

Self-Crosslinking and Cocrosslinking with Nitrile Rubber of Poly(vinyl chloride) with Pendent *N,N*-Diethyldithiocarbamate Group

JIANJUN GUAN,¹ CHANGYOU GAO,¹ WENJUN YANG,² JIACONG SHEN¹

¹ Department of Polymer Science and Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

² Institute of Rubber-Plastic Engineering, Qingdao College of Chemical Technology, Qingdao 266042, People's Republic of China

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ABSTRACT: In order to realize the self-crosslinking and cocrosslinking of poly(vinyl chloride) (PVC) with nitrile-butadiene rubber (NBR), PVC with pendent *N,N*-diethyldithiocarbamate groups (PVC-SR) was prepared from the reaction of PVC with sodium SR in butanone. The PVC-SR was self-crosslinked and the PVC-SR/NBR blend was cocrosslinked under heating at 170°C. The effect of the degree of functionality of PVC-SR on the torque, gel content, glass-transition temperature, and tensile properties was investigated. The results showed that the crosslinking reaction did not occur for PVC, NBR, or the PVC/NBR blend. Introducing the SR groups into PVC caused the crosslinking reaction to occur and the high gel contents of the crosslinked samples were obtained in 15 min. The degree of crosslinking increased with the degree of functionality of PVC-SR. The mechanism of the crosslinking reaction was discussed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 634–638, 2001

Key words: poly(vinyl chloride); functional polymer; crosslinking reaction; blend modification; nitrile rubber

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials in the plastics industry. Besides being used as a rigid material, it can also be used as an elastomer and for manufacture of blood bags, transfusion tubings, electric cables, wires, and so forth. The PVC elastomer that was blended with rubber [e.g., nitrile-butadiene rubber (NBR)], plasticizer, and a softening agent [e.g., dioctyl phthalate (DOP)] increased the flexibility, impact strength, and low

temperature properties of PVC. However, it is not a good elastomer because of the high deformation set under stretching, low resistance to heat, and easy migration of the plasticizer.^{1,2} The self-crosslinking of PVC and cocrosslinking of PVC with rubber^{3,4} could overcome these defects. In order to realize the crosslinking of PVC, procedures such as irradiation crosslinking, chemical crosslinking, and decomposing crosslinking were employed.⁵ Among them, chemical crosslinking attracted the most attention. However, conventional crosslinking methods such as sulfur-type vulcanization and peroxide vulcanization were either impossible or inadvisable because of the PVC's low reactivity and thermal stability. To accelerate the crosslinking reaction, one of the effective ways was to introduce the groups that were easy to combine into the PVC chains under

Correspondence to: J. Guan (jjguan@mail.hz.zj.cn).
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Table I Amount of NaSR Used and Degree of Functionality of PVC-SR Obtained

NaSR (g)	PVC-SR
0.25	17
0.35	25
0.70	50

processing conditions. Lakshmi and Jayakrishnan⁶ modified a medical PVC sheet with sodium *N,N*-diethyldithiocarbamate (NaSR) on its surface in a water solution and irradiation crosslinked it to reduce the migration of plasticizer. In this article PVC-SR with different degrees of functionality was prepared and used to enhance the self-crosslinking of PVC and cocrosslinking of PVC with NBR under heating. The results obtained are described and discussed.

EXPERIMENTAL

The solvents and other reagents used were all analytically pure and used without further purification.

Preparation and Characterization of PVC-SR

The PVC-SR was prepared by the reaction of PVC (DP = 1000, porous type, supplied by Qilu Petrochemical Co.) with NaSR (Shanghai Chemical Co., China). In a 250-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a temperature controller were placed PVC (3 g), butanone (120 mL), and a given weight of NaSR. The amounts of NaSR used are listed in Table I. The reaction continued under stirring and heating at 70°C for 5 h. The solution was then poured into a large amount of ethanol. The precipitated samples were reprecipitated from a THF-ethanol system and dried in a vacuum.

The content of chloride (Cl wt %) in the PVC-SR was determined by titrimetric analysis of the sample of combustion by the ISO1158-1984 method. The degree of functionality was determined according to the following equation:

degree of functionality of PVC-SR

$$= \frac{[35.5 - 62.5w(\text{Cl})]}{[35.5 + 102.81w(\text{Cl})]} \times 1000$$

The FTIR spectrum was obtained with an IFS66V FTIR recording spectrophotometer (Bruker Co.). The UV spectrum was determined at 25°C in THF on a Shimadzu UV-3100 UV-VIR-NIR recording spectrophotometer.

Preparation and Characterization of Crosslinked Samples

PVC (or PVC-SR) was kneaded with DOP and stabilizer, then melt mixed in a two-roll mill at 100°C for 10 min to ensure uniformity of the materials. The kneaded mixes (PVC or PVC-SR with DOP and stabilizer) were melt mixed for 5 min under the same conditions; masticated NBR (26 wt % acrylonitrile, Lanzhou Chemical Co., Lanzhou, China) was then added to the blend of PVC (or PVC-SR) with NBR, and mixing was continued for 3 min. The formulations of the mixes are given in Table II. The crosslinking reaction was completed by compression molding at 5000 kPa for 15 min at 170°C. This produced sheets that were approximately 1 mm thick.

Dumbbell-shaped specimens were made for tensile property measurements. This was done on a Instron machine at room temperature. The dimensions of the specimens were 40 × 10 mm, and a tensile speed of 50 mm/min was used in the measurements.

The rheographs of uncrosslinked samples were assessed using a Shawbury Curometer (H. W.

Table II Formulation of Polymer Compounds (phw)

	PVC	PVC-SR	NBR	Stearic Acid	Zinc Stearic	Barium Stearic	DOP
1	100	—	—	1.5	1.5	3	50
2	—	100	—	1.5	1.5	3	50
3	70	—	30	1.5	1.5	3	35
4	—	70	30	1.5	1.5	3	35

DOP, dioctyl phthalate; phw, parts by weight.

Wallace & Co. Ltd.), and tests were carried out at 170°C.

The crosslinked samples were extracted with THF for 48 h; the gel content was calculated from the equation

$$w(\text{gel}) = \frac{m_2}{m_1} \times 100\%$$

where m_1 and m_2 were the weight of the polymer before and after being extracted, respectively.

The glass-transition temperature curves of the polymers were measured using differential scanning calorimetry (DSC, Du Pont 910); 5–10 mg of samples were heated at a rate of 20°C/min.

The FTIR spectra of the grafted polymers were obtained on an IFS66V FTIR recording spectrophotometer (Bruker).

RESULTS AND DISCUSSION

Synthesis of PVC-SR

There were two facts that could confirm the nucleophilic substitution of PVC with NaSR: the

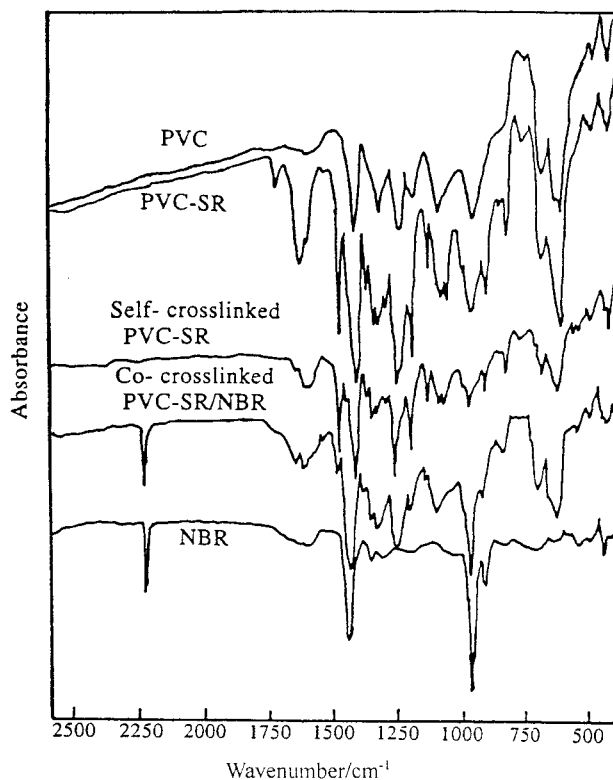


Figure 1 IR spectra of PVC, PVC-SR, self-crosslinked PVC-SR, cocrosslinked PVC-SR/NBR blend, and NBR.

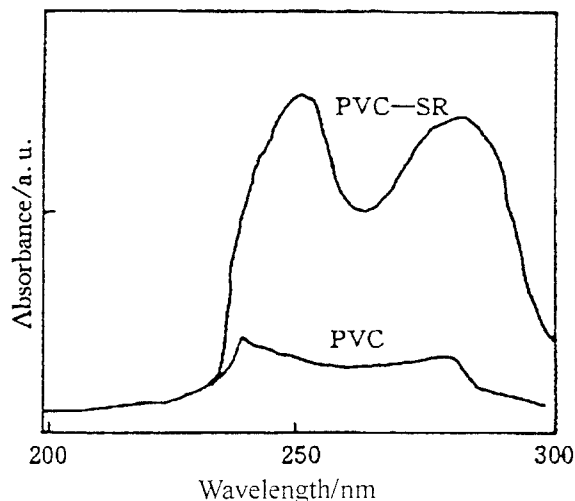


Figure 2 UV spectra of PVC and PVC-SR.

sodium chloride precipitated during the reaction, and the weight of the reacted samples increased. For example, when 3 g of PVC and 1 g of NaSR were reacted for 4 h at 70°C in 100 mL butanone, we obtained 0.19 g of sodium chloride and 3.37 g of dried polymer.

Figures 1 and 2 show the IR spectrum and UV spectrum, respectively, of the PVC-SR. Compared with the characteristic peak of —S—C(S)—N at 1644 cm^{-1} of PVC, conjugated peaks of —S—C(S)— and —C(S)—N— at 250 and 281 nm, respectively, were observed in the PVC-SR.

From the above results it could be seen that reacting with NaSR could functionalize the PVC. By controlling the amount of NaSR, PVC-SR with different degrees of functionality was obtained (Table I).

Confirmation of Crosslinking Reaction

The variation of the torque of PVC, PVC-SR, PVC/NBR blend, and PVC-SR/NBR blend as a function of time at 170°C was investigated. The results are shown in Figures 3 and 4. The torque of the PVC and PVC/NBR blend remained almost unchanged with the increase of time. After extraction with THF, there was no gel (Table III). This indicated that the PVC and PVC/NBR blend could not crosslink when heated at 170°C. Under the same conditions, however, the PVC-SR and PVC-SR/NBR blend crosslinked. The progressive rise in torque of the PVC-SR and PVC-SR/NBR blend with time was the result of the gradual formation of a network structure. Moreover, the gel was observed after extraction. When increasing of the degree of functionality of PVC-SR, the torque and

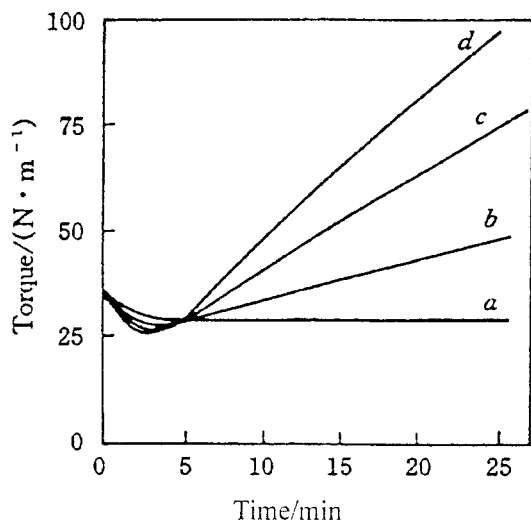


Figure 3 Rheographs of PVC and PVC-SR with different degrees of functionality at 170°C.

degree of gel increased, which meant that the degree of crosslinking increased.

As can be seen from Table III, the total gel content of crosslinked PVC-SR/NBR blend was higher than the gel content of the PVC-SR component, even if the PVC-SR component had the same degree of gel as the self-crosslinked PVC-SR. It could be considered that there was NBR gel in the total gel of the crosslinked blend, which was the crosslinked NBR component because of the action of the PVC-SR. In the IR spectra (Fig. 1) a characteristic peak of the CN group at 2237 cm^{-1} appeared apart from the characteristic peak

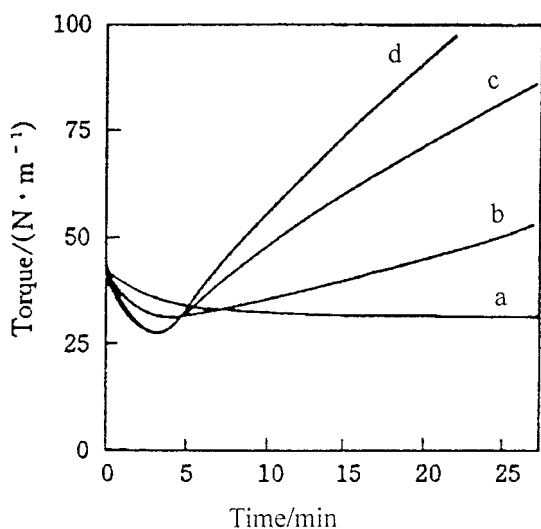


Figure 4 Rheographs of PVC/NBR (70/30) and PVC-SR/NBR (70/30) with different degrees of functionality at 170°C.

Table III Gel Content of Crosslinked Samples

	Degree of Functionality of PVC-SR			
	0	17	25	50
Gel content in PVC-SR (%)	0	60.0	94.5	96.0
Gel content in PVC-SR/NBR (%)	0	59.5	91.8	97.2
Maximum content of PVC in PVC-SR/NBR (%) ^a	0	42.0	66.2	67.2
Minimum content of NBR gel in PVC-SR/NBR (%)	0	17.5	25.6	30.0

PVC-SR/NBR = 70/30.

^a If PVC-SR has the same degree of reaction as self-crosslinking.

of PVC-SR, which further verified the existence of NBR gel in the total gel.

The glass-transition temperatures of uncrosslinked and crosslinked samples are shown in Figure 5. We found that the glass-transition temperature of the PVC-SR component in the crosslinked blend was lower than that of self-crosslinked PVC-SR, which meant that the cocrosslinking reaction occurred between the PVC-SR and NBR components. The glass-transition temperature of the PVC-SR component in the crosslinked blend was higher than that of the uncrosslinked PVC-SR, which was probably due to the high degree of crosslinking and self-crosslinking of the PVC-SR component.

In our previous study⁸ we found that the SR group was almost insensitive to thermal influ-

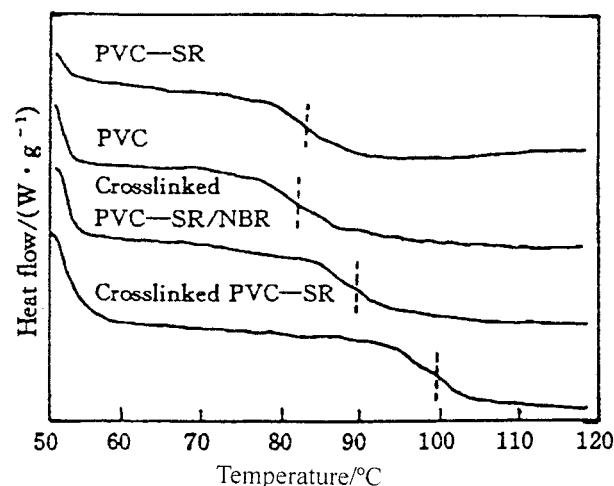


Figure 5 DSC curves of the obtained samples.

Table IV Properties of Crosslinked Samples

	Degree of Functionality of PVC-SR		
	17	25	50
Tensile strength (MPa)	12.5 (11.7)	17.7 (14.1)	12.1 (10.5)
Elongation at break (%)	200 (325)	121 (198)	89 (100)

The data in and out of the parentheses belong to crosslinked PVC-SR/NBR (70/30) and crosslinked PVC-SR, respectively.

ences when the temperature was lower than 100°C. From the above results, it could be concluded that partially substituted PVC with an SR group could self-crosslink and cocrosslink with NBR at high temperature and obtain a high degree of gel in a short time. This indicated that the SR group was not only photosensitive, but it was also thermosensitive at high temperature.

Discussion of Mechanism of Crosslinking

PVC could not self-crosslink under heating while the SR group substituted PVC self-crosslinked and cocrosslinked with NBR. Compared with PVC-SR, the peak of 1644 cm^{-1} for the extracted gel of self-crosslinked PVC-SR was low, which showed that the SR group dissociated during the crosslinking. PVC-SR could dissociate in two ways under heating or UV irradiation.⁷⁻⁹ One way was the forming of a macromolecular sulfur radical ($\text{PVC-S}\cdot$) and a small molecular carbon radical [$\cdot\text{C}(\text{S})\text{N}(\text{C}_2\text{H}_5)$]; the other way was the forming of a macromolecular carbon radical ($\text{PVC}\cdot$) and a small molecular sulfur radical [$\cdot\text{SC}(\text{S})\text{N}(\text{C}_2\text{H}_5)$]. It was confirmed that the SR group dissociated mainly in the first way. Because the sulfur radical has a high ability to combine, the self-crosslinking reaction of PVC-SR could be attributed to the combination of $\text{PVC-S}\cdot$ and forming double sulfur bonds between two PVC chains. In the PVC-SR/NBR blend the PVC-SR acted as a vulcanizator for NBR and the crosslinking reaction was realized by transferring of $\text{PVC-S}\cdot$ to the α -hydrogen of NBR. Therefore, there were three types of radical combinations in the blends: a combination of $\text{PVC-S}\cdot$ radicals, a combination of $\text{PVC-S}\cdot$ and $\text{NBR}\cdot$ radicals, and a combination of $\text{NBR}\cdot$ radicals. The occurrence of the three types of crosslinking reaction was verified by DSC curves of the blend: self-crosslinking of PVC-SR, self-crosslinking of NBR, and cocrosslinking of PVC-SR and NBR.

Properties of Crosslinked Samples

Table IV shows the properties of the crosslinked samples. The elongation at break of self-crosslinked and cocrosslinked samples decreased with the increase of the degree of functionality of PVC-SR. The tensile strength increased and then decreased when the degree of functionality was high (50), which was presumably due to the high density of crosslinking and severe stress of concentration.

CONCLUSION

The substitution reaction of NaSR on PVC could be performed in butanone medium, and the degree of functionality of PVC-SR could be controlled by adjusting the amount of NaSR. This functional polymer could be easily self-crosslinked and cocrosslinked with NBR under heating in a short time and it obtained a high degree of gel. It is possible that the functional PVC can serve as a coating to shield the surface of metal and nonmetal materials.

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