Enhanced Properties of Rubber Blends with Multi-Walled Carbon Nanotubes and Carbon Black

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Abstract

Natural rubber (NR) and styrene-butadiene rubber (SBR) were blended with Multi-walled carbon nanotubes (MWNTs) and carbon black (CB) as reinforcing fillers by a two-roll mill. The vulcanized NR/SBR rubber with different loading percentages of 1, 3, 10 phr (parts per hundred rubber) MWNTs were also compared to NR/SBR reinforced with 40, 45, 50 phr CB. The filler content in the compositions of 75/25 (NR/SBR) showed the short cure time, enhanced scorch time and cure rate index (CRI). MWNTs and CB increased the tensile modulus and tear strength of rubber blend. Increased filler loading of MWNTs and CB gave higher modulus and strength. As a result, combined application of NR/SBR rubber blend has improved the technological, mechanical, viscoelastic behavior of the obtained elastomeric materials compared to the samples using a single rubber.

KEYWORDS: Rubber blends; Multi-walled carbon nanotubes; Carbon black

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Introduction

Natural Rubber (NR) is a growing market in both global automotive and medical device industries. NR has good resilience, high strength, outstanding resilience, low compression set, resistance to wear and tear, and good electrical properties. For these reasons, NR is usually used in a wide range of applications [1, 2] but NR is very sensitive to heat oxidation because of the carbon-carbon double bonds in its chains. Furthermore, NR has low tensile strength and modulus and poor creeping characteristics unless highly vulcanized [3]. NR and styrene-butadiene rubber (SBR) have been blended for the complex shaped product which may be more easily fabricated during production [4, 5]. The blend of NR either with Polybutadiene (butadiene rubber BR) or Styrene-butadiene rubber (SBR) is widely used in tread compound and has become desirable and commercial interest.

A blending of the polymer is a mixture of two or more polymers that have been blended together to create a new material with different physical properties [6]. The polymer blend is a useful technique for the preparation and developing materials with properties superior to those of individual constituents. It is important especially from an industrial point of view to control the state of mixing of polymer blends [4, 5]. The properties of the blends can be manipulated according to their end use by correcting the selection of the component of polymers [6]. An adequate polymer blend process requires information and understanding of the blend behavior under production conditions. The knowledge of the correlation among melt viscosity, elasticity, pressure, and the process temperature is important for the design appropriate process equipment; and for assessment of the optimum process conditions to produce materials that have properties which are required [7].

They require reinforcing fillers to develop their optimum tensile strength and tear resistance. In the latter instance, the fillers are intentionally added to the polymer systems. Fillers not only reduce the cost of the material but also improve the mechanical and dynamic properties of the compounds [8]. Reinforcing fillers for elastomers include carbon black, silica, clay, plastics, and glass fibers. Carbon black, the commonly used reinforcing filler modifies the mechanical, electrical and aging properties [9]. Great interest has recently developed in the area of nanostructured carbon materials. Carbon nanostructures (CNS) are becoming commercially important with interest growing rapidly over the decade or so since the discovery of buckminsterfullerene, carbon nanotubes, and carbon nanofibers. Carbon nanotubes (CNTs) exhibit unique mechanical, electronic and magnetic properties, which have caused them to be widely studied [10]. This study, we developed an efficient NR/SBR mixing approach to disperse fillers well in rubber blend and carried out to investigate the effects of NR/SBR content, different fillers and filler loadings on the properties of the rubber composites. The fillers used were Multi-walled carbon nanotubes (MWNTs) and carbon black. We studied the vulcanizing mechanism: the cure time, scorch time and mechanical properties: tensile strength and crosslink density in rubber blend. Besides, we fabricated a series of novel rubber products and wide application of the rubber composites, and improve some fundamental understanding.

Materials and Methods

Materials

The multi-walled carbon nanotubes (MWNTs) was supplied by Chengdu Organic Chemicals Co., Ltd. Carbon black (Furnace black, N-330) was purchased from Polymer Innovation Co., Ltd. Natural rubber (RSS-3) was purchased from Hatyai Rubber Market, Thailand. Styrene-Butadiene Rubber (SBR-1502) that contents 23.5% bound styrene. Mercapto benzothiazole sulphenamide (MBTS), Diphenyl guanidine (DPG), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), Zinc oxide (ZnO), stearic acid and sulfur were procured from standard local suppliers.

Compound

A typical composition of the rubber blend composites was prepared by employing a NR matrix with uniform dispersion of MWNTs and carbon black throughout, is listed in Table 1. The MWNTs was added in amounts 1, 3, 5 and 10 parts per hundred of rubber (phr). The carbon black (CB) was added in amounts 40, 45, 50 phr.

Table 1 The composition of the rubber blends components.

Ingredients	Amount (phr)	
(NR)/(SBR)	75/25, 50/50, 25/75	
Zinc Oxide (ZnO)	3	3
Stearic Acid	2	2
Accelerators(MBTS+DPG)	1.5	1.5
Antioxidant (6PPD)	1	1
Sulphur	2	2
MWNTs	1, 3, 5, 10	-
CB	-	40, 45, 50

The ingredients were homogeneously mixed on a two roll mill. The duration of the mixing process was about 20 min for each ratio, then stored for 16 h before testing. The distinct cure time at 160 °C by a moving die rheometer MDR 2000 is in accordance with ASTM D5289-95 test method.

The rubber compounds were vulcanized at 160 °C on a hot press. The thickness of the rubber about 2 mm, according to the ASTM D412-80 standard testing method. The dumbbell and crescent test pieces were prepared for physical testing (300% modulus, elongation at break and tear resistance tested) following ASTM D412-68 and 624-54. At least five specimens were prepared for each case to obtain the mechanical properties of the rubber composites. Hardness was measured using a hardness testing machine according to ASTM D2240.

Results and Discussion

Cure Characterization Introduction

Cure rate index (CRI) is a measure for the rate of vulcanization based on the difference between optimum vulcanization and incipient scorch time [11]. The curing rate index (CRI) of the compounds cured with the same level of curative was calculated according to the equation as shown below:

$$CRI = \frac{100}{[t_{90} - t_{S2}]} \quad (1)$$

where t_{90} is the optimum cure time and t_{S2} is the scorch time. It can be seen from Fig. 1 that CRI decreased with increasing SBR loading. Table 2 shows a comparison of the curing time of CB/NR/SBR and MWNTs/NR/SBR composites at various concentrations of fillers. It was found that the rubber blend (75/25) showed the shortest cure time and the curing time decreased with increasing of CB and MWNTs. The curing time increased with increasing of SBR loading. The curing time of MWNTs/NR/SBR composite was higher than those of CB/NR/SBR composites; it tends to increase when the fillers content is more than 45 phr of carbon black due to the decrease in crosslink density as well as poor filler-rubber interaction.

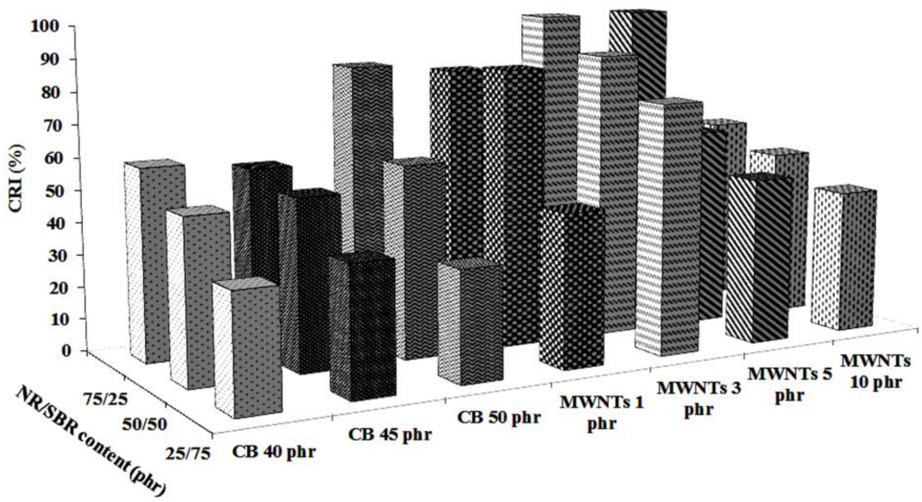


Fig. 1 Cure rate index of MWNTs/NR/SBR and CB/NR/SBR composites

The scorch time or time to incipient cure is a measure of the time at which vulcanization begins. The variations of scorch time of CB/NR and MWNTs/NR composites at various concentrations of fillers were shown in Table 1. It can be seen that the scorch time of MWNTs/NR/SBR composites was longer than those of the CB/NR/SBR.

Mechanical properties

The effect of different fillers and filler content on the tensile strength of the rubber blend is shown in Fig. 2. It was found that loading 45 phr of carbon black and 3 phr of MWNTs produced products with good tensile strength. The tensile strengths of the carbon black-filled rubber blend increased at the beginning and reached an optimum value when the carbon black filler content was 45 phr, then, the tensile strengths decreased with further increases in the carbon black loading. The initial increase in the tensile strength resulted in an increase in carbon black loading. The tensile strengths of the MWNTs–filled rubber blend increased at the beginning and reached optimum value when the MWNTs filler content was 3 phr, then, the tensile strengths decreased with further increases in the MWNTs loading. It could be explained by the reinforcing effect of fine filler and also by the increase in the crosslinking density of the rubber blend. The negative effect on the tensile strength observed at high filler loadings could be explained by the agglomeration of the filler [12].

Table 2 The effect of carbon black and MWNTs content on the cure time, scorch time and crosslink density of rubber blend at various quantities of fillers.

Reinforcement	NR/SBR (phr)	Cure Time (min)	Scorch Time (min)	Crosslink Density (10^{-4}) (mol cm^{-3})
CB 40 phr	25/75	3.40	0.56	1.41
	50/50	2.42	0.42	1.70
	75/25	2.07	0.38	1.57
CB 45 phr	25/75	3.07	0.51	1.82
	50/50	2.34	0.43	1.57
	75/25	2.15	0.37	1.38
CB 50 phr	25/75	3.48	0.53	1.40
	50/50	2.14	0.45	1.66
	75/25	1.53	0.36	1.50
MWNTs 1 phr	25/75	3.41	1.28	7.56
	50/50	2.19	1.02	6.55
	75/25	1.78	0.53	5.33
MWNTs 3 phr	25/75	2.56	1.26	7.24
	50/50	1.82	0.58	7.24
	75/25	1.48	0.46	6.38
MWNTs 5 phr	25/75	3.46	1.17	7.00
	50/50	1.86	0.39	7.09
	75/25	1.39	0.41	7.19
MWNTs 10 phr	25/75	3.51	1.26	7.47
	50/50	2.65	0.87	9.92
	75/25	2.11	0.41	6.06

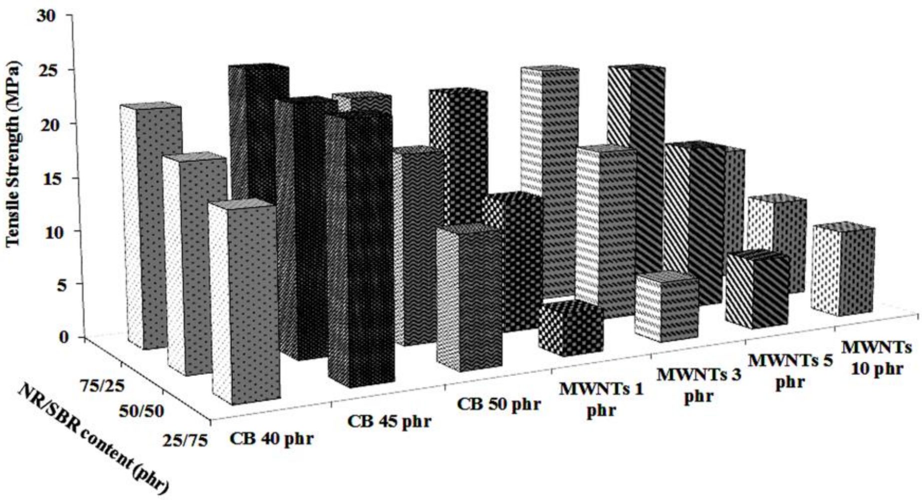


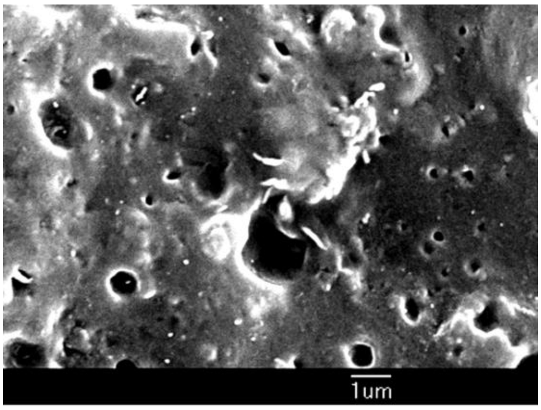
Fig. 2 The tensile strength of natural rubber composite at various quantities of fillers

Morphology properties and dynamic mechanical measurements

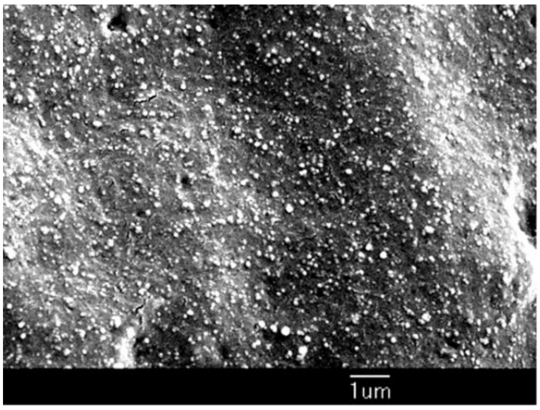
The structure of filler and the state of their dispersion in the NR/SBR blend were visualized using scanning electron microscopy. It can be observed from Fig. 5 that the filler is dispersed homogeneously in the rubbery matrix. The protruding dots in Figure 3 also suggest that the embedded filler were wrapped by the polymeric materials. Closer examination of the nanotubes reveals a thicker layer of rubber that seems to cover the filler surface. Temperature dependence on the dynamic mechanical properties storage modulus (E') of MWNTs/NR/SBR is shown in Fig. 4. It can be seen that the known increase in the storage modulus with the filler incorporation in the matrix. The peak height decreases considerably with higher MWNTs content. This behavior also indicates the strong reinforcement efficiency with only low content of MWNTs [13].

The temperature influence on the storage modulus of the NR/SBR rubber blend was evaluated in this section. Fig. 4 illustrates the influence of temperature on the storage modulus of the NR/SBR rubber blend at different filler contents. It was found that with an increase in temperature the storage modulus of samples decreases which are associated with the glass transition phenomenon of the elastomer chains. The value of the storage modulus increases as well with increasing filler loading. The distribution of fillers in the different phases of filled blends is estimated from the height of the local maxima of the loss modulus in the glass transition regime. Thereby, a linear increase of the maximum value of the loss modulus with rising NR/SBR rubber blends (75/25) is exploited that relates the enhanced energy dissipation of filled rubbers to the internal friction of the filler particles.

The influence of phase morphology and MWNTs distribution on energy storage and dissipation during dynamic excitations of rubber blends is discussed. The distribution of MWNTs in the different phases of filled blends is estimated from the height of the local maxima of the storage modulus in the glass transition regime. Thereby, a linear increase of the maximum value of the loss modulus with rising MWNTs concentration is exploited that relates the enhanced energy dissipation of filled rubbers to the internal friction of MWNTs particles. Results on MWNTs/NR/SBR blends indicate that MWNTs is preferably located in the NR phase. The concentration of MWNTs in the SBR phase is found in the case of MWNTs/NR/SBR rubber blends (10/75/25), as extensively described by NA. Yunus et al. [14]. More physical or chemical contacts between filler and the rubber matrix can reinforce the polymer matrix, compared with the rubber blend without filler. Modification of rubber using filler improves the vulcanization, mechanical and dynamic properties of rubber blend.

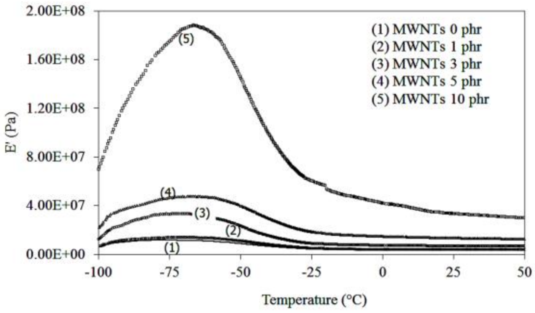


(a)



(b)

Fig. 3 SEM images of (a) MWNTs (3 phr) and (b) CB (45 phr) filled NR/SBR blends (75/25)



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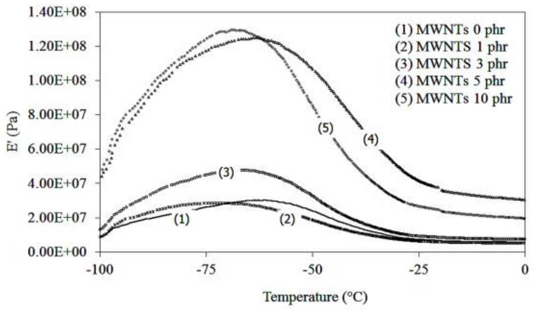

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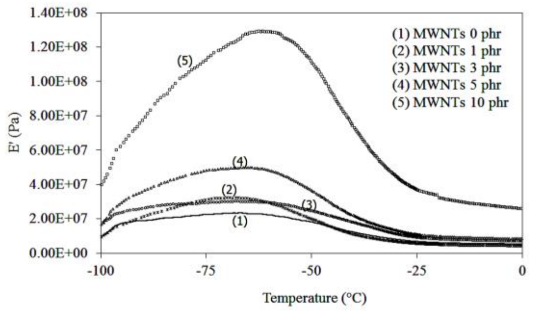

(c)

Fig. 4 Storage modulus E' as a function of the temperature for NR/SBR rubber blend at (a) 75/25, (b) 50/50, (c) 25/75 phr with MWNTs 1,3,5 and 10 phr

Conclusion

The rubber composites of natural rubber reinforced with Multi-walled carbon nanotubes (MWNTs) and carbon black were prepared by mechanical compounding. It was found that loading 45 phr of carbon black and 3 phr of MWNTs produced products with good tensile strength. CB/NR/SBR showed a maximum initial tensile strength at 45 phr of carbon black and 75/25 of NR/SBR while the MWNTs/NR/SBR showed increase tensile strength at 3 phr of MWNTs content. Finally, due to the high reinforcing activity of the Multi-walled carbon nanotubes as compared with carbon black, the special application of this filler can be extended to many ways where a large loading of carbon black are being used to get a high performance while a small loading of Multi-walled carbon nanotubes are also being used to get a high performance.

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