

Compatibility and nonlinear viscoelasticity of polychloroprene/polyvinyl chloride blends with nitrile butadiene rubber as a compatibilizer

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ABSTRACT: Miscible polychloroprene/polyvinyl chloride (CR/PVC) blends with nitrile butadiene rubber (NBR) as a compatibilizer were prepared. The effect of NBR on the compatibility between CR and PVC was mainly analyzed by studying the thermal behavior and the phase structure of CR/PVC blends. An obvious decrement in the T_g of PVC phase successfully provided an explanation for the compatibilization of NBR. Due to the improved compatibility between CR and PVC, the size of PVC particles in CR/PVC blends decreased a lot according to the scanning electronic microscopic images. The significant improvement of mechanical properties of CR/PVC blends was in good agreement with the better compatibility between CR and PVC phases. The softening effect of NBR on the nonlinear viscoelasticity of CR/PVC blends was also studied by RPA 2000. Temperature sweep test by RPA 2000, a less reported characterization method of T_g , was successfully applied to measure T_g of CR/PVC blends and study the compatibilization of NBR. The reason for better thermal stability and the thermal decomposition mechanism of CR/PVC blends were analyzed according to the results of TGA. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42448.

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INTRODUCTION

Polychloroprene (CR), commercially known as Neoprene, is a typical synthetic rubber with excellent mechanical properties, oil resistance, flame resistance and chemical resistance.^{1–3} But due to bad low temperature performance and storage stability,⁴ blends of CR with other polymers are often prepared instead to get better practical value. On the other hand, study on polymer blends has been one of the hot topics of polymer materials, because it is possible for polymer blends to combine excellent features of different components if they are blended properly.^{1,5}

Compared to the blends of CR with rubbers, topics of which mainly focus on the compatibility^{6–8} and the effect of fillers, such as carbon black,⁹ silica,¹⁰ and lubricant,¹¹ researches about CR/PVC blends are much less reported. In contrast to CR or PVC, CR/PVC blends possess many advantages, including lower cost, better aging resistance, better oil resistance, higher modulus and hardness. According to those published work, when the PVC concentration is lower than 50%, both of the tensile

strength (TS) and elongation at break (EB) of CR/PVC blends decrease gradually with the PVC proportion increasing. But when the PVC proportion is higher than 50%, TS and EB will increase again.¹² And a complete phase separation and the worst mechanical properties are observed when the ratio of CR and PVC is 50 : 50.^{12,13} Apart from the effect of the mixing ratio, processing temperature and screw speed of mixer are also reported to contribute a lot to the mechanical properties of melt-mixed CR/PVC blends.¹³ As regard to CR/PVC dilute solution, study on the compatibility by the Zelinger-Heidingsfeld criterion indicates that though PVC and CR are proved incompatible, CR/PVC blends can exhibit limited compatibility at high CR concentration.¹⁴ To sum up, the lower mechanical properties of CR/PVC blends than neat CR mainly result from the incompatibility between CR and PVC, which is always an important factor determining the final properties of common polymeric blends.^{1,5} In theory, the compatibility of CR and PVC are good because both of CR and PVC are polar polymers containing the same halogen and the solubility parameters of CR and PVC are very close to each other. So the incompatibility

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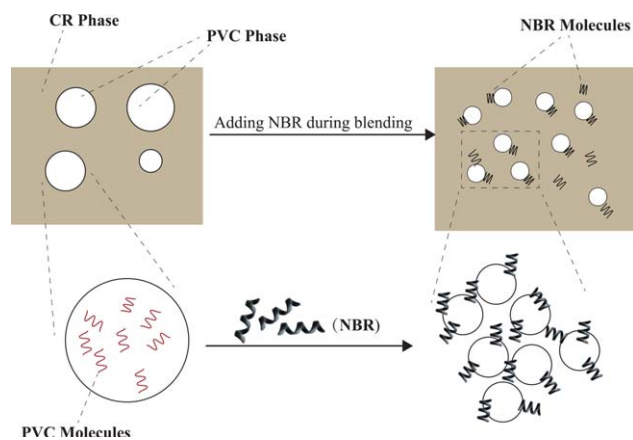


Figure 1. Phase structure of CR/PVC blends and the compatibilization of NBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between CR and PVC may be mainly attributed to the crystallization of CR, which results from the highly regular structure of CR chains.¹⁵

To enhance the compatibility of different components, many ways can be conducted, including adding compatibilizer,¹⁶ introducing the co-crosslinking reaction, co-crystallization and strong interaction between components.¹⁷ In this study, adding nitrile butadiene rubber (NBR) as the compatibilizer was used to improve the compatibility between CR and PVC. According to studies on the morphological properties of NBR/PVC published by other researchers, PVC/NBR blends is reported to be immiscible when the PVC content is greater than 50%.¹⁸ Matsuo¹⁹ found that when the acrylonitrile content of NBR was higher than 40%, the phase boundaries between NBR/PVC (100/15) blends was destroyed and the diameter of NBR particles decreased from about 0.3 to below 0.01 μm . So it can be concluded that the existence of strong interactions between PVC and NBR molecules results in a lower interfacial energy between PVC and NBR phase.^{20,21} As illustrated by Figure 1, the incompatibility between CR and PVC results in a typical “Sea-Island” phase structure in CR/PVC blends, in which CR is the continuous phase while PVC is the dispersed phase.¹² Due to the compatibilization of NBR, big PVC particles in CR/PVC blends are prone to break into small ones and the heterogeneity of PVC particles will disappear. Based on this analysis, miscible CR/PVC

blends with improved interfacial adhesion between CR and PVC phases is expected to be prepared with NBR as the compatibilizer.

In addition to the compatibilization, the effect of NBR on the nonlinear viscoelasticity of CR/PVC blends is another focus of this study. Rubber Process Analyzer 2000 (RPA 2000) is a new and effective method to study the curing parameters of rubbers, the interactions between filler–filler or filler–elastomer and the stress-softening behaviors of different rubbers or rubber blends.^{2,22–24} But this method is rarely reported to be used in studies of the nonlinear viscoelasticity of rubber-plastic blends or the compatibilization of the compatibilizer. Strain and frequency sweeps, the two most used test modes of RPA 2000,^{23,25} were used to study the effect of NBR on the nonlinear viscoelasticity of CR/PVC blends with different NBR contents. Like those typical methods used in the study on the compatibility of rubber blends, such as thermal analysis (DSC),²⁶ scanning electronic microscopy (SEM)²⁷ and dynamic mechanical analysis (DMA),²⁸ temperature sweep mode by RPA 2000 is proved another effective method to study the compatibility of polymers and their blends by measuring change of the T_g . But as the temperature of RPA 2000 cannot decrease to below 40°C, this method cannot measure T_g of components that are lower than 40°C.

EXPERIMENTAL

Materials

CR (M-40, ML[1+4] at 100°C: 48), ZnO, MgO (#150) and ethylenethiourea (ETU) of industrial grade were provided by Denki Kagaku Kogyo K.K, Japan. Stearic acid (SA) were bought from Sinopharm Chemical Reagent, China. Plasticized PVC was prepared by PVC with a degree of polymerization of 800 and other additives. NBR (NBR-3380, 33% acrylonitrile) was obtained from ZEON Co., Ltd, Japan.

Preparation of Samples

Formulations of CR/PVC blends prepared in this study are shown in Table I. Before blended with CR, PVC was firstly mixed with NBR in a mixing chamber (HAAKE PolyLab OS, Thermo Electron GmbH, Germany) at 120°C and 60 rpm. As

Table I. Formulations of CR/PVC Blends

Compounds/phr ^a	NBR0	NBR2.5	NBR5.0	NBR7.4	NBR10.0
CR/phr	80	80	80	80	80
^b PVC/phr	20	20	20	20	20
NBR/phr	0	2.5	5.0	7.5	10.0
MgO/phr	4	4	4	4	4
SA/phr	0.5	0.5	0.5	0.5	0.5
ETU/phr	0.5	0.5	0.5	0.5	0.5
ZnO/phr	5	5	5	5	5

^a Part per hundred CR + PVC.

^b Plasticized PVC.

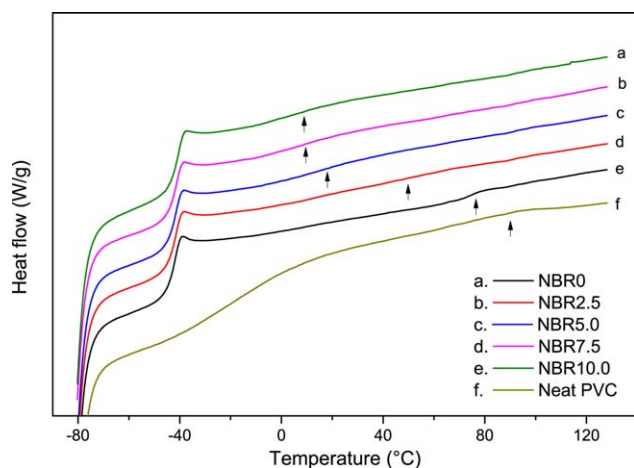


Figure 2. DSC curves of CR/PVC blends with different NBR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

HCl will be produced when the PVC is processed at high temperatures,^{12,29} MgO was also added into the chamber at this stage to prevent the generation of HCl. To get uniformly mixed and well dispersed CR/PVC blends, the pretreated PVC and CR gum were added into the mixing chamber again and mixed for another 6 min. Then CR/PVC blends were mixed with SA, ETU and ZnO on two-roll mills (LRMR-S-150/EW, Labtech Engineering Co., Ltd, Thailand) at room temperature. After having been kept for one day, the compounds were cured in a hydraulic presses (LP-S-50, Labtech Engineering Co., Ltd, Thailand) at 10 MPa, 153°C and to optimum time (t_{90}). The t_{90} and curing temperature were determined in RPA 2000.

Methods of Characterization

To study the compatibility of CR/PVC blends, T_g of vulcanizates was firstly measured by DSC (Q 2000, TA Instruments, USA) at 20°C/min under a N₂ flow. For eliminating the influence of thermal history, heat flow curves were got from the second heating process. DMA of samples with the size of 7 × 2 × 1 mm were conducted on DMA (Q800, TA Instruments, USA) in the tension mode from -80 to 130°C at a rate of 3°C/min. The strain and preload force are set as 0.01% and 0.01 N respectively. Scanning electron micrographs (Nova NanoSEM NPE218, FEI, Japan) of CR/PVC blends were carried out to study the phase structure by observing the cryogenically fractured surface of different specimens. Cryogenically fractured surfaces were dried in the vacuum oven at 80°C for 5 h after having been etched by tetrahydrofuran (THF) for 50 h. Mechanical properties of different vulcanizates were measured at a stretching rate of 500 mm/min on a material tester (Instron 4465, Instron Corp, USA) according to ASTM D412. And the hardness was determined using a Shore A durometer according to ASTM D2240.

Curing characteristics and nonlinear viscoelasticity test were conducted on a rubber process analyzer (RPA 2000, Alpha technologies, UK). For the test of curing characteristics, the temperature and frequency were kept at 153°C and 96 cpm

Table II. T_g (CR) and T_g (PVC) of CR/PVC Blends Measured by DSC

	NBR content				
T_g	0	2.5	5.0	7.5	10.0
$T_g(\text{CR})/^\circ\text{C}$	-41.5	-41.4	-41.2	-41.0	-40.5
$T_g(\text{PVC})/^\circ\text{C}$	75.4	40.8	17.3	9.4	9.0
$\Delta T_g/^\circ\text{C}$	116.9	82.2	58.5	50.4	49.5

respectively. In the nonlinear viscoelasticity tests by RPA 2000, strain frequency and temperature sweep tests were conducted after the blends having been vulcanized in the cavity. The frequency for strain sweep test and the strain for the frequency sweep test were set as 1 Hz and 1° respectively.² Both of strain sweep and frequency sweep tests were conducted at two different temperatures, 60 and 120°C. At last, the temperature sweep test were conducted from 40 to 130°C at 1 Hz and 1°.

TGA (Q5000 IR, TA Instruments, USA) was used to study effect of NBR on the thermal stability of CR/PVC blends with different NBR contents. With a nitrogen atmosphere, CR/PVC blends were heated from 40 to 800°C at 20°C/min.

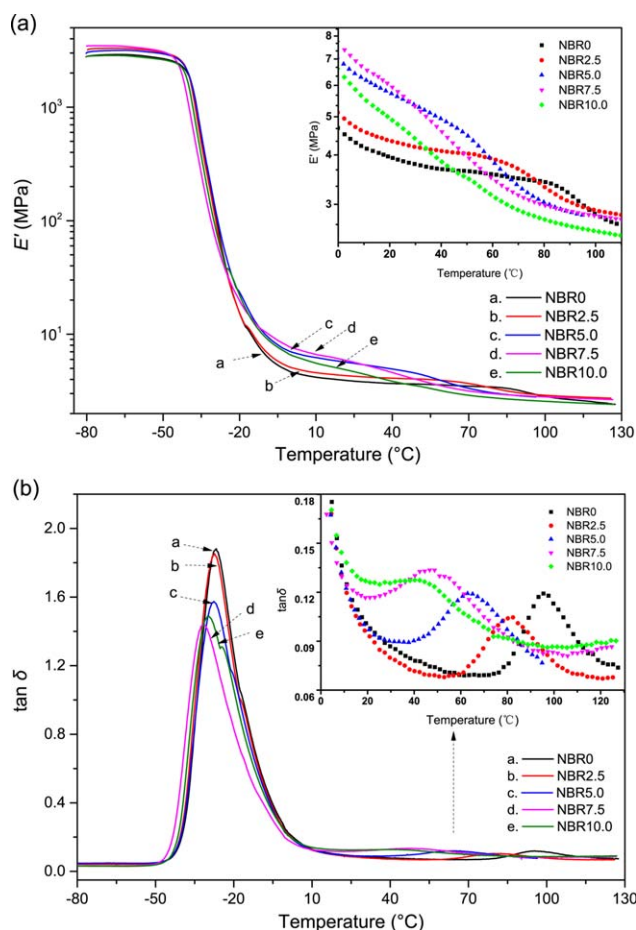


Figure 3. DMA curves of CR/PVC blends: (a) E' and (b) $\tan \delta$ as functions of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. T_g (CR) and T_g (PVC) of CR/PVC Blends Measured by DMA

T_g	NBR content				
	0	2.5	5.0	7.5	10.0
$T_g(\text{CR})/^\circ\text{C}$	-26.7	-27.3	-27.7	-31.5	-29.5
$T_g(\text{PVC})/^\circ\text{C}$	95.2	82.4	66.9	51.8	47.2
$\Delta T_g/^\circ\text{C}$	121.9	109.7	94.6	83.3	76.7

RESULTS AND DISCUSSION

Study of the thermal behavior can provide important information about the compatibility of rubber blends as the heat effects associated with the phase transitions can be measured exactly by DSC and DMA.³⁰ DSC curves of CR/PVC blends and neat PVC were presented in Figure 2 and Table II shows the T_g of

CR and PVC phases. The peak at -44°C and the stair above 0°C observed in Figure 2 correspond to the T_g of CR and PVC phases, respectively.³¹ Comparison between DSC curves of CR/PVC blends without NBR and the neat PVC shows that T_g of neat PVC are very close to that of PVC phase in CR/PVC blends, which indicates CR do not have an obvious effect on the T_g of PVC. This also proves the lack of strong interaction between CR and PVC molecules. According to Table II, with increasing NBR content from 0 to 10 phr, T_g of PVC decreases from 75.4 to 9.0°C gradually while T_g of CR phase just increases from -41.5 to -40.5°C . As a result, ΔT_g of CR/PVC blends that is defined as the difference of T_g (CR) and T_g (PVC) decreases from 116.9°C to 49.5°C gradually. This forcefully proves the existence of strong interaction between NBR and PVC molecules, which consequently improves the interfacial adhesion between CR and PVC phases. As a result, an improved

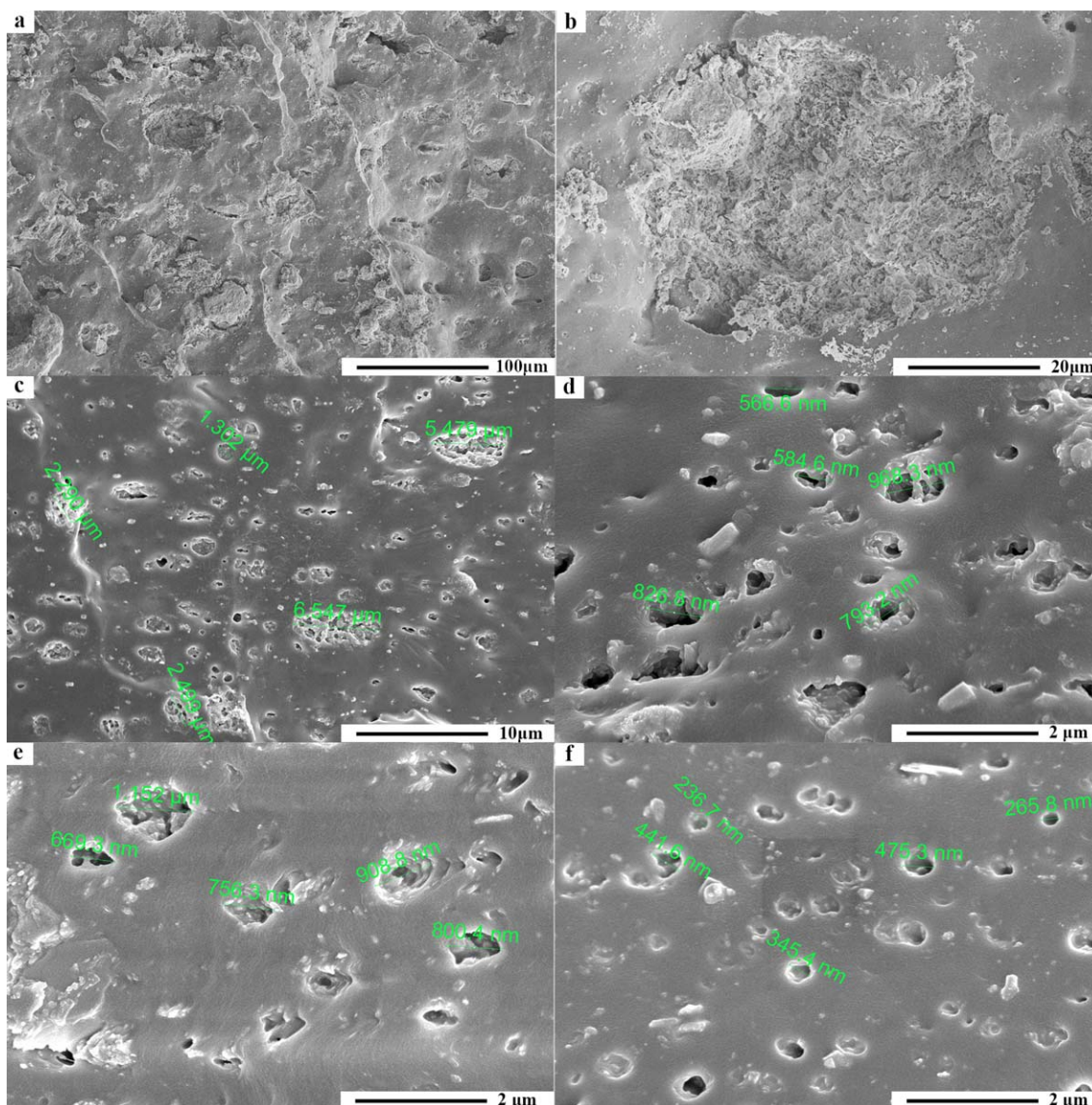


Figure 4. SEM pictures of vulcanizates of CR/PVC blends with different NBR contents: (a) and (b) 0 phr at different magnifications; (c) 2.5 phr; (d) 5.0 phr; (e) 7.5 phr; (f) 10 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Mechanical Properties of CR/PVC Blends

Mechanical characteristics	NBR content				
	0	2.5	5.0	7.5	10.0
TS/MPa	7.5	10.2	11.6	12.1	12.6
EB/%	320	306	395	450	534
Modulus at 100%/MPa	2.0	3.2	3.0	2.8	1.9
Modulus at 200%/MPa	4.3	6.7	5.4	5.0	3.5
Modulus at 300%/MPa	6.7	10.3	8.2	7.5	5.5
Hardness/Shore A	70	71	70	66	64

compatibility between CR and PVC phases can be achieved. But as the T_g of PVC phase is not obvious on the heat flow curves, thermal behavior of CR/PVC blends must be further measured by other effective methods to confirm the compatibilization of NBR.

The storage modulus (E') and loss tangent ($\tan \delta$) as a function of temperature for CR/PVC blends are illustrated in Figure 3. Figure 3(a) shows that when the temperature is lower than -50°C , E' of vulcanizates are very high because all of molecular segments of CR, PVC and NBR are frozen. But when the temperature is higher than -45°C , E' of vulcanizates sharply decrease due to the movement of CR chains. And when the investigated temperature is higher than 100°C , E' of all samples are very small and close to each other. It can be concluded that when the temperature is low enough for CR molecular segments to be frozen or high enough for PVC molecular segments to move, NBR does not affect the storage modulus of vulcanizates obviously. Figure 3(b) shows that there are two peaks in $\tan \delta$ curves, the first one of which is the T_g of CR phase³² and the other one is T_g of PVC.³³ And Table III presents values of these two T_g and ΔT_g , which are often different from those measured in DSC experiments.³⁰ With increasing NBR content from 0 to 10 phr, the T_g of PVC phase decrease from 95.2 to 47.2°C while T_g of CR just decrease from -26.7 to -29.5°C . And similar to the result of DSC experiments, ΔT_g of CR/PVC

blends decrease from 121.9 to 76.7°C gradually. This indicates that apart from the very obvious strong interaction between NBR and PVC molecules, NBR can also make it possible for CR segments to move at lower temperature. It is also noted that with increasing NBR content, the peak value of $\tan \delta$ for CR phase decreases while that of PVC phase increases. The peak in $\tan \delta$ of polymer is often higher than the peak in E' .³⁴ And when the glass transition of CR occurred, the E' of different samples are almost the same while there is a big difference in the E' , which is shown in the Supporting Information Figure S1. On the other hand, the existence of NBR molecules results in a much smaller size of PVC particles, which can increase the interaction between CR and PVC phases. As a result, the movement of CR molecules will be obviously obstructed at the glass transition. So the friction loss of CR molecules will be inhibited after NBR being added, which appeared as the decrease in the E' . So the most fundamental reason for the decrease in $\tan \delta$ for CR are the decrease in the size of PVC particles. For PVC phase, the increase in $\tan \delta$ should be mainly ascribed to the increase in the viscosity, which is attributed to the strong interaction between NBR and PVC molecules. So it can be concluded from DSC and DMA experiments that due to the stronger interfacial adhesion brought by the addition of NBR, T_g of PVC phase decreases obviously and the compatibility between CR and PVC increases gradually.

SEM images of CR/PVC blends with different NBR contents are shown in Figure 4. As PVC can be dissolved in the THF while vulcanized CR cannot be, distribution of holes on the fracture surface can be seen as the distribution of PVC particles in CR/PVC blends. So it is evident that in CR/PVC blends, CR is the continuous phase while PVC is the dispersed phase, which is in good agreement with the structure illustrated in Figure 1. It has

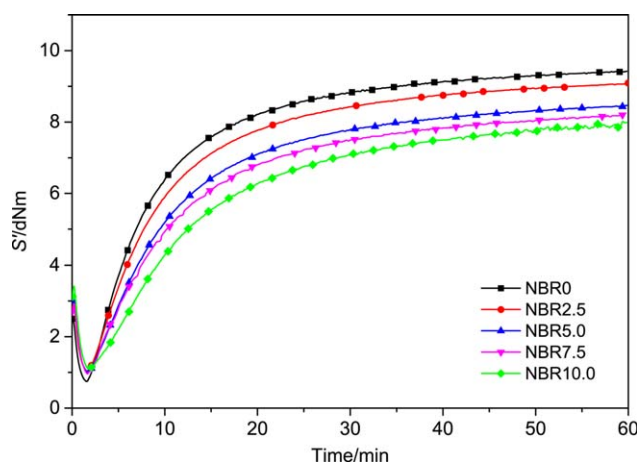


Figure 5. Curing curves of CR/PVC blends with varying NBR content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Curing Parameters of CR/PVC Blends

Cure characteristics	NBR content				
	0	2.5	5.0	7.5	10.0
t_{s1}/min	3.9	4.5	5.2	5.7	7.0
t_{90}/min	24.5	27.0	28.7	30.0	35.2
M_L/dNm	0.74	1.02	0.98	0.95	1.09
M_H/dNm	9.44	9.09	8.47	8.21	8.05
$\Delta M/\text{dNm}$	8.70	8.07	7.49	7.26	6.96

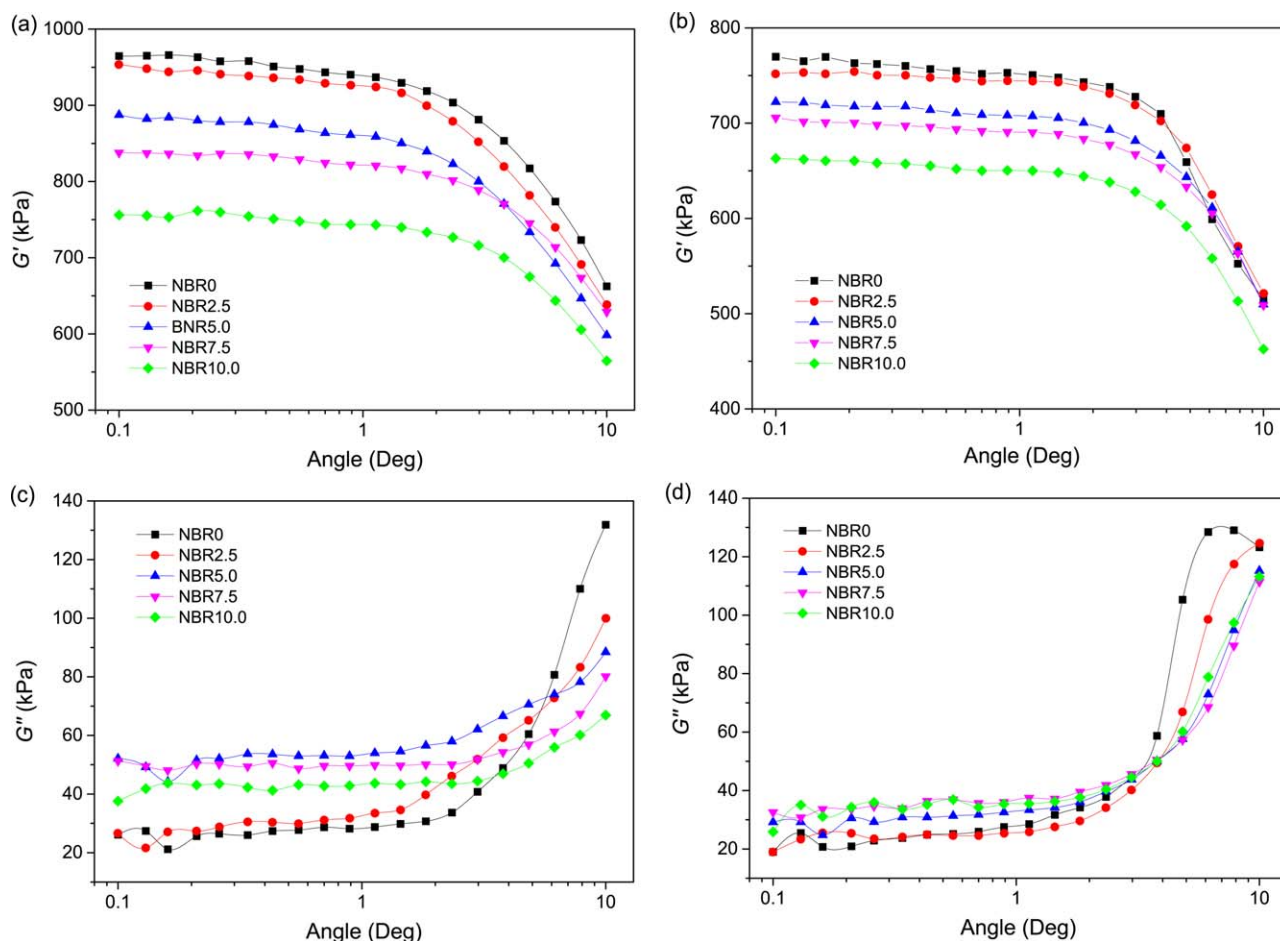


Figure 6. Strain dependence of G' and G'' for vulcanizates with different NBR contents: (a, c) G' and G'' at 60°C; (b, d) G' and G'' at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been reported that when the PVC content is small enough for the phase inversion to take place, PVC is likely to form the dispersed phase in CR/PVC blends.^{12,13}

For vulcanizates without NBR [Figure 4(a)], the fracture surface is very uneven and PVC is likely to form some large and irregular particles, size of which are as large as about 40 μm [Figure 4(b)]. This successfully demonstrated the incompatibility between CR and PVC. For samples [Figure 4(c–f)] with PVC particles having been pre-mixed with NBR, fracture surfaces become much smoother and sizes of PVC particles is much more uniform and smaller. It is observed that when the NBR content is 2.5 phr and 5.0 phr, there are still some large PVC particles on the fracture surface, which indicates the compatibilization of NBR is still not enough to totally reduce the interfacial energy between CR and PVC phases. But when NBR content is higher than 7.5 phr, there is no PVC particles large like what is shown in Figure 4(a). Measurements of particles by SEM shows that when the NBR content is 2.5, 5.0 and 7.5 phr, sizes of PVC particles are 3.62, 0.75 and 0.80 μm respectively. Figure 4(f) shows that the size of PVC in vulcanizates with 10 phr NBR is about 0.35 μm , which is much smaller than that of vulcanizates without NBR [Figure 4(a)]. This indicates that due to the strong interaction between PVC and NBR molecules,

large PVC particles can be completely damaged and turn into much smaller ones when NBR content is 10 phr. So it can be concluded that with the content increasing to 10 phr, the compatibilization of NBR is strong enough to eliminate the interfacial energy between CR and PVC phases and result in an obvious decrement on the size of PVC phase.

Table IV illustrates the mechanical properties of CR/PVC blends, including TS , EB , modulus (100%, 200%, and 300%) and hardness. It is observed that the TS and EB of CR/PVC blends are much smaller than that of neat CR, which are about 14MPa and 750%, respectively. This indicates that the inevitable incompatibility between CR and PVC results in a bad mechanical properties. As shown in Table IV, TS and EB of vulcanizates increase gradually with increasing NBR content from 0 to 10 phr. When NBR content is 10 phr, TS and EB are 12.6 MPa and 534% respectively, which are very close to that of neat CR. This proves that the compatibilization of NBR can obviously improve the TS and EB of CR/PVC blends. As PVC is the dispersed phase and CR is the continuous phase in CR/PVC blends, when the dumbbell-shaped samples of CR/PVC blends are stretched at a set speed, those rigid and big PVC particles are very likely to form stress concentration points as the deformability of PVC phase is much smaller than that of CR

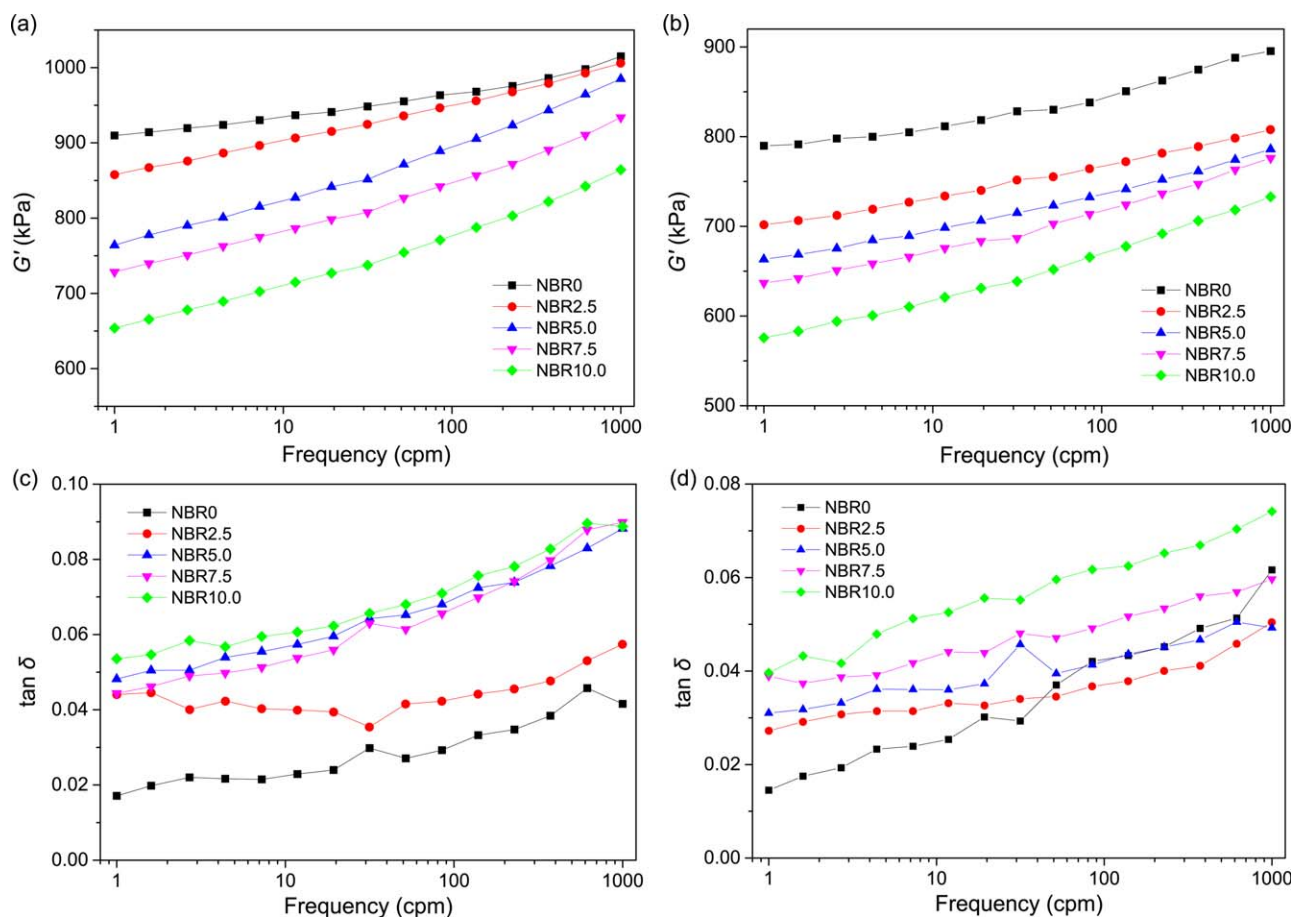


Figure 7. Frequency dependence of G' and $\tan \delta$ for vulcanizates with different NBR contents: (a, c) G' and $\tan \delta$ at 60°C; (b, d) G' and $\tan \delta$ at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phase. So mechanical properties of CR/PVC blends is worse than that of neat CR vulcanizates. With the addition of NBR, the strong interaction between NBR and PVC make it less likely for PVC to form rigid and big dimension particles in CR/PVC blends. So due to the inhibition effect on the formation of stress concentration points in CR/PVC blends, NBR can significantly improve the mechanical properties of CR/PVC blends. It is also observed that the hardness of CR/PVC blends decrease slightly with increasing NBR content. This indicates NBR has an important effect on the crosslinking density of CR/PVC blends along with a softening effect, which will be discussed in the curing and nonlinear viscoelasticity properties. And this effect is not enough when the NBR content is less than 5.0 phr, which is good agreement with the change of the curing curves.

Curing curves and curing parameters of CR/PVC blends are shown in Figure 5 and Table V, respectively. It is evident that with increasing NBR content from 0 to 10 phr, t_{s1} and t_{90} of vulcanizates both increase while M_H and ΔM ($M_H - M_L$) decrease gradually. So NBR can obviously reduce the vulcanization speed of CR/PVC blends, which can be explained by that with higher NBR content, the concentration of curing system for the entire compound is relatively reduced as NBR cannot be vulcanized by metal oxides. On the other hand, ΔM that is used to characterize the crosslinking density of vulcanizates³⁵

decreases gradually with increasing NBR content from 0 to 10 phr. This can be attributed to two reasons, the first one of which is the lack of vulcanization system for NBR. So this decrement of crosslinking density means that NBR can reduce the whole crosslinking density of the CR/PVC blends rather than the crosslinking density of CR. The second reason is that the effect of NBR on the CR/PVC blends is very different from that of fillers on CR or CR blends,^{2,35} as most of fillers can significantly increase the M_H of rubbers while a softening effect is observed here due to the addition of NBR. And according to the discussion above, this softening effect is mainly on the PVC phase as a result of the strong interaction between NBR and PVC molecules and the reduced interfacial energy between CR and PVC phases. So apart from the compatibilization, NBR can also decrease the vulcanization speed of CR/PVC blends and contribute a softening effect to CR/PVC blends.

To further analysis the softening effect of NBR on the CR/PVC blends, the nonlinear viscoelasticity of CR/PVC blends was studied. Strain and frequency sweeps at two investigated temperatures and temperature sweep tests by RPA 2000 are shown in Figures 6–8. Contrasts of storage modulus (G') and loss modulus (G'') at 60°C and 120°C (Figure 6) indicate that the effect of NBR on the vulcanizates at 60°C is bigger than that at 120°C, which may result from the effect of temperature on the

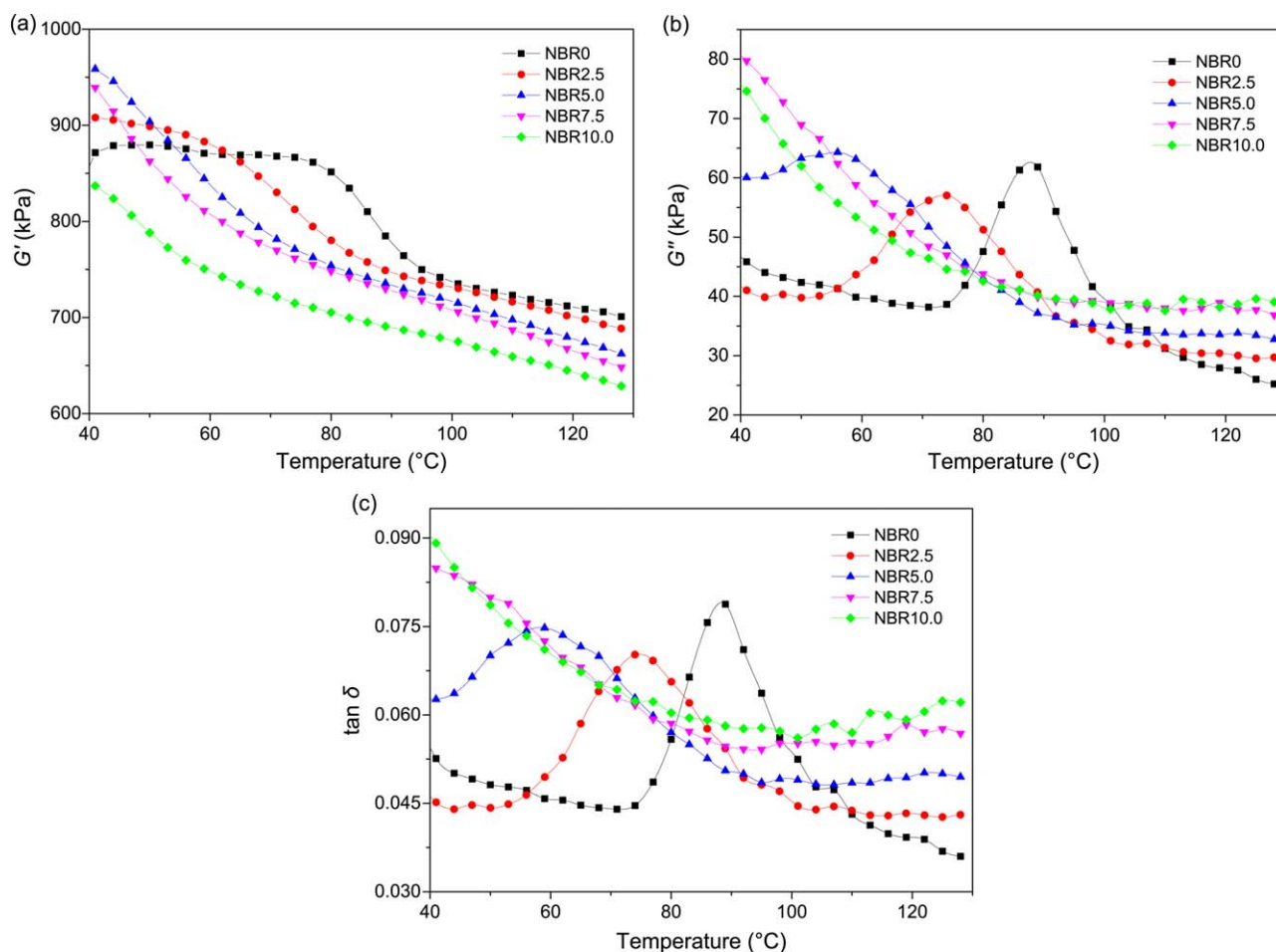


Figure 8. Temperature dependence of (a) G' , (b) G'' and (c) $\tan \delta$ for CR/PVC blends with varying NBR content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

softening effect of NBR. It is observed that G' curves [Figure 6(a,b)] does not change obviously when the strain angle is small, which indicates the vulcanizates of CR/PVC blends are in the linear viscoelastic (LVS) region. It is observed that the LVS region at 120 $^{\circ}\text{C}$, the range of which is about 0.1~3 $^{\circ}$, is bigger than that at 60 $^{\circ}\text{C}$. This indicates that the investigated temperature have an important influence on the range of the LVS region of CR/PVC blends. When the strain angle is high than a value, the G' of CR/PVC blends decreases sharply as a result of the destruction of polymer–polymer networks. With increasing NBR content from 0 to 10 phr, G' of CR/PVC blends [Figure 6(a,b)] decreases gradually at the whole investigated strain angle range. But G'' [Figure 6(c,d)] increases when the strain is in the LVS region while begins to decrease when the strain exceeds the LVS region. This indicates the effect of NBR on the nonlinear viscoelasticity also depends on whether CR/PVC blends are in LVS region or not. Studies about the effect of filler on rubbers show that with increasing contents of fillers, G' of rubbers increase while G'' decrease^{2,25} at the same time. That is to say that the effect of compatibilizers, such as NBR, on the viscoelasticity of CR/PVC blends is different from that of other fillers. When the polymer–polymer networks of CR having been destructed, the softening effect of NBR does not exist anymore.

Figure 7 illustrates the frequency dependence of G' and $\tan \delta$ of CR/PVC blends. For most of rubbers or rubber blends, G' is observed to increase with the sweep frequency increasing because the hysteresis of polymers is more obvious at high investigated frequency. So G' and $\tan \delta$ [Figure 7(a,d)] of CR/PVC vulcanizates both increase gradually with the frequency increasing from 1 to 1000 cpm. Like the result of strain sweeps, G' and $\tan \delta$ of CR/PVC blends at 120 $^{\circ}\text{C}$ are lower than those at 60 $^{\circ}\text{C}$ due to the influence of temperature. Apart from these, it is observed in Figure 7(a,d) that with increasing NBR from 0 to 10 phr, G' of CR/PVC blends decreases while $\tan \delta$ increases gradually at the same time. The increase of $\tan \delta$ [Figure 7(c,d)] proves that CR/PVC blends with higher NBR content performs more like rubber. It can be concluded that at a very large frequency range, NBR can significantly reduce the elasticity and improve the viscosity of CR/PVC blends obviously. According to the research published by Lamnawar,^{36,37} the contributions from two coexisting phases in PLA/PBAT blends can be studied by the Cole–Cole plots. And the addition of compatibilizer is proved to bring a significant increase in the relaxation times of PLA/PBAT blends.³⁸ But for rubber material, these analysis methods, such as Cole–Cole plots, are less used to study the effect of compatibilizer, which should be ascribed to the big

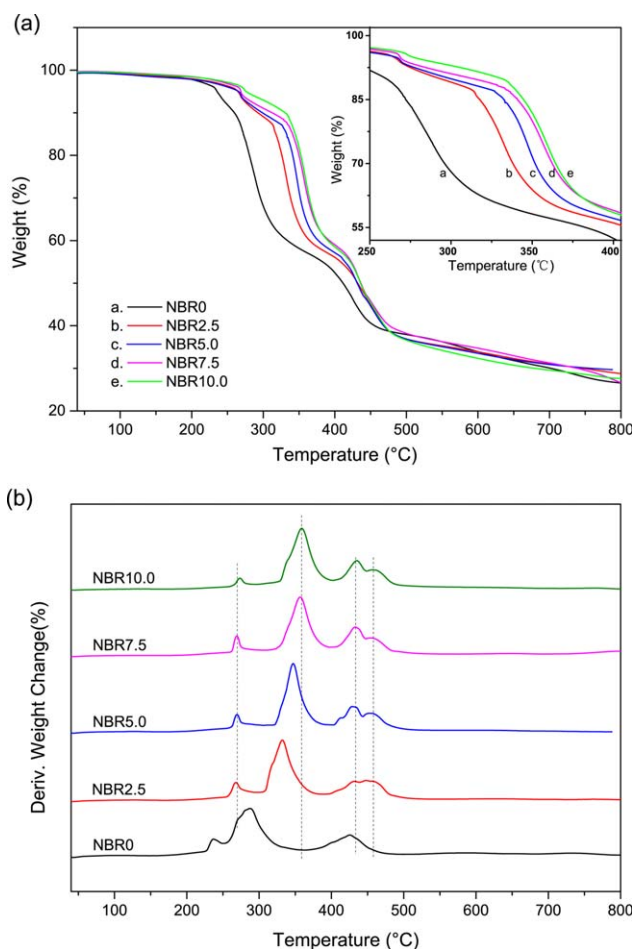


Figure 9. (a) TG and (b) DTG curves of CR/PVC blends with different NBR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

differences between the nonlinear viscoelasticity of resin blends and vulcanized rubbers. As shown in the Supporting Information Figure S3, the η^* of vulcanized CR/PVC blends is found to decrease linearly with the increase of frequency and no platform is observed at the low frequency range. After the vulcanization of CR, the relaxation process of PVC will not be observed on the $\eta''-\eta'$ curve and the linear correlation between η' and η'' does not change with the addition of NBR. So it can be concluded here the nonlinear viscoelasticity of CR/PVC blends measured by RPA 2000 mainly provides the information of the softening effect of NBR. On the other hand, the decrement in the size of PVC phase resulting from the compatibility of NBR is also speculated to be an important reason for the decrease in G' of CR/PVC blends.

The G' , G'' and $\tan \delta$ curves of CR/PVC vulcanizates in the temperature sweep are shown in Figure 8. Figure 8(a) shows that G' decreases gradually when the investigated temperature increasing from 40 to 130°C, which indicates a decrement in the elasticity of vulcanizates. It is interesting to find that there is a stair in G' curves of CR/PVC blends with 0 and 2.5 phr NBR and it disappears when the NBR content is higher than 2.5 phr. G'' and $\tan \delta$ [Figure 8(b,c)] curves show that there is a peak at the test temperature range, which are assigned as the

glass transition of PVC phase. When the NBR contents are 0, 2.5 and 5.0 phr, this peak was observed at 88.4°C, 74.5°C and 58.2°C respectively. Because the RPA test can't be conducted at very low temperature, so those peaks of vulcanizates with 7.5 and 10.0 phr are not observed at the investigated sweep temperature range. But slopes of $\tan \delta$ for vulcanizates with 7.5 and 10.0 phr near 40°C are both close to 0 and value of the former one is also smaller than that of the latter one. So it can be speculated that T_g of PVC phase decrease gradually with increasing NBR content from 0 to 10 phr. This shift of T_g sufficiently suggests the strong interaction between NBR and PVC molecules. Apart from the above analysis, it is also observed that when the temperature is higher than the T_g of the sample without NBR, G'' and $\tan \delta$ increase gradually with increasing NBR content from 0 to 10 phr. This is consistent with results of strain and frequency sweep experiments at 120°C. Apart from the verification of the compatibilization of NBR on CR/PVC blends, it can also be concluded that the temperature sweep by RPA 2000 is a very effective method to study the T_g of plastic or the polymer blends with plastic as one component.

The thermal stability of CR/PVC blends with different NBR contents has also been studied. Figure 9 shows the TGA and DTG curves of CR/PVC blends from 40°C to 800°C and Table VI presents values of the DTG peaks, corresponding mass losses and temperatures for selected mass losses ($T_{5\%}$, $T_{10\%}$ and $T_{30\%}$).³⁵ Table VI shows that when the NBR content increasing from 0 to 10 phr, the initial decomposition temperatures (IDT) (5% mass loss)^{35,39} of CR/PVC blends increases from 235.4°C to 275.9°C markedly. Similar to the change of IDT, $T_{10\%}$ and $T_{30\%}$ of CR/PVC blends also increase with the increment in the NBR content, which clearly indicates the thermal stability of CR/PVC blends can be significantly improved by the addition of NBR.

TG and DTG curves show that the degradations of CR/PVC blends occurs in three stages, which is different from the thermal degradation of CR.⁴⁰ The first stage starts at 200°C and ends at 300°C, the corresponding mass of which is about 5%. This mass loss is assigned as the evaporation of additives and the residual HCl in PVC. The additives discussed here are those small molecules in additives rather than DOP that begins to decompose at 350°C⁴¹ and it should also be noted that the residual HCl comes from the synthesis process of PVC. The second stage degradation, which starts at 250°C and lasts to 400°C, is one of the two main decomposition stages of CR/PVC blends. At this stage, the mass loss of CR/PVC blends ranges from 31~34% and this part is mainly assigned as the elimination of HCl⁴⁰ from CR and PVC molecules and the evaporation of some other additive in PVC, such as DOP. With increasing NBR content from 0 to 10 phr, the value of temperature at the DTG peak of this stage increases from 287.1°C to 358.9°C gradually. As shown in Supporting Information Figure S2, the maximum DTG peak of neat PVC was observed at this stage while the weight percentage of NBR is close to 100%. Due to the interaction between NBR and PVC, the size of PVC particles will decrease and a stable cladding layer formed by NBR appears on the surface of PVC particles, as shown in Figure 1. This stable cladding layer will inhibit the elimination of HCl from PVC

Table VI. Mass Loss at DTG Peaks and Temperatures for Selected Mass Loss of CR/PVC Blends

Thermal stability characteristics	NBR content				
	0	2.5	5.0	7.5	10.0
DTG peak values/°C	236.8	267.8	269.5	269.2	273.4
	287.1	332.2	347.2	356.8	358.9
	425.5	432.1	428.7	433.0	435.3
Mass loss at DTG peaks/%	5.4	5.9	6.1	5.3	4.6
	24.3	25.1	25.7	25.5	25.3
	53.9	50.0	49.1	48.7	49.8
Total mass loss/%	72.9	70.8	69.6	73.1	72.0
Temperature values for selected mass loss					
$T_{5\%}/^{\circ}\text{C}$	235.4	254.5	265.3	268.5	275.9
$T_{10\%}/^{\circ}\text{C}$	259.6	292.3	298.6	312.4	330.4
$T_{30\%}/^{\circ}\text{C}$	295.9	338.1	351.6	362.2	364.3

molecules and the attack of generated HCl on the CR and PVC molecules. The better thermal stability of DOP in this stage, the additives and residual HCl in the first stage are also related to the effect of this cladding layer.

The third stage degradation starts at 400°C and ends at 800°C, mass loss for which ranges from 27~33%. This part is mainly assigned as the weight loss of CR and PVC backbone and the volatilization of degradation products.⁴² With increasing NBR content, the position of the DTG peak is also observed to shift slightly. This indicates the effect NBR on the thermal decomposition of CR and PVC backbone is very less than that on the elimination of HCl. And after 500°C, there is little difference between the mass losses of all samples, which indicates the addition of NBR does not affect the thermal stability of CR/PVC blends any more. This is because most of NBR decomposes at the temperature range of 400~500°C, which can be well proved by the second DTG peak of CR/PVC blends in this stage and the only one DTG peak of neat NBR in Supporting Information Figure S2. To sum up, the effect of NBR on the thermal stability of CR/PVC blends mainly results from the effect of NBR cladding layer on the volatilization of the residual HCl in PVC and the elimination of HCl from CR and PVC molecules.

CONCLUSION

This study mainly dealt with the effect of the compatibilization of NBR on the thermal behavior, the mechanical properties, the nonlinear viscoelasticity and the thermal stability of CR/PVC blends. Analysis of thermal behavior suggests the compatibilization of NBR should be attributed to the strong interaction between PVC and NBR molecules. As a result of this interaction, the interfacial energy between CR and PVC phases can be obviously reduced and the compatibility of CR/PVC blends can be significantly improved. With the NBR content increasing from 0 to 10 phr, the size of PVC particles in CR/PVC blends decreases from 40 to 0.35 μm and becomes very uniform. In addition, the *TS* of vulcanizates increases from 7.5 MPa to 12.6 MPa and *EB* increases from 320% to 534%. Apart from the compatibilization, the softening effect of NBR was also proved by the study on the

hardness and the nonlinear viscoelasticity of CR/PVC blends. The decrease in *G'* of CR/PVC blends indicates that the compatibility of NBR have an important effect on the nonlinear viscoelasticity of CR/PVC blends by affecting the size of PVC phase. Temperature sweep tests by RPA 2000 was proved a new and effectively method to measure the T_g of polymer blends with plastic components. Better thermal stability of NBR and the effect of NBR cladding layer, which results from the interaction between NBR and PVC molecules, contribute a lot to the significantly improved thermal stability of CR/PVC blends.

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