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Co-crosslinking blend of incompatible polymers VI: poly(vinyl chloride) toughened with polyethylene via a co-crosslinking technique

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A binary blend which consists of two incompatible polymers such as poly(vinyl chloride) and polyethylene has been performed through a partial co-crosslinking reaction with peroxide to give a co-crosslinked blend with a uniform dispersion of small polyethylene particles and with an improved mechanical property. The results are obtained through the formation of a co-crosslinked product which acts as a potential solid phase dispersant as well as a well-bonded reinforcing interlayer on polyethylene particles uniformly dispersed in poly(vinyl chloride) matrix. The resulting blends (PVC/PE = 10/90 wt) give carbon spherules of 0.5 to 1 μm diameter through pressure-carbonization at 650° C for 1 h.

1. Introduction

For the production of the binary blends which consist of two incompatible polymers A and B, a co-crosslinking blend has been available [1–3]. The co-crosslinking blend can be obtained through the formation of a co-crosslinked product A–X–B by a co-crosslinking agent X. The co-crosslinked product which is formed at the interlayer of the two polymers, may play a role similar to that of block copolymer A–B which acts as a potential solid phase dispersant. In the previous paper [4, 5], blending of a plasticized poly(vinyl chloride) (PVC) and polyethylene (PE) which are typically imcompatible each other was found to achieve an acceptable level of toughness of the blends by the co-crosslinking reaction using 6-diallylamino-1,3,5-triazine-2,4-dithiol, 4,6-*bis*(diallylamino)-1,3,5-triazine-2-thiol or triallyl isocyanurate (TAIC) with peroxide. The result suggests that the PE can be used as a nonexudative softening agent for PVC in the place of the conventional plasticizer which may exude to the environment gradually from the products. In this paper, mechanical properties and blending performance are examined on the blends of PE and PVC without plasticizer obtained via the peroxide-co-cross-linking reaction with Zetpol and TAIC as a coagent. Zetpol is the trade name of partially saturated NBR (nitril content, 37%; iodine value, 14), which has a higher safety characteristic on processing at higher temperatures in the presence of peroxide.

TABLE I Effect of peroxide on change in T_s and E_b of PVC–PE blends

Formulation no.	PVC Compound (wt)					PE compound (wt)			Peroxide (wt) 1,3-*bis*(*t*-butyl peroxy-i-propyl)-benzene	Mechanical properties of blends‡ (100/50 wt)	
	PVC	MgO	RP101*	Zetpol†	TAIC	PE	Zetpol	TAIC		T_s (MPa)	E_b (%)
	100	1	1	10	–	100	10	–			
I			100				50		0	12.3	4
									1	22.3	30
	100	1	1	–	4	100	–	4			
II			100				50		0	11.7	0
									1	29.0	125
	100	1	1	10	4	100	10	4			
III			100				50		0	20.3	5
									1	36.1	180

*RP101: Ca–Ba–Zn stabilizer.
†Zetpol: partially saturated NBR.
‡Hot-pressed condition:160° C, 30 min under 5 MPa.

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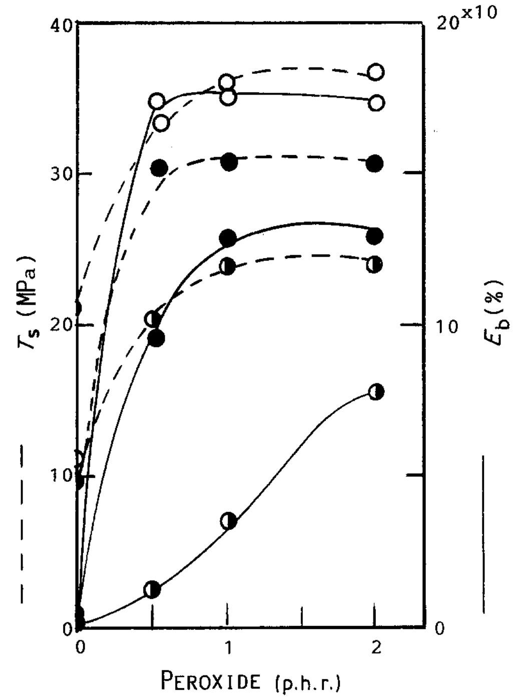

Figure 1 Change in T_s and E_b of PVC–PE blends (100/50 wt) as a function of peroxide content. (◑), (●), (○): formulations I, II, III in Table I, respectively.

2. Experimental techniques

2.1. Blending and co-crosslinking procedure

Each 10 g PVC (Geon 101EP, $\bar{p} = 1450$) or PE (Sumikasen LDPE, F 213B) was mixed with the additives given in Table I in a two-roll mill at 160 or 140° C for 5 min, respectively. The resulting PVC and PE sheets (10 g) were blended again in various compositions in the mill with the addition of peroxide at 160° C for 5 min. The blended sheet was then hot pressed at 160° C for 30 min under 5 MPa pressure to give co-crosslinked PVC–PE blend-sheets about 1 mm thick, which were used for mechanical testing.

2.2. Mechanical testing and determination

Tensile tests were carried out on a recording Autograph using a cross-head speed of 50 mm min^{-1} at 20° C. The crosslinking behaviour of the blends was determined using an oscillating disc rheometer at 160° C.

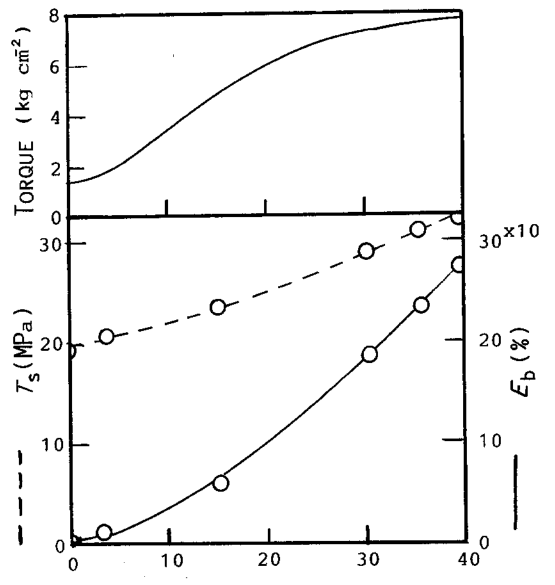

Figure 2 Change in T_s, E_b, and oscillating rheometer curve of PVC–PE blends (100/50 wt) as a function of hot-pressing time. Formulation is identified with III in Table I with 0.5 p.h.r. peroxide.

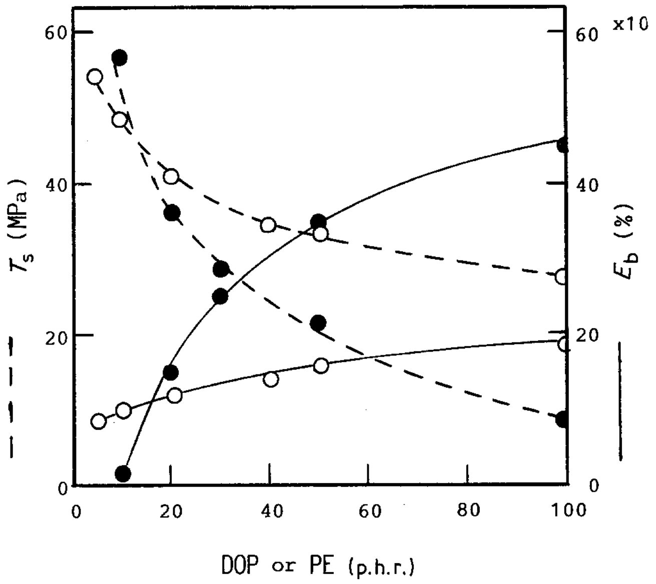

Figure 3 Change in T_s and E_b of PVC–PE blends and PVC–DOP blends as a function of PE and DOP content. (○) formulation III in Table I; (●) DOP was blended in place of PE in formulation III.

3. Results and discussion

3.1. Effect of peroxide to the elongation at break of the blends

As shown in Table I, the elongation at break (E_b) of the blends, which is a sensitive measure of compatibility, has been considerably improved by the addition of a small amount of peroxide during the blending process. The optimum amount of peroxide added to the blends is generally 0.5 to 1 p.h.r. as in Fig. 1. The preferred type of peroxide is dicumyl peroxide or 1,3-*bis*(*t*-butyl peroxy-i-propyl)-benzene (peroxymon) [5]. On increasing the amount over 1 p.h.r., E_b decreases with decrease in compatibility by over-crosslinking. As in Fig. 2, both the tensile strength (T_s) and E_b of the blends containing a small amount

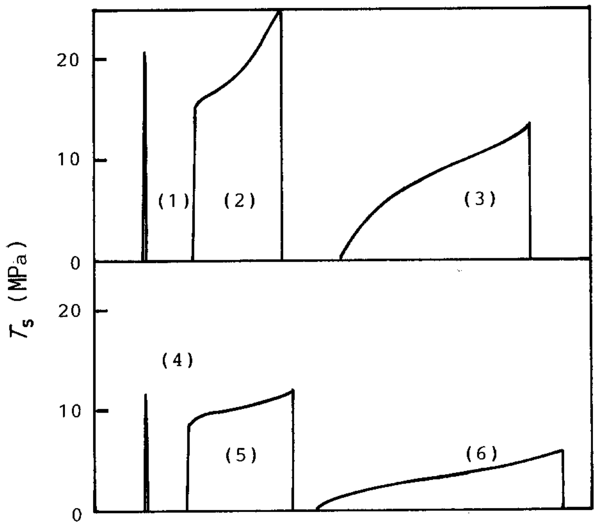

Figure 4 Stress–strain curves of blends. Base formulation is identified with III in Table I. Composition: (1) to (3) 100/50 wt; (4) to (6) 100/100 wt. (1, 4) PVC–PE blends without peroxide; (2, 5) PVC–PE blends with 1 p.h.r. peroxide; (3, 6) PVC–DOP blends with 1 p.h.r. peroxide.

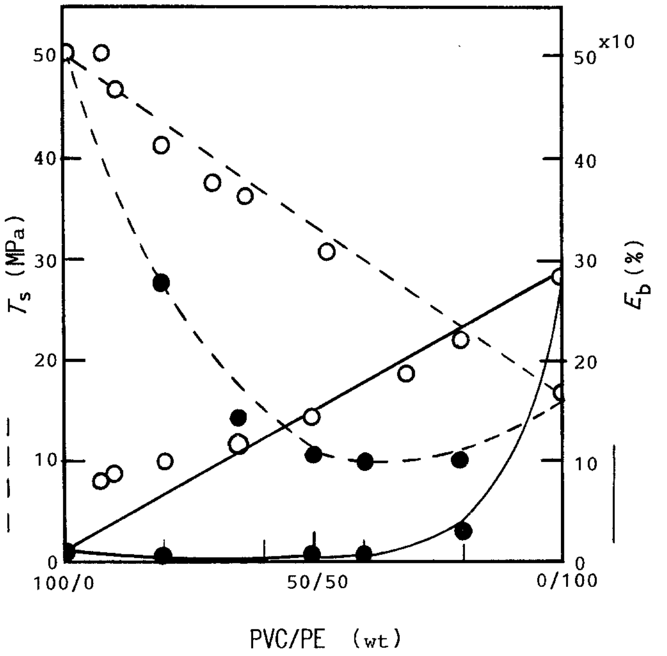

Figure 5 Change in T_s and E_b of PVC–PE blends as a function of composition. (○) Co-crosslinked blends by formulation III in Table I; (●) control blends of formulation III without peroxide.

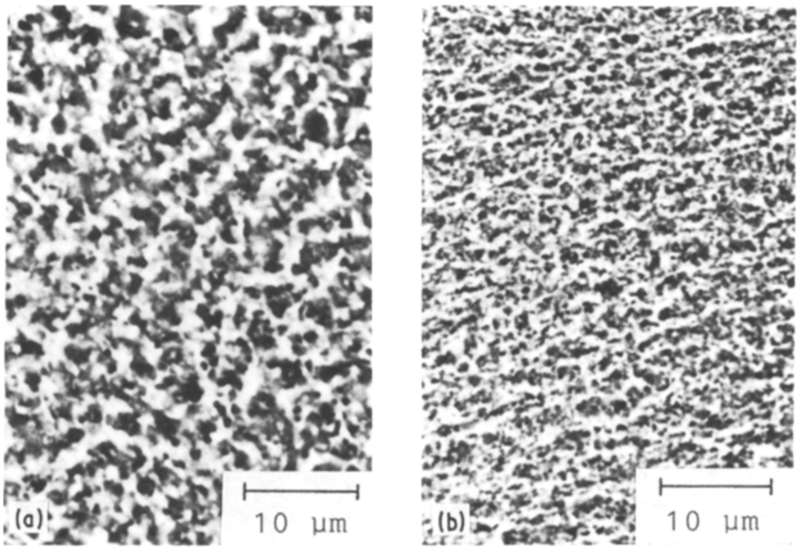

Figure 6 Phase-contrast photomicrographs of blends (PVC–PE = 100/150 wt). Formulation is identified with III in Table I. (1) Without peroxide, (2) with peroxide.

(0.5 p.h.r.) of peroxide, increase with increasing hot-pressing time, i.e. proceeding of partial crosslinking. The results suggest that co-crosslinked products formed at the interlayer contribute to an increase in the mechanical properties of the blends. Brownish discolouration in the PVC phase on hot pressing is hardly observed in the presence of Zetpol until after 30 min at 160° C [5].

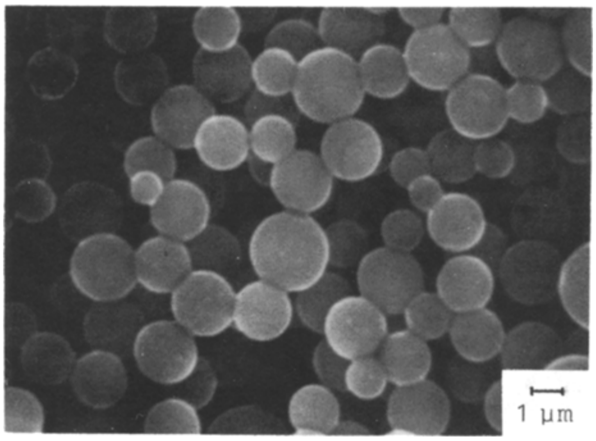

Figure 7 Carbon spherules obtained from PVC–PE (10–90) blends.

3.2. The mechanical properties of the co-crosslinked blends

T_s and E_b of the blends as a function of binary polymer composition is shown in Fig. 3 compared with those of plasticized PVC with DOP. T_s of the blends decreases and E_b increases with an increase in the PE content of the blends. This behaviour is not so remarkable when compared with the data of plasticized PVC, especially with an increased DOP content. An improved mechanical property of the co-crosslinked blends is also realized in the stress–strain curves of the blends in Fig. 4. Co-crosslinked blends (PVC–PE: 100/50 or 100 wt) show plastic deformation with yielding followed by a long elongation [2, 5], while blends without peroxide show a brittle fracture [1, 4]. In addition, the curves of the co-crosslinked blends [2, 5] show a characteristic pattern compared to the elastic deformation pattern of the cross-linked PVC plasticized with conventional plasticizer as DOP [3, 6]. E_b and T_s as a function of PE–PVC blend composition is shown in Fig. 5. It can be seen that E_b is a particularly sensitive measure of compatibility. E_b of the co-crosslinked blends shows a parallel behaviour to that of the binary component, while E_b of control blends without peroxide fall away to less than 10% of the E_b of pure PE. Fig. 6 shows the effect of co-crosslinking on the micrographs of the blends compared with a control. For a finely dispersed phase on the co-crosslinked blends, no such phase is observed on the control. The toughening behaviour in the co-crosslinked blends can be realized with a smaller size and uniform dispersion of PE in the PVC matrix, which act as a solid phase dispersants as well as well-bonded reinforcing filler particles [6, 7]. In conclusion, PVC has been found to be plasticized with PE through a co-crosslink-blending to give a co-crosslinked blend with an improved mechanical property.

3.3. Utilization of the co-crosslinked blends

The resulting co-crosslinked blends would be expected to have a unique property due to the blended component such as PE, with excellent shock resistant and abrasion resistant properties. In addition, carbon spherules 0.5 to 1 μm diameter as in Fig. 7, are obtainable through a pressure-carbonization [8, 9] of the resulting blends (PVC/PE = 10/90 wt) at 650° C for 1 h.

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