

Study of Viscoelastic Properties of White Carbon Black Reinforced Synthetic Polyisoprene*

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Abstract The viscoelastic properties of synthetic polyisoprenes (PI) reinforced by white carbon black (WCB) have been investigated and compared with WCB reinforced natural rubber (NR), including cure characteristics, physio-mechanical and dynamic mechanical properties. Compared with NR, PI loaded with the same amount of WCB (PI/WCB) exhibited shorter scorch time and optimal cure time, indicating that WCB fillers are comparatively easier to conjugate with PI. The tensile strength and elongation at break decreased with WCB filling in both PI and NR vulcanizates. The hardness of the rubber vulcanizates increased with the WCB filling in the rubber matrix. PI/WCB blends exhibited smaller hardness data, lower tensile strength, as well as lower elongation at break and tensile stress. Increasing the amount of WCB in rubber matrix induced the Payne effect. However, the Payne effect is much more obvious for the PI/WCB system, and PI/WCB also displayed higher storage modulus whereas lower loss modulus and loss tangent than NR/WCB, which could all be attributed to the poor dispersibilities of WCB in the PI matrix.

Keywords: Reinforcement; White carbon black; Synthetic polyisoprene; Natural rubber; Viscoelastic properties; Payne effect.

INTRODUCTION

Synthetic polyisoprene (PI) is a synthetic polymer obtained from solution orientated polymerization of isoprene monomers under the activation of catalysts. It resembles natural rubber (NR) in many aspects, such as chemical constitutions, stereo structures, as well as physio-mechanical properties^[1–3]. Thus it has been well acknowledged as the “synthetic natural rubber”. PI and NR are both economical rubbers and exhibit excellent physical properties, such as low dynamic responses and hysteresis, high levels of durabilities. Thus they have been widely used in the field of transportation for truck tyres, anti-vibration dampers, *etc.* Compared with NR, PI possesses narrow molecular weight distribution and little nonrubber components, which brings it with weaker cohesiveness, lower elastic modulus, and shorter fatigue lifetime, *etc.*^[4, 5]. However, the physical properties of PI could be readily tuned through modification since it can be obtained *via* chemical synthesis, thus making it a perfect candidate to meet the increasing requirements of low-cost rubbers yet with improved viscoelastic properties. For example, in the previous Soviet Union, PI almost replaced NR in tire industries^[6].

The enhancement of the processing and mechanical properties of rubbers could be done with the introduction of fillers due to the fluid dynamic effects and the strong interactions between fillers and rubber matrices^[7, 8]. In general, inorganic particulates, such as carbon black^[9], silica^[10], clay^[11] or short fibers^[12], *etc.*, have been utilized to cross-link and interact with the rubber matrix. Liu *et al.* studied the rheological properties

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and dynamic mechanical properties of carbon black reinforced PI and NR^[13]. They found that properties of PI/carbon black were improved, but there was a big difference between reinforced PI and NR mixtures. Recently, white carbon black (WCB) has been used to improve the properties of NR and PI. WCB is a kind of amorphous non-crystalline fine powder in the form of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. In light of its excellent properties such as strong chemical stability, high surface area, and good dispersibility, it has been widely applied in the field of paint, rubber, and so forth^[14, 15]. Zhao *et al.*^[16] studied the structure of filler networks and the dynamic viscoelasticity of WCB reinforced solution polymerized butadiene styrene rubber. However, to the best of our knowledge, systematic reports on the comparison of viscoelastic properties of white carbon black reinforced PI (PI/WCB) and NR (NR/WCB) are rare.

In this study, WCB was used as a filler to cross-link with PI and NR to reinforce their viscoelastic properties. Rubber process analyzer and dynamic mechanical analyzer were employed to analyze the mechanical properties of PI/WCB and NR/WCB. The variations of the mechanical properties, which include the cure characteristics and physio-mechanical properties, were explicitly investigated with WCB filling in the PI and NR vulcanizates. The dynamic properties of the storage modulus (G'), loss modulus (G''), and loss tangent ($\tan\delta$) were also evaluated and compared with for the WCB/rubber vulcanizates. Emphasis is on the differences of the effect that WCB had on the viscoelastic properties between the two final reinforced composites, namely, PI/WCB and NR/WCB.

EXPERIMENTAL

Materials

The polyisoprene rubber, LHIR-80 of Mooney viscosity ML (1 + 4) at 100 °C equal to 82, was supplied by LuhuaHongjin Chemical Co., Ltd (Zibo, China). The natural rubber was purchased from Indonesia (Bacon rubber, NO 1). WCB was obtained from TonghuaShuanglong Chemical Co., Ltd (Jilin, China). Triethanolamine and all the other auxiliary reagents of analytical grade were purchased and used without further purification.

Preparation of White Carbon Black Reinforced PI and NR

In a typical procedure, a 100 phr (parts by weight per 100 g of rubber) dosage of raw rubber (PI or NR) was first masticated on a two-roll mill for six times. After that, the milling was continued for another 3 min under a successive addition of 5 phr of zinc oxide, 2 phr of coactivator stearic acid, 1 phr of the accelerator CZ, and 1 phr of the antiager RD. A varying amount of WCB, *viz.*, 10, 20, and 30 phr, was then added and ground for 5 min. Finally, 2 phr of the vulcanizing agent sulphur was brought to the mixture, mixed evenly, and then plasticized for 1 min. The resulted rubber matrix was later vulcanized on a mold at 140 °C in a press with the time up to the optimum cure time, yielding in NR or PI composites loaded with varying weight percentages of WCB. Mixing composition of different ingredients is listed in Table 1. The applied pressure was 10.0 MPa.

Table 1. Formulation and compound designation for both PI/WCB and NR/WCB vulcanizates

Formulation ^a	Compound designation					
	PI-W10	PI-W20	PI-W30	NR-W10	NR-W20	NR-W30
Rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
CZ	1	1	1	1	1	1
RD	1	1	1	1	1	1
WCB	10	20	30	10	20	30
Sulphur	2	2	2	2	2	2

^a All weights are in phr (parts per 100 g of rubber); WCB: white carbon black

Characterization

The cure characteristics of different stocks were obtained using a no-rotor rheometer (GT-M2000-A) from Gotech. Hardness of the vulcanizates was conducted on a Shore A type durometer in accordance to GB/T23651-

2009. After the composite was cooled, tensile test specimens were prepared and tested according to GB/T528-1998. The tear tests were performed in terms of GB/T529-2008. Rubber process analyzer (RPA) was used to characterize the storage modulus, loss modulus, and loss factor. The temperature was fixed at 60 °C with a strain amplitude of 7% for the frequency scanning (0.1–30 Hz). Under the same fixed temperature, the strain scanning was performed at a frequency of 1 Hz, with a varying strain amplitude of 0.28%–98%. The dynamic mechanical properties were conducted using a dynamic mechanical analyzer (DMA/SDTA861e). The test samples were subjected to cyclic tensile strain at a frequency of 5 Hz. The temperature ranges from –120 °C to 100 °C with a heating rate of 5 K/min. The glass transition temperature (T_g) was obtained from the loss factor peak.

RESULTS AND DISCUSSION

The effect of WCB (filler) loading on the cure characteristics, physio-mechanical and dynamic mechanical properties (storage modulus, loss modulus, and loss tangent) for both PI/WCB and NR/WCB vulcanizates are discussed below.

Cure Characteristics

Cure data of PI/WCB and NR/WCB composites were recorded and summarized in Table 2. The scorch time (t_{s1}) and optical cure time (t_{c90}) represent measures of the time at which vulcanization begins and reaches completion, respectively. As shown in Table 2, t_{s1} and t_{c90} increase gradually with increasing the weight percentage of WCB for either PI/WCB or NR/WCB composites. The prolongation in t_{s1} and t_{c90} could be attributed to the low vulcanization efficiency of WCB because WCB has strong adsorption effect upon other additives, especially on accelerators. Normally, the more the content of WCB, the more obvious of the retardation effect. Moreover, WCB possesses abundant hydroxyl groups which could randomly adsorb onto accelerators and other radicals, resulting in an additional increase in t_{c90} . It should be noted that both the t_{s1} and t_{c90} of PI/WCB are much smaller than those of NR/WCB. This behavior could be ascribed to the comparatively easier conjugation between PI and WCB to form crosslinked networks^[17]. Activities among molecular chains of the rubber networks are consequently impeded and lead to a decrement in t_{s1} .

Table 2. Cure characteristics of rubber vulcanizates (140 °C)

	Sample codes					
	PI-W10	PI-W20	PI-W30	NR-W10	NR-W20	NR-W30
t_{s1} (m:s)	1:54	2:21	2:32	4:24	5:10	5:12
t_{c90} (m:s)	6:43	6:47	8:43	8:26	10:22	11:04
M_L (dN·m)	0.2	0.3	0.5	0.4	0.6	1.1
M_H (dN·m)	8.2	10.0	12.8	8.6	10.9	14.0
M_H-M_L (dN·m)	8.0	9.7	12.3	8.2	10.3	12.9

t_{s1} = scorch time; t_{c90} = optical cure time; M_L = elastic minimum torque; M_H = elastic maximum torque; M_H-M_L = Torque difference.

The minimum elastic torque (M_L) is commonly described as a representative of the uncured stock's elastic modulus and provides valuable information on rubber's processability. For WCB modified rubbers, M_L increases continuously when the WCB loading is increased, which indicates that WCB has a negative impact on the processability of the rubber. This might be due to the existence of multiple polar Si—OH groups which readily form strong van der Waals forces, resulting in reduced processability. PI/WCB shows lower M_L values than those of NR/WCB under the same amount of WCB fillers, suggesting that PI/WCB blends exhibit better mobilities. Due to the enhanced degree of crosslinking accompanied by the addition of WCB, the M_H values of both PI/WCB and NR/WCB are found to increase with increasing the weight percentage of WCB. Meanwhile, PI/WCB shows lower M_H and M_H-M_L values comparing to those of NR/WCB blends with the same amount of fillers. The torque difference (M_H-M_L) is acknowledged to be a measure of the difference between stiffness and shear modulus of the fully vulcanized and unvulcanized test specimens taken at the lower point of the vulcanizing curve. Wolff and Wang^[18] reported that M_H is dependent on the crosslink density of fillers.

Therefore it can be concluded that NR/WCB blends have higher degree of cross-link than PI/WCB vulcanizates considering the impact of rigid silica particles in WCB on torque^[19].

Physico-mechanical Properties

The physico-mechanical properties of different rubber vulcanizates as a function of WCB filling content are tabulated in Table 3, respectively. As can be seen, the hardness, tensile stress at given elongations (50%, 100%, and 300%), and tear strength of the WCB-filled NR and PI blends increase regularly with the increasement of the WCB loading in rubber matrix. This could also be ascribed to the increased crosslink density. To be noted, the increasement in hardness with WCB filling induced the enhancement of the resistance to abrasion of the rubber, leading to the ecological requirements of lowest rolling resistance and high durability in the tire industry. The tensile strength, on the other hand, drops only a little for both PI/WCB and NR/WCB vulcanizates. The minor decrease may be due to a slight agglomeration of WCB fillers inside the rubber matrix. However, the elongation at break decreases with increasing the content of WCB. This indicates that when the loading of WCB reaches 10 phr, the surplus WCB entangles among rubber matrix through physical actions, resulting in reduced reinforcement effect. Furthermore, separately existed WCB fillers have a dilute effect on the whole rubber networks, which also weakens the reinforcement. Furthermore, PI/WCB blends have lower values than NR/WCB in all the other four parameters except for the elongation at break. This result corresponds well with the lower crosslink density and smaller average molecular weight, as well as weaker intermolecular interactions in PI/WCB blends. Besides, NR/WCB blends exhibit stronger orientation during a stretching process and better crystallization abilities.

Table 3. Physico-mechanical properties of PI and NR with different contents of WCB

	Sample codes					
	PI-W10	PI-W20	PI-W30	NR-W10	NR-W20	NR-W30
Hardness, shore A	39	45	49	42	47	54
Tensile strength (MPa)	27.9	27.0	26.5	31.1	31.2	29.3
Elongation at break (%)	840	807	763	768	744	742
Se 50% (MPa)	0.6	0.6	0.7	0.7	0.8	0.9
Se 100% (MPa)	0.8	0.9	1.0	1.0	1.1	1.3
Se 300% (MPa)	1.5	1.9	2.2	2.2	2.7	3.2
Tear strength (kN·m ⁻¹)	26.7	32.8	34.0	30.2	49.4	62.7

Se X% = Tensile stress at X% elongation

Dynamic Mechanical Properties

Storage modulus, loss modulus, and loss tangent are usually the three main factors for characterizing the dynamic mechanical properties of rubber materials. For example, the rolling resistance, wet traction, and the heat originated from machine running are all dependent on the loss factor. Thus the dynamic mechanical properties play significant roles in the processing and applications of rubber composites.

The storage modulus (G'), which is proportional to the energy stored during a loading cycle, represents the stiffness of a viscoelastic material and is related to the traction property^[20]. For similar rubber systems, G' can be studied as a function of strain to analyze the rubber/filler interactions. The exact method was adopted by Fröhlich *et al.* to investigate the impact that fillers with different structures, diameters, and surfactivity have on the interface interactions among composite materials^[21]. An overload of the fillers (WCB), would probably cause agglomerations since they could not be evenly dispersed in rubber matrix. Under dynamic conditions, there is a larger risk to produce a hysteresis loss if the amount of WCB is high enough to form a WCB network in the rubber system. That is, G' is irrelevant to strain under low strain values, whereas a dramatic decrease will occur when the strain approaches a critical value. After that, it would remain constant at higher strains. This phenomenon is called Payne effect^[22]. Moreover, a permanent change, mainly referring to breakdown of the filler networks and the adhesive interface of filler/rubber system, will be caused in the interior of rubber blends under large strain amplitudes. Thus, in order to study the Payne effect of WCB reinforced rubbers (PI/WCB and

NR/WCB), we employed RPA (rubber process analyzer) strain scanning to investigate the variation of G' under both small or large strain values.

The graphical description of the variation of G' with strain of both PI and NR composites loaded with different amounts of WCB is shown in Fig. 1. When the WCB loading is 10 phr, G' barely changes with strain for either PI/WCB or NR/WCB, suggesting an inconspicuous Payne effect. However, it is clear that Payne effect becomes much more obvious with increasing the amount of WCB in the rubber matrix. In particular, a significant Payne effect appeared in the WCB-filled PI vulcanizates. Since Payne effect mainly reflects the formation of WCB-WCB networks, it is quite reasonable that the corresponding G' versus strain curves of 10 phr WCB show few changes under low strain values because the loading of 10 phr fillers could be finely dispersed in rubber matrix and a perfect rubber-WCB network is formed. In contrast, increasing the amount of WCB loadings, more and more WCB-WCB networks were formed due to agglomerations, resulting in enhanced G' . However, the WCB-WCB networks could be broken down when a larger strain amplitude is applied. Thus the storage modulus of all the six different rubber blends approaches an equal value. It can also be revealed that the fillers exhibit poorer dispersibilities in PI blends because the Payne effect in the PI/WCB system loading with 20 and 30 phr of fillers is much clearer. This finding is in accordance with the information conveyed from the “ $\Delta G'$ versus WCB content” plot, where $\Delta G'$, defined as the difference between the maximum and minimum G' values of the G' versus strain curves, represents the distribution of WCB-WCB networks, viz., the larger the $\Delta G'$, the poorer the dispersibility^[23].

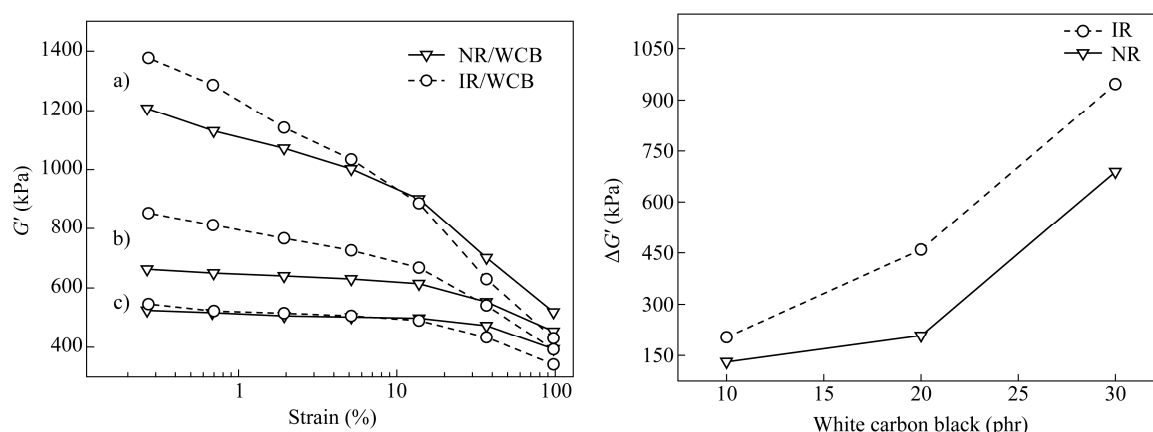


Fig. 1 G' versus strain and $\Delta G'$ versus WCB content of PI and NR vulcanizates loaded with varying amount of WCB: (a) 30 phr, (b) 20 phr, (c) 10 phr ($\Delta G'$ is the difference between the maximum and minimum G' values from the G' versus strain curves.)

The loss modulus G'' is proportional to the energy dissipated during a single loading cycle^[24, 25]. As depicted in Fig. 2, the value of G'' for both PI and NR vulcanizates is low when the WCB loading is 10 or 20 phr. The relevant curves remains almost flat under medium strains. After that, G'' increases with increasing strain amplitude. When 30 phr of WCB is loaded, the G'' factor of either PI-W30 or NR-W30 firstly increases rapidly with increasing strains and reaches a maximum, howbeit, a dramatic decline occurred afterwards. A theory of the breakdown and rebuilt of WCB-WCB networks is responsible for such an abnormal behavior. Since the white carbon black network has not been well developed with 10 or 20 phr of fillers, the G'' value is low. The resulted networks can be easily wrecked under high strains, thus G'' increases. The loss energy was mostly provided by the interactions among rubber molecules. Under lower strain amplitudes, the network is relatively strong enough to resist it from breaking down. G'' herein depends on the hydrodynamics of fillers, which means the formation of rubbers with high viscosities. Hence, G'' increases with increasement in the amount of WCB, leading to more WCB-WCB networks. The breakdown and rebuilt processes also increase, at the same time, the corresponding loss energy is amplified to carry out those procedures. The amplitude of

network breaking down rapidly enlarges as the strain goes up. If breaking down outperforms rebuilt, G'' begins to decline and reaches a minimum when the strain is high enough to make adequate yet irreversible damages to the network.

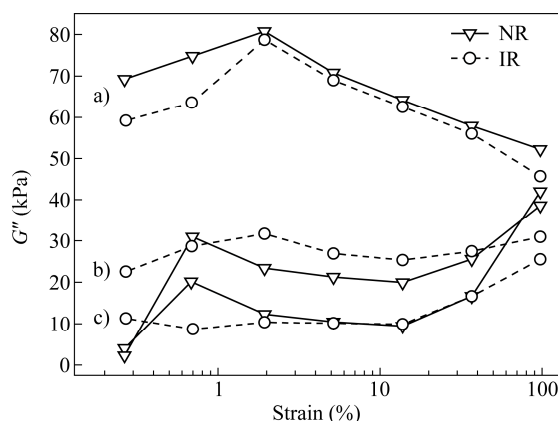


Fig. 2 G'' versus strain of PI and NR filled with varying WCB contents: (a) 30 phr, (b) 20 phr, (c) 10 phr

PI blends loaded with white carbon black show slightly larger G'' than NR/WCB composites, which is in agreement with the fact that the WCB filler exhibits a poorer dispersibility in the PI rubber matrix than that in the NR matrix (*vide supra*).

Figure 3 depicts the relationship between loss factor ($\tan\delta$) and strain amplitude in a white carbon black reinforced rubber system. Loss factor is the ratio of loss modulus G'' to storage modulus G' . It represents the mechanical damping or internal friction in viscoelastic materials. Usually, an introduction of inorganic fillers to a rubber matrix enhances the $\tan\delta$ value^[26]. Higher values of $\tan\delta$ indicate that the material is nonelastic, whereas lower ones correspond to elastic materials. Clearly, $\tan\delta$ tends to increase upon loading with larger amount of white carbon black for a given category of rubber. When the strain amplitude is enlarged, a peak value of $\tan\delta$ appears. This value also increases with increasing the content of WCB. Since $\tan\delta$ is proportional to the loss modulus, it is inevitably related to the breakdown and rebuilt of filler-filler networks. It has been discussed earlier that the loss energy increases with increasing filler-filler networks. Moreover, there is a strong hysteresis among rubbers' molecular chains. Larger amount of WCB will lead to increasement in occluded rubbers which would release much more rubber molecular chains, thus providing greater hysteresis. In conclusion, $\tan\delta$ becomes dependent on the strain amplitude with the increasement of white carbon black. Loss energy mostly comes from deformable rubbers under small strain amplitudes, which shelters the white carbon black networks from damages. Poor dispersion of white carbon black would result in many occluded rubbers that encapsulate a large proportion of rubber matrixes. Herein, the amount of deformable rubbers is reduced, leading to small $\tan\delta$ values at low strain amplitude. While under larger strains, the filling networks suffer from damages and the encapsulated deformable rubbers would be released. Plus the frictions among white carbon black particles produce another enlargement of loss modulus. Thus, $\tan\delta$ increases greatly under high strain amplitude and PI/WCB composites exhibit a larger loss energy.

The phase angle (δ) between stress and strain represents the viscous response to the material, where $\delta = 0^\circ$ stands for totally elastic and $\delta = 90^\circ$ stands for totally viscous. When δ equals 45° , storage modulus and loss modulus coincide with each other, and this point depends upon the applied frequency and temperature of the composites. To study the viscoelastic properties of WCB filled rubber composites, the variation of loss factor on frequency and temperature is studied as follows.

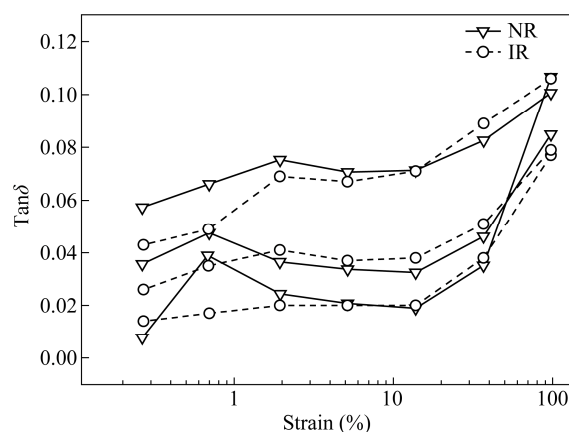


Fig. 3 $\tan\delta$ versus strain of vulcanizates filled with WCB (the amount of WCB is 30, 20, and 10 phr from top to bottom for each rubber system, respectively.)

The loss factor ($\tan\delta$) as a function of frequencies (Fig. 4a) is measured through dynamic mechanical analyses at 60 °C, with the strain amplitude to be 7%. Apparently, the WCB-filled PI compounds show an increase in $\tan\delta$ with increasing the amount of WCB loadings. When the loading is 10 and 20 phr, the loss tangent enlarges almost linearly upon enhancing the frequency. However, that of the one loaded with 30 phr of

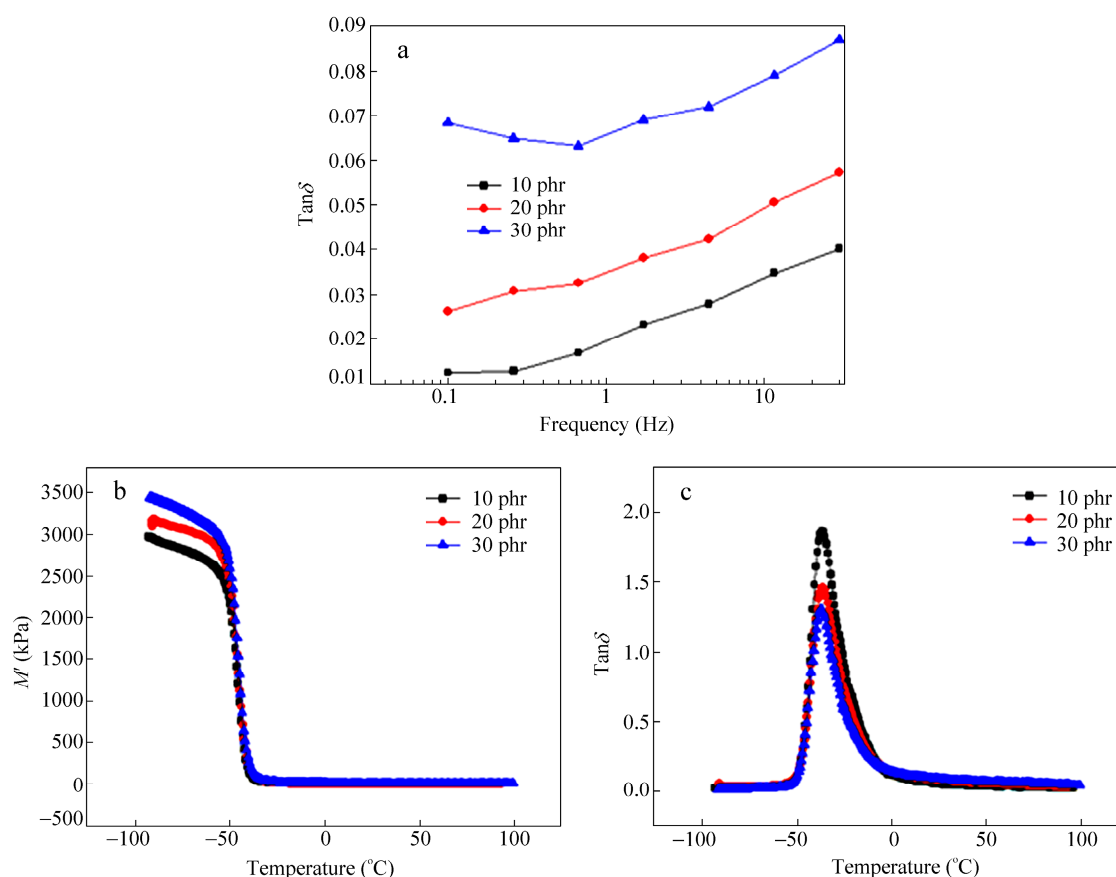


Fig. 4 $\tan\delta$ versus frequency (a), M' versus temperature (b), and $\tan\delta$ versus temperature (c) plots of PI blends loaded with different amounts of WCB

fillers decreases at first and later increases. These behaviors could also be ascribed to the frictions among intermolecular chains and rigid WCB particles.

Dynamic mechanical thermal analysis plots of elastic modulus (M') and $\tan\delta$ as a function of temperature at a frequency of 5 Hz are shown in Figs. 4(b) and 4(c), respectively. It is well accepted that the glass transition region is measured as a sudden and considerable change in the elastic modulus and a concurrent peak in the $\tan\delta$ curve^[27]. The temperature corresponding to the maximum $\tan\delta$ peak is called " T_g ", viz., the glass transition temperature, which is a significant factor of material dynamic properties. It is obvious that M' increases consistently with the increasing amount of fillers, especially at low temperatures. The $\tan\delta$ value shows a decrease as the loading of fillers increases. This can be a consequence of retarded mobilities of molecular chains when the temperature approaches T_g . Moreover, an increase in WCB loadings also leads to much more occluded rubbers, and thus starkly reduces the number of flexible rubber molecular chains^[28].

As shown in Table 4, the loss tangent at 0 °C and 60 °C represents the wet traction and rolling resistance of rubbers, respectively^[29–31]. The former one increases with increasing the amount of white carbon black. This result indicates that increasing of fillers is beneficial to enhance rubbers' wet traction. It also coincides well with the information obtained from the plot of $\tan\delta$ versus temperature, which is, a high $\tan\delta$ value at low temperatures favors the formation of rubbers with excellent wet traction. The latter one at 60 °C, on the other hand, shows similar trends in the relationship between $\tan\delta$ and the amount of fillers. However, this finding goes against the willing of reducing the rolling resistance. Thus the filling amount of white carbon black should be controlled appropriately to minimize filler-filler networks and reduce the rolling resistance.

Table 4. The loss factors of PI filled with different amounts of WCB at 0 °C and 60 °C

Temperature (°C)	Tan δ		
	PI-W10	PI-W20	PI-W30
0	0.115	0.139	0.140
60	0.031	0.046	0.061

CONCLUSIONS

In summary, it has been observed that PI/WCB composites exhibit shorter scroch time and optimum cure time when compared with NR blends loaded with the same amount of white carbon black. Whereas the NR matrix shows better dispersibilities of WCB fillers and possesses higher crosslinking densities. It is clear that NR system slightly outperforms PI system loaded with the exact same amount of WCB in its tensile strength and tensile stresses at given elongations. This result is in accordance with the fact that NR has higher average molecular weight and stronger orientation or crystallization among molecular chains during a stretching process. Nevertheless, the physio-mechanical properties for both PI and NR systems are almost the same. Thus PI can be used as an alternative to NR under some conditions.

We have studied in detail the structure-dynamic mechanical properties of both the NR/WCB and PI/WCB systems. The storage modulus, loss modulus, and loss tangent are investigated as a function of the amount of loaded fillers, strain amplitudes, frequencies, and temperatures to learn the differences between PI and NR systems. With increasing the amount of fillers, both PI and NR blends exhibit the obvious Payne effects. The most obvious Payne effect appears when the filler loading reaches 30 phr. Under the same loading amount of WCB, PI composites possess larger G' whereas smaller G'' and $\tan\delta$ values than those of NR systems. This is mainly due to the poor dispersion of WCB in the PI rubber matrix, resulting in many occluded rubbers. Finally, it was observed that the amount of filling white carbon black has an essential impact on the wet traction and rolling resistance parameters of rubbers. Thus it is very important to adjust the fillers' amount appropriately to require excellent physico- and dynamic-mechanical properties.

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