Study on phase dispersion-crosslinking synergism in binary blends of poly(vinyl chloride) with low density polyethylene

Chengwei Xu, Zhengping Fang*, Jianhua Zhong

Department of Chemistry, Hangzhou University, Hangzhou 310028, People's Republic of China

(Received 27 January 1995; revised 21 March 1996)

Influences of butadiene rubber (BR) on the structure and mechanical properties of poly(vinyl chloride) (PVC)/low density polyethylene (LDPE) blends and its synergism with crosslinking agent have been studied. As a solid phase dispersant, BR can promote the phase dispersion of PVC and LDPE, but cannot improve their interfacial adhesion. While dicumyl peroxide (DCP) can initiate the co-crosslinking of PVC and LDPE and hence improve their interfacial adhesion, its efficiency is limited because of the poor phase dispersion of the blend. When BR and DCP are added to the blend simultaneously, the probability of DCP existing at the interface will increase and more co-crosslinking products will form. Therefore, good synergism will be caused and the mechanical properties will be modified due to the improvement of the interfacial adhesion. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl chloride); polyethylene; blend)

INTRODUCTION

There are two major ways to improve the mechanical properties of polyvinyl chloride (PVC)/polyethylene (PE) blends. One is to add compatibilizer¹⁻⁵ and the other is to co-crosslink the two components⁵⁻⁸. In the previous papers⁹⁻¹³, we have found that there is a synergism between compatibilizer and crosslinking agent and the mechanical properties of the blends could be improved by using a compatibilization–crosslinking synergism technique.

Ghaffar *et al.*¹⁴ proposed a third way to enhance the properties of PVC/PE blend, i.e. to add a solid phase dispersant (SPD) to the blend. According to their opinion, the SPD is not necessary to increase the interfacial adhesion, but it can surely enhance the phase dispersion of the two components.

According to the proposed compatibilization-crosslinking synergism theory¹¹, we believe there is also a synergism between SPD and the crosslinking agent. This paper reports the results of our study on phase dispersion-crosslinking synergism in PVC/low density PE (LDPE) blend by using butadiene rubber (BR) as a SPD and dicumyl peroxide (DCP) as a crosslinking agent.

EXPERIMENTAL

Materials

The PVC (TK-700) used was a product of the Japanese Shin-Etsu Chemical Co. LDPE (2F2B, MFI = 2.0 g

10 min⁻¹, density 0.922 g cm⁻³) was a product of Shanghai Petrochemical General Works, China, BR was supplied by Qilu Petrochemical Co., while DCP was obtained from Gaoqiao Petrochemical Co., China.

Procedures and characterizations Refer to the previous paper¹¹.

RESULTS AND DISCUSSION

It is well known that PVC and LDPE are incompatible. During their melt blending, PVC and LDPE dispersed each other under the shearing force. However, LDPE worked as an outer lubricant in this system due to its low melt viscosity at the mixing temperature. The shearing force which affected the PVC phase was then weak and the phase dispersion was therefore insufficient. The domain size of PVC/LDPE (3/2, w/w and throughout) blend was found to be large (*Figure 1a*). This result is in accord with the prediction of White *et al.*¹⁵, i.e. blending polar and hydrocarbon polymers of greatly differing viscosity level is extremely difficult, while polymers of similar viscosity seem to blend easily.

The melt viscosity of PE will increase when it is mixed with several rubbers¹⁶. Thus, the rubbers could be blended with LDPE to decrease its lubrication effect and hence increase the shearing force affecting the PVC phase. In this case, the phase dispersion will be upgraded during the blending process and, because of the limited activity of the polymer chains, this phase morphology will be maintained after the sample is cooled, though it is not thermomechanically stable.

As a matter of fact, when 5 g of BR is added to PVC/LDPE (3/2) blend, the MFI decreases from $5.4 \text{ g} 10 \text{ min}^{-1}$

^{*}To whom correspondence should be addressed



Figure 1 Optical microscopic observations of the blends: (a) PVC/LDPE(3/2); (b) PVC/LDPE/BR(12/8/1)



Figure 2 Influence of BR content on (a) tensile strength and (b) elongation at break of the blends: (A) PVC/LDPE(3/2); (B) PVC/LDPE/DCP(60/40/1)



Figure 3 Influence of DCP content on (a) tensile stength and (b) elongation at break of the blends: (A) PVC/LDPE(3/2); (B) PVC/LDPE/BR(6/4/1)



Figure 4 Schematic presentation of mechanism of phase dispersioncrosslinking synergism

to $4.0 \text{ g} 10 \text{ min}^{-1}$ at 170° C. As a result, the phase dispersion is upgraded and the domain size is reduced (*Figure 1b*).

Figures 2 and 3 show the effects of BR and DCP on the tensile properties of PVC/LDPE blends. PVC/LDPE (3/2) blend has rather poor mechanical properties. especially in its elongational characteristics, owing to the incompatibility of the components. Unlike compatibilizer, BR does not improve the mechanical properties of PVC/LDPE blend. In one of our papers¹⁶, we found that BR acts as a tie molecule in PE/BR blends and thus improves the tensile elongation remarkably, whereas here in the PVC/LDPE/BR blend, elongation at break increases very slowly with increase of BR content. This result reveals that the mechanical properties of this blend are essentially dependent on the interfacial adhesion. The properties of component polymers take a minor role. BR, compatible with LDPE, but incompatible with PVC. can only promote the phase dispersion of PVC and LDPE. It cannot improve the interfacial adhesion.

The mechanical properties of PVC/PE blend has been found to be improved by blending them in the presence of a crosslinking agent⁶⁻¹³. Although the crystallinity of PE will decrease when the crosslinking agent is added, the improvement of the mechanical properties may still be attributed to the formation of a penetrated network of PE and the co-crosslinked product, PVC-x-PE, which plays a role as a compatibilizer of PVC and LDPE. However, because phase dispersion is not sufficient, the contact area between the two components is small. Thus, co-crosslinking, which must take place at the interface, becomes difficult when crosslinking agent is only added to the blend.

On adding BR and DCP to PVC/LDPE blend simultaneously, we found the tensile properties to be improved more dramatically. In this system, the interfacial area, and hence the probability of crosslinking agent existing at the interface, will increase due to the improvement of the phase dispersion promoted by BR. More co-crosslinked products will form which can induce the modification of interfacial adhesion. Thus, the effect of the crosslinking agent will be exerted more efficiently. *Figure 4* provides a brief description of the mechanism of phase dispersion-crosslinking synergism.

Figure 5 demonstrates the morphologies of tensile fracture surfaces of the blends. For the binary blend (Figure 5a), the domain size is large and the interface is clear, which reveals its poor phase dispersion and interfacial adhesion. The blend with DCP (Figure 5b) has also large domains, but its interface is blurred. In comparison, the blend with both DCP and BR (Figure 5c) has smaller domains, which shows good synergism between the two agents.

On examining *Figure 6*, the mechanical properties of PVC/LDPE blends with various compositions can be improved by means of phase dispersion-crosslinking synergism. It should be noted that the pure LDPE and LDPE/BR blend have good elongational characteristics, and it is reasonable to suppose that adding DCP to these blends will reduce the elongation at break due to the limitation of the crosslinked network. Evidently, PVC/LDPE blends with compositions approaching to 1/1 (from 3/7 to 7/3) have very poor properties. Addition of BR itself rarely has positive influence and DCP's modification effect is not satisfactory, whereas the synergism between BR and DCP has a much greater modification effect.

CONCLUSIONS

As a SPD, BR can promote the phase dispersion of PVC and LDPE, but cannot improve their interfacial



Figure 5 Scanning electronic micrographs of the tensile fracture surfaces of the blends: (a) PVC/LDPE(3/2); (b) PVC/LDPE/DCP(60/40/1); (c) PVC/LDPE/BR/DCP (60/40/5/1)



Figure 6 Influence of phase dispersion-crosslinking synergism on (a) tensile strength and (b) elongation at break of the blends with various PVC/LDPE ratios: (A) PVC/LDPE; (B) PVC/LDPE/DCP(2g); (C) PVC/LDPE/BR(5g); (D) PVC/LDPE/BR(5g)/DCP(2g)

adhesion. While DCP can initiate the co-crosslinking of the two components and hence improve the interfacial adhesion, its efficiency is limited because of the poor phase dispersion of the blend. When BR and DCP are added to the blend simultaneously, the probability of DCP existing at the interface will increase and more co-crosslinked products will form. Therefore, good synergism will be caused and the mechanical properties will be modified due to the improvement of the interfacial adhesion.

ACKNOWLEDGEMENT

This work is supported by the National Natural Science Foundation of China.

REFERENCES

- 1 Paul, D. R., Vinson, C. E. and Locke, C. E. Polym. Eng. Sci. 1972, **12**, 157
- 2 Paul, D. R., Locke, C. E. and Vinson, C. E. Polym. Eng. Sci. 1973, **13**, 202

- 3 Locke, C. E. and Paul, D. R. Polym. Eng. Sci. 1973, 13, 308
- 4 Xu, C. and Zhong, M. Zhongguo, Suliao (China Plastics) 1988, 53
- 5 Xu, C., Zhong, M. and Ge, S. Suliao (Plastics) 1988, 17, 15; Chem. Abstr. 1988, 109, 191302b
- 6 Nakamura, Y., Mori, K., Yoshida, Y. and Tamura, K. Kobunshi Ronbunshu 1984, 41, 531
- 7 Nakamura, Y., Mori, K., Nishira, H. and Tamura, K. Kobunshi Ronbunshu, 1985, **42**, 567
- 8 Nakamura, Y., Watanabe, A., Mori, K. and Tamura, K. *J. Polym. Sci. Part C* 1987, **25**, 127
- 9 Xu, C. and Bao, S. Zhongguo Suliao (China Plastics) 1991, 2, 43
- 10 Zhong, J. and Xu, C. Preprints of 1992 Symposium on Polymers, Changchun, China, 1992, p. 1053
- 11 Xu, C., Fang, Z. and Zhong, J. Angew Makromol. Chem. 1993, 212, 45
- 12 Xu, C., Zhong, J. and Fang, Z. Proceedings of 34th IUPAC Congress, Beijing, China, 1993, p. 642
- 13 Fang, Z., Xu, C., Bao, S. and Zhao, Y. Polymer 1997, 38, 131
- 14 Ghaffar, A., Sadrmohaghegh, C. and Scott, G. Eur. Polym. J. 1981, 17, 941
- 15 White, J. L. and Min, K. in 'Polymer Blends and Mixtures' (Eds D. J. Walsh, J. S. Higgins and A. Maconnachie), Martinus Nijhoff, Dordrecht, The Netherlands, 1984, p. 413
- 16 Fang, Z., Bao, S., Shan, X. and Xu, C. Hecheng Xiangjiao Gongye (China Sythetic Rubber Industry), 1992, 15, 290