispersion of the blends by modifying the viscosity ratio of blends; but it cannot increase the interfacial adhesion. Such a phase-dispersed structure is thermodynamically unstable. Consequently, a fine phase structure formed at high rotor speed (equivalent to high shear strength) will become coarser when the rotor speed decreases.

CONCLUSIONS

The dispersed phase morphology as a function of mixing time and rotor speed was investigated for LDPE/PVC, LDPE/PVC/BR, and LDPE/PVC/CPE blends. Binary blends of LDPE and PVC reach a metastable phase structure after mixing for 15–25 min. Such a dispersed phase structure is easy to coarsen when

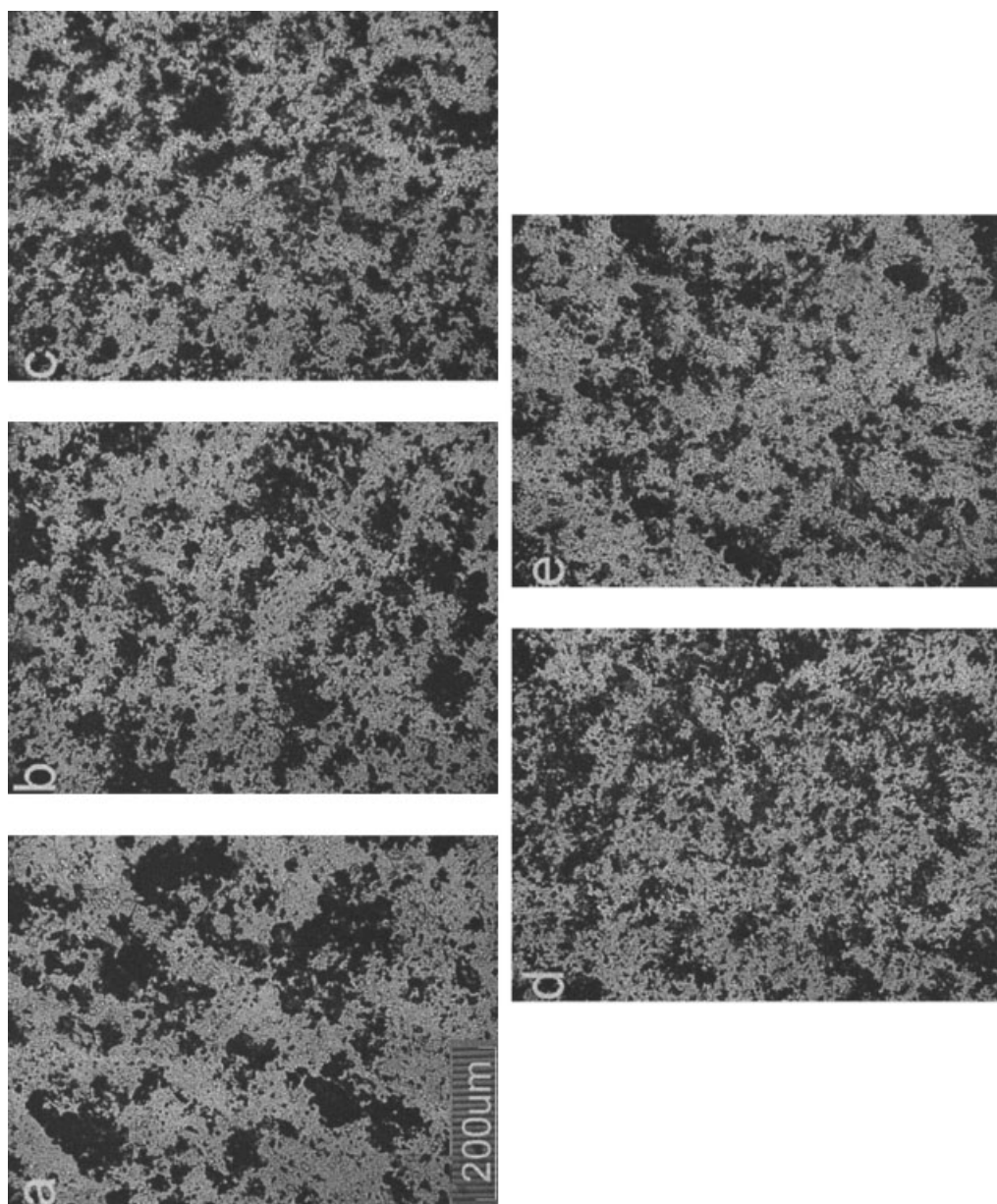


Figure 4 Optical micrographs of LDPE/PVC/CPE (70/30/7.5) blends for different mixing times (in minutes) at 50 rpm during melting mixing: (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

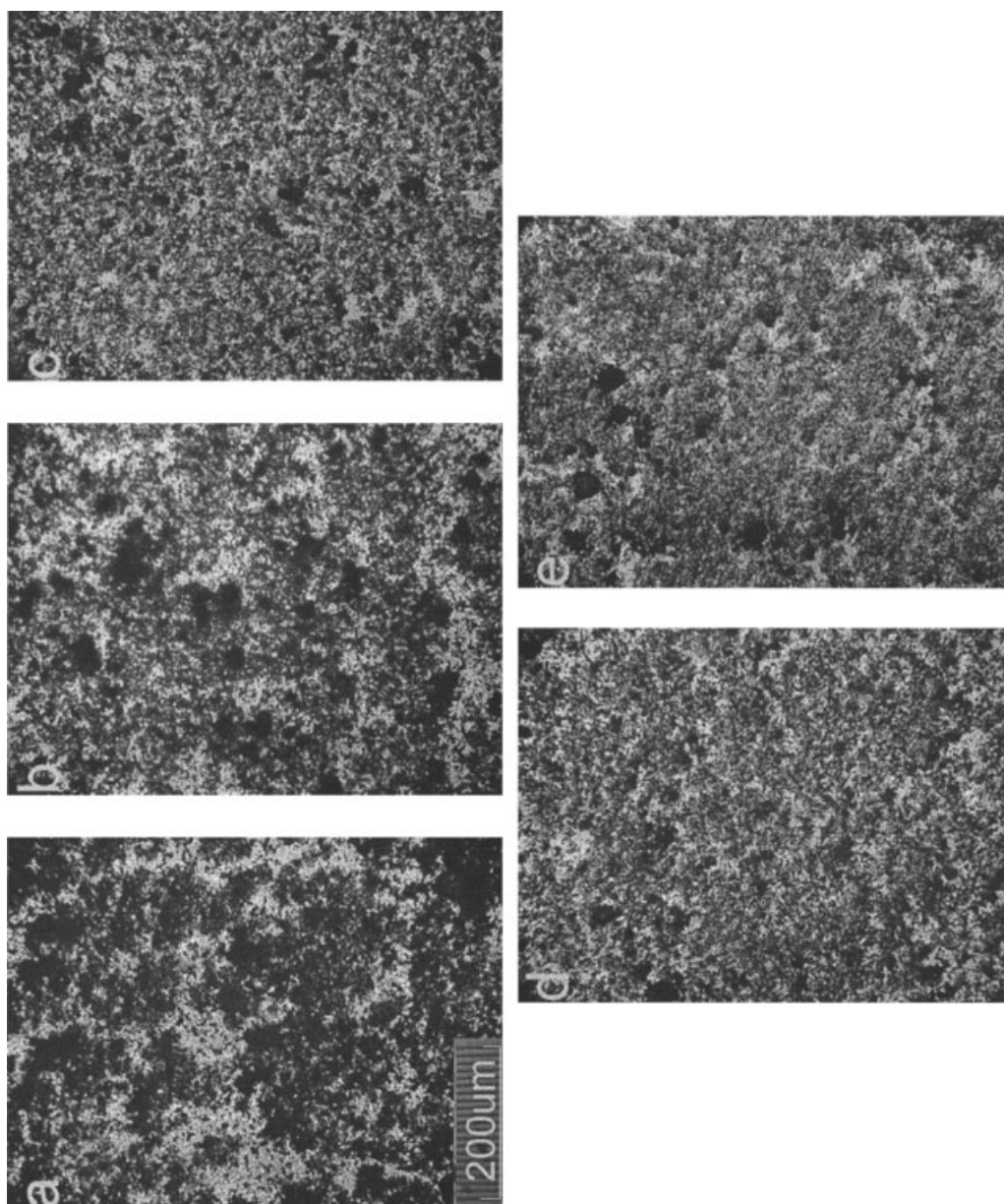


Figure 5 Optical micrographs of LDPE/PVC/CPE (70/30/7.5) blends for different mixing times (in minutes) at 150 rpm during melting mixing: (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

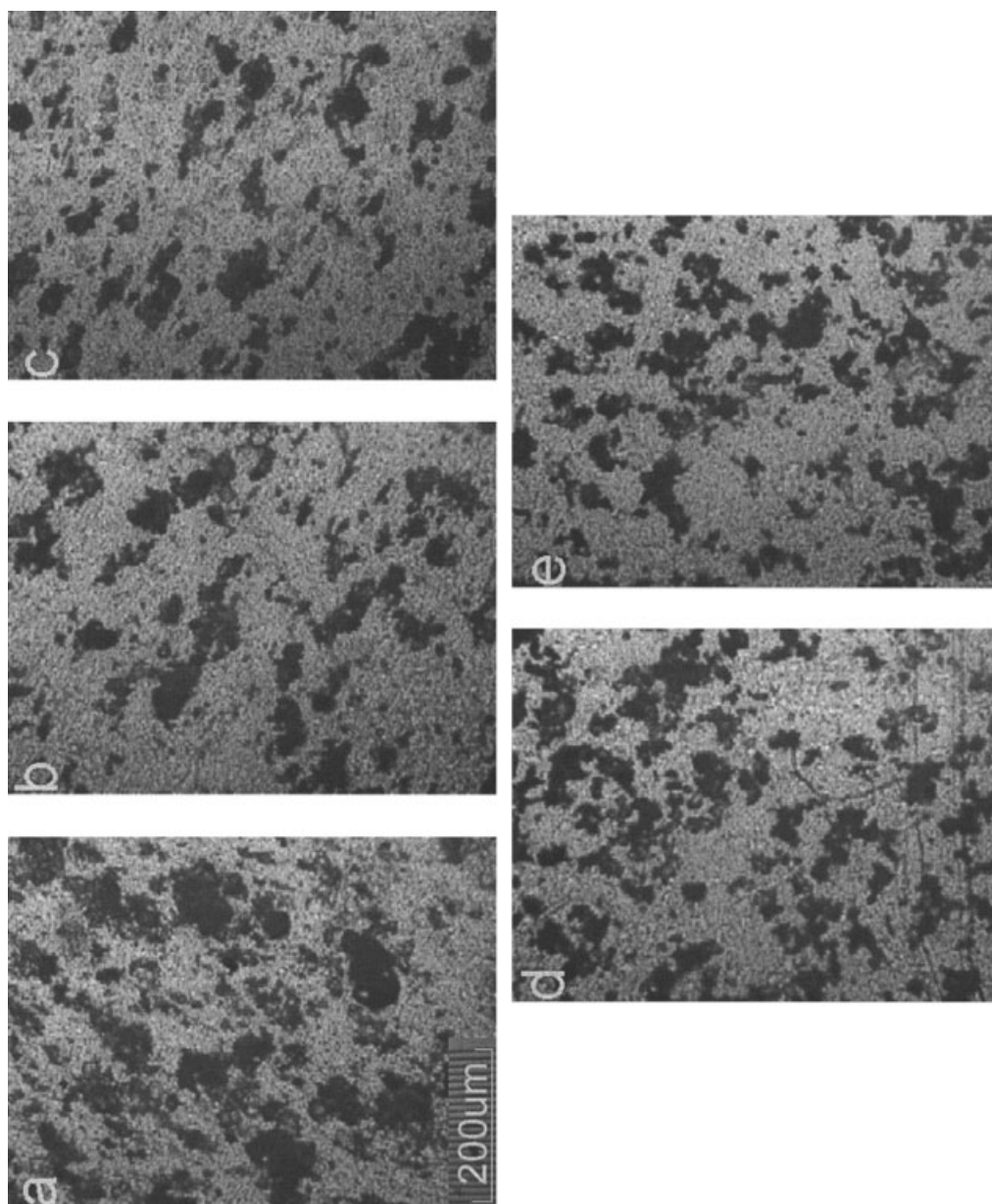


Figure 6 Optical micrographs of LDPE/PVC/BR (70/30/7.5) blends for different mixing times (in minutes) at 50 rpm during melting mixing: (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

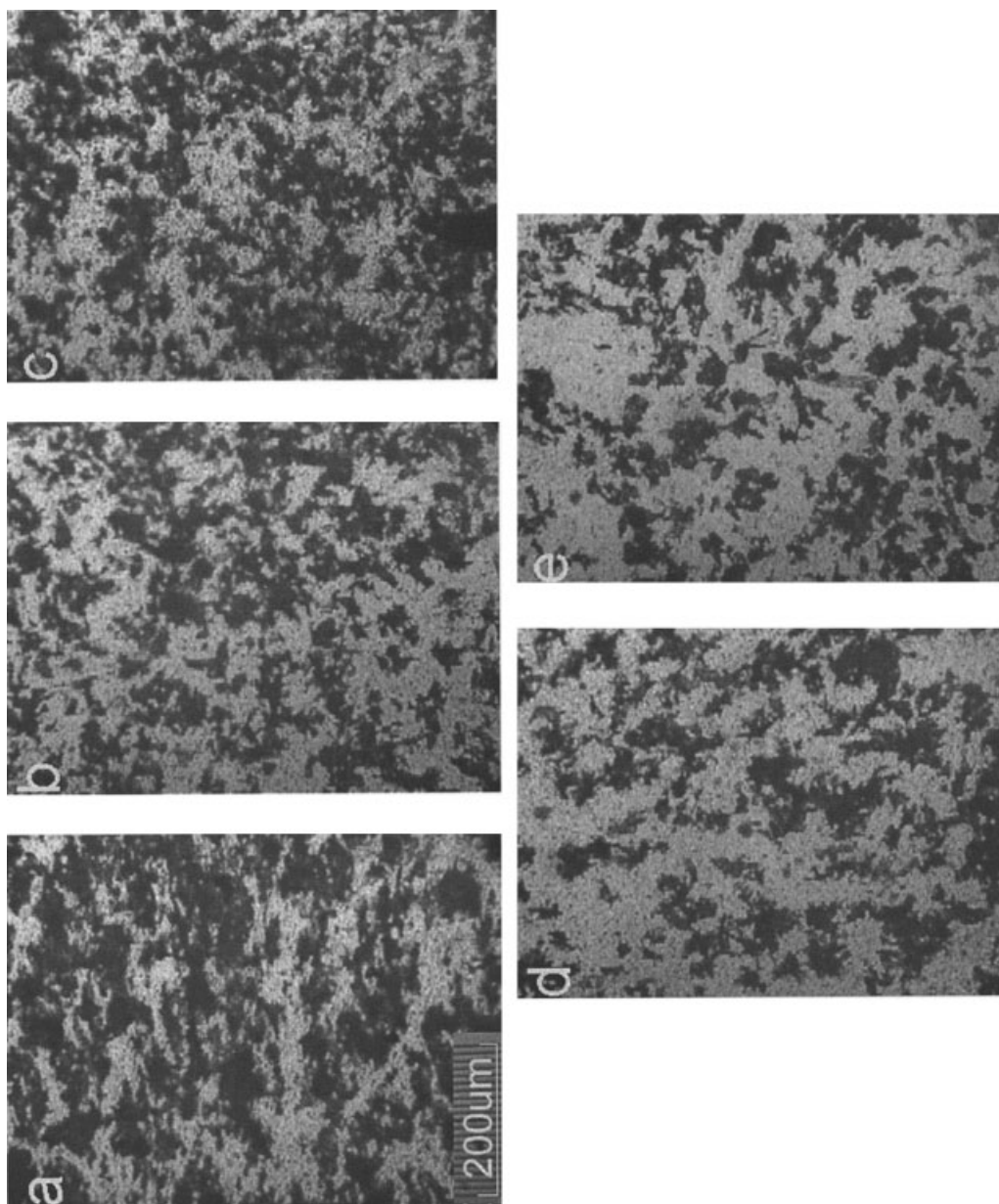


Figure 7 Optical micrographs of LDPE/PVC/BR (70/30/7.5) blends for different mixing times (in minutes) at 150 rpm during melting mixing: (a) 5; (b) 15; (c) 25; (d) 35; (e) 40.

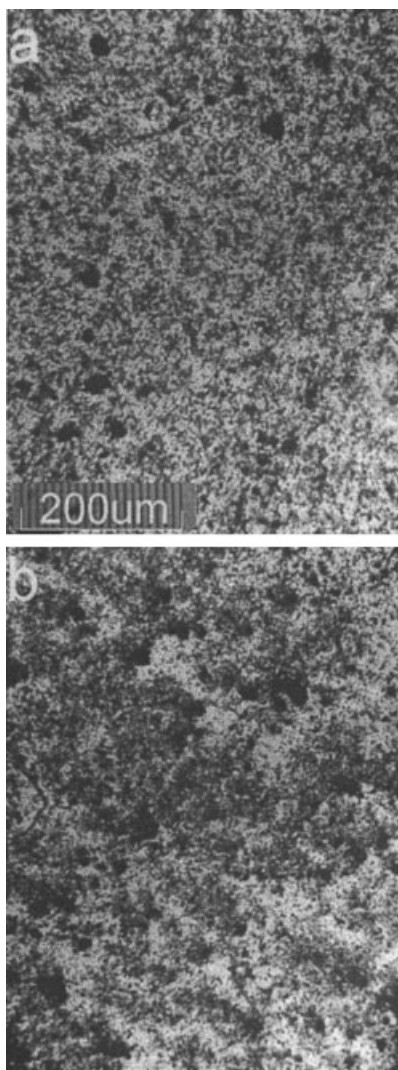


Figure 8 Morphology evolution of LDPE/PVC/CPE (70/30/7.5) blends: (a) optical micrograph of the blends after mixing 25 min at 150 rpm; (b) optical micrograph of (a) after mixing another 25 min at 50 rpm, showing an even finer phase structure.

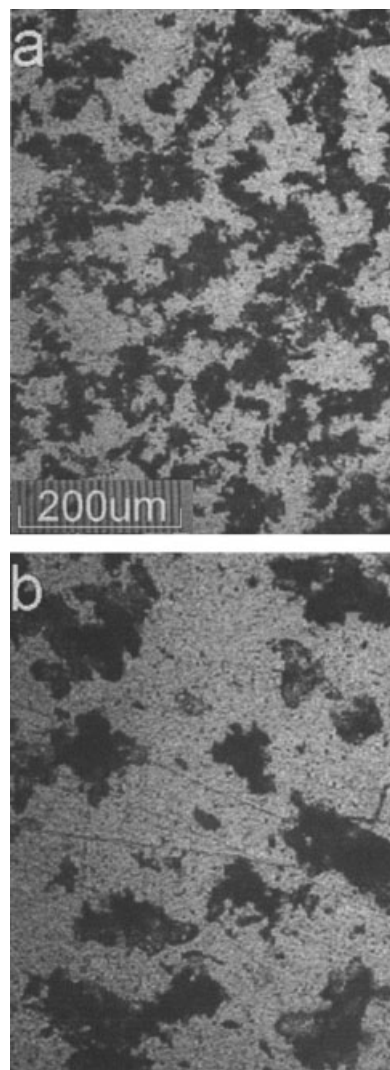


Figure 9 Morphology evolution of LDPE/PVC/BR (70/30/7.5) blends: (a) optical micrograph of the blends after mixing 25 min at 150 rpm; (b) optical micrograph of (a) after mixing another 25 min at 50 rpm, showing the coalescence of the dispersed phase.

the shear strength decreases. As a phase dispersant, BR or SBR can accelerate the phase dispersion process. But it cannot stabilize the phase structure. In comparison, the compatibilizer, CPE or NBR, can improve the phase dispersion and stabilize the finely dispersed phase structure.

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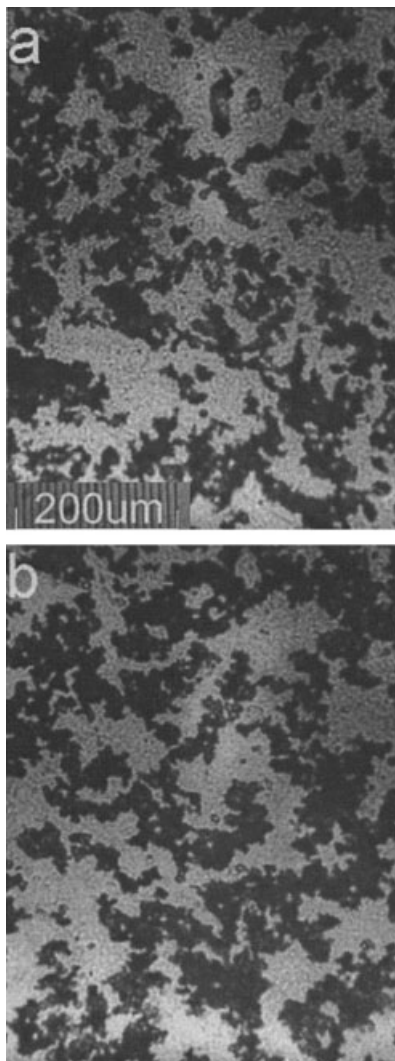


Figure 10 Morphology evolution of LDPE/PVC/NBR (70/30/7.5) blends: (a) optical micrograph of the blends after mixing 25 min at 150 rpm; (b) optical micrograph of (a) after mixing another 25 min at 50 rpm, showing an even finer phase structure.

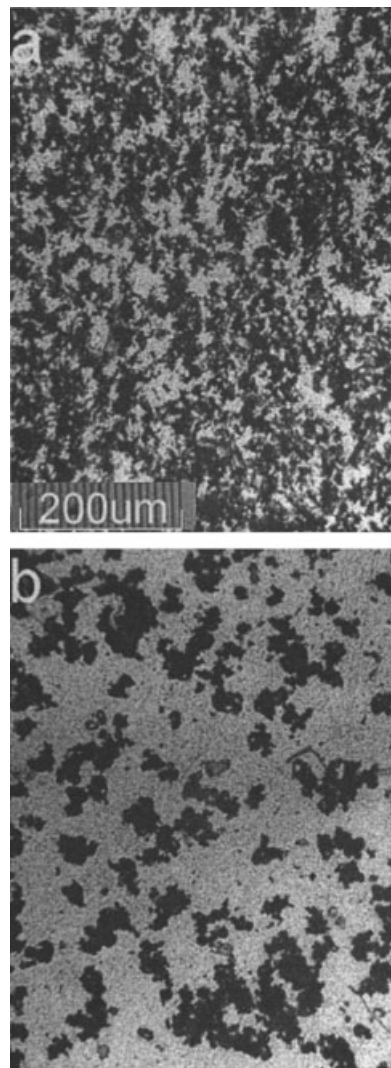


Figure 11 Morphology evolution of LDPE/PVC/SBR (70/30/7.5) blends: (a) optical micrograph of the blends after mixing 25 min at 150 rpm; (b) optical micrograph of (a) after mixing another 25 min at 50 rpm, showing the coalescence of the dispersed phase.

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