

CROSSLINKING AND COMPATIBILIZATION IN BLENDS OF POLYSTYRENE AND POLYETHYLENE*

FANG Zhengping (方征平) XU Chengwei (许承威) XIANG Yichong (项义崇)
WU Jianhua (吴建华) and XU Huanchi (徐欢驰)

(*Department of Chemistry, Hangzhou University, Hangzhou 310028, China*)

Abstract This paper investigated the influences of butadiene rubber (BR) and dicumyl peroxide (DCP) on thermal and rheological behaviour, morphology and mechanical properties of PS/LLDPE/SBS blend. Addition of DCP alone was found to decrease the mechanical properties of PS/LLDPE/SBS blend due to the decomposition of PS. When BR was added together with DCP, it is found that the co-crosslinking of BR, SBS and PE takes place, and the decomposition of PS is reduced simultaneously because of the consumption of the free radicals in the crosslinking process. Synergism was thus realised which resulted in the improvement of the ductility of blend.

Keywords Polystyrene; Polyethylene; Blends; Compatibilization; Crosslinking

INTRODUCTION

Polystyrene (PS) is usually toughened by incorporation of a disperse rubbery component which is partially compatible with PS. Mechanical properties of binary blends of polystyrene and polyethylene (PE) are rarely better than those of PS homopolymer. Attempts have been made to improve the blend performance by enhancement of the interfacial adhesion of the components through addition of a compatibilizer^[1~5] or by direct coupling between PS and PE^[6~8].

Phase dispersion (or compatibilization)-crosslinking synergism is an effective method to improve the properties of incompatible polymer blends. It has been successfully applied in binary blends of polyvinyl chloride with polyethylene^[9~13]. However, it seems difficult to realise such a charming synergism in PS/PE blend by using styrene-butadiene-styrene triblock copolymer (SBS) as a compatibilizer and dicumyl peroxide (DCP) as a crosslinking agent because PS is decomposed easily in the presence of a peroxide. In this paper, we will study the possibility of phase dispersion-crosslinking synergism in PS/PE blend by adding BR in this blend together with SBS and DCP.

* The project is supported by the National Natural Science Foundation of China.

Received February 3, 1997

EXPERIMENTAL

Materials

Polystyrene (PS 535, MFR=0.79g/10min) is a product of Zhanjiang Zhongmei Chemical Industries Ltd., China. Linear low density polyethylene (LLDPE 218W, MFR=2.2g/10min) is product of Saudi Basic Industries, Co., Saudi Arabia. SBS (YH-805, Star type, S/B=40/60, MFR=0.6g/10min) was supplied by Yueyang Chemical General Works, China. Butadiene rubber (BR) and DCP were obtained from Qilu Petrochemical Company and Gaoqiao Petrochemical Company, China.

Procedures

Polymer blends were generated by melt mixing on a two-roll mixer with the front and rear roll temperature of 155°C and 135°C, respectively. The well-mixed piece was transferred to a compression mould and pressed at 180°C under 20MPa for 10min to form a sheet. The blend compositions in this paper are given as weight ratios.

Characterisations

Rheologic measurements were performed in a HBI system 90 Rheologic instrument at 170°C and 30rpm. The temperature and torque were recorded with mixing time.

Samples of ca. 1g were extracted with toluene in a Soxhlet extractor at a bath temperature of 150°C for 50h. Elementary analysis was performed to determine carbon and hydrogen contents of the samples before and after extraction.

Specimens of $55 \times 6 \times 4\text{mm}^3$ (with a notch of 1mm in width and 1.3mm in depth) were used to measure the impact strength with a UT/10/40 impact instrument (Hungary AVK. Unrapest) at 10 ~ 15°C. Morphology of the fracture surfaces was observed through a Hitachi S-570 scanning electronic microscope.

Thermal transition temperatures of the blends were determined from DSC curves measured on a Perkin-Elmer 7 differential scanning calorimeter. Samples were first heated to 150°C for 5min and cooled down with a rate of 100°C/min. DSC scans were then performed with a heating rate of 10°C/min.

RESULTS

Rheological behaviour

LLDPE and SBS are easy to crosslink at 190°C in the presence of DCP, whereas PS tends to decompose at the same condition. Fig. 1 shows the influence of DCP on rheological behaviour of PS and PS/LLDPE/SBS systems. Temperature of the

material in the chamber reached a balance after ca. 5min. For PS/DCP system, there was a rapid decrease in torque between 5min to 9min, which corresponded to the decomposition of polystyrene. While for PS/LLDPE/SBS/DCP system, there was a competition between the crosslinking of PE and SBS and the decomposition of PS. An increase in torque appeared between 6min to 7min, revealing that the influence of crosslinking of PE and SBS was stronger than the influence of decomposition of PS during this period. The torque decreased afterwards, revealing that the decomposition of PS took a major role.

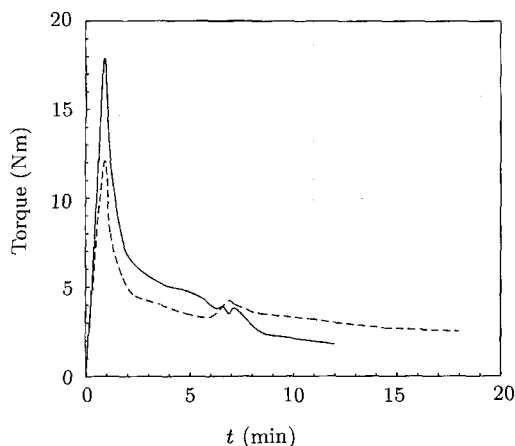


Fig. 1 Influence of DCP on rheologic behaviour of PS (solid line) and PS/LLDPE/SBS (85/15/9) blend (dotted line).

Selective extraction

Among the components in PS/LLDPE/SBS/BR/DCP (85/15/9/7/0.2) blend, only PE (weight content 12.91%) cannot dissolve in toluene. However, the remaining part of the sample extracted by toluene was 13.65% which was higher than PE content. And the molar ratio of the insoluble part was also higher than that of PE (Table 1). Combining the result of rheologic test, BR and SBS were expected to crosslink together with PE in this sample.

Table 1 Molar ratios of carbon and hydrogen of the components in PS/LLDPE/SBS/BR/DCP (85/15/9/7/0.2) blend

Material	C/H ratio (mol/mol)
LLDPE	0.50/1
PS	1.00/1
SBS	0.74/1
BR	0.67/1
Toluene-insoluble part	0.57/1

Impact strength

Fig. 2 and 3 show that the impact strength of PS/LLDPE/SBS (85/15/9) blends decreases when DCP or BR is added alone. However, when DCP and BR were added together, they showed a very good synergism. For the blend containing 0.2g

DCP, the impact strength (σ_i) increased with increasing BR content. σ_i reached to 17kJ/m^2 at BR content of 9g, about twice as much as the value of the blend without BR and DCP. For the blend with fixed BR content (7g), σ_i increased sharply with the increase of DCP and reached a maximum (18kJ/m^2) at DCP content of ca. 0.15g. σ_i decreased slowly with the further increase of DCP content.

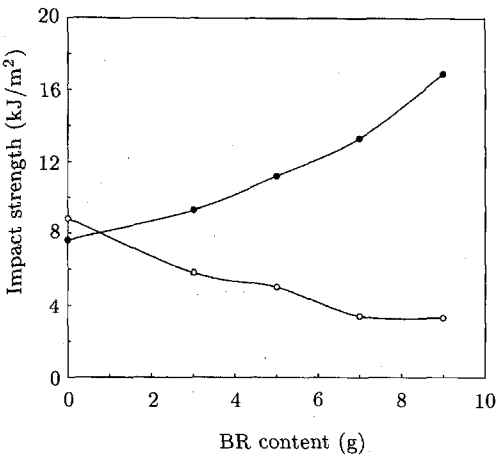


Fig. 2 Influence of BR content on notched impact strength of PS /LLDPE/SBS (85/15/9) (cycle) and PS/LLDPE/SBS/DCP (85/15/9/0.2) (point) blends

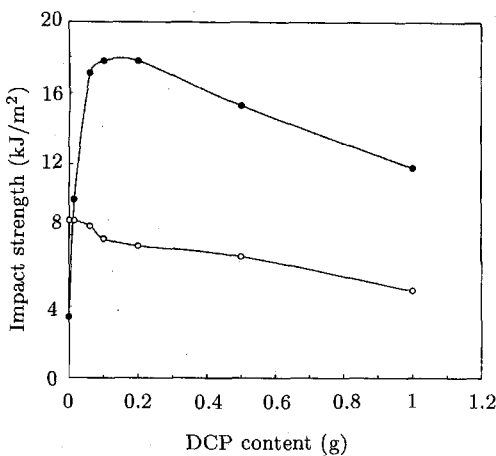


Fig. 3 Influence of DCP content on notched impact strength of PS /LLDPE/SBS (85/15/9) (cycle) and PS/LLDPE/SBS/BR (85/15/9/7) (point) blends

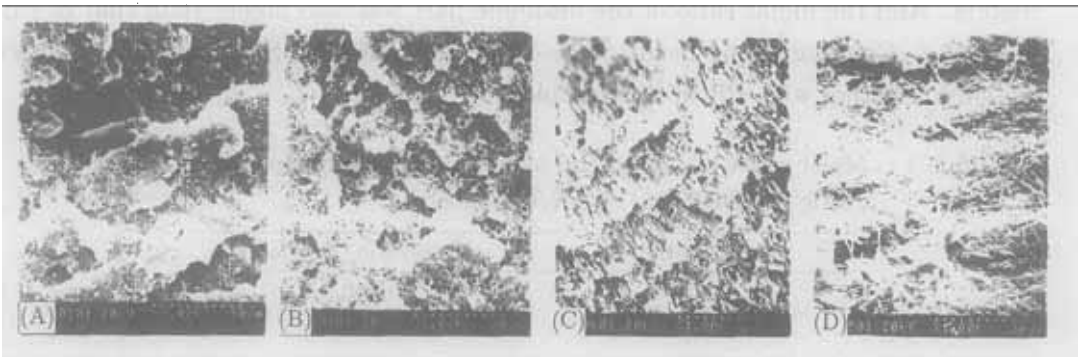


Fig. 4 SEM observations of some blends
(A) PS/LLDPE/SBS (85/15/9); (B) PS/LLDPE/SBS/BR (85/15/9/7); (C) PS/LLDPE/SBS/BR/DCP (85/15/9/7/0.1); (D) PS/LLDPE/SBS/BR/DCP (85/15/9/7/0.3)

Morphology

Scanning electron microscopic observations showed that the domain size increased when 7g BR was added in PS/LLDPE/SBS (85/15/9) blend alone. When 0.1g DCP was added together, the spherical domains vanished and many tiny fibres

protruded out from the fracture surface. It is easy to conclude that a transition from brittle fracture to tough fracture takes place before and after DCP is added. In the blend containing 0.3g DCP, the domains appeared again and the fracture seemed to peeled off one layer upon another, manifesting a less tough fracture than the blend containing 0.1g DCP.

Thermal behaviour

$T_{g,PS}$ ($92^{\circ}C$) and $T_{m,PE}$ ($115^{\circ}C$) in PS/LLDPE/SBS blend are lower than their original values. Addition of BR into PS/LLDPE/SBS blend induced $T_{g,PS}$ and $T_{m,PE}$ to move toward higher temperatures. When DCP was added to this four-component blend, $T_{g,PS}$ and $T_{m,PE}$ decreased again to the position near their values in PS/LLDPE/SBS blend.

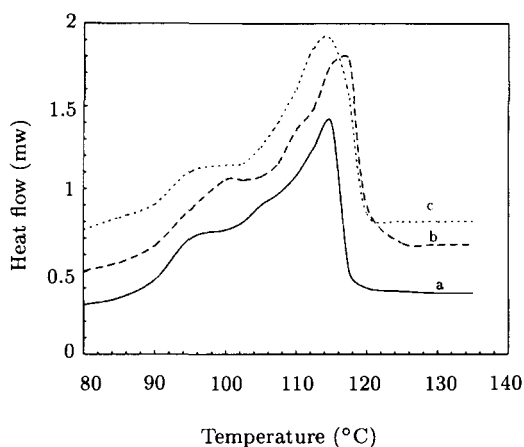


Fig. 5 DSC scans of some blends. (a) PS/LLDPE/SBS (85/15/9); (b) PS/LLDPE/SBS/BR (85/15/9/7); (c) PS/LLDPE/SBS/BR /DCP (85/15/9/7/0.2)

DISCUSSION

Polystyrene and polyethylene are immiscible polymers. Binary blends of PS/LLDPE have a two-phase structure with big domains and poor interfacial adhesion. In ternary blends of PS/LLDPE/SBS, SBS distributes in the interface between PS and LLDPE, leading to the improvement of the interfacial adhesion. $T_{g,PS}$ and $T_{m,PE}$ are thus decreased due to the influence of the other phase.

Fig. 6 gives a brief description of the synergism between BR and DCP in PS/LLDPE/SBS blend. The solubility parameter of BR ($17.15J^{1/2}cm^{-3/2}$, calculated by Small^[14]) is between those of PS ($18.66J^{1/2}cm^{-3/2}$) and PE ($16.6J^{1/2}cm^{-3/2}$). When BR is added to PS/LLDPE/SBS blend, it is more likely to distribute in the interphase. Because the butadiene block of SBS is easier to mix with BR than PE, SBS is more possibly to distribute in the interface of PS and BR. This will reduce the compatibilization effect of SBS on PS/PE and thus induce an increase in domain size. Consequently, $T_{g,PS}$ and $T_{m,PE}$ recover to their original values and the impact strength decreases.

When DCP is added to the blend together with BR, in-situ crosslinking will

take place in PE, SBS and BR component (as revealed by the result of rheological behaviour and selective extraction). The co-crosslinked products (SBS-x-PE, SBS-x-BR, BR-x-PE) improve the interfacial adhesion between polyethylene and butadiene block of SBS. At the same time, the decomposition of PS is reduced because of the consumption of the free radicals in the crosslinking process. In this way, the impact strength increases remarkably and $T_{g,PS}$ and $T_{m,PE}$ decreases again.

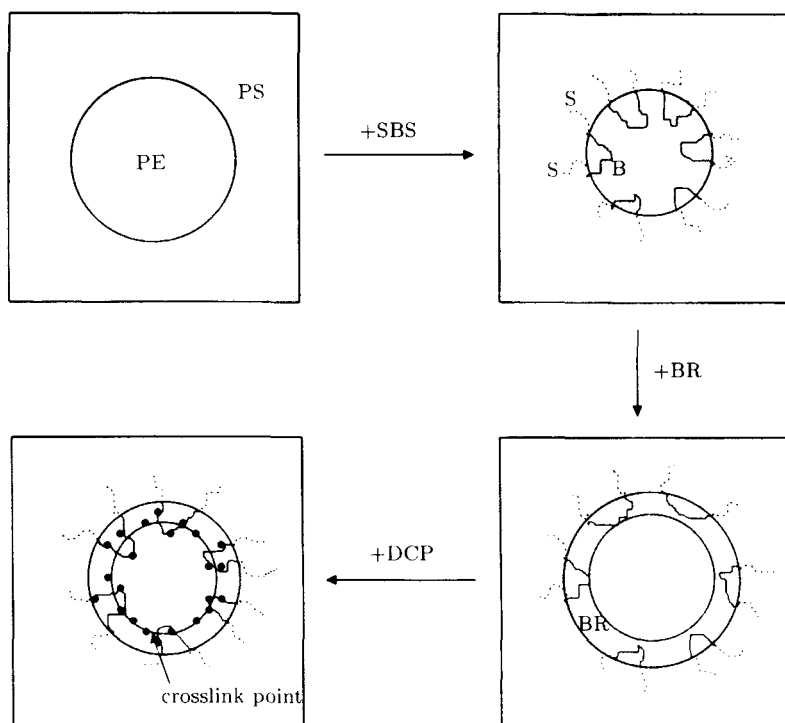


Fig. 6 Schematic presentation of phase dispersion-crosslinking synergism in PS/LLDPE/SBS blend

When too much DCP is added, the effect of decomposition will surpass the effect of crosslinking. In this cases, the toughness of the blend will decrease with increasing DCP content.

CONCLUSION

When BR is added to PS/LLDPE/SBS blend alone, it is likely to form an inter-phase between PS and PE. The compatibilization effect to SBS will reduce owing that butadiene block of SBS are restrained in BR phase. When DCP is added to PS/LLDPE/SBS blend alone, it will induce the decomposition of polystyrene.

When DCP and BR are added together, co-crosslinking between PE, SBS and BR will take place which leads to an improvement of interfacial adhesion. At the same time, the decomposition of PS is reduced due to the consumption of the free radicals in the crosslinking process. Synergism is thus realised which leads to a remarkable improvement in the impact strength of the blend.

REFERENCES

- [1] Locke, C.E., Paul, D.R., *J. Appl. Polym. Sci.*, **1973**, *17*, 2791
- [2] Heikens, D., Hoen, N., Barentsen, W., Piet, P., Laden, H., *J. Polym. Sci., Symp.*, **1978**, *62*, 309
- [3] Hajian, M., Sadrmohaghegh, C., Scott, G., *Eur. Polym. J.*, **1984**, *20*, 135
- [4] Friese, K., Michler, G., Steinbach, H., Hamann, B., Runge, J., *Angew. Makromol. Chem.*, **1986**, *141*, 185
- [5] Fayt, R., Jerome, R., Teyssie, Ph., *J. Polym. Sci. Phys.*, **1989**, *27*, 775
- [6] Baker, W.E., Saleem, M., *Polymer*, **1987**, *28*, 2057
- [7] Van Ballegoole, P., Rudin, A., *Polym. Eng. Sci.*, **1988**, *28*, 1434
- [8] The J.W., Rudin, A., *Polym. Eng. Sci.*, **1991**, *31*, 1033
- [9] Xu, C., Bao, S., *China Plastics (in Chinese)*, **1991**, (2), 43
- [10] Xu, C., Fang, Z., Zhong, J., *Angew. Makromol. Chem.*, **1993**, *212*, 45
- [11] Fang, Z., Xu, C., Bao, S., Zhao, Y., *Chinese Science Bulletin*, **1995**, *40*(19), 1671
- [12] Xu, C., Fang, Z., Zhong, J., *Polymer*, **1997**, *38*(1), 155
- [13] Fang, Z., Xu, C., Bao, S., Zhao, Y., *Polymer*, **1997**, *38*(1), 131
- [14] Small, P.A., *J. Appl. Chem.*, **1953**, *3*, 71