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Investigation of the Properties of Co-Crosslinked Blends of Polyvinyl-Chloride with Polyethylene

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Various methods were used to study the effects of co-crosslinking reaction between polyvinyl chloride and polyethylene on the properties of blends. The compatibility of blend was investigated by dynamic mechanical analysis, scanning electron micrographs, differential scanning calorimetry, and stress-strain. Evidence was found for the two-phase nature of the blends. The compatibility of blend was improved when crosslinking reaction took place in blend systems, and blends exhibited high impact strength, tensile strength and elongation at break. This paper also discusses the relationships between morphologies and mechanical properties of blends.

KEY WORDS Co-crosslink, PVC/PE blend, compatibility, morphology, copolymer.

INTRODUCTION

Although polyvinylchloride is the most popular and widely used rigid plastics, brittleness restricts wider application.¹ Many researches have been made to toughen the brittle plastics by introducing rubber components. Polyethylene is another polymer with flexible molecular chain and lower glass transition temperature, thus can be used as a good modifier of PVC. However, simple blending of PVC and PE can not produce the blends of practical application due to thermodynamic immiscibility. There are high interfacial tension and poor adhesion between the phases of incompatible blends like as PVC/PE systems.^{2,3} The compatibility of PVC/PE blend can usually be improved by adding a third polymer component which acts as the compatibilizer to enhance the interaction force between PVC and PE.⁴

In this paper the binary blending of PVC and PE with good mechanical properties was made through a partially co-crosslinking reaction with crosslinking agent and peroxide initiator.⁵ Various methods have been used to determine the compatibility

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TABLE I
Composition of co-crosslinked PVC/PE blends

Sample No.	Composition(wt%)							
	PVC	PE	TAIC	DCP	4432	MgO	DOP	
I	1	100	0	0	0	1.5	1	0
	2	95	5	4	1	1.5	1	0
	3	90	10	4	1	1.5	1	0
	4	85	15	4	1	1.5	1	0
	5	80	20	4	1	1.5	1	0
II	6	90	10	4	0	1.5	1	0
	7	90	10	4	0.5	1.5	1	0
	8	90	10	4	1.5	1.5	1	0
	9	90	10	4	2.0	1.5	1	0
	10	90	10	4	2.5	1.5	1	0
III	11	90	10	0	1	1.5	1	0
	12	90	10	2	1	1.5	1	0
	13	90	10	3	1	1.5	1	0
	14	90	10	6	1	1.5	1	0
IV	15	90	10	4	1	0	1	0
	16	90	10	4	1	0.5	1	0
	17	90	10	4	1	2.5	1	0
	18	90	10	4	1	3.5	1	0
	19	90	10	4	1	4.5	1	0
V	20	95	0	0	0	1.5	1	5
	21	90	0	0	0	1.5	1	10
	22	85	0	0	0	1.5	1	15

of polymer blend. The effects of PE, crosslinking agent, initiator, and stabilizer on the co-crosslinking reaction and the properties of PVC/PE blends were studied.

EXPERIMENTAL

Materials

The polyvinylchloride (PVC), XS-3 type, was Tianjin Chemical Factory with $M_n = 10^5$. The High Density Polyethylene (HDPE), MI = 20–25 g/10 min, was purchased from Beijing Qianjin Chemical Factory. Triallyl isocyanurate (TAIC),

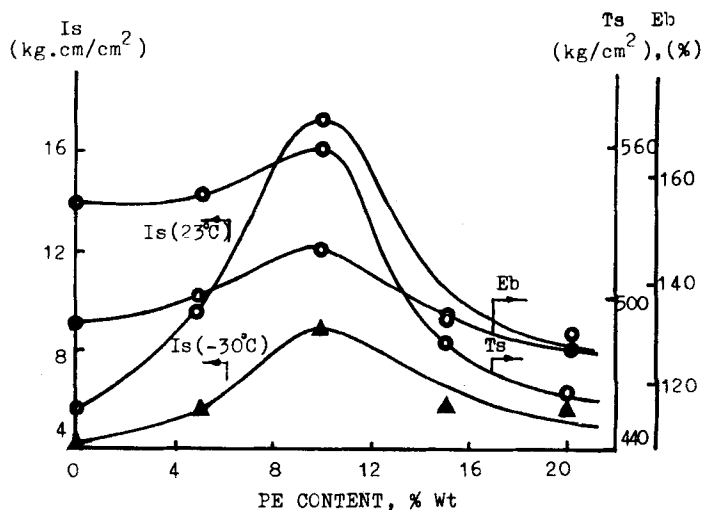


FIGURE 1 Polyethylene (PE) content versus impact strength (*Is*), tensile strength (*Ts*), and elongation at break (*Eb*) of co-crosslinked PVC/PE blends.

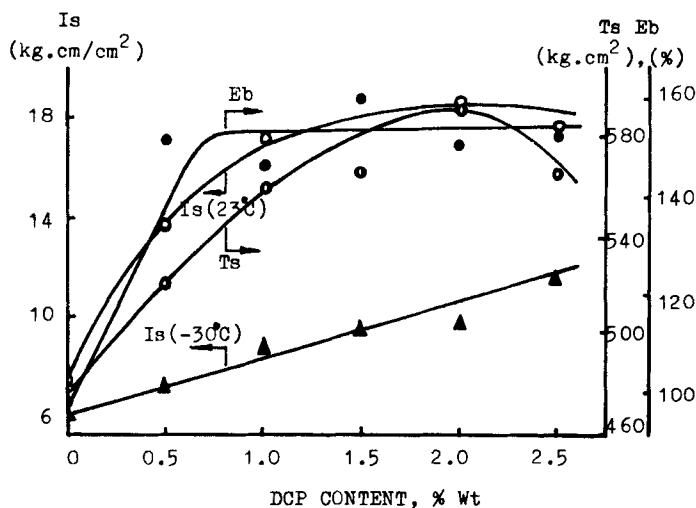


FIGURE 2 Documyl peroxide (DCP) content versus impact strength (*Is*), tensile strength (*Ts*), and elongation at break (*Eb*) of co-crosslinked PVC/PE blends.

Dicumyl Peroxide (DCP), Dibutyltin Mercaptide (4432), MgO, and Di(2-ethyl hexyl) Octyl Phthalate (DOP) were purchased as commercial chemical pure agent.

Sample Preparation

PVC/PE blends with compositions illustrated in Table I were melt-blended on a laboratory two-roll mill at 165°C for 10 min. The weight percentage of the added TAIC, DCP, 4432 and DOP was identified as their weight fraction in the PVC/PE blends. The samples were compressed into sheets with a hydraulic press at 180°C

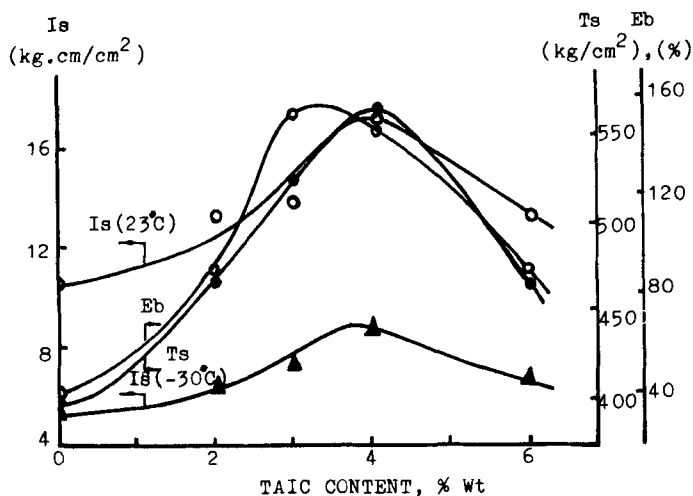


FIGURE 3 Crosslinking agent (TAIC) content versus impact strength (I_s), tensile strength (T_s), and elongation at break (E_b) of co-crosslinked PVC/PE blends.

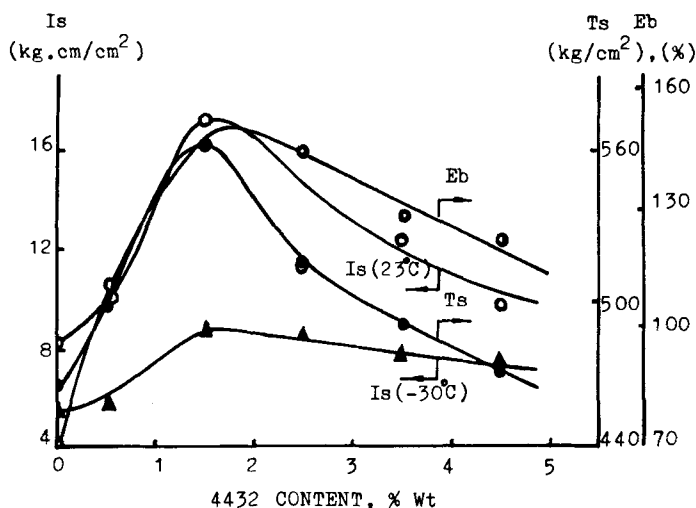


FIGURE 4 Stabilizer (4432) content versus impact strength (I_s), tensile strength (T_s), and elongation at break (E_b) of co-crosslinked PVC/PE blends.

and 19 MPa for 25 min and then cooled to room temperature. Both tensile and Charpy impact strength test specimens were machined from the molded sheets.

Experimental Methods

Stress-strain experiments were made using WD-10 tensile testing apparatus at 23°C and crosshead speed 5 cm/min, samples were cut on GB1040-79 (Chinese standard). The impact strength was tested with X CJ-500 Charpy impact tester at 23°C and -30°C, samples were cut on GB1043-79 (Chinese standard).

Dynamic mechanical analysis (DMA) data was collected at 110 Hz and 2°C/min

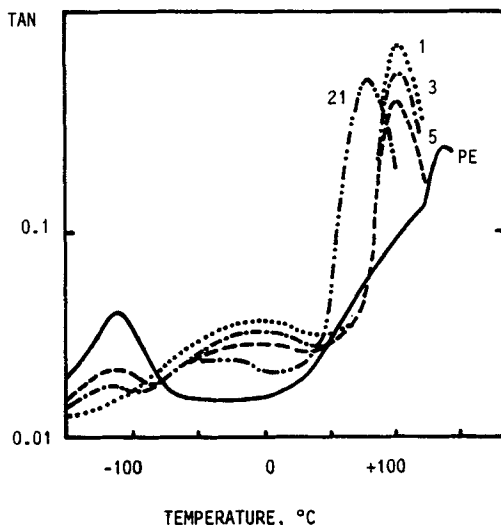


FIGURE 5 Dynamic mechanical spectra of co-crosslinked PVC/PE blends with different PE or DOP content.

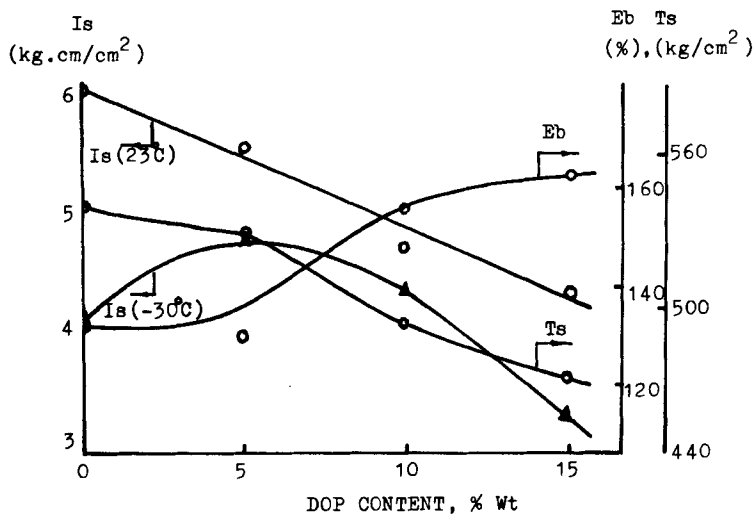


FIGURE 6 Plastifier (DOP) content versus impact strength (T_s), tensile strength (T_s), and elongation at break (E_b) of co-crosslinked PVC/PE blends.

by a Japanese vibron DDV-II EA viscoelastometer, temperature range was $-150^{\circ}\text{C} \sim +150^{\circ}\text{C}$, thickness of test specimen was $0.1 \sim 0.3$ mm.

Differential scanning calorimetry (DSC) were recorded by means of a Shanghai DSC CDR-1 type instrument. Sample weights were 20 mg. Heating rate was $20^{\circ}\text{C}/\text{min}$.

Fracture surfaces of samples were observed through a Japanese HITACHI X-650 scanning electron microscopy (SEM).

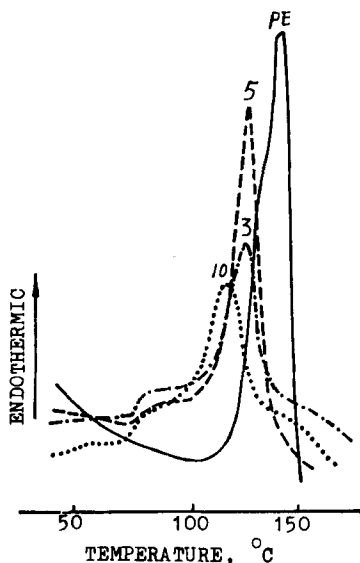


FIGURE 7 DSC spectra of co-crosslinked PVC/PE blends with different PE and TAIC content.

RESULTS AND DISCUSSION

The effects of PE content on the mechanical properties for co-crosslinked PVC/PE blends are shown in Figure 1, impact strength, tensile strength and elongation at break increase with increasing PE content, and pass through a maximum value at about 10%. It is obvious that the properties of PVC/PE blends depend on the degree of crosslinking and PE content. When keeping 4432, TAIC, DCP and MgO a constant weight percentage, the crosslinking reaction between PVC and PE generated a constant amount PE-co-PVC copolymers acting as the compatibilizer of blends in the interface of phases, thus there is a suitable composition of blend which exhibits combining of each component in the blends. When PE content is less than 10% it can not play a reinforcing and toughening role, when PE content is more than 10%, the crosslinking polymers acting as the compatibilizer are too less to produce enough copolymers on the interface to obtain a good compatibility, the mechanical properties of blends are poor.

Figure 2 shows that impact strength, tensile strength, and elongation at break increase with increasing dicumyl peroxide (DCP) content. The more DCP content, the more crosslinked macromolecules. When DCP content is about 1.0 ~ 2.0% impact strength and tensile strength of blends reach the maximum value, which indicates that more DCP is not necessary for initiating the crosslinking reaction to form the copolymer compatibilizer. There is a proper proportion of component at which the best properties of blends can be obtained.

The effects of triallyl isocyanurate (TAIC) on the mechanical properties are shown in Figure 3. Results show that impact strength, tensile strength, and elongation at break increase with increasing TAIC content and again pass through a maximum value at about 4% TAIC content. In fact, TAIC content controls the crosslinking density of blend which is the key factor for improving the compatibility

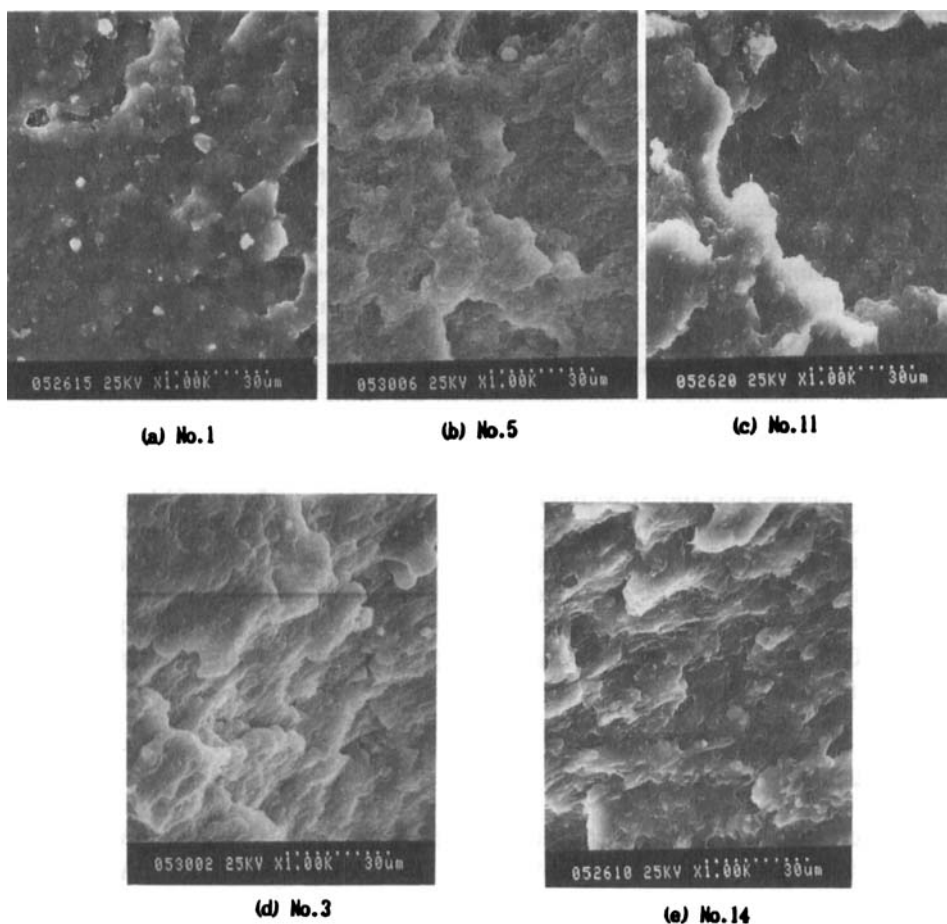


FIGURE 8 Scanning electron micrographs of fracture surface for co-crosslinked PVC/PE blends with different TAIC content (c, d, e) and PE content (b, d).

of PVC and PE, and the improvements of mechanical properties of blends are contributed through the formation of a crosslinked polymer which acts as a solid-phase dispersant.

As shown in Figure 4, stabilizer (4432) is another factor which influences the properties of blends. Too small amounts of stabilizers maybe lead to the reduction of the properties of blends due to probably thermal degradation of PVC. However, it has to be noted that the stabilizer terminates not only the free radicals generated by degradation of PVC, but also the free radicals by DCP, thus a suitable stabilizer content should be used to prevent the thermal degradation of PVC and initiate the crosslinking reaction between PVC and PE.

Summarizing the above results, the blends of PVC with PE are successfully performed by a partial co-crosslinking reaction between PVC and PE. In addition, it seems that the synergism occurs when the composition of blend is suitable. This synergism was also observed in other blends.^{5,6}

The interfacial adhesion between PVC and PE remarkably influences the prop-

erties of blends. Figure 5 shows the dynamic mechanical spectra of PE, PVC, PVC/PE, and PVC/DOP. It can be noted that the T_g of PVC is 100.6°C and the T_g of PE is -111.2°C. After mixed, two T_g s can still be recognized in the DMA curves. This indicates that the blends possess a two phase nature. However, the T_g s of PVC in PVC/PE blends drop to 97°C (90/10) and 95°C (80/20) respectively, that strongly suggests the improvement of compatibility of blend. The T_g of PVC increases with decreasing PE content, it is obvious that the crosslinking density should influence the interfacial layer structure of blends. From Figure 6, the effect of DOP on the dynamic mechanical spectrum can also be observed. The plastifier DOP significantly influences the T_g of PVC, which demonstrates the plastifier makes conformation change easier.^{7,8} The addition of DOP also influences the mechanical properties of PVC/PE blends.

Figure 7 indicates that the melting point of PE shifts to lower temperature when the PE content and DCP content are changed. This is because the compatibility of PVC/PE blend is improved due to crosslinking reaction between PVC and PE.

Figure 8 shows that the SEM micrographs of fracture surfaces of blends indicate that the stretched deformation pattern of dispersed PE particles is observed on the failure surfaces of co-crosslinked blends (b, c, d, e) comparing brittle deformation of PVC (a) after blends were treated with DCP and TAIC. Changing the TAIC content, the micrographs of blends are different. As shown in Figure 8 (c, d, e), the TAIC makes the fracture surfaces of blends matrix yielding and the characteristic of tough failure.

CONCLUSION

The effects of co-crosslinking reaction between PVC and PE on the properties of blends have been studied by DMA, SEM, DSC and stress-strain. Addition of crosslinking agent (TAIC) and initiator (DCP) to PVC/PE blends generates the copolymers in the interfacial surface between PVC phase and PE phase, these copolymers can act as the compatibilizer of PVC/PE blends, the compatibility of blend is significantly improved, the similar results had been observed by author's other works.^{9,10} By controlling carefully the proportion of TAIC, DCP and component polymer, the good compatibility of blend can be obtained, thus the properties of blends can be remarkably improved. The synergism is also observed in the blend systems, it means that when the composition of blend is suitable impact strength, tensile strength, and elongation at break pass through a maximum value. In fact, the synergism is response to the degree of crosslinking of blends. It is obvious that the superior properties of blends depend on the proper co-crosslinking morphology of blend, and it is the cross-linking reaction that determines all of these properties of blends.

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