

Phase Dispersion–Crosslinking Synergism in Binary Blends of Poly(vinyl chloride) with Low-Density Polyethylene: Entrapping Phenomenon in PVC/LDPE/DCP Blend

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ABSTRACT: The co-crosslinked products and the entrapping phenomenon that may exist in a poly(vinyl chloride)/low density polyethylene/dicumyl peroxide (PVC/LDPE/DCP) blend were investigated. The results of selective extraction show that unextracted PVC was due to not being co-crosslinked with LDPE but being entrapped by the networks formed by the LDPE phase. SBR, as a solid-phase dispersant, can promote the perfection of networks of the LDPE phase when it is added to the PVC/LDPE blends together with DCP, which leads to more PVC unextracted

and improvement of the mechanical properties of PVC/LDPE blends. Meanwhile, the improvement of the tensile properties is dependent mainly on the properties of the LDPE networks. Finally, the mechanism of phase dispersion–crosslinking synergism is presented. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1296–1303, 2003

Key words: poly(vinyl chloride) (PVC); polyethylene (PE); crosslinking; networks

INTRODUCTION

A blending technique is an efficient way for the modification of general plastics and treatment and recycling of plastics wastes. Most of the polymer blends, however, are immiscible at the molecular level. The immiscibility between polymeric pairs is responsible for the poor phase structure and mechanical properties of polymer blends. Various methods have been used for compatibilizing polymer blends, namely, the introduction of strong specific interaction (e.g., hydrogen bonding,^{1,2} cocrystallization,^{3,4} and chemical reactions^{5,6}), the addition of a block or graft copolymer,⁷ and the formation of interpenetrating networks and crosslinking.^{8–10} The addition of a crosslinking agent in the blend may form a semi-interpenetrating or interpenetrating networks and co-crosslinked products during the melt-mixed process.^{11,12} The co-crosslinked products that are formed at the interlayer of two-component polymers may act as an *in situ* compatibilizer. Also, the formation of semi-interpenetrating networks can enhance the mechanical properties of the matrix phase.

The binary blends of poly(vinyl chloride) (PVC) and polyethylene (PE) are typically immiscible with a poor phase structure and mechanical properties. Therefore, enhancing the compatibility of PVC and PE is a key technology to obtain polymer blends with desirable properties. In our former article,¹³ a compatibilization–crosslinking synergism technique was proposed to improve the mechanical properties of PVC and PE. A compatibilizer can promote the phase dispersion of PVC and PE and their interfacial adhesion. Then, the probability of a crosslinking agent existing at the interface will increase and more co-crosslinked products will be formed. Therefore, compatibilization and crosslinking are both exerted sufficiently. Further studies showed that the core of the compatibilization–crosslinking synergism technique is phase dispersion–crosslinking synergism,^{14–17} that is, not only can a compatibilizer promote the dispersion of incompatible polymer blends, but also a solid-phase dispersion (SPD)¹⁸ and a crosslinking agent have a good synergism which can remarkably improve the mechanical properties of incompatible polymer blends.

In previous articles,^{14,19} we found that an SPD butadiene rubber (BR) or styrene-butadiene rubber (SBR) and the crosslinking agent dicumyl peroxide (DCP) have a good synergism in the improvement of the mechanical properties of incompatible PVC/low-density PE (LDPE) blends. Although synergism has been applied to the treatment of commingled plastic waste,²⁰ up to now, studies have been limited to the

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TABLE I
Influence of Crosslinking on the Characteristics of PVC/PE Blend and PVC/SBR Blend

Samples	Composition (g)	Ext (%)	Ext' (%)	Ext/Ext' (%)	Tensile strength (MPa)	Elongation at break (%)
PVC/LDPE	100/10	87.9	87.0	101.0	12.7	80
PVC/LDPE/DCP	100/10/1	89.1	86.2	103.4	11.0	52
PVC/LDPE	50/50	49.8	47.8	104.2	7.1	11
PVC/LDPE/DCP	50/50/1	38.6	47.8	80.8	7.2	39
PVC/LDPE	10/100	10.4	9.6	108.3	8.4	50
PVC/LDPE/DCP	10/100/1	7.8	9.6	81.2	8.2	99
PVC/SBR	100/10	97.1	96.1	101.0	5.7	42
PVC/SBR/DCP	100/10/1	86.7	86.2	100.6	9.7	85
PVC/SBR/DCP/TAIC/MgO	100/10/1/2/1	87.5	84.3	103.8	10.8	97

rheology, morphology, and mechanical properties. Thorough analyses of the involved processes and the formed polymer structure have not been published yet.²¹ In this article, the co-crosslinked products and

the entrapping phenomenon that may exist in the PVC/LDPE/DCP blend were investigated and the mechanism of phase dispersion-crosslinking synergism in a PVC/LDPE/SBR/DCP blend is discussed.

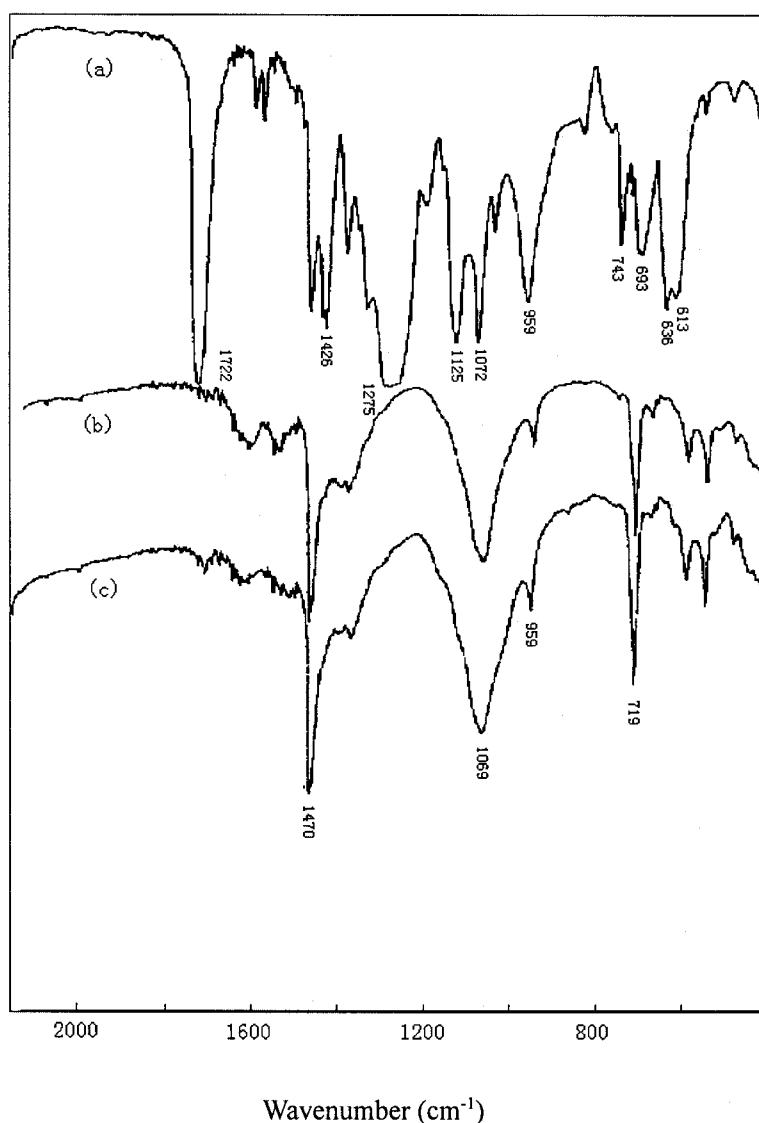


Figure 1 FTIR spectra of (a) PVC/LDPE, (b) extracted PVC/LDPE, and (c) extracted PVC/LDPE/DCP.

The results will contribute to the understanding of the formed polymer structure of immiscible polymer pairs with the crosslinking agent.

EXPERIMENTAL

Materials

PVC (WS-800S) was a product of Shanghai Chloroalkali Chemical Co., Ltd. (China). LDPE (2F2B, MFR = 2.0 g/10 min, density 0.922 g/cm³) was supplied by the Shanghai Petrochemical Co., Ltd. (China). Gaoqiao Petrochemical Co. (Shanghai, China) supplied the DCP, while SBR (1500) was obtained from the Jilin Chemical Industry Stock Co. Ltd. (Jilin, China). Tetrahydrofuran (THF) was a product of the Hangzhou Shuanglin Chemical Reagent Co. (Hangzhou, China).

Processing

PVC and its additives (weight ratio: PVC/DOP/3PbO · PbSO₄/2PbO · PbHPO₄/HSt = 100/32/3/3/1) were mixed and milled (front roll 155–160°C, rear roll 145–150°C) for 5 min. (For simplification, the plasticized PVC prepared is written as PVC in the following part of this article.) LDPE, SBR, or nitrile-butadiene rubber (NBR) was milled (front roll 140°C, rear roll 135°C) together with PVC. Finally, the crosslinking agent was added and mixed for 5 min. The well-mixed piece is then transferred to a preheated compression mold and hot-pressed at 160°C under 14 MPa, then annealed at ambient temperature to give a blend sheet for testing.

Characterization

Samples of about 1 g were extracted by THF in a Soxhlet extractor at a bath temperature of 82°C for 50 h. The weight ratio of the extractable part, *Ext*, was calculated by

$$Ext = \frac{(w_1 - w_2)}{w_1}$$

where w_1 and w_2 indicate the weight of the sample before and after extraction, respectively.

The components of the samples that were included before and after extraction were qualitatively monitored by Fourier transform infrared spectroscopy (PK-6000 FTIR) in the form of a film or KBr wafer. The T_g of the samples was determined by an Advanced Rheometric Expansion System (2ARES-9A) over a range of temperatures from 20 to 90°C with measurements being made at 10 Hz. The results obtained allow the $\tan \delta$ values to be found for the materials over the range of temperatures employed. The T_g values were taken at the peak temperature in the $\tan \delta$ curves in the ARES

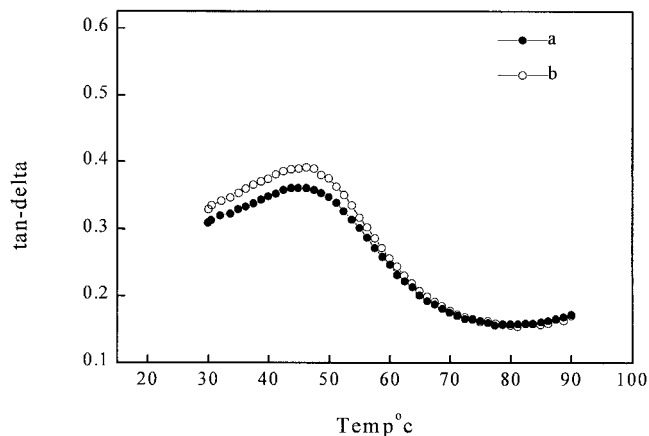


Figure 2 Dynamic mechanical spectra of PVC in (a) PVC/LDPE and (b) PVC/LDPE/DCP.

measurements. The melt viscosity of the LDPE/SBR blend was measured under 13.5 kPa of stress shear at 160°C with an XLY-2 capillary rheology instrument. The phase morphology of the sample was examined with an optical microscope. For enhancing the phase contrast between the PVC and LDPE phases, the film of the sample was treated with a θ -like solvent²² before observation. A tensile test was performed according to the GB1040-89 standard (similar to ISO527-1993) on an XL-250 tensile instrument at 20°C and a cross-head speed of 50 mm/min, using type III (dumbbell) samples.

RESULTS AND DISCUSSION

Co-crosslinking of PVC and LDPE

According to the results of selective extraction presented in an earlier article,¹¹ we proposed that DCP could initiate the co-crosslinking of PVC and LDPE for a minor part of PVC was unextracted in the PVC/LDPE (1:1) blend. But we are curious as to whether there are other possibilities: For example, the crosslinked LDPE could form tight networks, which could entrap PVC chains and make it unextractable by the solvent. For avoiding the entrapment, only 10 g of PE was blended with 100 g of PVC to investigate the co-crosslinking. In such a system, PE forms the dispersed phase and PVC forms the matrix. As shown in Table I, PVC in the PVC/LDPE/DCP (100/10/1) blend is absolutely extracted. The FTIR spectrum [see Fig. 1 (c)] shows that there is no characteristic absorption (such as 1426 or 1256 cm⁻¹) of PVC²³ for the sample of the PVC/LDPE/DCP blend after extraction. Furthermore, Figure 2 demonstrates that the T_g of PVC in the PVC/LDPE/DCP (100/10/1) blend is the same as that in the PVC/LDPE (100/10) blend. All these results sustain that few PVC chains crosslinked themselves or co-crosslinked with LDPE when only DCP was added.

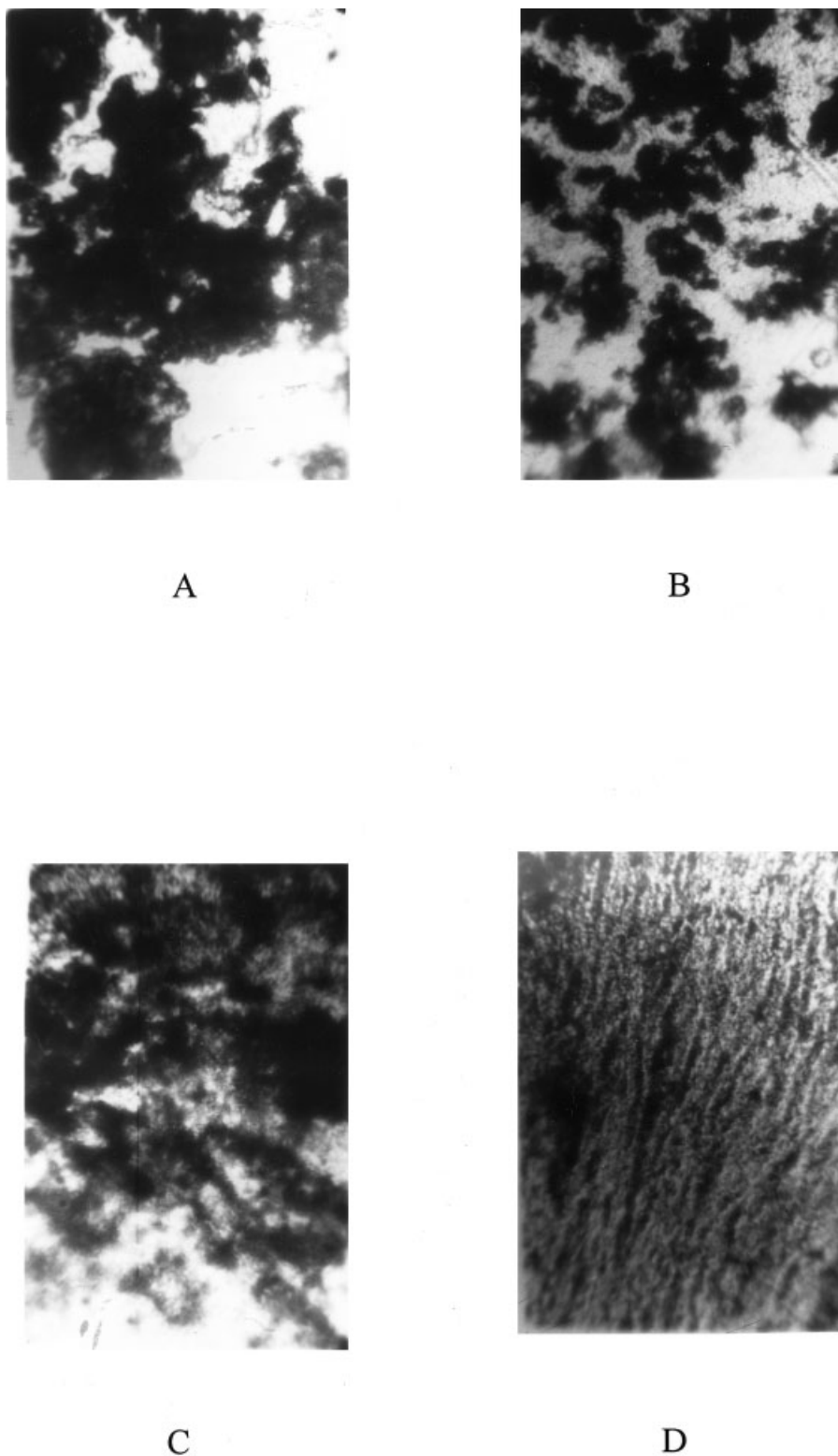


Figure 3 Phase contrast microscope observation of PVC/LDPE/SBR/DCP blends ($\times 120$): (A) 50/50/0/0; (B) 50/50/1.5/0; (C) 50/50/0/0.9; (D) 50/50/1.5/0.9.

Entrapping phenomenon in PVC/LDPE/DCP blends

As shown in Table I, the results of the PVC/LDPE/DCP (100/10/1) blend extracted by THF show that

PVC can be extracted completely. When it comes to the PVC/LDPE/DCP (50/50/1) blend and the PVC/LDPE/DCP (10/100/1) blend, the weight ratios of the extractable part (*Ext*) of 38.6 and 7.8%, respectively,

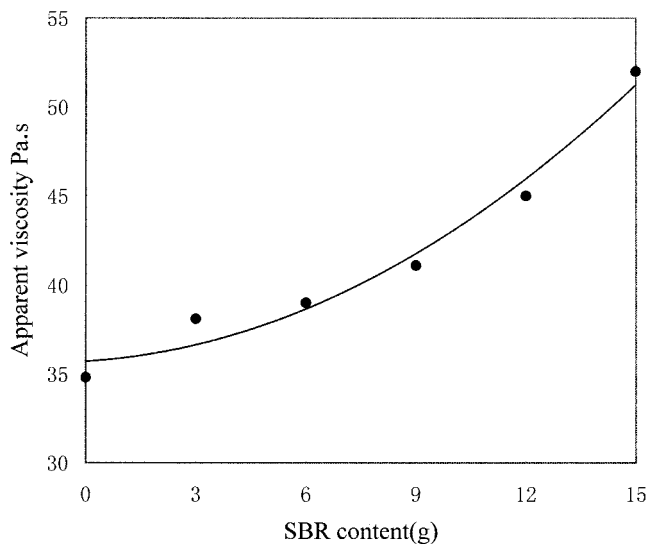


Figure 4 Influence of SBR on the apparent viscosity of the LDPE/SBR blend.

show that PVC cannot be extracted completely by the THF solvent. We affirmed that no co-crosslinking products of PVC and LDPE were formed when DCP was added to the PVC/PE blends alone. So, we believe there must be the formation of semi-interpenetrating networks composed of crosslinked LDPE and uncrosslinked PVC. In the PVC/LDPE/DCP (100/10/1) blends, a minor part of LDPE (10 g) forms a dispersed phase, which has no ability to form a continuous crosslinking network due to the disturbance of the major part of PVC (100 g); hence, PVC was exposed to the THF solvent absolutely. When there is 50 g LDPE or 100 g LDPE in the blends, LDPE forms the continuous phase and the effective crosslinking networks of LDPE are formed with the assistance of DCP. The crosslinking networks of LDPE firmly entrap the PVC chains. This prevents a minor part of PVC from being exposed to the THF solvent.

In the PVC/LDPE (100/10) blend, it is a well-known fact that PVC is incompatible with LDPE, so the dispersed-phase LDPE acts as an isolator, which inevita-

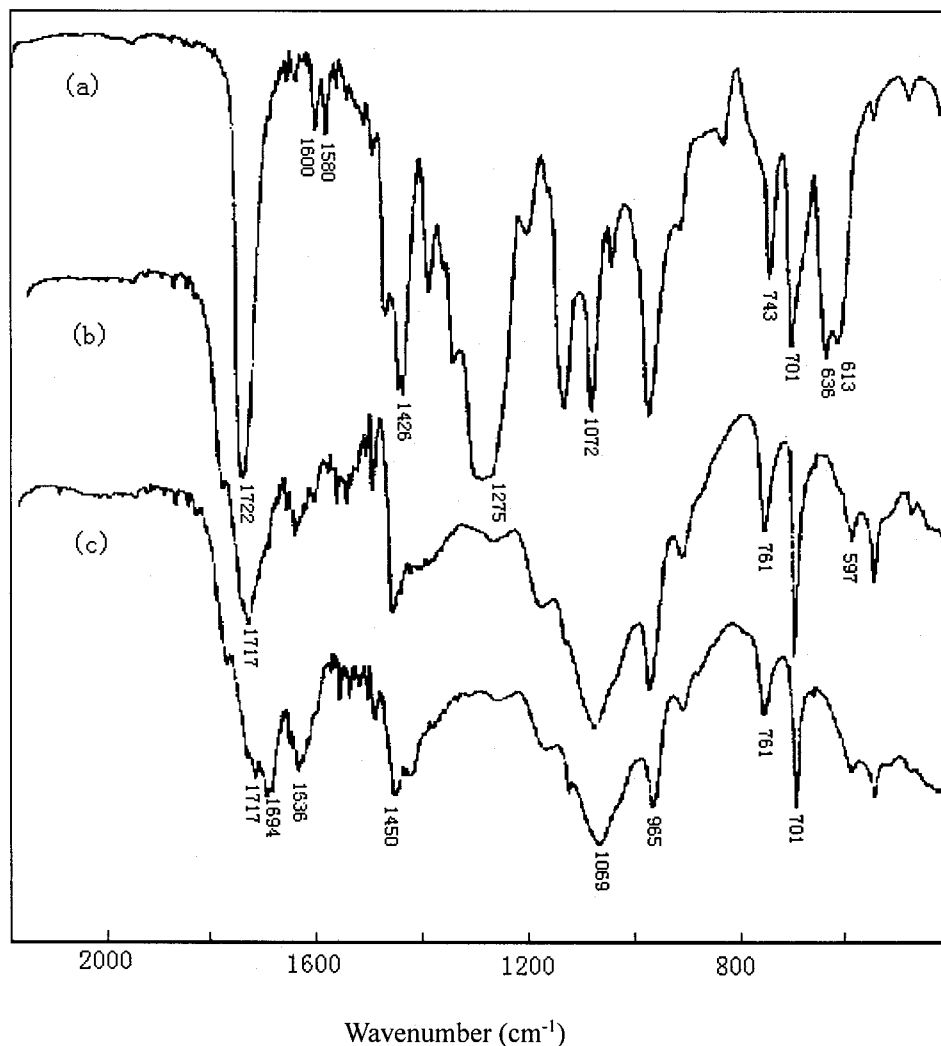


Figure 5 FTIR spectra of (a) PVC/SBR, (b) extracted PVC/SBR/DCP, and (c) extracted PVC/SBR/DCP+TAIC+MgO.

bly leads to the poor tensile properties of the blend. When DCP is added to the blend alone, only the LDPE phase is crosslinked. Consequently, the LDPE phase becomes less adhesive to the PVC phase. So, the tensile properties are lower than those of the PVC/LDPE blend. As to the PVC/LDPE (50/50) blend and the PVC/LDPE (10/100) blend, owing to the formation of the networks of the LDPE phase, the elongation at break is promoted. That the tensile strength of the two blends with DCP is similar to that without DCP shows that there is no co-crosslinking products formed in the interface.

Influence of SBR on the entrapping phenomenon

SBR was added to the PVC/LDPE blend as an SPD. Figure 3 shows that SBR can enhance the phase dispersion of PVC and LDPE. We believe it to be attributed to that SBR can increase the melt viscosity of the LDPE phase (as shown in Fig. 4) and, hence, decrease the viscosity ratio between the PVC phase and the LDPE phase.

Experiments were done to make clear whether the added SBR could induce PVC co-crosslinking with LDPE in the presence of the crosslinking agent or the composite crosslinking agent (including DCP, triallyl isocyanurate (TAIC), and MgO). As shown in Table I, the values of Ext/Ext' were 101.0, 100.6, and 103.8%, respectively, revealing that PVC cannot be crosslinked with SBR. This was also demonstrated by the absence of the characteristic absorption (such as 1426 or 1256 cm^{-1}) of PVC in the extracted PVC/SBR/DCP blend and the extracted PVC/SBR/DCP+TAIC+MgO blend in their FTIR spectra as shown in Figure 5. However, the results of the dynamic rheological behavior in Figure 6 show that the T_g 's of the blends with the crosslinking agent or the composite crosslinking agent are decreased, compared with that of the blend without the crosslinking agent. It may be attributed to

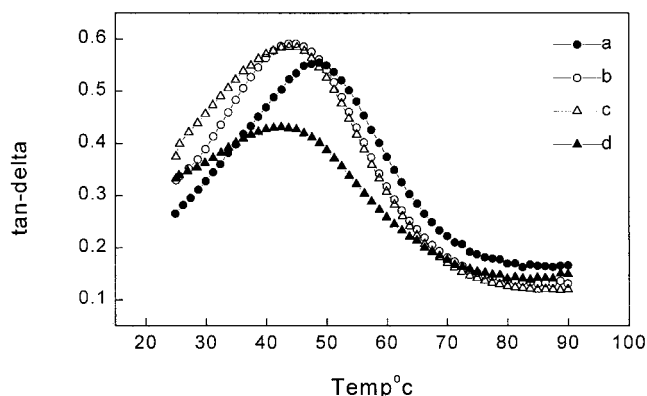
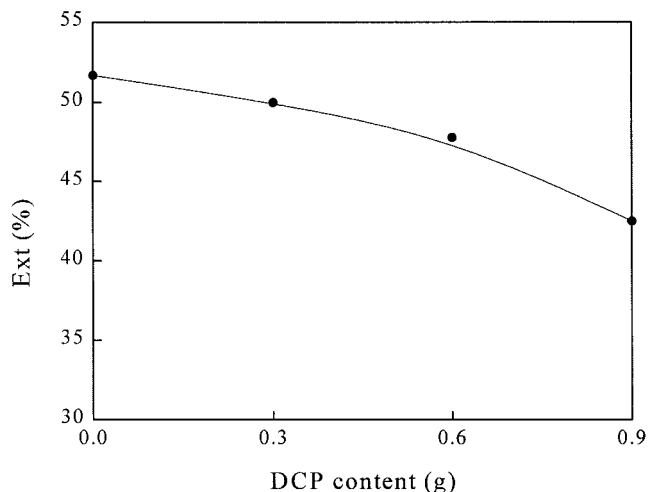
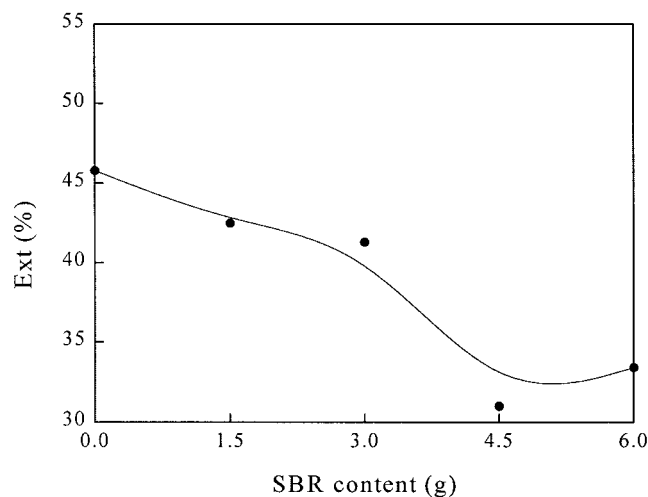


Figure 6 Dynamic mechanical spectra of PVC in (a) PVC/SBR, (b) PVC/SBR/DCP, (c) PVC/SBR/DCP+TAIC+MgO, and (d) PVC.



(a)

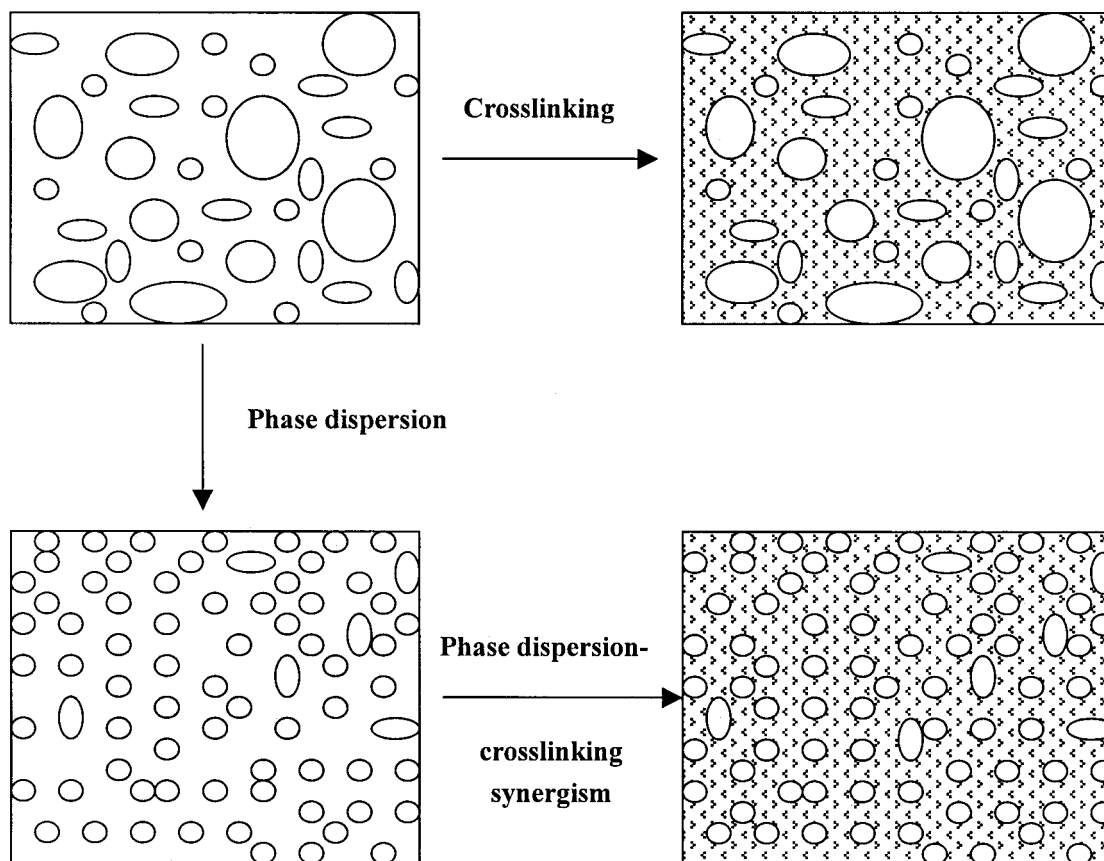


(b)

Figure 7 Influence of DCP and SBR content on the Ext of PVC in (a) PVC/LDPE/SBR (50/50/1.5) blend and (b) PVC/LDPE/DCP (50/50/0.9) blend.

the fact that the dioctyl phthalate (DOP) is transferred from the PVC phase to the SBR phase. From Figure 6(a,d), we find that the T_g of the (a) PVC/SBR blend moves toward high temperature compared with that of (d) PVC. However, when a crosslinking agent is added to the PVC/SBR blend, the SBR phase is crosslinked. The crosslinked SBR has less ability to absorb DOP from PVC. So, the T_g in the blend with a crosslinking agent returns to low temperature.

Figure 7(a,b) shows the effects of SBR and DCP on the weight ratio of extractable PVC. From Figure 7(a), we find that SBR combined with DCP could cause more PVC to be unextractable in the PVC/LDPE blends. It also indicates that the extractable PVC in the PVC/LDPE blends is reduced with increase of the DCP and SBR content, while it was proved above that SBR could not induce PVC to be crosslinked. By ana-



Scheme 1 Mechanism of phase dispersion-crosslinking synergism; domain is PVC and matrix is LDPE.

lyzing the phase morphology of the blends using an optical microscope (see Fig. 3), we found that the blends form a semi-interpenetrated network structure composed of a crosslinked LDPE phase and an uncrosslinked PVC phase.

From Figure 3(A,B), with the help of SBR, the morphology of PVC/LDPE becomes better, which brings about a better structure of the LDPE crosslinked networks [see Fig. 3(C,D)]. As we know, the better the structure of the LDPE networks is, the more chances there will be that PVC can be entrapped. Moreover, because SBR is easily crosslinked in the presence of DCP, it can act as a crosslinking coagent of LDPE and help to entrap more PVC. Additionally, the more DCP, the higher the density of the crosslinked networks of LDPE, which makes PVC less extractable. The mechanism of phase dispersion-crosslinking synergism is elucidated in Scheme 1.

Tensile properties of the blends

Figures 8 and 9 show the effects of the SBR and DCP content on the tensile properties of the PVC/LDPE/SBR/DCP blend. From Figure 9, we find that when SBR and DCP are added to the blends simultaneously the tensile properties of the blends were modified.

Through studying the entrapping phenomenon in the PVC/LDPE/SBR/DCP blend, we infer that the tensile properties of the blends are dependent mainly on the properties of the LDPE crosslinked networks; uncrosslinked PVC merely acts as finely divided polymeric filler. Therefore, the mechanical properties of

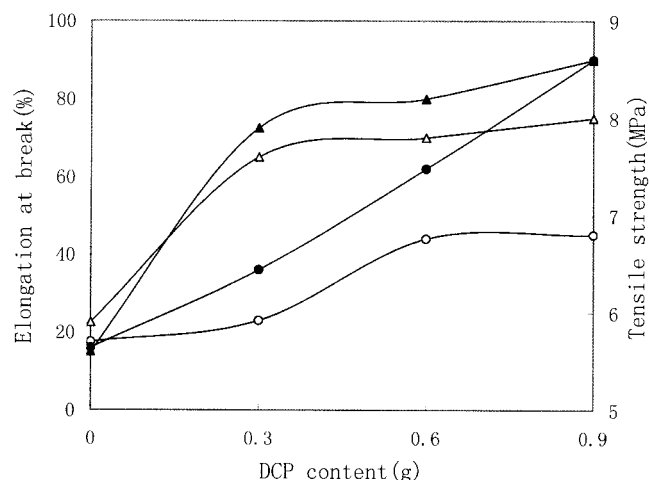


Figure 8 Influence of DCP content on (○,●) elongation at break and (△,▲) tensile strength: (hollow) PVC/LDPE (50/50); (solid) PVC/LDPE/SBR (50/50/1.5).

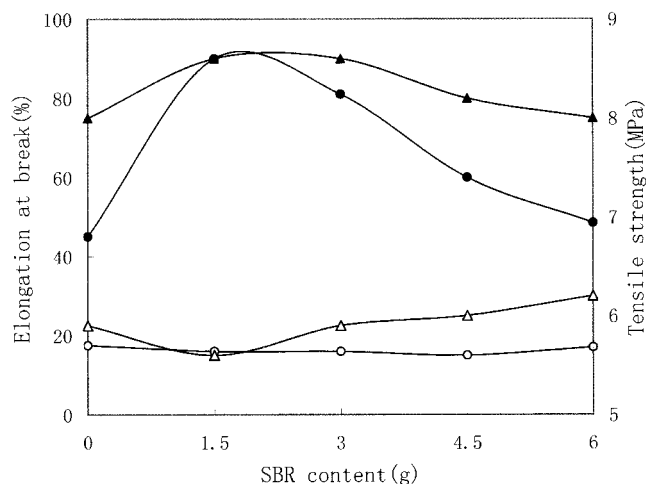


Figure 9 Influence of SBR content on (○,●) elongation at break and (△,▲) tensile strength: (hollow) PVC/LDPE (50/50); (solid) PVC/LDPE/DCP (50/50/0.9).

the PVC/LDPE blends may be improved by modifying the perfection of the networks. From Figures 8 and 9, with an increment of the SBR content, the tensile properties of the PVC/LDPE blends show little modification. However, the tensile properties of the PVC/LDPE blend and the PVC/LDPE/SBR blend could be improved remarkably with the help of DCP. Especially, when 1.5 g SBR and 0.9 g DCP were added simultaneously, the blend showed a tensile strength of 8.6 MPa and an elongation at break of 90% versus 5.9 MPa and 17.5%, respectively, for the blends without SBR and DCP. The morphology of the blends shows a continuously fine structure of LDPE crosslinked networks [see Fig. 3(D)].

As we know, SBR can promote the phase dispersion of PVC and LDPE, but cannot improve their interfacial adhesion. While DCP can initiate the crosslinking of the LDPE phase and, hence, improve the tensile properties, the crosslinked networks are not perfect because of the poor phase dispersion of the blends. When SBR and DCP are added to the blends simultaneously, the LDPE phase is distributed continuously around the blends and the continuous perfect crosslinked networks of LDPE are formed. Therefore, good synergism results and the tensile properties are modified due to the formation of the more continuous crosslinked networks and fine phase dispersion.

However, the tensile properties of the blends reduce slowly with a further increment of SBR, especially their elongation properties. This is due to that excess SBR will attract DCP to the rubber phase, which leads

to highly crosslinked SBR and, consequently, less elasticity and more of the isolator in the blends.²⁴

CONCLUSIONS

The entrapping phenomenon that exists in the PVC/LDPE/DCP blend demonstrates that unextracted PVC was entrapped by the networks formed by the LDPE phase and not by the existence of the co-crosslinked product PVC-*x*-LDPE. SBR, as an SPD, can promote the perfection of the crosslinking networks of the LDPE phase when it is added to the PVC/LDPE blend together with DCP, which results in a good synergism and the improvement of the mechanical properties of the PVC/LDPE blend.

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References

- Tarlou-Smith, R. E.; Register, R. A. *Macromolecules* 1993, 26, 2802.
- Meaurio, E.; Cesteros, L. C.; Katime, I. *Macromolecules* 1997, 30, 4567.
- Ree, M.; Kyu, T.; Stein, R. S. *J Polym Sci Part B Polym Phys* 1987, 25, 105.
- Tang, T.; Li, H.; Huang, B. *Macromol Chem Phys* 1994, 195, 2931.
- Li, H.; Chiba, T.; Higashida, N. *Polymer* 1997, 38, 3921.
- Huang, C. C.; Chang, F. C. *Polymer* 1997, 38, 4287.
- Xu, S.; Zhao, H.; Tang, T. *Polymer* 1999, 40, 1537.
- Sanchez, M. S.; Ferrer, G. G.; Cabanilles, C. T. *Polymer* 2001, 42, 10071.
- Mathew, A. P.; Packirisamy, S.; Thomas, S. *J Appl Polym Sci* 2000, 78, 2327.
- Wu, C. F. *J Appl Polym Sci* 2001, 80, 2468.
- Fang, Z.; Xu, C.; Bao, S.; Zhao, Y. *Polymer* 1997, 38, 131.
- Zhu, S. H.; Chan, C. M.; Wong, S. C.; Mai, Y. W. *Polym Eng Sci* 1999, 39, 1998.
- Xu, C.; Fang, Z.; Zhong, J. *Angew Makromol Chem* 1993, 212, 45.
- Xu, C.; Fang, Z.; Zhong, J. *Polymer* 1997, 38, 155.
- Fang, Z.; Xu, C.; Bao, S.; Zhao, Y. *Kexue Tongbao (Sci J)* 1995, 40, 1246.
- Xu, C.; Zhong, M.; Guo, S. *Shuliao (Plastics)* 1988, 17(2), 15.
- Xu, C.; Bao, S. *Zhongguo Shuliao (China Plast)* 1991, 5(2), 43.
- Ghaffar, A.; Sadrmohegh, C.; Scott, G. *Eur Polym J* 1981, 17, 941.
- Fang, Z.; Ma, G.; Cai, G.; Xu, C. In *Preprints of 1999 Symposium on Polymers*, Shanghai, China, 1999; p f-242.
- Fang, Z.; Zeng, M.; Cai, G. *J Appl Polym Sci* 2001, 82, 2947.
- Cor, K.; Martin, V.; Christophe, P. *Prog Polym Sci* 1998, 23, 707.
- Zhong, J.; Xu, C. *Zhongguo Shuliao (China Plast)* 1991, 5(3), 31.
- Shen, D. *Infrared Spectroscopy, Applications in Polymers*; Science: Beijing, 1982.
- Wu, P.; Zhang, L. In *Blending Modification of Polymers*; Wu, P., Zhang, L., Eds.; China Light Industry: Beijing, 1996; p 106.