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Material Properties

Curing characteristics, tensile properties and morphology of palm ash/halloysite nanotubes/ethylene-propylene-diene monomer (EPDM) hybrid composites

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Palm Ash (PA)/Halloysite Nanotubes (HNTs)/Ethylene-Propylene-Diene Monomer (EPDM) hybrid composites were prepared by incorporation of hybrid nanotubes into EPDM rubber matrix on a laboratory size two-roll mill. The effects of palm ash/halloysite nanotube weight ratio on the curing characteristics, tensile properties and morphology of the hybrid composites were studied. Curing time (t_{90}), scorch time (t_2), maximum torque, tensile strength and tensile modulus (M100 and M300) were increased whereas elongation at break was decreased with increasing halloysite nanotube content. Morphological studies of tensile fracture surfaces of PA/HNTs/EPDM hybrid composites indicated that HNTs has better adhesion to the EPDM matrix as compared to palm ash.

1. Introduction

The concept of reinforcement for rubbers is complex but, generally, reinforcement is added to rubbers to enhance certain properties and at the same time reduces the cost of the rubber compound [1]. Currently, there are more than 100 types of reinforcement that have been reported in the literature, however, only a few have been commercialized and used extensively [2]. The principal advantage of composite materials lies in the possibility of combining physical properties of the constituents to obtain enhanced properties, for example physical, mechanical or optical [3]. The great demand for composite materials in many fields has brought to the forefront the very complex problem of developing new types of composite material in which reinforcement from two or more types of filler/fibres is combined to produce so called hybrid composite materials [4]. The incorporation of hybrid fillers into polymer matrix has been a popular field of research in recent years [2,5–10].

The Malaysian palm oil industry plays an important role as it serves as the largest palm oil producer and exporter in the world. According to the Malaysian Palm Oil Council (MPOC) [11], Malaysia currently accounts for 51% of world palm oil production and 62% of world exports. The mass production of palm oil generates solid waste, such as palm oil kernels and seeds, which are being used as fuel for a combustion process to generate steam in palm oil mills. The by product of the combustion, the ash, is highly abundant in Malaysia and the waste is either transported to an approved dump site or dumped illegally. Dumping requires large areas of land, which is a limited resource, and is an environmentally–unfriendly activity which creates many problems.

Over the years, much research had been carried out in various fields on the utilization of palm ash and oil palm fibre [6,12–15]. At the same time, in recent years Halloysite Nanotubes (HNTs) have been incorporated as a new type of reinforcing filler in polymers such as epoxies, polypropylenes and elastomers [16–22]. Halloysite is a super fine clay material with the formula ($Al_2Si_5(OH)_4.H_2O$ 1:1)

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and often occurs naturally as an ultramicroscopic hollow tube with a multi-layer wall. HNTs appear to have the same geometry as multi-walled carbon nanotubes (MWCNTs) but their unique crystal structure, low density of hydroxyl functional groups and tubular shape gives an advantage to the HNTs in terms of not forming agglomerations and ease of dispersion in a polymer matrix [16,22,23–25]. Therefore, the objective of this article is to study the potential of PA/HNTs hybrid fillers in EPDM composites. In this study, the effect of PA/HNTs weight ratio on the curing characteristics, tensile properties and morphology of PA/HNTs/EPDM hybrid composites is reported.

2. Experimental

2.1. Materials

Ethylene-Propylene-Diene Monomer (EPDM), Keltan 778Z, with 67% ethylene content and 43% ENB, and 63 ML (1 + 4) 125 °C, purchased from Bayer (M) Ltd., was used as the matrix. Palm ash was obtained from United Oil Palm Mill, Penang, Malaysia, and Halloysite Nanotubes (HNTs), (ultrafine) were supplied by Imerys Tableware Asia Limited, New Zealand. Both palm ash and halloysite nanotubes were dried in a vacuum oven at 80 °C for 24 h to expel moisture. The palm ash was then sieved with Endicott sieves (BS 410) to obtain an average particle size of 75 μm. The elemental composition of palm ash obtained with a Rigaku RIX3000 X-Ray Fluoroscence Spectrometer (XRF Spectrometer) is listed in Table 1. Halloysite nanotube particles are tubular in shape and have typical dimensions of 150 nm–2 μm long, 20–100 nm outer diameter and 5–30 nm inner diameter [16]. The elemental composition of halloysite nanotubes was as follows [26]: (wt.%) $Si\text{-}O_2$, 49; Al_2O_3, 34.8; Fe_2O_3, 0.35; TiO_2, 0.12; Na_2O, 0.25; MgO, 0.15. The other compounding ingredients used were zinc oxide, stearic acid, 2-mercapto benzothiazole (MBT), tetramethyl thiuram disulfide (TMTD), and sulphur, all of which were supplied by Bayer (M) Ltd and used as received. Toluene was supplied by Baker–Aldrich (M) Ltd.

Table 1
Elemental composition of palm ash. [27].

Component	Weight (%)
Na_2O	0.13
MgO	3.0
$A1_2O_3$	0.84
$Si\text{–}O_2$	10.0
P_2O_5	2.4
SO_3	1.8
Cl	4.1
K_2O	27.0
CaO	3.4
TiO_2	0.032
MnO	0.046
Fe_2O_3	0.29
CuO	0.012
ZnO	0.025
Br	0.011
Rb_2O	0.076
SrO	0.012
ZrO_2	Trace
C	46.0

2.2. Preparation of palm ash/halloysite nanotubes/EPDM hybrid composites

The compounding of palm ash, HNTs, EPDM and other ingredients, as shown in Table 2, was done using a conventional 160 mm × 320 mm two-roll mill model XK160. The curing characteristics of the hybrid composites, such as cure time (t_{90}), scorch time (t_2) and maximum torque, were determined by a Monsanto Rheometer MDR 2000 according to ISO 3417 at 160 °C. The compounds were later compression moulded at 160 °C based on the respective t_{90} values.

2.3. Measurement of tensile properties

Dumb-bell shaped test pieces were cut from the moulded sheets previously conditioned for 24 h at room temperature. Tensile tests were performed using an Instron Machine IX3366 at a crosshead speed of 500 mm/min according to ISO 37. Data, such as tensile modulus (M100 and M300), tensile strength and elongation at break (E_b), were obtained from the tests.

2.4. Measurement of rubber–filler interactions

Measurement of the rubber–filler interaction was determined through swelling of the composite in toluene according to ISO 1817. Test pieces with dimensions of 30 mm × 5 mm × 2 mm were prepared from the moulded sheets. Prior to the testing, the initial weight of the test pieces was recorded. The test pieces were then immersed in toluene and conditioned at 25 °C in a dark environment for 72 h. After the conditioned period, the pieces were weighed again. The pieces were then dried in an oven at 70 °C for 15 min and let cool at room temperature for another 15 min before final weighing. The Lorenz–Park equation was applied in the study of rubber–filler interaction [28]. The swelling index was calculated based on the following equation:

$$Q_f/Q_g = ae^{-z} + b$$

where subscripts f and g refers to filled and gum vulcanizates, respectively; z is the ratio by weight of the filler to the rubber hydrocarbon in the vulcanizates; a and b are constants. In this study, the weight of toluene uptake per gram of rubber hydrocarbon (Q) is calculated as follows:

$$Q = \frac{Swollen\ Weight(W_s) - Dried\ Weight(W_d)}{Initial\ Weight(W_i) - 100/Formula\ Weight}$$

Table 2
Formulation of Palm Ash/Halloysite Nanotubes/EPDM Hybrid Composites.

Materials	Composites (phr)
EPDM	100
Zinc Oxide	5
Stearic Acid	1.5
MBT	0.8
TMTD	1.5
Sulphur	1.5
Palm Ash/HNTs 30/0 (control), 20/10, 15/15. 10/20, 0/30	