Study on the Self-Crosslinking Behavior Based on Polychloroprene Rubber and Epoxidized Natural Rubber

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ABSTRACT: This work has studied the impact of curing temperature and rubber compositions on the self-crosslinking behavior of the polychloroprene rubber (CR) and epoxidized natural rubber (ENR) blend. Variation of the temperature and blending ratios, rheological results have shown a better crosslinking result at 160°C with the optimum CR ratio at 75%. Then, Arrhenius equation was applied to verify the crosslinking kinetic and first-order kinetics has been verified. The chemical reaction routes proposed by differential scanning calorimetry have also been analyzed. Moreover, dynamic mechanical analysis and field emission scanning electron micrographs combined with energy-dispersive X-ray analysis were done to evaluate the phase compatibility. Based on the experimental results, a proposal "cross-promotion" reaction is drawn to conclude the self-crosslinking of CR and ENR. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1084–1090, 2012

Key words: polymer blends; rubber; self-crosslinking

INTRODUCTION

It is well known that vulcanization has attracted close attention since the rising of the rubber vulcanizate and its extensive applications in both domestic and industrial fields. In the recent years, for the finding of self-crosslinking, it has been demonstrated that rubber blends with reactive functional groups can undergo self-crosslinking without addition of external vulcanizing agents.[1–6] Self-crosslinking is well chosen as an alternative way to prepare polymer blend with improved overall properties. Numerous studies on plastic/rubber blend such as poly(vinyl chloride)/epoxidized natural rubber (ENR) blend have disclosed that the blending temperature, which determines the crosslinking behavior, plays great role on the physical properties of the blend.[1–3] Although the relating work of self-vulcanizable rubber blends is critically low, most of the works are limited to the physical compatibility.[4–6] So, as a promising work has both academic and industrial value, it is urgent to undertake a detailed study to explore the chemical nature of self-crosslinking.

Both polychloroprene rubber (CR) and ENR have been chosen as the study subject for self-crosslinking due to their possession of reactive groups.[7–15] The crosslinking of CR has been elucidated to be the extension of the thermal-induced polymerization.[16] Besides, it has been illustrated that the initial vulcanization of CR is the release of hydrochloride from the allylic chloride of 1,2-isomers and then the transition of the other isomers into allylic structure to crosslink.[17] During the vulcanization of CR, metallic oxides such as zinc oxide plays great role and serves as acid-acceptor.[18] Moreover, the studies on the crosslinking of ENR have found that ENR with high epoxide level undergoes facile ring expansion in the presence of acid, that is, leading to the formation of five, six, and seven-membered-cyclic ethers, where five-membered furanized structures are most probably formed.[7,8]

This study follows a previous part[4,5] and concentrates on the vulcanization investigation of CR and ENR binary blend. Detailed experiments and analysis were undertaken on the thermal enthalpy variation to verify the intercrosslinking of CR and ENR. And the crosslinking kinetic study was analyzed based on Arrhenius equation,[19] which substantiates the self-crosslinking of ENR and CR is a first-order course. Combining the fact that the best mechanical properties for ENR/CR is with the weight ratio of 25/75, we conclude that it is the "cross-promotion" reaction lies between ENR and CR that leads to intercrosslinking and good mechanical properties for the blend.

EXPERIMENTAL

Materials and sample preparation

ENR with 50 mol % epoxidation-random copolymer of 2-methyl-2-butane and 2,3-epoxy-2-methyl butane (ENR-50)[20] was kindly supplied by the Institute of Agro-Food Science and Technology, Chinese Academy of Agricultural Sciences, China. CR, indicated as CR-2442 (high crystallization, ML (1 + 4)100°C 76–90) was purchased from Changshou Chemical Co., China. Rubber samples were prepared in a laboratory two-roll mill at room temperature. The preparation of the vulcanizate was carried out at 160°C for 60 min under 10 MPa pressure using a Yadong Tech hot press. The molded sample was sandwiched with aluminum foils. Besides, to give a clear description of the blend, the sample designation was given as S_n, where n indicates the weight percent of CR.

Measurements

Curing characteristics using oscillating disk rheometer

Gum rubber was prepared for vulcanization test. The cure characteristics of the stocks were measured using an ODR (model 110E) at series of set temperatures from 140 to 180°C, with an interval of 10°C and stepwise increase.

Cure kinetics using differential scanning calorimetry

Differential scanning, calorimetric experiment was performed on a thermal analyzer model under nitrogen atmosphere with a flow rate of 50 mL/min, using a DSC 204 (NETZSCH, Germany) at 10°C/min. The sample was set in an aluminum pan and cover.

Miscibility studies using dynamic mechanical analysis

Dynamical mechanical tests were undertaken in tension mode, between −100°C and 60°C at 1 Hz, using a TA Q-80 (TA Instruments, USA). The strain amplitude used was 0.0025 cm, and the heating rate was 2°C/min.

Swelling properties determination

To fully determine the crosslinking nature of the sample, three solvents, that is, acetone, toluene, and chloroform were used. Their Hildebrand solubility parameters are 9.9, 8.9, and 9.3, respectively.[21] Square samples with side length 1.5 cm were used for swelling experiments. Samples were immersed in solvents in test bottles and kept at room temperature in a circulated air oven. The samples were weighed at periodic intervals. The weighing was continued till equilibrium swelling was attained.[22] Five parallel experiments for each sample had been done, and the average polymer weight ratio (w_2) value was acquired according to $w_2 = w_{ds}/w_s$ (w_{ds} and w_s relate to the weight of deswollen and swollen samples).

Mechanical properties using tensile tester

Tensile studies were performed using an Instron Testing Machine, Model 5567, according to ASTM D 412-87 with a tensile rate at 500 mm/min. No less than five pieces of each sample were tested, and the average value was obtained.

Morphology and phase compatibility characterization

Field emission scanning electron micrographs (FESEM) and energy-dispersive X-ray (EDX) analysis were carried out on a XL 30 ESEM FEG scanning electron microscope (Micrio Fei Philips, Holand). Samples were quenched in liquid nitrogen and smashed with steel rod. The side section was chosen and coated with an ultrathin film of gold to make them conductive before observation. The relative weight ratio of carbon, chloride, and oxygen had been applied to characterize the phase compatibility of vulcanized ENR/CR, because ENR had oxygen element while CR had chloride.

RESULTS AND DISCUSSION

The crosslinking behavior was first determined with the Oscillating Disk Rheometer. The relative influence of composition and cure temperature on vulcanization parameters of CR and ENR-50 blend is listed in Table I. In which, the scorch time, optimum cure time, and the corresponding torque values, which offer links to the curing rate and degree, are shown. Most dominantly, for a set cure temperature, a decrease of scorch safety is observed with increase of CR. Besides, taking the influence of curing temperature into consideration, the optimum time shows a minimum value at 160°C, which indicates that the fast cure rate was achieved at 160°C. Based on the thermal-induced crosslinking nature of CR and ENR,[8,16] this could be attributed to the optimum balance of crosslinking and degradation. Further experimental results and discussion are shown below.

Cure rate index (CRI) as a direct characterization of cure rate was calculated as shown in

$$CRI = \frac{100}{t_{90} - t_{10}} \qquad (1)$$

where t_{90} is the optimum cure time and t_{10} is the scorch time.[23] Response values of CRI as a function

TABLE I
Vulcanization Parameters of ENR/CR Blends as a Function of Blend Ratio

Cure parameters	Temperature (°C)															
	150				160				170				180			
	S_{25}	S_{50}	S_{75}	S_{100}	S_{25}	S_{50}	S_{75}	S_{100}	S_{25}	S_{50}	S_{75}	S_{100}	S_{25}	S_{50}	S_{75}	S_{100}
$M_H{}^a$ (N*M)	0.79	1.26	1.61	1.38	0.79	1.38	1.51	1.32	0.66	1.12	1.45	1.44	0.60	0.96	1.22	1.29
$M_L{}^b$ (N*M)	0.60	0.49	0.43	0.24	0.51	0.62	0.33	0.24	0.31	0.26	0.17	0.21	0.16	0.18	0.14	0.21
$t_{10}{}^c$ (min)	8.08	5.32	5.22	4.53	4.88	3.45	3.28	3.50	2.82	2.52	2.08	1.4 9	1.57	1.48	1.42	1.35
$t_{90}{}^d$ (min)	45.25	20.95	16.22	8.55	38.68	18.42	11.45	15.70	45.38	38.08	26.82	34.13	48.1	39.5	27.2	19.3

[a] Maximum torque.
[b] Minimum torque.
[c] scorch time.
[d] Optimum cure time.

of blend ratio and cure temperature are shown in Table II. It is found that the CRI increases with the addition of CR at a given cure temperature, that is, the most effective participation is observed in S_{75}. Besides, taking the influence of cure temperature into consideration, the CRI value shows a maximum at 160°C. Therefore, the optimum activation for crosslinking is achieved for S_{75} at 160°C.

Figure 1 shows the comprehensive differential scanning calorimetric curve of the blend. The top left figure shows the differential scanning calorimetry (DSC) curve ranged from 130 to 190°C is offered. For further discussion, S_{75} was taken as an example. It is easy to find that there is a low endothermic peak at about 140°C (peak 1), an exothermic subacromial peak at 160°C (peak 2), and a dominant exothermic peak at around 238°C (peak 3). These three concerned thermal peaks may relate to the release of allylic chloride,[17] intercrosslinking of ENR and CR and further crosslinking of CR that is, Cis and Trans 1,4-isomers, respectively. Additionally, there are dominant exothermic peaks at higher temperature than 238°C, which are due to the thermal-induced degradation of macromolecules. As mentioned in the previous work, Sadequl et al.[9] has elucidated that the ring-opening of epoxy groups should be at no less than 155°C. Hence the initiation and activation of the oxirane groups of ENR needs more energy and higher temperature than the crosslinking of CR. However, higher temperature will purge the degradation of the main molecule chains, while degradation reactions could decrease

the crosslinking density. Therefore, there exists an optimum cure temperature, that is, 160°C as illustrated earlier.

Figure 2 offers the curing curves of ENR/CR blends at 160°C. Taking the optimum cure time into consideration (Table I), the increase of ENR ratio has dominantly retarded the curing course. Besides, the variation of the blend ratio also results in a substantial increase of maximum torque (M_H) in the order of $S_{25} < S_{100} < S_{50} < S_{75}$. Because of the fact that M_H is directly proportion to the crosslinking density, the crosslinking density ranks in the order of $S_{25} < S_{100} < S_{50} < S_{75}$, which indicates that CR takes important role in the self-crosslinking of ENR/CR blend.

The swelling experiment was applied to distinguish the physical crosslinks from the chemical ones. The relative influence of solvent on the swelling properties is shown in Table III. It is reported that the solubility parameter of CR and ENR-50 is

TABLE II
Cure Rate Index (CRI) of ENR/CR Blends as a Function of Temperature

Temperature (°C)	S_{25}	S_{50}	S_{75}
140	–	4.13	5.24
150	2.99	6.52	8.98
160	3.05	6.74	12.10
170	2.50	2.82	4.03
180	2.15	2.63	3.83
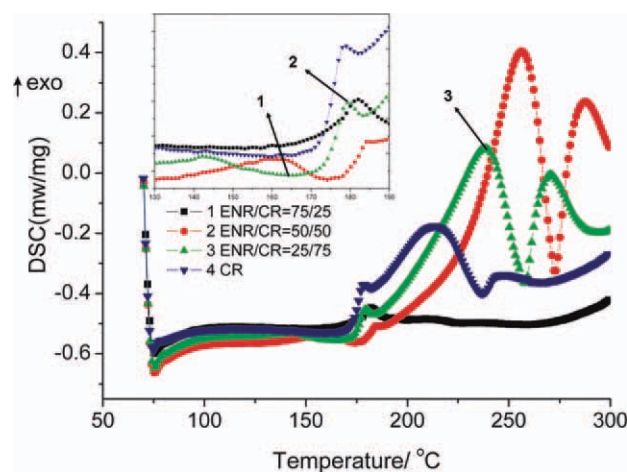
Figure 1 Differential scanning calorimetry curves of ENR/CR binary blends among which endothermic peak 1 is assigned to the release of hydrochloride; exothermic peaks 2 and 3 arise from the intercrosslinking of ENR-CR and intracrosslinking of CR, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
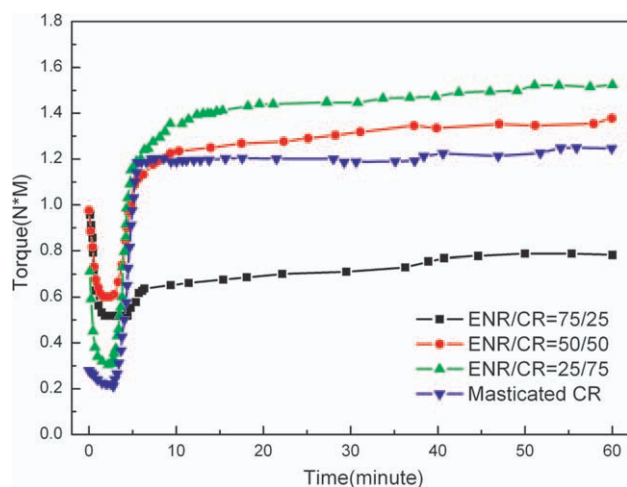
Figure 2 Curing curves of ENR/CR blend with varying weight ratio of CR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

9.5[24] and 8.9,[25] respectively. And, acetone, toluene, and chloroform, which have the approximate solubility parameters to those of the rubbers', are chosen as the solvents. The crosslinking density is indicated by polymer weight ratio (w_2), and the higher w_2 values indicate high degree of crosslinking. It is easy to find that the blend shows enhancive crosslinking density with the increase of CR ratio. However, for neat CR, the crosslinking density values are varied with the applied solvent. For example, the swelling results with acetone and chloroform indicate less effective crosslinking than the blends, which is contrast to that with toluene. The above-mentioned results could be attributed to the occurrence of special interaction between CR and ENR except for the thermal-induced crosslinking of CR.[26] The existence of this interaction had been elucidated in the work of Nagoda et al.[6] However, the physical crosslinking, for example, hydrogen bonding, charge transfer in the self-vulcanized system is not as stable as the conventional sulfur bridges or C—C ones, and so it could be destroyed in the existence of some proper solvents as justified by swelling result with toluene.

To explore the kinetic parameters of vulcanization, a few works had been done by the assumption and confirmation that the cure reaction was a first-order

TABLE III
Swelling Properties[a] of the Blend as a Function of Solvents

Solvent	S_{25}	S_{50}	S_{75}	S_{100}
Acetone	0.4554	0.6359	0.7157	0.3231
Chloroform	0.0527	0.1171	0.1326	0.0540
Toluene	0.1026	0.1779	0.2130	0.6399

[a] The average polymer weight ratio (w_2) value was accepted to evaluate the variation of the swelling properties.

kinetic course.[19] According to the relative work of Sadequl et al.,[9] response kinetic equation for the self-vulcanization process was obtained from the torque-time values of the vulcanization curve. On the consideration of the first-order reaction, which expressed by Eq. (2), as follows:

$$\ln\left(\frac{M_H - M_L}{M_H - M_t}\right) = kt \qquad (2)$$

where k is the vulcanization kinetic constant which indicates the slope, and M_H, M_L, and M_t correspond to the maximum torque value, the minimum torque value, and the torque value at time t, respectively. Take the S_{75}, for example, the $\ln(M_H - M_L)$ is constant, the related $\ln(M_H - M_t)$ versus t are shown in Figure 3. Noting that the plots $\ln(M_H - M_t)$ versus t, a straight line graph is obtained, indicating the cure reaction followed first-order kinetic. Furthermore, the relation of vulcanization rate depended on reciprocal temperature was calculated with the help of Arrhenius equation, as shown in

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

or

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \qquad (4)$$

where A is the pre-exponential factor, R represents the gas constant, T is the absolute temperature, and E_a indicates the apparent activation energy for the curing process. The relative influence of blend ratio and temperature on rate constant and E_a are shown in Table IV. From which, it is found that the cure
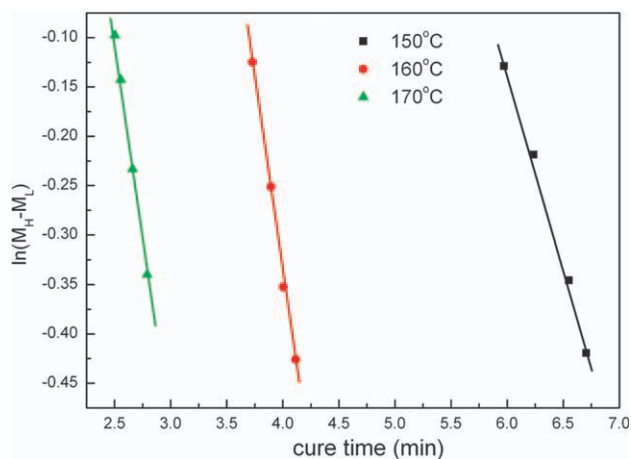
Figure 3 Plots of Eq. (2) for S_{75} at various temperatures. Solid lines indicate the linear fitting results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
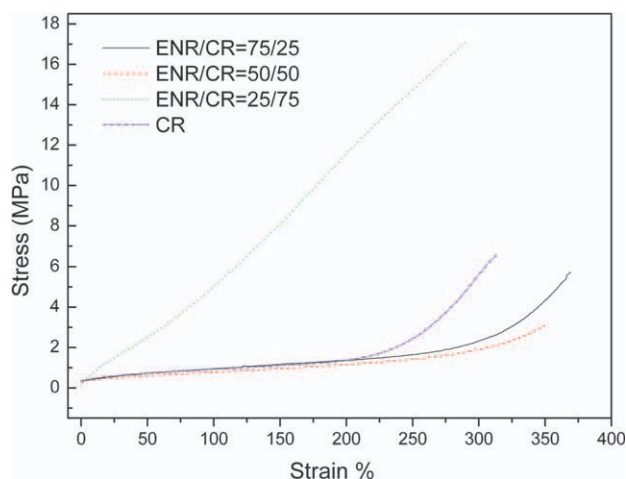
TABLE IV
Kinetic Parameters of Vulcanization of ENR/CR Blends as a Function of Blend Ratio

Sample	Rate constant, k (min$^-$)			E_a (kJ/mol)
	150°C	160°C	170°C	
S_{25}	0.1734	0.4059	0.1460	129.5
S_{50}	0.3211	0.6712	0.6393	112.3
S_{75}	0.3953	0.7951	0.8395	106.4

TABLE V
Mechanical Properties of Rubber Blend as Function of CR Ratio

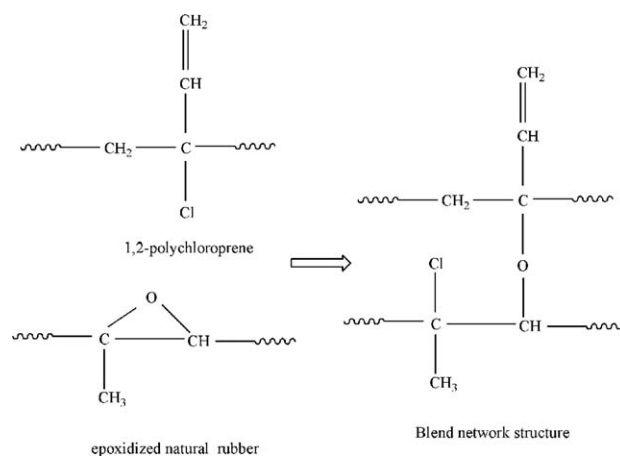| Sample	Modulus (MPa)[a]			T_B[b] (MPa)	ξ_B[c] (100%)
	M_{100}	M_{200}	M_{300}		
S_{25}	0.94	1.36	2.32	5.74	3.69
S_{50}	0.77	1.16	1.89	3.11	3.5
S_{75}	5.03	11.57	–	17.1	2.9
S_{100}	0.92	1.36	5.6	6.6	3.14

[a] Tensile modulus at different elongation, that is, M_{100} (100%), M_{200} (200%), and M_{300} (300%).
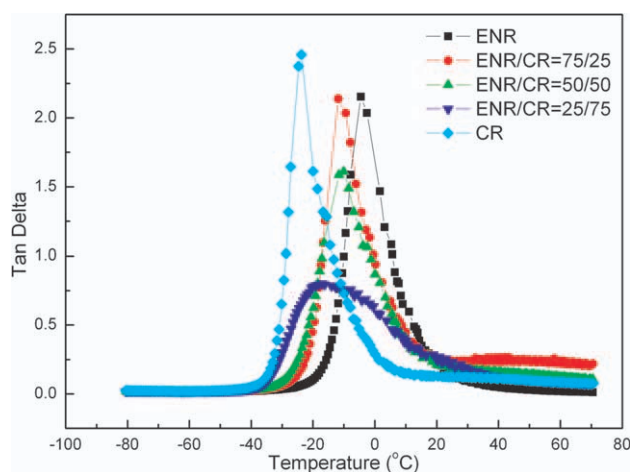[b] Tensile strength.
[c] Elongation at break.

rate grows with the increase of CR while the E_a decreases in the order of S_{25}, S_{50}, and S_{75}; for each blend ratio, the maximum rate constant appears at 160°C. Lower E_a value indicates that self-crosslinking proceeds more easily. This result also implies that the optimum cure temperature is 160°C and increase the amount of CR would promote the self-vulcanization course.

The stress–strain curves for the ENR/CR blends vulcanized at 160°C are shown in Figure 4, and detailed mechanical properties are summarized in Table V. From the tensile results, it is found that the sample containing 75 wt % CR shows much higher tensile modulus value, while the mechanical properties get worse with the increase in ENR. Because of the similarity of polarity, CR and ENR-50 can get semimiscible blend with the existence of special interaction, that is, donor–acceptor, ion–dipole, and dipole–dipole.[12] Incorporating the fact that ENR retains many oxide groups that can promote the initial crosslinking of CR; on the other hand, the accumulation of HCl will promote the ring opening of ENR.[7] So, the best mechanical properties at ENR/CR = 25/75 is well explained with the "cross-promotion" reaction. The proposal crosslinking between ENR and CR is sketched in Figure 5. As shown in Figure 5, active chloride in 2-chloro-2-bu-

tenyl will react with the epoxide group of ENR and new intercrosslinking C—O—C bond takes place. This reaction initiates from the dehydrochlorination of 2-chloro-2-butenyl and accompanying formation of the active carbocation, which will react with the epoxy groups of ENR and lead to the formation of chlorohydrin groups that can perform as further reactive sites.[13,14]

On the deduction of "cross-promotion," there may be more intermediate phase in the blend. To give an illustration, the variation of loss factor tangent (tan δ) of ENR/CR with temperature is shown in Figure 6. It is found that the binary blend at all blend ratios has one single transition peak, that is, T_g, which intermediates between those of ENR and CR, indicating the dynamical miscibility of the blend. It is worth noting that the base of the tan δ of the blend is slightly wider while the height of the peak is lower than those of ENR and CR. These could be attributed to the increase of crosslinking that has been referred in the work of Prud-homme et al.[27] Detailed parameters of the transition behavior are shown in Table VI. It is observed that S_{75}

Figure 4 Stress–strain curves of the ENR/CR blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 5** Schematic figure of proposal crosslinking of CR and ENR.

Figure 6 Dynamic mechanical analysis (tan loss factor) curves of ENR/CR blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

has the broadest transition range. Because the width of the transition zone is treated as an indication of miscibility or compatibility,[28] the observed broadening of tan δ peaks reflecting the presence of microheterogeneities in the blends. And it can be attributed to partial interpenetrating network formation involving thermal-vulcanized CR and crosslinked ENR/CR phases.[15] Furthermore, the FESEM–EDX results (the sample is ENR/CR = 25/75, which vulcanized at 160°C) are shown in Figure 7. As reflected in Figure 7(a), the vulcanized ENR/CR blend shows flat surface morphology and no detectable phase segregation features. Meanwhile, the EDX analysis for the area shown in Figure 7(a) is offered as Figure 7(b). It is easy to find that there are both chloride and oxygen element existing in the focus area. Meanwhile, we can also get the relative weight ratio of carbon, chloride, and oxygen by EDX analysis. The related weight ratios of carbon, chloride, and oxygen are 70.68%, 24.93%, and 4.4%, respectively. The coexistence of chloride and oxygen affirms that there are both CR and ENR existing in the scanned zone as shown in Figure 7(a). Hence, the vulcanized ENR/CR has partial compatible structure.

TABLE VI
Glass Transition Properties of ENR/CR Blend

Sample	Initial temperature (°C)	Terminal temperature (°C)	Transition range (°C)
S_0	−26.9	39.4	66.3
S_{25}	−31.5	19.4	50.9
S_{50}	−35.6	25.3	60.9
S_{75}	−44.4	39.4	83.8
S_{100}	−39.4	8.17	47.6
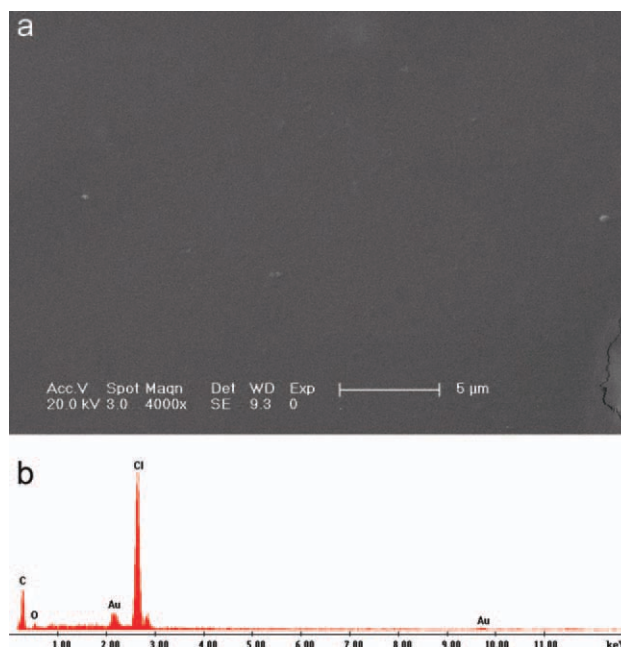
Figure 7 SEM micrographs (a) and corresponding EDX spectra of elements (b) of S_{75} sample. The energy of the X-ray character emitted from the element of carbon (C), oxygen (O), and chloride (Cl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

By studying the vulcanization behavior and mechanical properties, it is interesting to note that thermal-induced vulcanization of CR and intercrosslinking of ENR/CR are the main part of the "self-vulcanization" in ENR/CR blend system. The presence of oxides' groups promotes the thermal-vulcanization of CR, the resulting accumulation of HCl promotes the ring-opening of ENR, and then intercrosslinking is promoted. The optimum mechanical properties of the rubber blend, that is, ENR/CR = 25/75 is attributed to the "cross-promotion" chemical intercrosslinking reaction, which is proved to be a first-order course as indicated by Arrhenius equation.

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