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Material properties

Mechanical and electrical properties of natural rubber and nitrile rubber blends filled with multi-wall carbon nanotube: Effect of preparation methods

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ABSTRACT

Carbon nanotube (CNT)/NR masterbatches prepared by predispersing and conventional methods were mixed with NBR for preparing CNT-filled 50/50 NR/NBR blends. The amount of CNT in the blends was varied from 0 to 6 phr. At a given CNT loading, hardness, modulus, tensile strength and tear strength of the blends containing the masterbatches prepared by the predispersing method were significantly higher than those prepared by the conventional method. This was simply due to the better CNT dispersion in the blends. Additionally, dynamic mechanical results showed that the maximum tan δ of the vulcanizates containing the masterbatches prepared by the predispersing method was lower than that of the corresponding conventional samples. This behaviour indicated the stronger reinforcing efficiency when the masterbatch prepared by the predispersing method was utilized. In addition, the volume resistivity of the P blends was lower than that of the corresponding C blend by about 2 orders of magnitude when only 2 phr of CNT was added. Moreover, thermal conductivity of the P blend having 4 phr of MWCNT was 1.7 times higher than that of the corresponding sample prepared by the conventional method.

1. Introduction

Rubber blending is commercially important because it gives a balance of properties which one rubber alone cannot provide [1]. Blend of natural rubber (NR) and nitrile rubber (NBR) imparts rubber with a balance in tensile strength and oil resistance [2–4], while the other mechanical properties of the blend such as tear strength and abrasion resistance can be improved by the addition of reinforcing fillers [3–6]. Among reinforcing fillers, carbon nanotubes (CNTs) are currently attractive because of their excellent mechanical, thermal and electrical properties [7,8]. Thus, the incorporation of CNT into rubber is expected to impart the rubber composites with properties which are suitable for producing electromagnetic interference (EMI) shielding products, such as EMI O-rings and seals [9–15]. Generally, CNT can be divided into two main types single-wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT). The MWCNT are frequently used in rubber composites because they gives higher electrical conductivity than SWCNT at the same degree of CNT dispersion [16,17]. However, previous studies have shown that dispersion of MWCNT in rubber matrix is rather poor because they tend to form highly entangled agglomerates like felted thread, resulting in poor mechanical and electrical properties [18,19]. Recently, many methods have been

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adopted to improve dispersion of CNT [18–23]. Villmow and coworkers [21] attempted to enhance dispersion of the MWCNT in a poly(lactic acid) matrix by using a twin-screw mixer having high mechanical shear [21]. However, this process brings about a serious breakage of the MWCNT leading to a decrease in length and effective aspect ratio, and a consequent decrease in electrical conductivity of the composite [21]. Yue reported that the addition of MWCNT dispersed in organic solvent by ultrasonication into HNBR results in a significant improvement of the mechanical and electrical properties when only 2 phr MWCNT is added [22]. In addition, incorporation of MWCNT suspension, prepared by using the ultrasonic process, into 50/50 SBR/BR blend gives higher mechanical properties and electrical conductivity than the corresponding blend prepared by conventional mixing method due to improvement of MWCNT dispersion [18,20].

This research aims to investigate the mechanical, dynamic, thermal and electrical properties of 50/50 NR/NBR blends. Blends with various MWCNT loadings were prepared by mixing NBR with MWCNT/NR masterbatches prepared by two different methods, and their properties were determined.

2. Experimental

2.1. Materials

Nitrile rubber (KRYNAC® 3345 F) with acrylonitrile content of 33 wt% and natural rubber (STR 5L) were purchased from Caldic (Thailand) Ltd. (Bangkok, Thailand) and Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. (Samutprakarn, Thailand), respectively. CNT used as filler was MWCNT (Nanocyl™ NC7000) bought from Nanocyl S.A. In. (Sambreville, Belgium). The activators consisting of stearic acid and zinc oxide (ZnO) were obtained from Chemmin Co., Ltd. (Samutprakarn, Thailand). N-tert-butyl-benzothiazole sulfenamide (TBBS) and tetrabenzylthiuram disulfide (TBzTD) used as the accelerators were purchased from Reliance Technochem Co., Ltd. (Bangkok, Thailand). Antioxidant used in this work was N-isopropyl-N′-phenyl-p-phenylenediamine (IPPD) obtained from MDR International Co., Ltd. (Bangkok, Thailand). Elemental sulfur (S_8) was purchased from The Siam Chemical Public Co., Ltd. (Bangkok, Thailand). A non-ionic surfactant (Nonidet P40) and ethyl alcohol were obtained from RCI Labscan Co., Ltd. (Bangkok, Thailand).

2.2. Preparation of CNT/NR masterbatch

CNT/NR masterbatches containing various CNT contents (from 0 to 12 phr) were prepared by using the predispersing and conventional methods. For the predispersing method, 15 %w/w_{CNT} of the non-ionic surfactant was added to a mixture of CNT and ethanol. Then, the mixture was agitated gently by using an ultrasonic bath (B2510-MTH; Branson ultrasonic corporation, Danbury, USA) for approximately 2.5 h. Thereafter, the mixture was mixed with masticated NR on a two-roll mill (LRM150; Labtech engineering Co., Ltd., Samutprakarn, Thailand) at 80 °C for 10 min. For CNT/NR masterbatches prepared by using the conventional method, the CNT powder was mixed directly into NR on the two-roll mill using the same mixing conditions. The CNT/NR masterbatches obtained from the two methods were then used to prepare 50/50 NR/NBR blends.

2.3. Preparation of 50/50 NR/NBR blends and compound testing

The formulations of all NR/NBR compounds are shown in Table 1. 50/50 NR/NBR blends containing the CNT/NR masterbatches prepared from the predispersing and conventional methods were denoted as “P” and “C”, respectively. The number following the letters indicates the amount of CNT in the blends. Each CNT/NR masterbatch and other ingredients, except the curatives, were mixed with NBR by using a laboratory-size internal mixer (Brabender Plasticorder R2000; Brabender, Duisburg, Germany) at a temperature of 50 °C, a rotor speed of 50 rpm and a fill factor of 0.7. The total mixing time was 8 min. After discharging, the compound was sheeted on a two roll-mill (LRM150; Labtech engineering Co., Ltd., Samutprakarn, Thailand) for 1 min. Then, the curatives were added and mixed for 5 min. Thereafter, 10 end-roll passes were made. Later, cure characteristics of all compounds were determined by using a moving die rheometer (TechPro rheotech MD+; Alpha Technologies, Ohio, USA) at 150 °C. Then, the compounds were vulcanized at 150 °C in a compression mold according to their cure time (t_{c100}) to produce sheets and test pieces which were stored at room temperature for at least 24 h before determination of properties.

2.4. Mechanical property measurement

Hardness of the vulcanizates was measured using a Shore A durometer (model H17A, Wallace Instruments, Cambridge, UK) based on ISO 7619-1. Specimens for tensile and tear tests were prepared from compression molded sheets having thickness of about 1 mm and tested by using a universal tester (model 5566; Instron Corporation, Massachusetts, USA) in accordance with ISO 37 (die C) and 34-1 (crescent test piece), respectively. The specimens were tested by using a 1 kN load cell and a crosshead speed of 500 mm/min. The values of tensile and tear properties were the average of 4–5 specimens.

Table 1
NR/NBR compound formulations.

Ingredient	Amount (phr[a])									
	P0	P2	P4	P5	P6	C0	C2	C4	C5	C6
NR	50	–	–	–	–	50	–	–	–	–
NBR	50	50	50	50	50	50	50	50	50	50
CNT/NR masterbatch[b]	–	52	54	55	56	–	52	54	55	56
Stearic acid	1	1	1	1	1	1	1	1	1	1
Zinc oxide	3	3	3	3	3	3	3	3	3	3
IPPD	1	1	1	1	1	1	1	1	1	1
TBBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TBzTD	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Sulfur	2	2	2	2	2	2	2	2	2	2

[a] Parts per hundred parts of rubber.

[b] Masterbatches prepared from the predispersing and the conventional methods were used to prepare P and C compounds, respectively.