

Study on Nitrile–Butadiene Rubber/Poly(propylene carbonate) Elastomer as Coupling Agent of Poly(vinyl chloride)/Poly(propylene carbonate) Blends. I. Effect on Mechanical Properties of Blends

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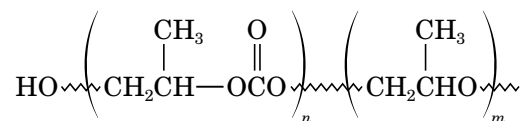
ABSTRACT: Nitrile–butadiene rubber/poly(propylene carbonate) (NBR–PPC) elastomer was studied as a coupling agent of the blends of poly(vinyl chloride) (PVC) with poly(propylene carbonate) (PPC). It greatly improved the PVC/PPC system mechanical properties that were dependent on the amount and composition of the coupling agent. When the coupling agent consisted of a 70/30 ratio of NBR/PPC (in which NBR had 34% nitrile content) and 2.5 phr of benzoyl peroxide (BPO) initiator and underwent a prevulcanization, the blends of PVC/PPC displayed excellent mechanical properties by adding 8 phr of the coupling agent. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1107–1111, 1997

Key words: poly(vinyl chloride); poly(propylene carbonate); coupling agent; blend; mechanical properties

INTRODUCTION

Poly(vinyl chloride) (PVC) is one kind of all-purpose plastic that is consumed in large quantities. But PVC homopolymer is a stiff and brittle material. Its soft products are usually created by adding a quantity of plasticizer, usually a small-molecule plasticizer.^{1,2} Current general small-molecule plasticizers, for example, dioctyl phthalate (DOP), are easy to vaporize and transport to the surface from the plasticized PVC products. Polymeric plasticizers for PVC have been studied,³ but most dissimilar polymers are immiscible or polymeric plasticizers are too expensive.⁴ So study on various coupling agents is one of the important fields of polymer alloy research.

Poly(propylene carbonate) (PPC, synthesized by our Institute) is a new kind of hydroxyl-terminated aliphatic polycarbonate that it costs less than PVC. It is composed of carbon dioxide and propylene epoxide with the following molecular structure⁵:



Its viscosity-average molecular weight (\bar{M}_η) is from 5000 to 20,000 under present synthesis facilities. To expand its applied field, we studied PPC as a polymeric plasticizer of PVC. We discovered that PVC/PPC blends were immiscible, and partially crosslinked nitrile–butadiene rubber (NBR)–PPC elastomer could compatibilize them and greatly improve their mechanical properties.⁶ This research systematically studied the effects of NBR–PPC elastomer composition, processing

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Table I Effect of Coupling Agent Content of Properties of 100/20 phr PVC/PPC Blends

	Coupling Agent (phr)				
	0	3	8	13	18
Tensile strength (MPa)	29.1	21.7	22.5	10.1	7.8
Elongation at break (%)	2	2	111	45	65
Impact resistance (kJ/m ²)	2.8	1.5	5.4	7.6	8.7
Crosslinking density ($\bar{M}_c \times 10^3$)	—	6.1	5.0	7.4	8.2

(—) It was proved that the blends without coupling agent all dissolved in THF.

conditions, and crosslinking degree on the mechanical properties of PVC/PPC blends.

EXPERIMENTAL

Materials

PPC, a copolymer of carbon dioxide and propylene epoxide, was produced by our Institute. Its viscosity-average molecular weight was 10,000 as measured by a Ubbelohde viscosimeter in benzene solution at $35 \pm 0.1^\circ\text{C}$.⁷ PVC (SG-5 type, number-average molecular weight 62,000–54,000) was produced by the Forth Chemical Plant in Baotou, China.

NBRs N220S (nitrile percentage 41%) and N41 (nitrile percentage 26%) were made in Japan. To obtain different nitrile contents of NBR, these two types of NBR were mixed in different ratios. For example, N220S type NBR was mixed with an equal amount of N41 to yield NBR with 34% nitrile content.

2-Mercaptobenzimidazole (MB), benzoyl peroxide (BPO), DOP, tetrahydrofuran (THF), stabilizer, and lubricant were made in China.

Processing of Coupling Agent (NBR–PPC Elastomer)

A mixture ratio of NBR, PPC, MB, and BPO were uniformly mixed on a XKR-160A type of two-roll mixer at room temperature, and compressed by a QLB-D flat vulcanizing heater under 20 MPa at 130°C .

Mixing of PVC/PPC Blends

PVC, PPC, NBR–PPC elastomer, DOP, stabilizer, and lubricant were mixed at room temperature

and processed for several minutes by the two-roll mixer at 170°C .

Model Pressing of PVC/PPC Blends

The blends were preheated for 5 min, pressed for 10 min under 20 MPa at 170°C by the flat vulcanizing heater that exuded gas twice during pressing, and coolly pressed for several minutes.

Tensile Test

The blend samples were manufactured and measured by a DXLL-2500 electronic tensile machine according to GB 1040-79 of China. The extension speed was 15 mm/min.

Impact Test

The blend samples were manufactured and measured by a WPM cantilever beam impact resiliometer according to GB 1043-79 of China. The impact resistance measured was notched impact strength.

Determination of Crosslinking Density

The small pieces of blend samples were extracted by THF for 48 h, and about 10% insoluble residuals were obtained. This may have been caused by the addition of prevulcanizing coupling agent.

For measuring their crosslinking densities, the 1×1 cm cylinder blend samples (height \times diameter) were heated to 90°C , pressed with another 50 g weight every 10 min, and their compression strains were recorded. Their crosslinking densities were calculated according to the relation between compression strength and compression strain,⁸

Table II Effect of NBR/PPC Ratio of Coupling Agent on Properties of PVC/PPC Blends

	NBR/PPC Ratio				
	100/0	80/20	70/30	60/40	50/50
Tensile strength (MPa)	16.2	19.6	22.5	8.9	6.0
Elongation at break (%)	18	30	111	3	1
Impact resistance (kJ/m ²)	2.8	4.2	5.4	1.7	1.7

$$F = \frac{3\rho RT}{M_c} \times \frac{A_0}{h_0} \times \Delta h \quad (1)$$

where ρ was the density of the sample, A_0 and h_0 were cross-section area and height of cylinders unpressed, F and Δh were total pressure strength and pressure strain, and \bar{M}_c was the crosslinking density of the sample, for example, the average molecular weight between the two crosslinking points.

RESULTS AND DISCUSSION

Effect of Coupling Agent Content on Properties of PVC/PPC Blends

PPC cannot obviously decrease the processing temperature of PVC and evidently cannot prevent PVC from decomposing when PPC alone plasticizes the PVC.⁶ A small amount of DOP, stabilizer, and lubricant were added to the PVC/PPC blends, resulting in some improvement in processing behavior, heat stability, tensile strength, and toughness, but not ductility. Coupling agent is thought to compatibilize PVC/PPC blends and make further improvement on the processing behavior and ductility of blends. It was reported that NBR/PPC elastomer has an interpenetrating polymer network structure in certain conditions⁹ and that PVC is compatible with NBR.¹⁰ So it was supposed that NBR-PPC elastomer with a controlled structure would be a good compatibilizer for PVC/PPC blends. The coupling agent was prepared by blending 70 phr NBR, 30 phr PPC, 2.5 phr BPO, and 1.5 phr MB and then heating it at 130°C under 20 MPa for 10 min as found in the literature.⁹ In the PVC/PPC blends there were 100 phr PVC, 20 phr PPC, and a series of different contents of the coupling agent. The mechanical properties of PVC/PPC blends are listed in Table I. It was obvious that 8 phr was an optimum content of coupling agent for improving the mechanical properties of

PVC/PPC blends. These results may have been caused by the existence of a probable ideal interfacial action between the PVC and PPC phases in the PVC/PPC blends. Therefore, the basic formula of PVC/PPC blends consisted of 100 phr PVC, 20 phr PPC, 8 phr coupling agent, and a small amount of DOP, stabilizer, and lubricant. This basic formula was used in the following study of PVC/PPC blends.

Effect of NBR/PPC Ratio of Coupling Agent on Properties of PVC/PPC Blends

It was necessary to make a further study on PVC/PPC blends with 8 phr NBR-PPC elastomer. Coupling of NBR-PPC elastomer in PVC/PPC blends was supported by its partially crosslinked structure. If the ratio of the NBR/PPC in the elastomer was varied, intermolecular chemical linking and the chain's condensed state in the elastomer would evidently change. So the elastomers with various structures had different affects on the properties of the PVC/PPC blends.

By using the above basic formula, the NBR/PPC ratio of the coupling agent was changed, which led to the variation of the mechanical properties of the PVC/PPC blends shown in Table II. The results indicated that a 70/30 ratio of NBR/PPC had a better affect than other lower or higher NBR/PPC ratios. The reason why NBR-PPC elastomer can compatibilize PVC/PPC blends is that NBR is compatible with PVC and there are crosslinking bonds between the NBR and PPC in the elastomer. To create some interaction between PPC and PVC, chemical crosslinking bonds between NBR and PPC should be cooperatively proportional to the interaction between compatible NBR/PVC. Experimental data showed that the reasonable ratio of NBR/PPC was 70/30.

Effect of Nitrile Content of NBR in NBR-PPC Elastomer on Properties of PVC/PPC Blends

The nitrile content of NBR has a great affect on the compatibility between PVC and NBR,^{11,12} and it

Table III Effect of Nitrile Percentage of NBR on Properties of PVC/PPC Blends

	NBR Amount in NBR-PPC Elastomer					
	N220S (phr)	70	50	35	20	0
	N41 (phr)	0	20	35	50	70
	Nitrile Percentage of NBR					
	41	37	34	30	26	
Tensile strength (MPa)	19.1	19.2	22.5	15.4	8.6	
Elongation at break (%)	21	27	111	19	12	
Impact resistance (kJ/m ²)	1.8	4.1	5.4	3.9	2.5	
Crosslinking density ($\bar{M}_c \times 10^3$)	5.3	5.2	5.0	5.8	6.0	

probably influences the interaction between PPC and NBR. For understanding the influence of the nitrile content of the NBR, a series of NBRs with different nitrile contents were used; the resultant coupling agent was a component in the basic formula of the PVC/PPC blends. The mechanical properties of these blends are shown in Table III and Figure 1. The results indicated that the properties of PVC/PPC blends were the best when the nitrile percentage of NBR was about 34%; tensile strength, impact resistance, and elongation at break of the blend were all better than those of any other blends with other nitrile percentages of NBR. This is different from the fact that the compatibility between PVC and NBR

increases with a rising nitrile percentage of NBR¹⁰ probably because the increase of NBR's nitrile percentage increases the compatibility of NBR/PVC. But it is probably a disadvantage for forming the chemical linking bonds between NBR and PPC at the same time. In the NBR-PPC system, the hydrogen attached to the α carbon of the acrylonitrile group or to the *ortho*-methylene carbon atom that connects to the C=C bond is easily activated by oxygen to produce a free radical⁹ and then to crosslink with the PPC main chain.

Effect of BPO Content of Coupling Agent on Properties of PVC/PPC Blends

BPO was used as the initiator of the coupling agent. Its amount probably had a certain effect on the crosslinking structure of the coupling agent, and then affected the properties of PVC/PPC blends. If the amount was too small, interaction between NBR and PPC in the coupling agent would not be strong enough to make a great coupling action. But if it was too much, NBR and PPC were all crosslinked in the elastomer and there was little interaction between PVC and NBR when this highly crosslinked coupling agent was added to the PVC/PPC blends.

Table IV shows the effect of BPO content on the mechanical properties of PVC/PPC blends. It was obvious that 2.5 phr was the best content of BPO in the elastomer.

Effect of Pre vulcanization Time of NBR-PPC Elastomer on Properties of PVC/PPC Blends

In the following, the basic formula was used but the NBR-PPC elastomer was pre vulcanized for a differ-

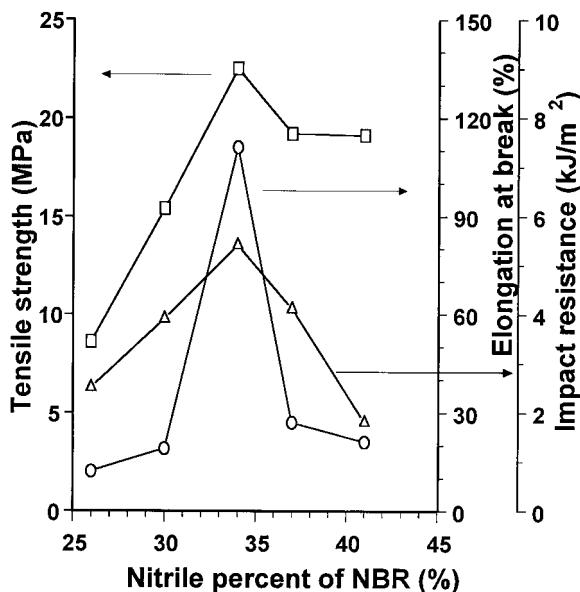


Figure 1 Mechanical properties of PVC/PPC blends vs. nitrile content of NBR.

Table IV Effect of BPO Content on Properties of PVC/PPC Blends

	BPO Amount (phr)				
	0	1.0	2.5	4.0	4.5
Tensile strength (MPa)	17.0	17.7	22.5	22.1	16.1
Elongation at break (%)	18	12	111	18	17
Impact resistance (kJ/m ²)	6.0	6.8	5.4	5.1	5.3
Crosslinking density ($\bar{M}_c \times 10^3$)	—	5.9	5.0	4.2	6.1

(—) It was proved that the blends without BPO all dissolved in THF.

ent time. Figure 2 shows the effect of the elastomer's prevulcanization time on the mechanical properties of the blends. When increasing the elastomer's prevulcanization time, tensile strength and impact resistance gradually decreased. When vulcanization time was more than 20 min, elongation at break dramatically decreased. A possible reason is that the vulcanization time of the coupling agent was so long that the coupling agent itself was crosslinked completely, the NBR in the coupling agent could not cause interaction between itself and the PVC, and then the NBR-PPC elastomer was not influential on the interfacial action between the PVC and PPC phases.

CONCLUSIONS

1. NBR-PPC elastomer can promote the compatibility of PVC/PPC blends.

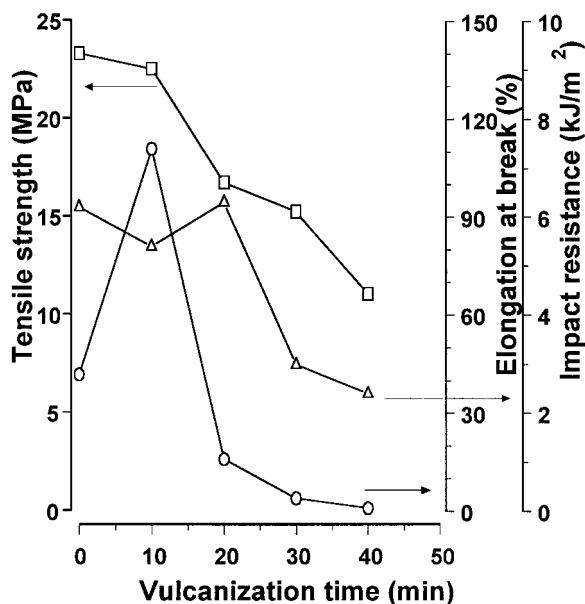


Figure 2 Mechanical properties of PVC/PPC blends vs. prevulcanization time of NBR-PPC elastomer.

2. NBR-PPC elastomer greatly improved the mechanical properties of PVC/PPC blends.
3. When NBR-PPC elastomer consisted of a 70/30 ratio of NBR/PPC (in which NBR had 34% nitrile content) and 2.5 phr of BPO initiator and underwent a prevulcanization, PVC/PPC blends displayed excellent mechanical properties with 8 phr elastomer.

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REFERENCES

1. M. Gyor, A. Rockenbauer, L. Jokay, and F. Tudos, *Polym. Bull.*, **15**, 525 (1986).
2. F. Gallego, M. E. Munoz, J. J. Pena, and A. Santamaria, *Eur. Polym. J.*, **24**, 327 (1988).
3. X. J. Zheng, H. P. Henry, and Y. F. Lu, *J. Polym. Sci., Part C: Polym. Lett.*, **26**(6), 255 (1988).
4. T. Ougizawa and T. Inoue, *J. Mater. Sci.*, **23**, 718 (1988).
5. L. B. Chen, X. X. Lin, and H. S. Chen, *Chin. J. Appl. Chem.*, **5**(4), 7 (1988).
6. S. J. Wang, Y. H. Huang, and G. M. Cong, *Polym. Bulletin*, to appear.
7. L. B. Chen, J. Lin, J. X. Jin, and G. C. Huang, *J. Macromol. Sci.-Chem.*, **A26**, 361 (1989).
8. E. F. Cluff, E. K. Gladding, and P. Pariser, *J. Polym. Syst.*, **45**, 341 (1960).
9. Y. H. Huang, X. H. Yang, S. L. Zhao, G. M. Cong, and L. B. Chen, *J. Appl. Polym. Sci.*, to appear.
10. D. H. Liu, *Handbook of the Synthetic Rubber Industry of China*, Chemical Industry Press, Beijing, 1991.
11. L. A. Utracki, *Polym.-Plast. Technol. Eng.*, **22**, 27 (1984).
12. K. E. George, R. Joseph, D. J. Francis, and K. T. Thomas, *Polym. Eng. Sci.*, **27**, 1137 (1987).