

In situ crosslinking and its synergism with compatibilization in polyvinyl chloride/polyethylene blends

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In situ crosslinking was performed in a polyvinyl chloride (PVC)/high density polyethylene (HDPE) (weight ratio 50/50) blend using a crosslinking system composed of dicumyl peroxide, triallyl isocyanurate and magnesium oxide. The results of selective solvent extraction and scanning electronic microscopy reveal that a semi-interpenetrated network of crosslinked HDPE and uncrosslinked PVC forms during this process and the mechanical properties of the blend are thus improved. However, few PVC molecules are crosslinked and the phase dispersity is not good enough when only crosslinking agents are added. When powdery nitrile rubber (*p*-NBR) is added simultaneously to the blend, it improves the phase dispersity of PVC and HDPE and at the same time attracts the crosslinking agents to the interfacial layer. In this way, a good synergism between *p*-NBR and the crosslinking system occurs. A great number of co-crosslinked products (PVC-*x*-PE) forms which induces remarkable improvements in the interfacial adhesion of two phases and hence the mechanical properties of the blend. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Due to the shortage of crude oil and environment considerations, the polymer fabrication industry is paying increasing attention to the possibility of recycling polymer wastes. The key problem to be solved before processes for recycled products become economic is the inferior mechanical properties of polymer blends formed from the common thermoplastics. Among them, polyvinyl chloride (PVC) and polyolefins (POs, including polyethylene, PE, and polypropylene, PP) have the largest scale fabrication and application. Blends of PVC and POs possess very poor mechanical properties because of their poor miscibility and for this reason, the study of PVC/PO blends is of interest in both industrial and academic fields.

The simplest but most widely used method to improve the mechanical properties of PVC/PE blends is to add a compatibilizer^{1–5}. Nakamura *et al.*^{6–9} proposed another possibility, that of adding a crosslinking agent. The co-crosslinked product PVC-*x*-PE which is formed at the interlayer of two component polymers, may play a role similar to that of block copolymer which acts as a potential compatibilizer. A plasticized PVC/PE blend is formed to achieve an acceptable level of toughness by this method. In one of their reports⁹, they used a partial saturated nitrile rubber (Zetpol, nitrile content 37 wt%) as a crosslinking coagent. The formed blends had a good phase dispersion and tensile properties, but they took no notice of the function of NBR which we¹⁰ confirmed as being a good compatibilizer

of PVC and PE and, furthermore, having good synergism with crosslinking agent.

In this paper, PVC/HDPE blends, obtained via *in situ* crosslinking with dicumyl peroxide (DCP) as an initiator and triallyl isocyanurate (TAIC) and magnesium oxide (MgO) as coagents, have been examined by selective solvent extraction and scanning electronic microscopy. Synergism between this crosslinking system and a compatibilizer, powdery nitrile rubber (*p*-NBR), will be also discussed.

EXPERIMENTAL

HDPE (DMD 6158, Qilu Petrochemical General Works, China) was premixed with *p*-NBR (Chemigum P83, nitrile content 33 wt%, Goodyear, USA) in a two roll mill (front roll 135–140°C, rear roll 130–135°C) for 10 min and put aside for further use.

PVC and its additives (weight ratio: PVC/DOP/3PbO·PbSO₄/2PbO·PbHPO₃/CaSt = 100/33/2/1/1) were mixed with TAIC and MgO and milled (front roll 155–160°C, rear roll 145–150°C) for 10 min. The premixed HDPE/*p*-NBR sheet was then loaded and mixed together. Finally, DCP was added and mixed for another 10 min to perform the *in situ* crosslinking. The well mixed piece was then transferred to a pre-heated compression mould and hot pressed at 170°C under 20 MPa for 15 min to give a blend sheet for testing.

Samples of *ca* 1 g were extracted by tetrahydrofuran (THF) in a Soxhlet extractor at a bath temperature of 100°C for 50 h. The weight ratio of the extractable part, Ext, was calculated by

$$\text{Ext} = (W_1 - W_2)/W_1$$

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Table 1 Influences of crosslinking agent and p-NBR on the characteristics of PVC/HDPE blends

Sample		A	B	C	D
Composition	PVC (g)	50.0	50.0	50.0	50.0
	Additives of PVC (g)	18.5	18.5	18.5	18.5
	HDPE (g)	50.0	50.0	50.0	50.0
	DCP (g)		1.5	1.5	1.5
	TAIC (g)		2.0	2.0	2.0
	MgO (g)		0.5	0.5	0.5
	p-NBR (g)			2.5	15.0
	Properties	Tensile strength (MPa)	1.7	16.2	21.3
Elongation at break (%)		10	77	90	190
Crystallinity of HDPE (%)		68.4	53.2	53.3	50.4
Ext (%)		56.0	54.3	22.3	14.5
Ext' (%)		57.8	55.9	54.8	49.8
Ext/Ext' (%)		96.9	97.1	40.7	29.1

where W_1 and W_2 are the weight of sample before and after extraction.

The morphologies of the extracted samples were examined by a Hitachi S-570 scanning electronic microscope. The crystallinities of polyethylene in blends were determined from d.s.c. curves measured on a Perkin-Elmer 7 differential scanning calorimeter with a heating rate of $10^\circ\text{C min}^{-1}$. Tensile test was performed on a XL-250 tensile instrument at 20°C and a cross-head speed of 250 mm min^{-1} .

RESULTS AND DISCUSSION

In *Table 1*, the expected weight ratios of the extractable part, Ext', are calculated by assuming that PVC and its additives (whether crosslinked or not) are extractable in THF, while HDPE and crosslinked p-NBR are not extractable. Thus the ratio Ext/Ext' is used to demonstrate the extent of co-crosslinking between PVC and HDPE.

In the PVC/HDPE blend without crosslinking agent, the weight ratio of extractable part is 56.0%, 96.9% of the expected value. The small gap between the measured value of Ext and the expected one can be explained by the occlusion of some soluble components in the HDPE phase.

As shown in *Table 1*, PVC/HDPE binary blends have very small values of tensile strength and elongation at break. The blend with crosslinking agent shows plastic deformation, with remarkable increased tensile strength and elongation at break. However, the value of Ext/Ext' remains near to 100%, compared with that of the blend without crosslinking agent. This result reveals that few PVC chains co-crosslink with HDPE when only crosslinking agent is added.

The morphologies of the extracted samples with and without crosslinking agent are quite different, as shown in *Figure 1*. The sample without crosslinking agent shows a more open and coarse morphology. It seems that the

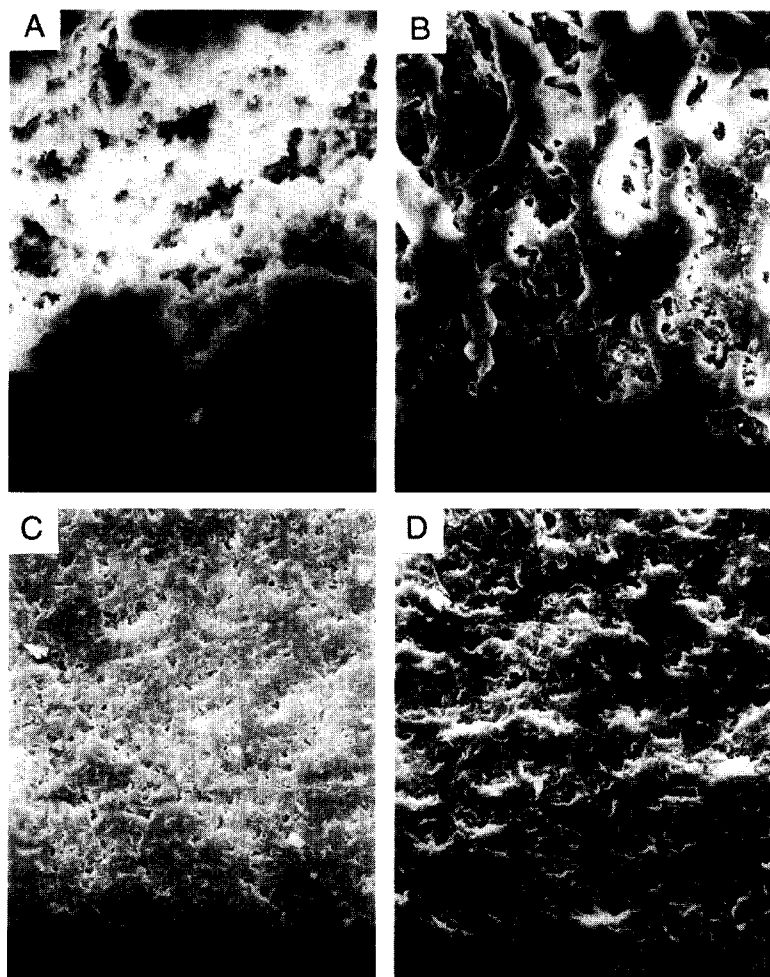


Figure 1 Scanning electronic microscope observations on the surface of the blends after extraction. Compositions are given in *Table 1*

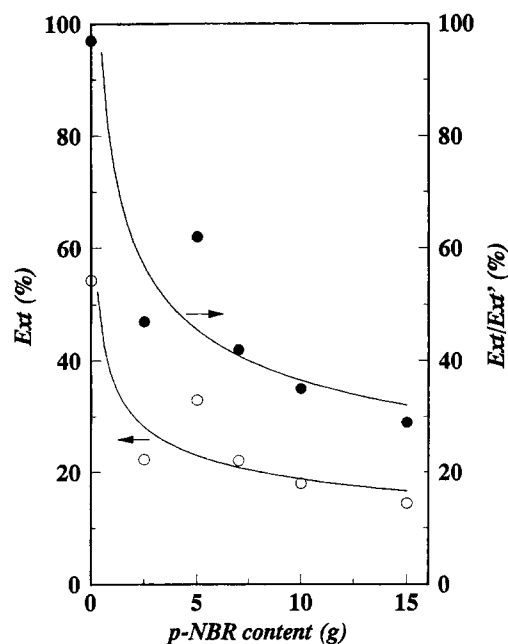


Figure 2 Influence of p-NBR content on the extractability of the PVC/HDPE/crosslinking agent blend (sample B in Table 1) in THF

PE phase is less continuous and few connections exist between the two separated phases. On the other hand, the sample with crosslinking agent shows a PE network formed by self-crosslinking. This can also be shown by the decrease of the crystallinity of PE as shown in Table 1. Simultaneously, the extracted PVC phase is still continuous, as can be confirmed by the voids in the PE phase. The improvement of the mechanical properties seems to be essentially owing to the formation of this semi-interpenetrated network.

It is noticed that the addition of p-NBR in the blend results in a finer morphology. The average dimension of the voids, being formed by extracted PVC phase, decreases remarkably, indicating the modification of the phase dispersity. No void can be observed in the blend with 15 g p-NBR.

NBR has been confirmed to have good miscibility with both PVC¹¹ and PE¹², and to be a compatibilizer of PVC/LDPE¹⁰. Figure 2 shows that, when a small amount of p-NBR is added to the blend together with the crosslinking agent, the weight ratio of extracted components will decrease markedly. Considering crosslinked PVC molecules become insoluble in THF, this result reveals the formation of a considerable amount of co-crosslinked products of PVC-x-PE. This ratio decreases further with increasing p-NBR content.

In one of our previous papers¹³, we performed a phase dispersion-crosslinking synergism technique to improve the miscibility, as well as the mechanical properties of PVC/LDPE blends and gave a brief description of the mechanism. In fact, NBR can be considered as a particular kind of phase dispersant, which can not only improve the phase dispersity by means of enhancing the shearing force during melt blending, but also increase the interfacial adhesion between the two phases. We premixed it with HDPE in this study to reduce the viscosity gap between HDPE and PVC, which is very important

for improving the dispersity of the two component polymers¹⁴. Furthermore, NBR, owing to its highly polar nitrile groups, also has strong polar-polar interactions with DCP and TAIC. Thus, the possibility of a crosslinking agent existing at the interfacial layer obviously increases with the increase of NBR content due to the improvement of the phase dispersity as well as the attraction of NBR on the crosslinking agents. Consequently, more co-crosslinked products are formed which can induce the modification of interfacial adhesion of the two phases, and hence improve the mechanical properties of the blend.

CONCLUSION

From the results of selective solvent extraction and scanning electronic microscopy, we can conclude that when the crosslinking agent alone is added to the PVC/HDPE blend, *in situ* crosslinking will take place only in the HDPE phase. The mechanical properties of the blend will improve due to the formation of a semi-interpenetrated network composed of crosslinked HDPE and uncrosslinked PVC. When p-NBR is added simultaneously to the blend, it improves the phase dispersity of PVC and HDPE and at the same time, attracts the crosslinking agents to the interfacial layer. In this way, a good synergism is caused which induces the formation of a large number of co-crosslinked products and a remarkable improvement of the mechanical properties of the blend.

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