

## Effect of C5 Petroleum Resin Content on Damping Behavior, Morphology, and Mechanical Properties of BIIR/BR Vulcanizates

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**ABSTRACT:** In this work, the white-silica-filled vulcanizates of brombutyl rubber (BIIR)/cis 1,4 polybutadiene rubbers (BR) with hydrogenated aromatic hydrocarbon (C5) petroleum resins were prepared by compression molding, and the effects of C5 petroleum resin content on the damping behaviors and mechanical properties of BIIR/BR vulcanizates were investigated by foam force rheometer, dynamic mechanical analysis (DMA), scanning electron microscopy, and mechanical measurements. The results of this study showed that, the C5 resins could retard the vulcanization, and reduce the crosslink density and Mooney viscosity of vulcanizates. The DMA curves exhibited two independent peaks of loss factor ( $\tan\delta$ ) corresponding to the glass transition of BR and BIIR vulcanizates, respectively. The addition of C5 resin had a positive impact on the damping of BIIR/BR vulcanizates, with the increment content of C5 resin, the main  $\tan\delta$  peaks shifted significantly to higher temperature and the effective damping temperature range was broadened remarkably, especially in the range of the BIIR glass transition. The mechanical properties such as tensile strength and abrasion performance were influenced by the C5 resin and the changes in mechanical properties were mainly due to the decline of crosslink density and the improvement of filler dispersion. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 510–515, 2013

**KEYWORDS:** blends; crosslinking; glass transition; mechanical properties; morphology

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### INTRODUCTION

With the development of modern industry, transportation, aerospace aviation, military fields and other science field, machinery and equipment, and other high-tech product constantly tend to be high speed and automation, and thus inevitably produce a series of problems, such as vibration and noise. In addition, the precision of mechanical equipment processing and the quality of the products are affected. Therefore, noise and vibration control have become a serious problem in current science field. Polymers have been widely used for noise and vibration control in recent years, because of a unique combination of low modulus and inherent damping.<sup>1,2</sup> Damping is influenced by dynamic mechanical properties such as the temperature dependence of storage modulus  $E'$ , loss modulus  $E''$ , and the ratio  $E''/E'$  as loss factor  $\tan\delta$ .<sup>3,4</sup> The excellent damping materials are usually desirable to have high values of  $\tan\delta$  over wide temperature and frequency ranges. For example,  $\tan\delta$  above 0.3 is often demanded over a temperature range of at least 50–80°C for machinery applications in the constrained layer damping of structure vibrations,<sup>5</sup> but homopolymers usually possessed narrow effective damping temperature ranges of only 20–30°C around

their glass transition temperatures. Many approaches for broadening the glass transition temperature of the polymer so as to improve the effective damping range have been investigated. One of the most conventional ways is to mix several kinds of polymers with different  $T_g$  (glass transition temperature). Interpenetrating polymer network in which the phase-separated domain is limited to a very small size has been conformed to be a very effective structure as high-performance damping materials. Addition of inorganic filler in polymer matrix is also a quite useful method to improve the damping behavior, which is due to the friction between the filler and the chains of polymer. Recently, as found in some researches of scholars, addition of some small molecules like hydrocarbon resins in polymer matrix could broaden the effective damping range and improve the loss peak. For example, Wu and Wu<sup>6</sup> investigated the damping properties in blends of poly(styrene-*b*-isoprene-*b*-styrene) and hydrogenated aromatic hydrocarbon (C9) resin, and the main  $\tan\delta$  peak shifted to higher temperatures and the useful damping temperature range was broadened. Thaijaroen<sup>7</sup> studied the effect of aromatic hydrocarbon resins on mechanical properties and dynamic properties of vulcanizates, and the effect of resins

on the retardation of vulcanization is observed and the changes in mechanical properties due to the reduction in crosslink density are correlated. Good compatibility between natural rubber and all three tackifiers is verified by a single  $\tan\delta$  peak detected for each vulcanizate in temperature ramp test. In most of these studies, the materials have been shown to exhibit useful damping behaviors in the temperature ranges around room temperature. However, it is inevitable that the addition of hydrocarbon resins always brings about the change in mechanical properties of the rubber.

C5 fraction is a by-product of ethylene production, which accounts for about 10–14% of ethylene production. C5 petroleum resin is a thermoplastic resin based on C5 fraction as raw materials, after pretreatment, polymerization, flash technology. It is a kind oligomer, has molecular weights ranging from 300 to 3000, and usually exhibits a glassy state at room temperature. This resin is commonly referred to as tackifying resins and added to elastomers to improve the surface bonding strength, and these resins have favorable compatibility with elastomers.

Brominated butyl rubber (BIIR) is a halogenated isobutylene-based polymer, having excellent damping properties, air impermeability, elasticity, and vulcanization activity,<sup>8</sup> but the abrasion performance of BIIR is pretty poor. Cis polybutadiene rubbers not only have the excellent abrasion performance, but also have the lower rolling resistance and favorable processability. In addition, the BR could achieve covulcanization with the BIIR, and improve the abrasion performance of the BIIR vulcanizate.<sup>9</sup>

In this article, we have investigated the effects of C5 resin content on the cure property, damping behavior, morphology, and mechanical properties of BIIR/BR vulcanizates, aiming at a new material of excellent damping over a broad temperature range with favorable mechanical properties, especially the abrasion performance.

## EXPERIMENTAL

### Materials and Sample Preparation

The raw rubbers used were BIIR2255 (EXXON<sup>TM</sup>) and BR9000 (Yanshan Petro-Chemical Industry Corporation, China); C5 petroleum resin was commercial grade (softening point: 95–105°C; Hengtai petrochemical company, China). Five compounds containing different content of C5 resin were prepared. BIIR and BR were mixing in a two roll mill (SK-160, Shanghai Shuangyi Rubber & Plastic Machinery, China) for 5 min, and then the petroleum resin was added. Other ingredients were added after the rubber and the resin mixing together. The formulations of individual compounds were displayed as follows: BIIR 30, BR 70, silica 50, sulfur 1, ZnO 1, stearic acid 3, TMTM 1, and DM 1 phr (parts per hundred of rubber). C5 content was varied from 0 to 20 phr. The temperature of the rubber compounds during mixing was 50–65°C. Finally, with the end of mixing, the rubber was recovered from the two roll mill and kept at ambient temperature (23°C) for at least 24 h, before the measurements of Mooney viscosity and cure properties. After these measurements were completed, the rubber compounds were cured in a compression mold at 150°C with a

**Table I.** Vulcanization Parameters of BIIR/BR/C5 Compounds

Compounds	1	2	3	4	5
C5 loading (phr)	0	5	10	15	20
Scorch time, $t_{s2}$ (min)	2.6	2.8	3.0	3.4	3.7
Optimum cure time, $t_{90}$ (min)	6	5.8	6	6.7	6.9
Minimum torque, $M_L$ (dN m)	9.2	7.1	6.7	6.5	5.2
Maximum torque, $M_H$ (dN m)	32.7	27.5	22.5	20.3	17.5

pressure of 10 MPa, and the curing time was according to the results of cure measurements (Table I). Pieces of rubber were cut from the milled sheet. Each piece was placed in the center of the mold to enable it to flow in all directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubber, the thin sheets  $13 \times 11 \times 2.0$  mm<sup>3</sup>, and the thick sheets  $10 \times 10 \times 6$  mm<sup>3</sup> were used, from which various samples for further tests were cut.

### Vulcanization Measurements

The scorch time ( $t_{s2}$ ), which is the time for the onset of cure, and the optimum cure time ( $t_{90}$ ), which is the time for the completion of cure, and  $M_H$  (maximum torque),  $M_L$  (minimum torque) and  $(M_H - M_L)$ , which are the arguments for crosslink degree, were measured from the cure traces generated at 150°C by an Foam Force Rheometer (M-2000-FA, GOTECH, Taiwan) according to ASTM D 5289-95.

### Mooney Viscosity

The Mooney viscosities of BIIR/BR/C5 compounds were measured at 100°C in a single-speed rotational Mooney viscometer (GT-7080S2, Gotech, Taiwan) according to ASTM D 1646-99.

### Crosslink Density Measurements

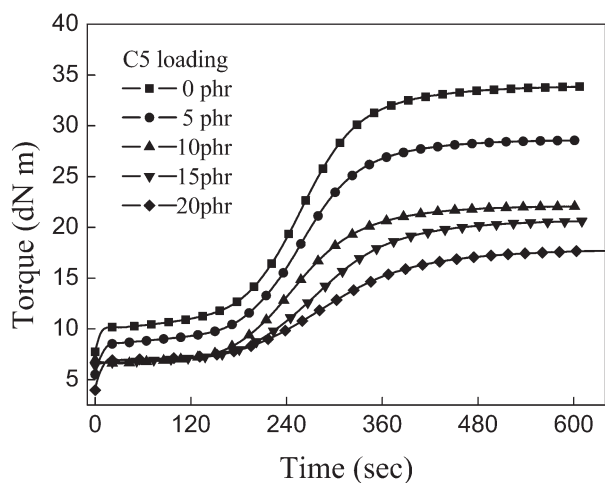
The solvent used for the crosslink density determination was toluene. The samples were then placed individually in 50 mL of the solvent in labeled bottles and allowed to swell for 48 h at 21°C. The solvent was removed after this time elapsed, and the samples were dried in air for 0.5 h. The samples were subsequently dried in vacuum oven at 80°C for 24 h. The crosslink density was then calculated as eqs. (1)–(3).<sup>10–13</sup>

$$\mu_{cs} = \frac{\rho}{2} \left( \frac{1}{M_{CS}} - \frac{1}{M_n} \right) \quad (1)$$

where  $\mu_{cs}$  is the crosslink density,  $M_n$  is the number molecular weight.  $M_{CS}$  is the molecular weight of the network chain between crosslinks, which is given by the Flory-Rehner relationship for a 4-functional network.

$$M_{cs} = - \frac{0.5\rho V_1 (v_r^{1/3} - 0.5v_r)}{\ln(1 - v_r) + \chi v_r^2 + v_r} \quad (2)$$

where  $v_r$  is the volume fraction of polymer at the equilibrium degree of swelling and  $v_1$  is the molar volume of solvent;  $\chi$  is an interaction parameter between the polymer and the swelling agent known as the Flory-Huggins interaction parameter.



**Figure 1.** Variation of torque versus time for BIIR/BR/C5 compounds.

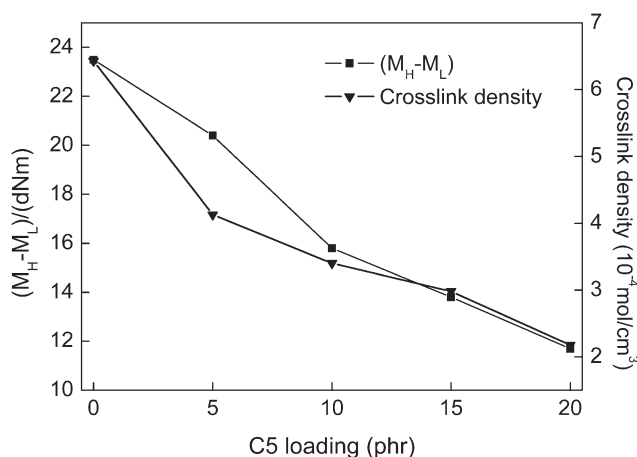
To calculate  $M_{cs}$  for the cured samples,  $v_r$  was evaluated using

$$v_r = \frac{(W_d - W_f)/\rho}{[(W_d - W_f)/\rho] + [(W_s - W_d)/\rho_s]} \quad (3)$$

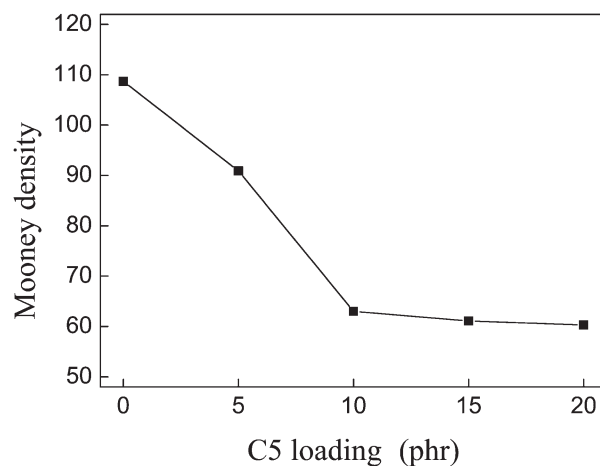
where  $W_d$  is the weight of the sample after swelling and drying,  $W_f$  is the weight of nonextractable filler in the sample,  $W_s$  is the weight of the swollen sample and  $\rho_s$  is the density of the solvent (0.8669 g/cm<sup>3</sup> for toluene).

### Mechanical Property Measurements

For measuring the hardness of the rubbers, square samples 6 mm thick and 10 mm length were used. The samples were then placed in a ShoreA hardness tester (LX-A, Shanghai, China) according to ASTM D2240: 2005. The tensile properties were performed on a universal testing machine (DXLL-5000, Shanghai, China), according to ASTM D412 : 1998 and ASTM D642 : 2000 separately with a cross-head speed of 500 mm/min. The abrasion loss was measured on a DIN abrasion testing machine (GT-7012-D, Gotech, Taiwan) according to ASTM D5963-2004.



**Figure 2.** Variation of  $(M_H - M_L)$  and crosslink density versus C5 loading for BIIR/BR/C5 compounds.



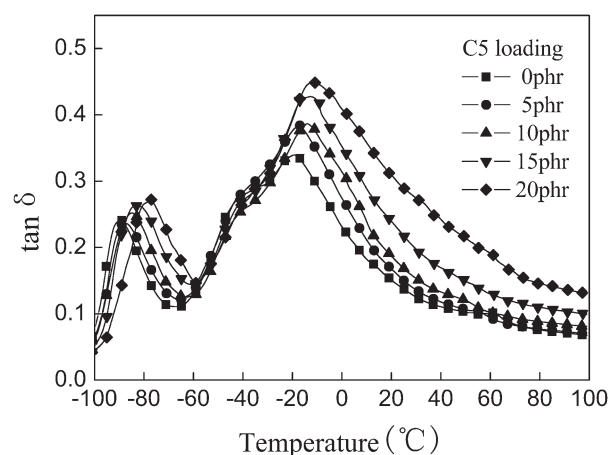
**Figure 3.** Variation of Mooney viscosity versus C5 loading for BIIR/BR/C5 compounds.

### Morphology Evaluation

The samples were placed in liquid nitrogen for 3 min and were then fractured to create two fresh surfaces, and then the cryogenic fractured surfaces were gold-sputtered. Dispersion of the silica particles and sectional structure in the rubber was assessed by a scanning electron microscope (JSM-6360LV, JEOL, Tokyo, Japan) with an accelerating voltage of 10 kV.

### Dynamic Mechanical Analysis (DMA) Measurements

$\tan\delta$  is the ratio between the loss modulus and storage modulus. The loss modulus represents the viscous component of the modulus and includes all the energy dissipation processes during dynamic strain, and storage modulus represents the stiffness component of the modulus. The  $\tan\delta$  of the rubber vulcanizates was measured in EPLEXOR 500N DMA (GABO Instruments, Germany). Test pieces 10 mm long, 10 mm wide, and ~6 mm thick were used. The tests were performed under compression mode, at 10 Hz frequency, 5% static strain, and 0.5% dynamic strain, and the sample temperature was increased from  $-100$  to  $100^\circ\text{C}$  at  $2^\circ\text{C}/\text{min}$  steps.



**Figure 4.** Temperature dependence of  $\tan\delta$  for BIIR/BR/C5 vulcanizates.

**Table II.** Details of Dynamic Mechanical Analysis for BIIR/BR/C5 compounds

Compounds	1	2	3	4	5
C5 loading (phr)	0	5	10	15	20
$Tan\delta_{max}/T_{max}$					
$T_{low}$	0.24/-89	0.24/-86.5	0.25/-84.9	0.26/-83	0.27/-77
$T_{high}$	0.34/-19	0.38/-17	0.39/-14.1	0.43/-11.9	0.45/-9.1
$T_{high} - T_{low}$	70	68.5	70.8	71.4	67.9
Temperature ( $tan\delta \geq 0.3$ )	-33.1 - -11.1	-37.1 - -3.0	-34.2-2.6	-31-9.0	-30.9-23.3
Range (°C)	22.0	34.1	36.8	40.0	54.2

## RESULTS AND DISCUSSION

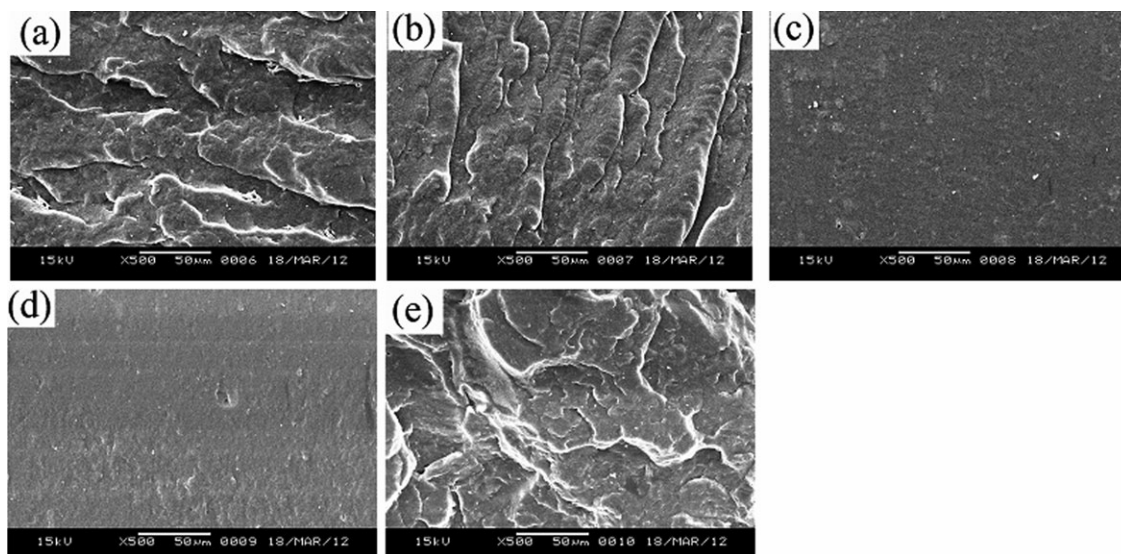
### Vulcanization Behaviors and Mooney Viscosity

The influences of C5 resin loading on the vulcanization behavior of the BIIR/BR/C5 compounds are shown in Figures 1 and 2. The scorch times, optimum cure times, and the torques of individual compounds were shown in Table I. Obviously, the presence of C5 resin in the compounds not only retarded the rate of vulcanization, but also reduced the crosslink density as can be observed from the reduction in the ( $M_H - M_L$ ) between the maximum and minimum torque of individual cure curve. The effect of C5 resin on crosslink density of compounds was more significant with increasing loading of C5 resin as shown in Figures 1 and 2. An explanation to this phenomenon could be partly attributed to the adsorption of accelerator onto the molecules of C5 resin, which comprise some polar fractions.<sup>14</sup> Therefore, partial loss of effective accelerator brings about the decline of crosslink density. In addition, the concentration of vulcanization agents could decline with the increment loading of C5 resin, as a result, the cure rate was retarded. The effects of C5 resin loading on Mooney viscosity of BIIR/BR/C5 compounds are shown in Figure 3. The Mooney viscosity reduced sharply with increase in C5 resin from 0 to 10 phr, and then remained basically unchanged with the continuous increase of

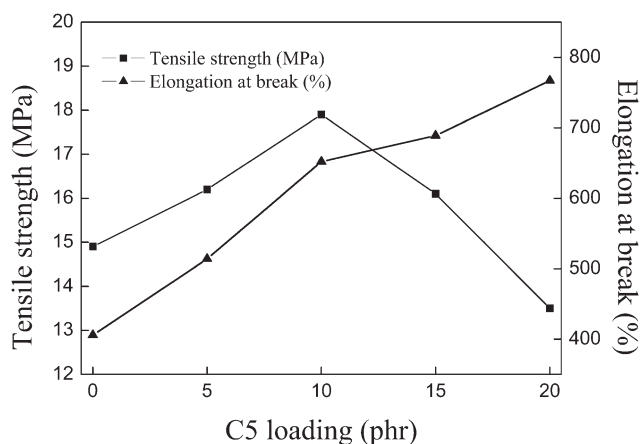
C5 resin. As shown in Figure 3, C5 resin in the compounds reduced the Mooney viscosity similar to physical diluents. In addition, this could be partly attributed to the declined of the gel content of BIIR/BR compounds with increase in C5 loading. But the effect of excess C5 resin was not obvious in BIIR/BR/C5 composites. This problem also indicated that C5 could not decline Mooney viscosity unlimitedly in composites.

### Damping Behavior

The effect of C5 resins on the dynamic characteristics of the BIIR/BR/C5 vulcanizates was studied by analyzing the temperature dependent behavior of  $tan\delta$ . Generally, the compatibility between different materials can be displayed by considering its dynamic characteristics, especially the variation of  $tan\delta$  since this parameter represents relaxation processes of components in the mixture.<sup>15</sup> The variation of  $tan\delta$  of the BIIR/BR/C5 vulcanizates is displayed in Figure 4, and the detail data are also recorded in Table II. As shown in Figure 4, the peak in  $tan\delta$  near  $-80$  and  $0^\circ\text{C}$  reflect the glass transitions for the BR and BIIR domains, respectively. In general, the  $tan\delta$  peak also reflects the glass transition temperature ( $T_g$ ) of the material. With the increase of C5 resins loading, the two independent  $tan\delta$  peaks of the blends shifted significantly to higher



**Figure 5.** SEM images of BIIR/BR/C5 vulcanizates [C5 loading: (a) 0 phr; (b) 5 phr; (c): 10 phr; (d):15 phr; (e): 20 phr].



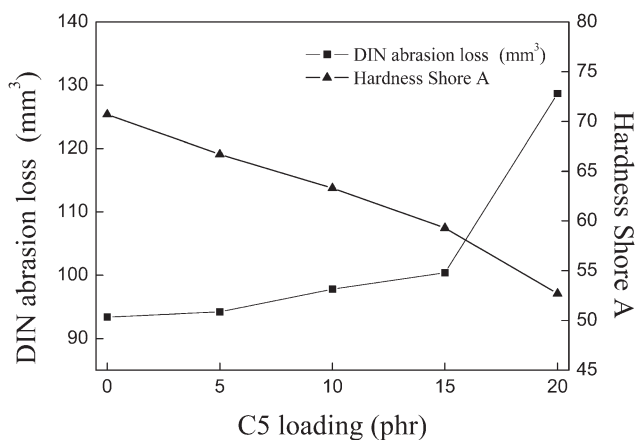
**Figure 6.** Tensile strength and elongation at break versus C5 resin loading for BIIR/BR/C5 vulcanizates.

temperatures, and the  $\tan\delta_{\max}$  also increased as shown in Table II. This is due to the fact that the  $T_g$  of most solid-form petroleum resin lies at much higher temperature than that of the base rubber,<sup>16,17</sup> and the two peaks of  $\tan\delta$  detected for each vulcanizate also indicate good compatibility between the resin and the matrix rubber, thereby bringing about the shift of the  $T_g$  of the BIIR and BR to higher temperature. In the molecular-level point of view, the increase in  $T_g$  implies that the presence of C5 resin causes the reduction in free volume within the matrix.<sup>11</sup> The effective damping temperature range of the BIIR/BR/C5 vulcanizates was broadened with the increase of C5 resins, especially in the range of the BIIR glass transition, and the damping temperature range ( $\tan\delta \geq 0.3$ ) was broadened remarkably from 22.0 to 54.2°C. However, the  $\tan\delta$  peak width of the BR glass transition was slightly changed with the adding of the C5 resin, this could be due to the high cis synthetic and the lower hysteresis compare with the BIIR. In addition, the difference of  $T_g$  between two matrix rubbers ( $T_{\text{high}} - T_{\text{low}}$ ) changed slightly with increase of the C5 resin, indicating the addition of C5 resin could not improve the compatibility between the BIIR and the BR.

### Morphological and Mechanical Properties

As shown in Figure 5(a), for the unfilled resin case, the poor dispersion of white silica was observed. With the increment loading of C5 resin, the interface of compounds became smoother from better dispersion of the silica. The addition of C5 resin, improved the dispersion of the silica. With the C5 resin loading increasing to 20 phr, the broad size distribution of dispersion phase indicated there exists silica particles agglomeration. This was attributed to the decline of crosslink density, influencing the filler-rubber interaction and reducing the surface hydrophobicity of the silica. In addition, the phase-separation morphology of these five compounds was not observed by scanning electron microscopy (SEM), although DMA spectra exhibited two glass transitions corresponding to the BIIR and BR.

The loading of C5 resin in the rubber matrix affected mechanical properties of the vulcanizates as summarized in Figures 6 and 7. The tensile strength of the vulcanizates was progressively



**Figure 7.** DIN abrasion loss and Hardness Shore A versus C5 resin loading for BIIR/BR/C5 vulcanizates.

increased with increasing C5 resins from 0 to 10 phr, and then dropped obviously with the continuous increment of C5 resins. The increment of the tensile strength is mainly due to the improvement of white silica dispersion as shown in SEM images (Figure 5), and the excellent dispersion could increase the relative volume content of silica in the matrix. Thus, the tensile strength got some improvement. However, with the continuous increment of C5 resins, the crosslink state was affected seriously by the excess C5 resins, which could cause the decline of the filler-rubber interaction and the interface strength of two rubber matrixes. Finally, the tensile strength reduced. Both the elongation at break and the abrasion losses of the vulcanizates increased gradually with increasing of C5 resins, but the increase rate of the abrasion losses was quite slowly. The increase of elongation at break can be explained by the higher extensibility of the rubber network improving by the C5 resins. The increase in the DIN abrasion of the vulcanizates could partly arise from the lower achievable crosslink-density. In addition, the lower crosslink-density could decline the interaction between the silica and matrix. The serious decline of crosslink-density is the most important factor to lead a rapid increase in DIN abrasion loss. The observed behavior could be partly due to the nature of C5 resins itself, which are capable of increasing internal friction within the rubber matrix, thereby bringing about the deterioration in abrasion loss,<sup>18,19</sup> but the effect of 5–15 phr C5 resins on the abrasion loss of blends was almost negligible. The decrease of hardness also could be arisen from the lower achievable crosslink-density.

### CONCLUSIONS

The effects of C5 resin loading on damping behavior and mechanical properties of BIIR/BR with C5 resin vulcanizates have been investigated. For this study, the C5 resins could retard the vulcanization, and reduce the crosslink density and Mooney viscosity of the blends. With increment in C5 resin content, the main  $\tan\delta$  peak shifted significantly to higher temperatures and the effective damping temperature range was broadened remarkably, especially in the range of the BIIR glass transition. The tensile strength improved with the increase content of C5 resin,

and reached the peak value with the content of C5 resin increasing up to 10 phr. The hardness declined, the elongation at break and the DIN abrasion loss increased with increment of C5 resin, but the effect of 5–15 phr C5 resins on the abrasion loss of blends was almost negligible. Therefore, the vulcanizates of BIIR/BR with C5 resin could be considered as a competent candidate for damping materials with the excellent mechanical properties.

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