

NR/XSBR Nanocomposites with Carbon Black and Carbon Nanotube Prepared by Latex Compounding

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Abstract

Two series of natural rubber/carboxylated styrene butadiene rubber (NR/XSBR) (80/20) nanocomposites containing different loadings of carbon black (CB) (3-9 phr) and carbon nanotube (CNT) (0.1-0.4 phr) have been prepared by a latex stage compounding method. Before mixing with NR/XSBR blended latex, CB and CNT were dispersed and stabilized in water by ball milling with the aid of surfactant. The obtained compounded latex was cast into sheet on a glass mold and thereafter cured in an oven at 80°C for 3 h. The tensile properties (tensile strength, modulus at 300% strain, elongation at break), dynamic mechanical properties (loss tangent, storage modulus) and thermal stabilities (degradation temperatures, % char) of the vulcanizates were evaluated. The results showed that the addition of either CB or CNT enhanced the tensile strength, modulus at 300% strain, storage modulus and thermal stability, but reduced the elongation at break of the NR/XSBR blend in a dose dependent manner, except that the tensile strength peaked at an optimum filler level, declining at higher filler loadings. The CNT-filled nanocomposites provided a comparable tensile strength with that of the CB-filled nanocomposites but at about 25-fold lower loading. This reinforcing effect is attributed to the greater aspect ratio and specific surface area of CNT.

Key words: Natural rubber, Carboxylated styrene butadiene rubber, Carbon black, Carbon nanotube

Introduction

Carboxylated styrene-butadiene rubber (XSBR) latex is derived from an emulsion based polymerization of butadiene, styrene and a small amount of unsaturated carboxylic acid, such as acrylate, methyl acrylate or itaconic acid, amongst others, where the carboxyl groups are randomly distributed along the polymer chains.^(1,2) XSBR in latex form can be considered as nanopolymer sphere dispersion in an aqueous medium. The presence of carboxyl groups in XSBR molecules leads to an increased polarity, bonding properties and resistance to hydrocarbon solvents and oils as compared to those of styrene-butadiene rubber (SBR).⁽³⁻⁵⁾ The incorporation of XSBR into natural rubber (NR) helps to improve the solvent, oil and thermal resistance properties and to lower the

gas permeability of NR.^(1,4-6) The latices of NR and XSBR are easily mixed, with their blends being compatible and offering a fine scale dispersion of these two components.^(1,4,5,7) The latex compounding method has many advantages, including an environmental friendliness, a low cost and being an easily controlled process, plus it is quite promising in terms of the ability for viable industrialization. Moreover, the latex products exhibit superior properties as compared to dry rubber articles, due to the absence of a mastication step during compounding.⁽⁸⁾ The vulcanizate of NR/XSBR blends can also be obtained by the conventional sulfur-curing system.⁽⁵⁾ The mechanical properties, thermal stability, aging properties and gas permeation of NR/XSBR latex blends have been extensively studied.⁽⁴⁻⁶⁾ However, reinforcing fillers are commonly incorporated into rubbers to increase the range

of properties and to fulfill the industrial needs. Therefore, the attractive properties of NR/XSBR blends lead to the on-going studies of these blends as matrices for rubber nanocomposites. Carbon black (CB) is the most important reinforcing filler used in the rubber industries, but it is not so effective for rubber latex due to its large particle dimensions and tendency to agglomerate.⁽⁹⁻¹²⁾ Therefore, carbon nanotube (CNT) has been used to replace CB in rubber compounds prepared by the latex compounding method. CNT is one of the ultimate reinforcing nanofillers for polymer nanocomposites, because of its very high aspect ratio (up to 10^4), surface-to-volume ratio, Young's modulus and tensile strength.⁽¹³⁻¹⁶⁾ The efficiency of CNT as a reinforcing agent is primarily attributed to its high aspect ratio that offers extensive physical entanglement and stress transfer from the polymer matrix to the CNT.⁽¹³⁻¹⁸⁾ However, there are only a few reports dealing with the incorporation of CNT into rubbers and, to our knowledge, no study has reported on the influence of CNT as a reinforcing agent for NR/XSBR blends. Due to its unique and superior properties, CNT might offer a suitable reinforcing effect for the latex of NR/XSBR blends at a much lower loading level as compared with the currently used CB filler. Here, in this study, different loading levels of CB (3-9 phr) and CNT (0.1-0.4 phr) were used to reinforce a 80/20 NR/XSBR blend by a conventional latex compounding method. The NR/XSBR-based nanocomposites so obtained were then characterized for their tensile properties, dynamic mechanical properties and thermal stability behaviors.

Materials and Experimental Procedures

Materials

NR latex with a 60 wt% dry rubber content (DRC), potassium oleate, potassium hydroxide (KOH), sulfur (S), zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC), Wingstay L antioxidant and CB (N 330) with diameter of 28-36 nm were obtained from the

Rubber Research Institute of Thailand. XSBR latex with a 52 wt% DRC was donated by Siam Synthetic Latex Company. A multi-walled CNT with an average diameter of 15 nm was purchased from EM-Power Co., Ltd. The representative CNT image visualized by transmission electron microscopy (TEM) on a Jeol JEM-1230 is shown in Figure 1. The CNT can highly entangle with one another and form an interconnecting structure. The aqueous dispersions of S, ZnO, ZDEC, Wingstay L, CB and CNT were prepared using voltamol and bentonite as the dispersing agents in a ball mill for 72 h. Potassium oleate and KOH were used as 10% (w/v) aqueous solutions.

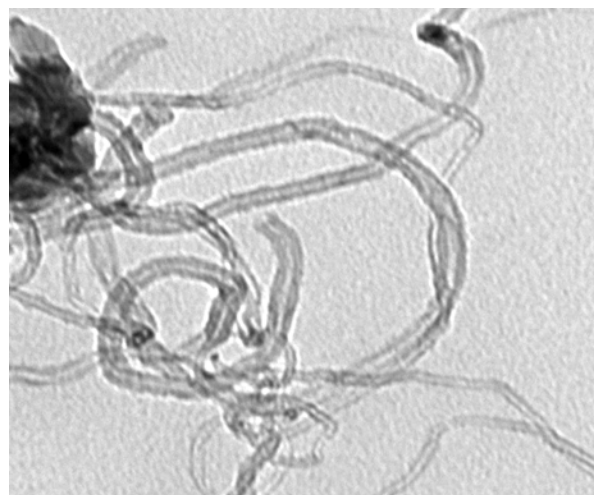


Figure 1. Representative TEM image of the multiwalled CNT.

Sample Preparation

NR and XSBR latices were compounded in an aqueous solution/dispersion according to the recipes given in Table 1. Compounding was performed at an ambient temperature ($\sim 25^\circ\text{C}$) using a mechanical stirrer at 150 rpm for ~ 30 min so as to achieve uniformity. The latex compounds were then cast onto glass molds ($20\text{ cm} \times 20\text{ cm} \times 0.15\text{ cm}$), allowed to air-dry for 24 h and subsequently cured in an oven at 80°C for 3 h.

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Table 1. Formulations of the sulphur-curing system for the rubber compound (based on dry weight) used in this study.

Materials	Amount (phr)	Amount (phr)
60% (w/w) NR latex	80.0	80.0
50.5% (w/w) SBR latex	20.0	20.0
10% (w/v) Potassium oleate solution	0.2	0.2
10% (w/v) KOH solution	0.5	0.5
50% (w/v) ZDEC dispersion	1.0	1.0
50% (w/v) S dispersion	1.5	1.5
50% (w/v) Wingstay L dispersion	1.0	1.0
50% (w/v) ZnO dispersion	1.0	1.0
20% (w/v) CB dispersion	0, 3, 5, 7, 9	-
2% (w/v) CNT dispersion	-	0, 0.1, 0.2, 0.3, 0.4

Measurement of Tensile Properties

The tensile properties of the vulcanizates were evaluated according to the standard ISO 37 (Type 2), using dumbbell-shaped specimens at a constant cross-head speed of 500 mm/min, with an Instron IX-1011 testing machine and a load cell capacity of 1 kN. The values of the tensile strength, modulus at 300% strain and elongation at break were averaged from at least five sample measurements for each composition.

Dynamic Mechanical Analysis (DMA)

The loss tangent ($\tan \delta$) and storage modulus (E') as a function of the temperature, were assessed by dynamic mechanical analysis (DMA), using a Mettler Toledo, DMA/SDTA 861^e instrument under the shear mode at a fixed frequency of 1 Hz with a heating rate of 3°C/min from -80°C to 100°C and under a nitrogen atmosphere.

Thermogravimetric Analysis (TGA)

The thermal stability of the samples was determined using a thermogravimetric analyzer (TGA) (Mettler Toledo, TGA/SDTA 851^e) under a nitrogen atmosphere. The heating rate was 20°C/min in the temperature range between 50°C and 1000°C.

Results and Discussion

Tensile Properties

The tensile properties, in terms of the tensile strength, modulus at 300% strain and elongation at break, of the neat 80/20 NR/XSBR blend and its nanocomposites with different CB and CNT loadings prepared through conventional latex compounding are summarized in Figure 2. The tensile strength, modulus at 300% strain and elongation at break of the neat rubber blend were about 18.7 MPa, 2.2 MPa and 684%, respectively. The tensile strength and modulus of the nanocomposites filled with either CB or CNT were all higher than those of the unfilled rubber blends. The tensile strength of the nanocomposites increased with increasing CB and CNT loading levels up to their optimum (maximal) values at about 21.7 MPa and 21.4 MPa at 5 phr and 0.2 phr (Figure 2a), respectively, which are about 14.4 to 16% higher than that of the unfilled rubber blend. Therefore, it is necessary to add a 25-fold higher level of CB to obtain a comparable tensile strength as the CNT nanocomposite. This is likely to be because CNT has much higher aspect ratio and specific surface area, resulting in high interaction between the CNT and rubber matrix as compared with CB. However, the reinforcing effects of both CB and CNT loadings decreased sharply at higher levels (above 5 phr and 0.2 phr, respectively), and at a CB loading level of 9 phr were only slightly higher than that of the unfilled rubber blend. This decrease in the tensile strength may be attributed to the agglomeration of CB and CNT in the rubber matrix.

The modulus at 300% strain also increased steadily with increasing CB and CNT loadings, but continued to increase at CB and CNT loading levels above those that were optimal for the tensile strength (Figure 2b). This is due to the fact that fillers with a higher stiffness than the matrix can effectively increase the modulus of the composites by restricting the mobility and deformability of the rubber chains, particularly at high filler loadings. However, the increase in the modulus with increasing filler levels was more marked for CB than CNT, but required higher loading levels. Thus, the incorporation of CB at 9 phr in the composite resulted in an 86.4% increase in the modulus, whilst that of the nanocomposite with CNT at 0.4 phr was increased about 31.8%. However, the nanocomposite filled with 0.4 phr of CNT has a comparable modulus to the composite filled with ~4 phr of CB (as extrapolated from Figure 2b), and thus a 10-fold higher CB than CNT level was required.

The elongation at break of the nanocomposites decreased continuously with increasing CB and CNT loadings (Figure 2c), which is a common trend for composites filled with stiff particles, since they impede the rubber chain movement during deformation. Furthermore, at high filler loadings, the agglomeration of CB and CNT will impart a higher resistance on the chain mobility, leading to an enhanced modulus and so reduce the elongation at break of the composites. However, the elongation of the composites is largely retained. The incorporations of CB at 9 phr and CNT at 0.4 phr resulted in a reduction of the elongation at break of about 29.2% and 14%, respectively, relative to the neat rubber blend.

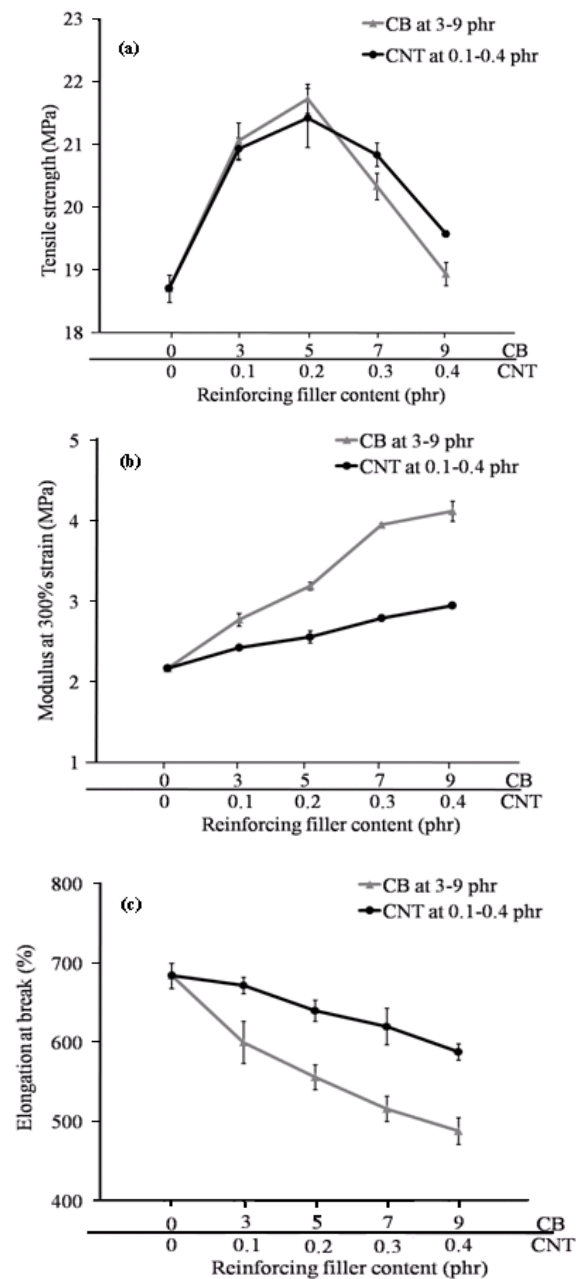


Figure 2. Tensile properties of NR/XSBR-based nanocomposites filled with different CB or CNT loadings: (a) tensile strength, (b) modulus at 300% strain and (c) elongation at break.

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Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties, in terms of $\tan \delta$ and E' , of the neat 80/20 NR/XSBR blend and its nanocomposites were evaluated from -80 to 100°C. Figures 3 and 4 show the influence of CB and CNT loadings, respectively, on the $\tan \delta$ and E' as a function of temperature for the nanocomposites, whilst the glass transition temperatures (T_g s) of NR and XSBR obtained from the $\tan \delta$ peaks and E' at -80°C of all compositions are summarized in Table 2. The variation in $\tan \delta$ with temperature of the neat rubber blend and its nanocomposites filled with CB and CNT revealed two $\tan \delta$ peaks at -60 to -43.4°C and 30 to 50°C, that were assigned to the T_g s of NR and XSBR, respectively (Figures 3a and 4a). This indicates that the blends are not compatible and so form a two-phase structure in the blend and nanocomposites. The T_g s for both NR and XSBR of each rubber nanocomposite tended to increase with increasing CB or CNT loading levels (Figures 3a and 4a; Table 2), and so the thermal motion of the rubber chain segments was constrained by the CB and CNT particles.

With respect to the variations in the E' with temperature, the E' of each composition decreased with increasing temperatures due to the decrease in stiffness of the samples (Figures 3b and 4b). A significant influence of the CB and CNT content on the E' occurs at a temperature below the T_g of NR. The data presented in Table 2 reveal that at -80°C, a temperature selected below the T_g of NR, the E' of the nanocomposites tends to increase considerably with increasing CB or CNT loadings in comparison with that of the neat rubber blend, most likely due to the stiffening of the rubber matrix, as described previously. Thus, the data for the changes in E' with increasing CB or CNT loading levels are in agreement with that for the tensile modulus.

Table 2. DMA data of NR/XSBR-based nanocomposites filled with different CB or CNT loadings.

Filler content	Storage modulus (E') at -80°C (MPa)	T_g (°C) from $\tan \delta$ peak	
		NR phase	XSBR phase
Unfilled	319.9	-60.2	30.0
3 phr CB	396.2	-52.2	34.4
5 phr CB	524.6	-51.1	36.7
7 phr CB	595.2	-46.7	47.2
9 phr CB	624.5	-43.4	50.0
0.1 phr CNT	355.8	-54.4	30.5
0.2 phr CNT	411.2	-54.4	34.6
0.3 phr CNT	458.8	-49.8	35.3
0.4 phr CNT	509.0	-50.0	36.0

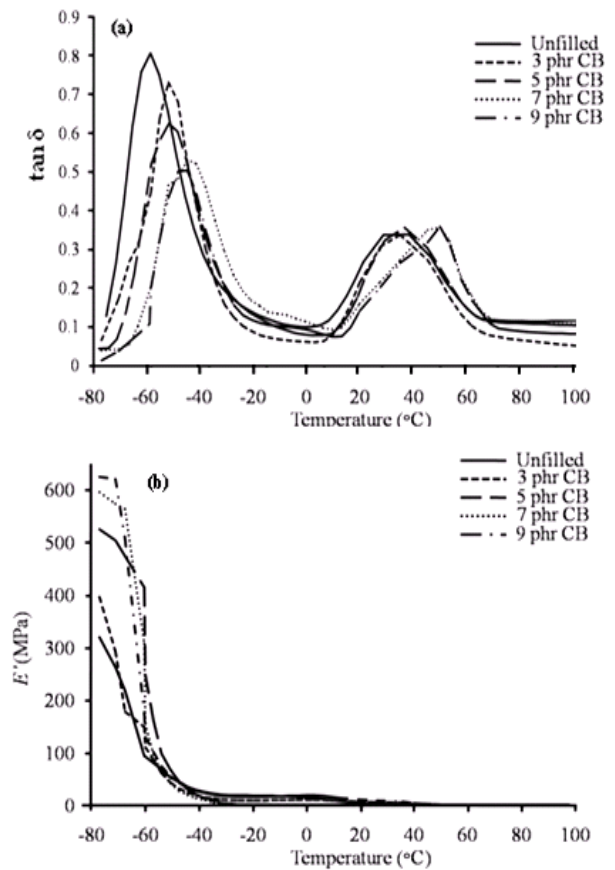


Figure 3. Representative DMA thermograms of NR/XSBR-based nanocomposites filled with different CB loadings: (a) $\tan \delta$ and (b) E' .

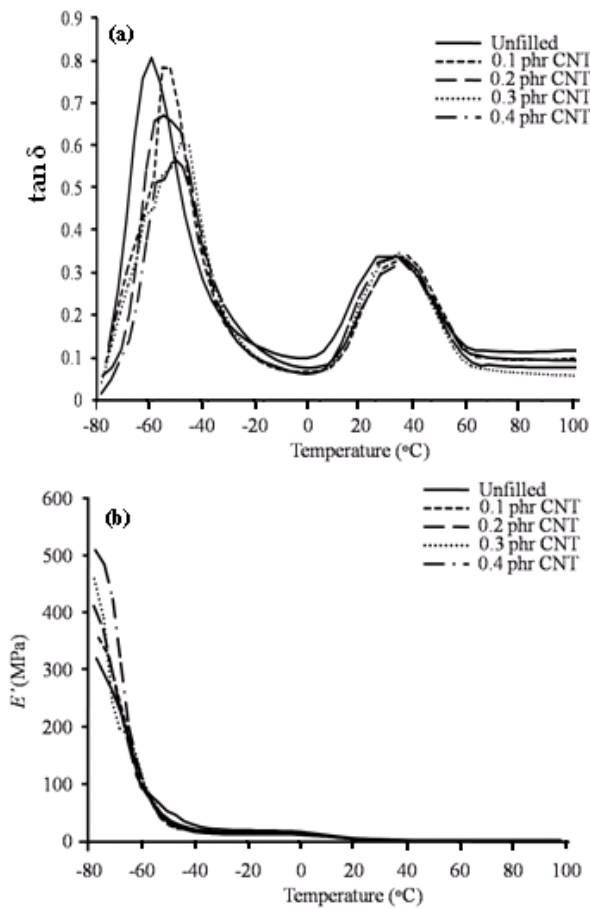


Figure 4. Representative DMA thermograms of NR/XSBR-based nanocomposites filled with different CNT loadings: (a) $\tan \delta$ and (b) E' .

Thermogravimetric Analysis (TGA)

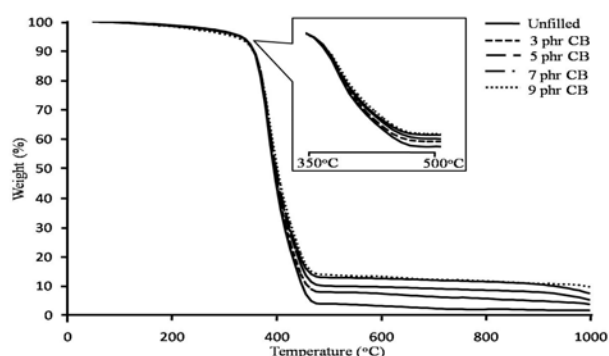
TGA was performed in order to evaluate the thermal stability of the samples. The thermal degradation curves of the neat 80/20 NR/XSBR blend and its composites filled with different loadings of CB and CNT are broadly similar to that of the neat rubber blend (Figure 5). Table 3 summarizes the values of the temperatures for the onset (T_{onset}), end set ($T_{\text{end set}}$), 50% weight loss ($T_{50\%}$) and %char obtained from the TGA curves in Figure 5. The initial degradation of the neat rubber blend occurs at about 350.4°C and continues to degrade up to 454.6°C. The thermal stabilities of the nanocomposites filled with either CB or CNT are improved, shifting the T_{onset} , $T_{\text{end set}}$, $T_{50\%}$ and % char residue

towards higher values with increasing CB or CNT loading levels (Table 3). Thus, the T_{onset} and $T_{\text{end set}}$ of the nanocomposites filled with CB (3-9 phr) increased with increasing CB loadings by about 3.9 to 12.7°C and 0.4 to 7.8°C, respectively, whilst those of the nanocomposites filled with CNT (0.1-0.4 phr) also increased with increasing CNT loadings by about 2.5 to 10°C and 0.5 to 5.7°C, respectively, as compared to the neat rubber blend. Moreover, the percentages of the final char residue in the TGA thermograms increased with increasing loading levels of CB or CNT in the nanocomposites. Given that the higher % residual char residue exceeds that of the added filler mass, this then indicates that the nanocomposites have a better thermal stability than the neat rubber blend.⁽¹⁹⁻²⁰⁾ Additionally, the higher content of the final char residue can thermally insulate the polymer by not allowing oxygen to easily enter the combustion area and so subsequently increase the flame resistance of the sample.⁽²¹⁻²⁴⁾

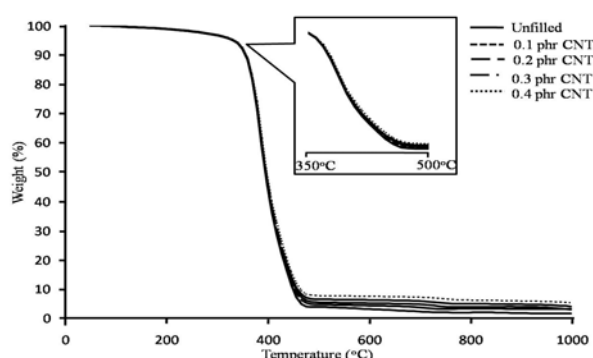
Table 3. TGA data of NR/XSBR-based nanocomposites filled with different CB or CNT loadings.

Filler content	T_{onset} (°C)	$T_{50\%}$ (°C)	$T_{\text{end set}}$ (°C)	%char
Unfilled	350.4	392.9	454.6	3.4
3 phr CB	354.3	394.8	455.0	7.8
5 phr CB	357.7	396.6	460.0	9.9
7 phr CB	360.4	397.6	461.9	12.6
9 phr CB	363.1	401.1	462.4	13.3
0.1 phr CNT	352.9	393.9	455.1	4.5
0.2 phr CNT	355.5	395.5	458.3	5.4
0.3 phr CNT	358.5	395.6	459.2	6.4
0.4 phr CNT	360.4	397.7	460.3	7.7

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(a)



(b)

Figure 5. Representative TGA curves of NR/XSBR-based nanocomposites filled with different loadings of (a) CB and (b) CNT.

Conclusions

In this work, a conventional latex compounding method was utilized to prepare NR/XSBR-based nanocomposites filled with various levels of either CB or CNT. The main focus was to investigate the effects of CB and CNT loadings on the tensile, dynamic mechanical and thermal properties of the prepared composites. The results showed that filling with either CB or CNT enhanced the tensile strength, modulus at 300% strain, storage modulus and thermal stability, but reduced the elongation at break of the NR/XSBR blend. A similar optimal tensile strength of NR/XSBR-based nanocomposites was achieved with either 5 phr of CB or 0.2 phr of CNT, and so CNT can provide a

comparable reinforcing effect to that of CB but at a very low (25-fold lower) filler loading, due to its high aspect ratio and specific surface area. The addition of either CB or CNT to the NR/XSBR blend effectively enhances the char formations and consequently improves the flame retardant of the samples. Moreover, the DMA results confirmed that loading with CB or CNT fillers both stiffened the NR/XSBR-based nanocomposites.

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