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Material Properties

Effect of preparation methods and carbon black distribution on mechanical properties of short pineapple leaf fiber-carbon black reinforced natural rubber hybrid composites

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ABSTRACT

The aim of this work is to improve the performance of natural rubber reinforced with a hybrid of pineapple leaf fiber with carbon black. When there are multiple components to be mixed into a rubber matrix, mixing can be carried out in more than one way. Thus, in this study, the effects of preparation method and the resulting carbon black distribution on the mechanical properties of the hybrid composite were evaluated. Pineapple leaf fiber (PALF) and carbon black contents were fixed at 10 parts (by weight) and 30 parts (by weight) per hundred parts of rubber (phr), respectively. In order to improve the dispersion, PALF with rubber was prepared as a masterbatch. Carbon black was added to the compound either as a single portion or as two separate portions, one in the PALF masterbatch and the other in the main mixing step. It was found that, despite using the same final compound formulation, the mixing scheme significantly affected the medium strain region of the vulcanizate stress-strain curve. No stress drop in this strain region was observed for the two-step mixing scheme. Models for composites with different preparation methods are proposed and discussed.

1. Introduction

Generally, particulate fillers are used in rubber composites to improve and modify the mechanical properties. The presence of certain types of filler usually leads to increases in modulus, strength, abrasion and tear resistance [1,2]. These are known as reinforcement fillers and good examples are carbon black and silica. Short fiber reinforced rubber composites can be used where large deformation is not desirable. Such applications include, for example, hoses, belts, tires and seals.

In addition to many types of synthetic fibers, natural fibers such as flax, jute, sisal, oil palm, bamboo and pineapple leaf have been used as the reinforcing component in rubber composites [3–6]. Generally, the mechanical properties of a composite depend on those of the matrix and such fiber properties as strength, dispersion, aspect ratio, content and orientation. The mechanical properties also depend on the mechanism of stress transfer from the matrix to the fiber. Since the mechanical properties of pineapple leaf fiber (PALF) stand out among natural fibers and are close to those of glass and aramid fibers, it is very attractive as a rubber reinforcement. Our research group has published the use of short PALF for the reinforcement of nitrile rubber (NBR) [7–9] and natural rubber (NR) [10–12]. The level of improvement in mechanical properties obtained in NR is less than that obtained in NBR composites due to greater difference in polarity between the matrix rubber and the reinforcing fiber. It has been shown that, by reducing the NR molecular weight, significant improvement of mechanical properties in the low strain regions can be obtained.

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However, the use of low molecular weight NR as the matrix may be considered disadvantageous as the mechanical properties of the final composites at very high strains remain rather poor. This latter point can be overcome by the use of a hybrid particulate filler [9].

Therefore, the aims of this study are to avoid using low molecular weight NR as the matrix with a PALF/NR masterbatch and to improve the vulcanizate high strain properties by using carbon black as hybrid filler. Preparation methods are designed such that normal NR is the matrix and the dispersed PALF is surrounded by low molecular weight NR to provide better stress transfer. In addition, rather than charging all carbon black in one step as in our previous work, an additional step in carbon black incorporation is introduced to make certain that carbon black is evenly distributed in both normal and low molecular weight NR phases. Mechanical properties of the vulcanizates are compared and their representative models proposed.

2. Experimental

2.1. Materials

PALF: Pineapple leaves were collected from cultivation areas in Ban Yang District, Amphoe Nakhon Thai, Phitsanulok Province, Thailand. The fresh leaves were cut across the long axis to be 6 mm long before being fed into a disc milling machine following the milling technique developed in our laboratory [13]. The soft tissue of the leaves and fiber bundles were crushed into paste. The paste was dried and sieved to separate PALF from non-fibrous materials. The yield, shape, and size distribution PALF prepared by this method have been reported elsewhere [13].

NR: Natural rubber was STR5L grade purchased from MBJ Enterprise Co. Ltd. Thailand.

Rubber chemicals: Carbon black was N330 grade manufactured by Thai Carbon Black Public Co., Ltd. Peptizer was Struktol A60, Struktol, USA. Other rubber chemicals were commercial grade.

2.2. Preparation of PALF masterbatch

The PALF masterbatch (MBF) containing 30% wt of PALF in NR matrix was prepared on a laboratory two-roll mill (Nishimura, Tokyo, Japan). NR was first masticated with peptizer for 1 min before adding PALF. The total mixing time was 16 min.

2.3. Preparation of CB masterbatch

Carbon black (CB) masterbatch containing 40% wt of carbon black was prepared with a small scale internal mixer (Brabender Plasticorder R2000; Brabender, Duisbury, Germany) at a temperature of 50 °C, a rotor speed of 40 rpm and a fill factor of 0.7. The total mixing time was 15 min.

2.4. Preparation of PALF-carbon black masterbatch

PALF-carbon black masterbatch (MBFCB) containing PALF in a carbon black filled NR matrix was prepared on a laboratory two-roll mill. First, the carbon black masterbatch was diluted with NR to give a matrix containing 30 phr carbon black. This mastication was continued for 30 min. Then, PALF was added to this carbon black filled NR matrix with the ratio of PALF:matrix set at 30:70. The mixing was continued for another 10 min.

2.5. Preparation of rubber composites

Rubber compounds containing fixed amounts of PALF, carbon black and chemicals were prepared on a laboratory two-roll mill. Compound formulations are displayed in Table 1. Mixing was carried out by first masticating the rubber for 2 min in all cases, except 16 min for NR(16)10F, before the PALF was introduced. This was followed by the carbon black and rubber chemicals. Mixing was carried out at room temperature with a total mixing time of 15 min after mastication. PALF was either added directly on the mill during mixing (NR10F) or pre-dispersed by preparing a masterbatch as described above (NR10MBF). For those compounds containing carbon black, it was added using two different schemes. In one scheme, carbon black was added in a single portion and the code name is NR10MBF-30CB. In the other, carbon black was added in two separate portions, i.e. one in the PALF masterbatch preparation step and the other in the main mixing step. The code name for this composite is NR10MBFCB-30CB. After the mixing of each compound was complete, the compound was collected as sheets using a narrow nip to align the fiber in the machine direction [7]. The rubber compounds were vulcanized in a hydraulic press at approximately 10 MPa and 150 °C using a 1 mm thickness mold. The compression time was set according to t_{c90} (the time at which 90% of cure has taken place) obtained from a Moving Die Rheometer (MDR). The test specimens were stored at room temperature for least 24 h before their properties were determined.

2.6. Characterization

Cure behavior was studied with a Moving Die Rheometor (MDR) (Rheo TECH MD+, Alpha Technologies, Akron, USA). Tensile properties, hardness and tear strength of cured composites were measured according to ISO 37 (Type C), ISO 7619 and ISO 34 (Type B), respectively. Test specimens were cut in the longitudinal fiber orientations. The tests were carried out on a universal testing machine (Instron 5569, High Wycombe, UK) fitted with a long travel contact-style extensometer. A crosshead speed of 500 mm/min and a 1 kN load cell were used. Tensile strength, moduli or stresses at 10%, 50%, and 100% strains, elongation at break and tear strength were determined. Hardness was measured with a Shore A durometer (Wallace, H17A). The mean value of at least 5 test pieces is reported for each property. The tensile fracture surfaces of the composites were observed with a scanning electron microscope (SEM) (Hitachi Tabletop Microscope; model TM 1000, Japan).

3. Results

3.1. Cure characteristics

The cure characteristics of the different rubber compounds are displayed as torque-time curves in Fig. 1. Numerical values for these are tabulated in Table 2. When PALF was added to the compounds, the scorch time decreased slightly while the maximum torque increased significantly over that of NR. The maximum torques for NR(16)10F and NR10MBF, which contain the same amount of PALF (10 phr), are comparable.

When carbon black was added to the compound (NR10MBF-

Table 1
Formulations of mixtures.

Compounds/Ingredient	Amount (phr)						
	NR	PALF	CB	ZnO	Stearic acid	CBS[a]	Sulfur
NR10F	100	–	–	5	2	1	2
NR(16)10F	100	10	–	5	2	1	2
NR10MBF	100	10	–	5	2	1	2
NR10MBF-30CB	100	10	30	5	2	1	2
NR10MBCBF-30CB	100	10	30	5	2	1	2

[a] CBS = N-Cyclohexyl-2-benzothaiazolesulfenamide.