

A Study on the Compatibility and Physical Properties of Chlorinated Polyethylene Rubber/Nitrile Rubber Blends

Zhen Xiu Zhang,¹ Chun Hua Chen,¹ Xin Wen Gao,¹ Jin Kuk Kim,² Zhen Xiang Xin¹

¹Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology, Ministry of Education, Qingdao 266042, People's Republic of China

²School of Nano and Advanced Materials Engineering, Gyeongsang National University, Gyeongnam, Jinju 660-701, South Korea

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ABSTRACT: The miscibility and some physicomechanical characteristics of chlorinated polyethylene rubber (CPE) and nitrile rubber (NBR) blends have been investigated. Calculation of the heat of mixing, differential scanning calorimetry, and scanning electron microscopy analysis showed that CPE was miscible with NBR in all proportions. The cure and scorch times decreased with the increase in NBR content, whereas the maximum torque increased. The tensile strength, 100% modulus, elongation at break, tear strength, and compression set decreased

with increasing of NBR content. After aging, hardness and tensile strength increased, and there was no drastic change in elongation at break on aging. The thermal aging resistance and the abrasion resistance of NBR are improved after blending with CPE, but the oil resistance decreased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1180–1185, 2011

Key words: nitrile rubber (NBR); chlorinated polyethylene; blends; compatibility; oil resistance; thermal aging; abrasion resistance

INTRODUCTION

Rubber blends are widely used in rubber industry for a variety of reasons which included improving of physical properties, improving service life, easier processing, and reducing product cost.^{1–3} The blend can offer a set of properties that can give it the potential of entering application area not possible with either of the polymers comprising the blend. A review of rubber blends was published by Ronald⁴ and different methods were used for studying polymer-polymer blends.⁵ Chlorinated polyethylene, ASTM designation CM or commonly referred to as chlorinated polyethylene (CPE), possesses high resistance to hydrocarbon oil, heat, and weathering, which is attributed to the addition of chlorine atoms, on the polyethylene backbone. CPE also has excellent flex fatigue characteristics, abrasion resistance, and resistance to refrigerant chemicals at high temperatures. CPE can provide performance and cost advantages over other elastomer systems, such as polychloroprene, nitrile rubber (NBR), chlorosulfonated polyethylene, NBR/PVC blends.⁶ Blends of CPE and other polymers have received wide attention in the literature.^{7–13} The role of CPE as a compatibilizer has also been investigated.¹⁴ Severe and

White¹⁵ studied the miscibility of hydrogenated nitrile rubber with CPE and found that strong interactions between the functional groups are responsible for miscibility. Sirisinha and coworkers^{16–19} extensively studied the compatibility, rheological, dynamic mechanical, and physicomechanical properties of CPE/NR blends. Maity and Das²⁰ reported that CPE formed interchain crosslink bonds with polyurethane.

Nitrile rubber (NBR) was commercialized as an oil-resistant rubber but always had problems with ultraviolet light and ozone attack. So blending of NBR with CPE should improve the oil resistance of CPE, as well as the heat aging resistance of NBR. Also, CPE-NBR blends are cost effective when compared with NBR. In fact, these blends are expected to have a unique set of properties essential for many applications.

In this study, the blend miscibility of CPE and NBR was studied in the complete composition range using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) techniques. The physicomechanical characteristics of the blends were also reported.

EXPERIMENTAL

Materials

The CPE (CM 135B), which contained 35 wt % chlorine, was supplied by Qingdao Haijing Chemical

Correspondence to: Z. X. Xin (xzx@qust.edu.cn).

TABLE I
Blend Formulations of CPE and NBR

Chemical	Amount (phr ^a)				
	A	B	C	D	E
CPE	100	75	50	25	0
NBR	0	25	50	75	100
DCP	2.5	2.5	2.5	2.5	2.5
TAIC	3.5	3.5	3.5	3.5	3.5
MgO	4	4	4	4	4
Stabilizing agent	0.5	0.5	0.5	0.5	0.5

^a phr: parts per hundreds of rubber.

Co., China, nitrile rubber (NBR3430) was supplied by Bayer Company, Germany, which contained 34 wt % acrylonitrile and had a Mooney viscosity [$M_L(1 + 4)$] at 100°C of 30; the curing agent was dicumyl peroxide (DCP) supplied by Canton Gold Prosperity Co., China; magnesium oxide (MgO) and triallyl isocyanurate (TAIC) were obtained from Atman Chemical Industry Co., China.

Blend preparation

The blends (Table I) were prepared on a laboratory size two roll-mill (X(S)K-160, Shanghai, China) at a roller temperature of 70–80°C. The CPE was first charged to the two-roll mill and allowed 1 min for melting. Thereafter, the masticated NBR was added. After the homogenization of the rubber blend, the other ingredients were added in the following order: stabilizing agent, MgO, DCP, and TAIC. The processing time after each component addition was about 2 min. The 2-mm thick slabs were then press cured under the pressure of 10 MPa at 165°C.²¹ The vulcanization parameters of the blends were measured on a moving die Rheometer (Model GT-M-2000-A, High Speed Rail Technology Co., Taiwan).

Mechanical properties measurement

Tensile strength, modulus, and elongation at break were measured on six dumbbell specimens for each sample according to ASTM D412-92, and the tear resistance was determined according to ASTM D642-00 using computerized test instrument (High Speed Rail Technology Co., Taiwan) at a crosshead speed of 500 mm/min. The compression set value was determined by the constant strain method keeping 48 h for 100°C, according to ASTM D395-03. The hardness of samples was measured according to ASTM D2240-04 with a durometer and Shore A scale at room temperature. Abrasion resistance of rubbers (volume losses) according to ASTM D5963-04 was measured by an abrasion tester (Taiwan, China).

Oil resistance and thermal aging properties measurement

Oil resistance measurements of blend vulcanizates were carried out according to ASTM D471-79. The test specimens were immersed in ASTM oil no. 3 (IRM 903 oil, Nibo Changtai Company, China) at 100°C for 72 h. Thereafter, the test specimens were removed from the oil, quickly dipped in acetone, and blotted lightly with filter paper to remove excess oil from the surfaces. The percentage of change in volume and quantity of the specimen after oil immersion were used to determine the oil resistance of the blends.

For the determination of thermal aging properties, the specimens were placed in an oven equipped with an air circulating system at the test temperature of 100°C for 72 h, according to ASTM D573-04. The aged specimens were then measured for tensile properties. The changes in tensile properties after thermal aging were used to determine thermal aging resistance.

Scanning electron microscopy (SEM)

SEM micrographs of fracture surface of all samples after tensile measurement were obtained using a model JSM6700 (Japan) scanning electron microscope. To characterize the different phases present in the blends, the fractured surfaces were etched with *N,N*-dimethylformamide solvent for 10 min to remove the NBR phase. The surface was then coated by a thin gold layer.

Differential scanning calorimetry (DSC)

DSC was carried out on a DSC-204 (NETZSCH) in nitrogen atmosphere. The temperature was increased at the heating rate 10°C/min in the range of –75 to 20°C.

RESULTS AND DISCUSSION

Thermodynamics of CPE/NBR blends

Thermodynamic miscibility and homogeneity can be attained when the following condition is fulfilled:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \quad (1)$$

where ΔG_m , ΔH_m , and ΔS_m are the Gibb's free energy, the enthalpy, and entropy of mixing at temperature T , respectively.

However, if two high-molecular weight polymers are blended, the gain in entropy, ΔS_m is negligible; therefore, the sign of ΔG_m always depends on the value of the enthalpy of mixing ΔH_m . The extent of homogeneity of CPE/NBR blends can be evaluated

TABLE II
Parameters of CPE and NBR

	δ (J/cm ³) ^{1/2}	ρ (g/cm ³)	M (g/mol)
CPE	19.2	1.116	107
NBR	19.5	0.946	90.5

from the heat of mixing of CPE/NBR blend system, calculated according to the following equation.²²

$$\Delta H_m = \left\{ W_A M_A \rho_A (\delta_A - \delta_B)^2 \times \left[\frac{W_B}{(1 - W_B) M_B \rho_B + (1 - W_A) M_A \rho_A} \right]^2 \right\}^{1/2} \quad (2)$$

where W , M , ρ , and δ are the weight fraction, molecular weight of monomer unit, polymer density, and solubility parameter, respectively, and subscript A and B refers to CPE and NBR, respectively. The parameters of CPE and NBR related to eq. (2), which were shown in Table II.

Table III showed the effect of changes in the weight fraction of CPE on ΔH_m calculated with eq. (2). It can be seen that the maximum value of $\Delta H_m = 2.515 \times 10^{-2}$ J/mol appeared at a 0.75 weight fraction of CPE. Schneier²² calculated the ΔH_m values of many polymer pairs and showed that for compatible polymer pairs, the value could vary from about 4×10^{-3} to 4×10^{-2} J. Therefore, the CPE/NBR blends were miscible in the composition range.

Differential scanning calorimetry (DSC) analysis

DSC measurement of glass-transition temperature is widely used to investigate the miscibility of blends, provided that the glass-transition temperatures (T_g) of the pure components are clearly distinguishable. It is expected that a miscible polymer blend should present a single glass-transition. The value of such T_g is generally located between those of the parent polymers and depends on the blend composition.

The glass-transitions temperatures T_g of CPE, NBR, and CPE/NBR blends were reported in Figure 1, the CPE/NBR blends exhibited a single T_g intermediate between those of the pure components, indicating that these systems were miscible in the tested compositions.^{23,24} In each case, the T_g value was affected by the blend composition; it gradually

TABLE III
 ΔH_m of CPE/NBR Blends

CPE (wt %)	75	50	25
CPE/NBR ΔH_m ($\times 10^2$ J/mol)	2.515	1.153	1.129

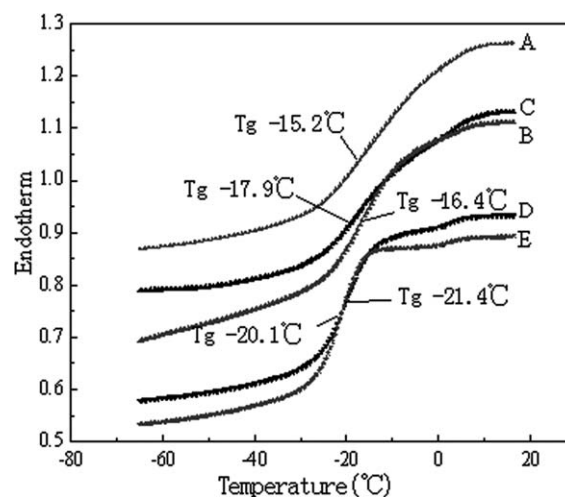


Figure 1 DSC thermogram of various CPE/NBR blends (A) CPE/NBR = 100/0, (B) CPE/NBR = 75/25, (C) CPE/NBR = 50/50, (D) CPE/NBR = 25/75, and (E) CPE/NBR = 0/100.

shifted to higher temperatures with increasing CPE content.

SEM analysis

Morphology is a major factor which can determine how the extent to which the blends are compatible. SEM micrographs of the fractures for the CPE/NBR blends were presented in Figure 2. It was found that the characteristic morphology depended on the blend ratio of CPE/NBR. The SEM micrographs illustrated that the NBR phase was dispersed in continuous domains as shown in Figure 2(a,b), the boundaries of the cavities were obscure, indicating that the interfacial adhesion was between the NBR and CPE phase. The domain size of the dispersed NBR-phase increased with increasing NBR content, since the process of particle coalescence was favored by increasing the concentration. When the NBR content was 75 wt %, pronounced phase coalescence occurred which resulted in a much coarser morphology as shown in Figure 2(c).

Vulcanization characteristics

Table IV showed the cure characteristics of the CPE/NBR blends under investigation. Regular variations in maximum torque, minimum torque, scorch time, and optimum cure time (t_{90}) have been observed for the blends. It can be seen that as the content of NBR increased in the blend systems, the maximum torque increased, which indicated the enhancement in crosslink density of the blends. Pure CPE showed maximum cure time. Optimum cure time decreased with an increase in NBR content in the blends. This showed that the rate of vulcanization

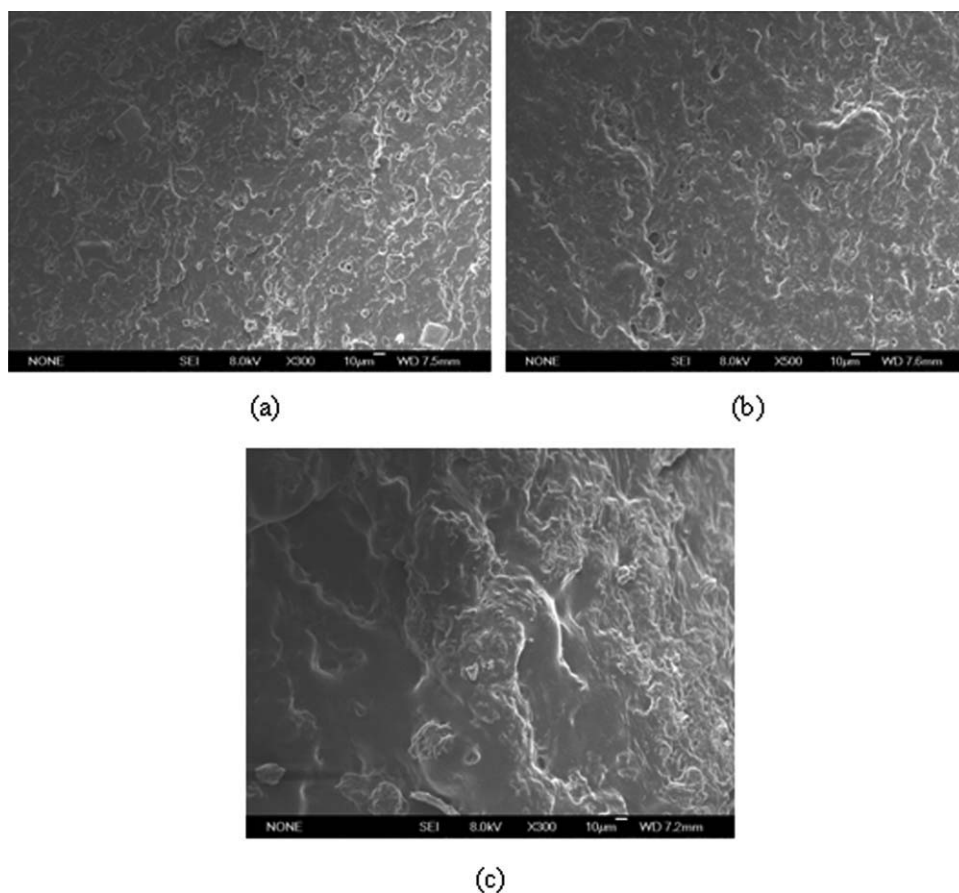


Figure 2 SEM micrographs of various CPE/NBR blends: (a) CPE/NBR = 75/25; (b) CPE/NB = 50/50; (c) CPE/NBR = 25/75.

was more in blends containing more NBR. Scorch time (t_{10}) is a measure of the premature vulcanization of the materials. As shown in Table IV, the scorch time decrease with higher content of NBR in the blends. This showed that the scorch safety was higher for the blend with higher content of CPE rubber.

Mechanical properties

The relationship between tensile strength of the blends and the blend ratio of CPE/NBR were shown in Figure 3. It was observed that the tensile strength decreased with increasing of the NBR content in the

blend, which indicated that the CPE phase was responsible for the high tensile strength of the blends. Similarly, the elongation at break result was shown in Figure 3 revealed that as the amount of NBR in blends increased, the elongation at break gradually decreased. This is due to the noncrystallizable property of NBR.²⁵ Figure 4 showed the effect of blend ratio on the modulus at 100%. It was obvious that

TABLE IV
Cure Characteristics of CPE/NBR Blends

Item	t_{10} (s)	t_{90} (s)	M_L (Kg cm)	M_H (Kg cm)
A	65	1120	1.77	11.29
B	56	995	1.24	11.65
C	50	818	0.95	11.87
D	49	670	0.64	11.96
E	51	658	0.41	12.35

t_{10} : scorch (premature vulcanization of a rubber compound) time; t_{90} : cure time; M_L : minimum torque; M_H : maximum torque.

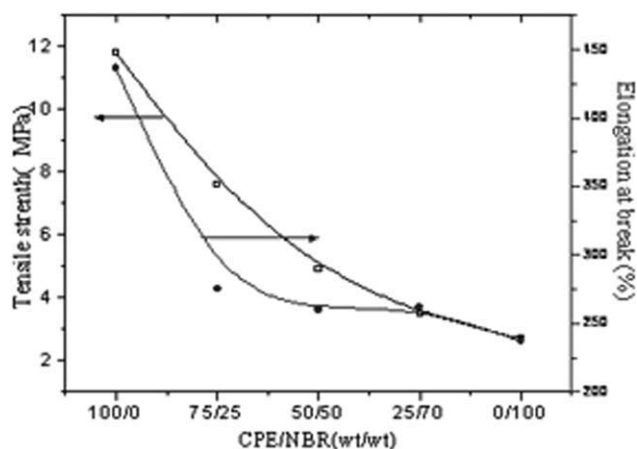


Figure 3 Tensile strength and elongation at break of CPE/NBR blends with various blend ratio.

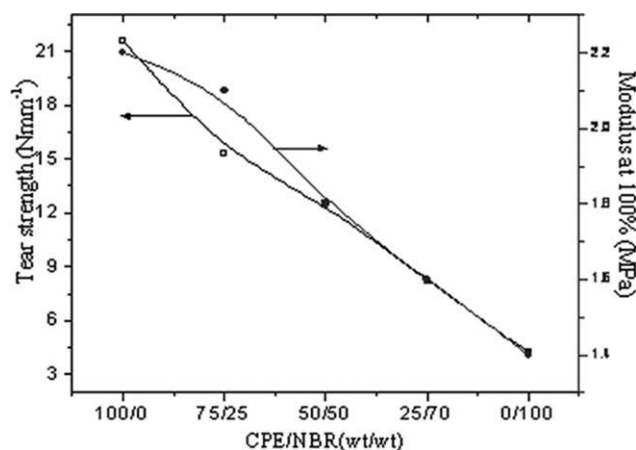


Figure 4 Tear strength and modulus at 100% of CPE/NBR blends with various blend ratio.

higher content of CPE in the blends had higher modulus. This meant that the CPE in the blend would enhance crosslinking as modulus at 100% was a measure of degree of crosslinking. Figure 4 also showed the effect of blend ratio on the tear strength of CPE/NBR blends. The tearing behavior was influenced by the viscoelastic properties of the polymer. The results could be explained that CPE was self-reinforced rubber or crystalline rubber. It can bring induced crystallization after tearing, which greatly improved strain ability and had high tear strength. The tear strength of CPE/NBR blends tended to decrease with increasing NBR content.

Compression set value was strongly dependent on the elastic recovery of the vulcanizate, it can be seen from the Figure 5 that the compression set of the blends decreased with increasing in content of NBR. This is because NBR has good molecular chain flexibility and lower hysteresis loss, namely it has smaller compression set compared with CPE.

The abrasion resistances of the blends have been expressed in terms of volume loss. The abrasion loss of CPE/NBR blends varied in the range of 140 to 320 mm³ (Fig. 5). It was evident that the abrasion loss of CPE/NBR with NBR content up to 50% by weight was close to that of pure CPE, however, with NBR content >50 wt %, abrasion loss of the blend started to increase. The abrasion was a phenomenon involving tear hysteresis, so when NBR content

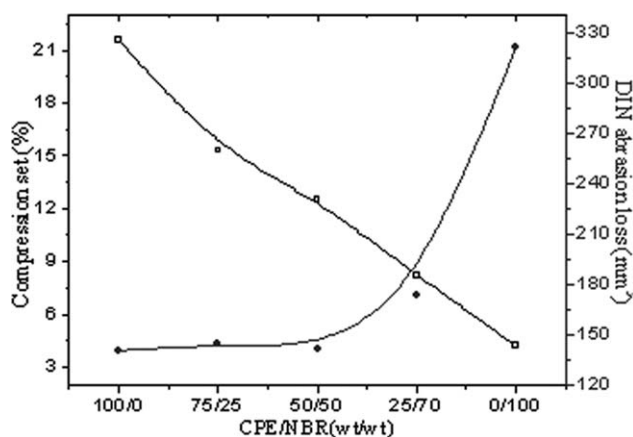


Figure 5 Compression set and DIN abrasion loss of CPE/NBR blends with various blend ratio.

>50 wt %, abrasion loss was dominated by higher concentration of the NBR matrix material which gave rise to increased abrasion loss.

Thermal aging resistance

The thermal aging resistance of CPE/NBR blends was shown in Table V. It was known that crosslinking could be occurring in CPE or NBR rubber under thermal aging. As a result, its tensile strength and hardness increased, whereas the elongation at break decreased. During thermal oxidation, chlorine loss gives C=C in the main chain. These cause local stiffening and become preferential sites for thermo-oxidation and crosslinking. The magnitude of the increase in tensile strength depends on blend ratio. It is known that saturated backbone of CPE exhibits good resistance to the thermal aging compared with unsaturated nature of NBR. So, the improvement in the thermal aging resistance of NBR is accomplished by blending with CPE.

Oil resistance

Figure 6 showed percent change in volume corresponding to degree of oil resistance of the various CPE/NBR blends. As expected, the percentage change in volume descended with the increase of NBR content in the blend. This is because both CPE

TABLE V
Change in Mechanical Properties After Aging of CPE/NBR Blends with Various Blend Ratio After Aging

Item	CPE/NBR				
	100/0	75/25	50/50	25/75	0/100
Hardness (Shore A) change/%	+5	+3	+3	+2	+2
Tensile strength change rate/%	+38	+35	+33	+29	+18
Elongation at break change rate/%	+2	-2	-5	-9	-10

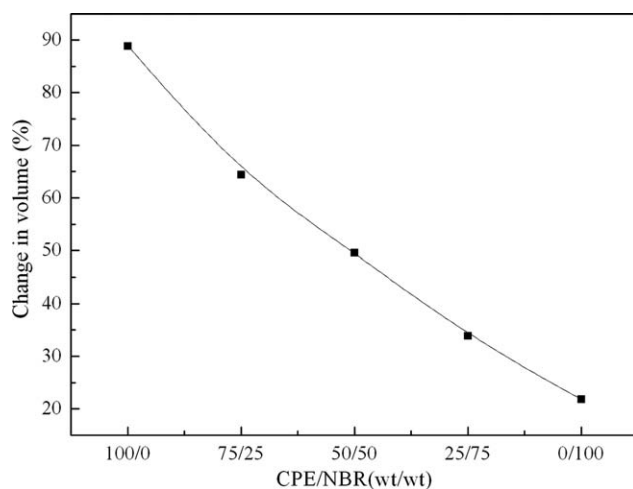


Figure 6 Changes in volume of various ratio of CPE/NBR blends after immersion in oil.

and NBR are high polar rubber, whereas the polarity of nitrile group in the acrylonitrile is much larger than polarity of chlorine group in the CPE. As a result, with increasing of NBR content leads to a greater degree of oil resistance in the blend.

CONCLUSIONS

1. The miscibility of CPE with NBR was estimated by the calculation of ΔH_m , which was related to the difference between the solubility parameters of CPE and NBR. The calculated values of ΔH_m for the entire composition range shows that the CPE was compatible with NBR. The glass-transition temperatures obtained from DSC thermograms exhibit a single T_g indicating miscibility of CPE and NBR. The SEM micrographs also suggested the compatibility in binary blends of CPE and NBR.
2. The effect of blend ratio on the curing behavior and physical properties of CPE/NBR blends has been studied. The cure and scorch times decreased with the increase in NBR content, whereas the maximum torque increased. The

incorporation of CPE into NBR improved the thermal aging and mechanical properties of the blends, but the oil resistance decreased.

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