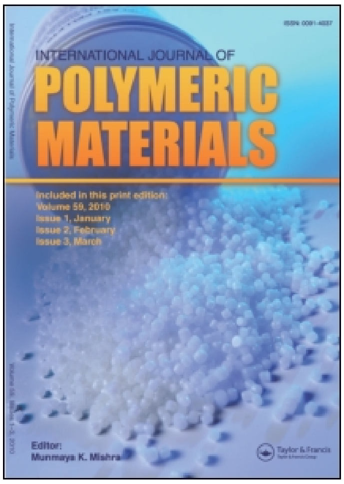

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The effect of dynamic vulcanization on mechanical properties and water absorption of silica and rubberwood filled polypropylene/natural rubber hybrid composites

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THE EFFECT OF DYNAMIC VULCANIZATION ON MECHANICAL PROPERTIES AND WATER ABSORPTION OF SILICA AND RUBBERWOOD FILLED POLYPROPYLENE/NATURAL RUBBER HYBRID COMPOSITES

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Dynamic vulcanized silica and rubberwood filled polypropylene (PP)/natural rubber (NR) hybrid composites were prepared using a Brabender plasticorder at 150°C and a rotor speed of 50 rpm for 12 minutes. The effectiveness of the dynamic vulcanization was indicated by the Brabender plastograms. The mechanical and water absorption properties of hybrid composites with different concentration of sulfur were investigated. Significant enhancement in mechanical properties, viz. tensile strength, stress at peak, Young modulus and flexural modulus were observed for dynamically vulcanized hybrid composites compared to unvulcanized hybrid composites. This has been attributed to the increase in crosslink density, which was manifested by a reduction of water absorption and increase of stabilization torque at the end of mixing stage with increasing sulfur concentration.

Keywords: dynamic vulcanization, polypropylene, natural rubber, silica, rubberwood

1. INTRODUCTION

Over the last decade, short-fiber reinforcement of plastic composites has gained considerable attention as a viable alternative to particulate filler reinforcement [1]. The growth of lignocellulosic-plastic

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composites has been attributed to the density factor of the lignocellulosic filler, in addition to other advantages such as greater deformability, less abrasiveness to expensive molds and mixing equipments, and of course, lower cost [2]. Dynamic vulcanization is a process of vulcanization of an elastomer during its melt mixing with a thermoplastic, which results in the production of a new class of materials called thermoplastic vulcanizates [3, 4]. They offer a substantial economic advantage with respect to the fabrication of finish parts. The improvement in properties resulting from dynamic vulcanization are reduced permanent set, improved ultimate mechanical properties, greater resistance to attack by fluids, improved high temperature utility, greater stability of phase morphology in the melt, greater melt strength and more reliable thermoplastic fabricability [5]. In previous works [6, 7], we have reported the use of rubberwood fibers in natural rubber compounds. Tensile modulus of the composites increases with the filler loading. The incorporation of filler reduces the elasticity of the rubber matrix, resulting in more rigid composites. However, tensile strength and elongation at break show the opposite trend. In this work the effect of dynamic vulcanization on mechanical properties and water absorption of silica and rubberwood filled polypropylene/natural rubber hybrid composites were examined. Rubberwood powder was used as a filler together with a commercial filler, *viz.* silica. It is believed that hybrid composites would enlarge the domain of applications shown by the existing conventional composites, which normally use high-density inorganic fillers, such as glass fiber, mica or silica.

2. EXPERIMENT

2.1. Materials

Polypropylene (PP) used was purchased from Polypropylene Malaysia Sdn. Bhd, Malaysia, with a melt flow index and a density of 12.0 gm/10 min and 0.903 g/cm^3 respectively. Natural rubber (SMR L) was obtained from Rubber Research Institute of Malaysia (RRIM). Rubberwood powder (consisting, of about 76% of holocellulose and 26% of lignin) was produced by grinding untreated rubberwood fibers obtained from Pan Malaysia Wood Mill (M) Ltd., Penang. An Endecotts sieve was used to obtain filler size of 270–400 mesh (38–53 μm). Silica (Vulcasil S) was obtained from Monsanto Company. All rubber chemicals were obtained from Bayer (M) Ltd., Penang.

TABLE 1 Formulation used in Dynamically Vulcanize of Silica and Rubberwood Filled PP/NR Hybrid Composites

Ingredient	% (by weight)
PP	80
NR	20
Rubberwood	20
Silica	20
Curative system:	
Zinc oxide	1.0
Stearic acid	0.4
CBS[a]	0.4
TMTD[b]	0.5
Sulfur	0, 0.5, 1.0, 1.5, 2.0

[a] N-cyclohexyl-2-benzothiazol-2-sulphenamide.
[b] Tetramethylthiuram disulphide.

2.2. Compounding and Processing

The formulation used is shown in Table 1. Natural rubber was initially preheated for one minute and subsequently melt mixing was carried out in a Brabender Plasticorder Model PLE 331 coupled with a mixer/measuring head (W50H) at a temperature of 180°C and a rotor speed of 50 rpm for 10 minutes for control blend and 12 minutes for vulcanize blends. Mixing sequence is shown in Table 2. At the end of 10 minutes for control blend and 12 minutes for vulcanize blends, they were taken out and sheeted through a laboratory mill at 2.0 mm nip setting. Samples of the composites were compression moulded in an electrically heated hydraulic press. Hot press procedure involved preheating at 190°C for six minutes followed by compressing for four

TABLE 2 Mixing Sequence of Components in Preparation of the Composites

Time (min)	Operation
0	Loading of NR
1	Rotor started
3	Addition of rubberwood and silica (filler)
5	Addition of PP
9	Addition of curatives*
12	Dump

*For control blend, total mixing time was 10 minutes without the addition of curatives.

minutes at the same temperature and subsequent cooling under pressure for another four minutes.

2.3. Testing

Tensile tests were carried out according to ASTM D 412 on a Testometric tensometer M500. 2 mm thick dumbell specimens were cut from the molded sheet with a Wallace die cutter. A cross head speed of 50 cm/min was used and the tests were performed at 25 ± 3°C. The flexural test was conducted according to ASTM D 790, that is a three point bending system, using a similar tensile test machine. The samples with dimensions of $15 \times 1.5 \times 0.3$ cm were tested at a cross head speed of 5.0 mm/min.

2.4. Water Absorption Test

Samples were immersed in distilled water at 30°C. Weights of the samples were recorded at different times. Samples were wiped with tissue paper to remove surface water before weighing. Finally the weight gain and the weight loss were calculated [8].

(a) Weight Gain

Water absorption (*i.e.*, weight gain) was determined by the following

$$\mathrm{Wg} = \frac{\mathrm{We} - \mathrm{Wo}}{\mathrm{We}} \times 100$$

where Wg = % of weight gain; We = equilibrium weight after water treatment; Wo = oven dry weight before water treatment.

(b) Weight Loss

Samples that were immersed in water were then dried at 70°C for 24 hour, after which they were cooled at the ambient temperature under normal conditions. Their final weights were taken to determine the weight loss according to the following equation:

$$\mathrm{W}_1 = \frac{\mathrm{Wo} - \mathrm{Wt}}{\mathrm{Wo}} \times 100$$

where Wt = oven dry weight after immersion in water.
Wo = oven dry weight before water treatment.
W_1 = % of weight loss.

2.5. Morphological Study

The fracture surface of the composites from the tensile test was investigated with a Leica Cambridge S-360 scanning electron microscope (SEM). The objective was to get some information regarding fibers dispersion and bonding quality between fiber and matrix and to detect the presence of microdefects, if any. The fracture ends of the specimen were mounted on an aluminum stub and sputer-coated with a thin layer of gold to avoid electrostatic charging during examination.

3. RESULT AND DISCUSSION

3.1. Brabender Curves

Figure 1 shows the Brabender torque-time curves for dynamic vulcanization of silica and rubberwood filled PP/NR hybrid composites. The explanation for the curves is as follows: NR was charged to the mixing chamber at 0 minutes (at A) and was allowed to preheat for 1 minute. Therefore, at the first minute of mixing cycle (A–B), zero torque was registered as rotor was not moving. When rotor was started at first minutes, a sudden rise in torque can be seen (B–C) due to the

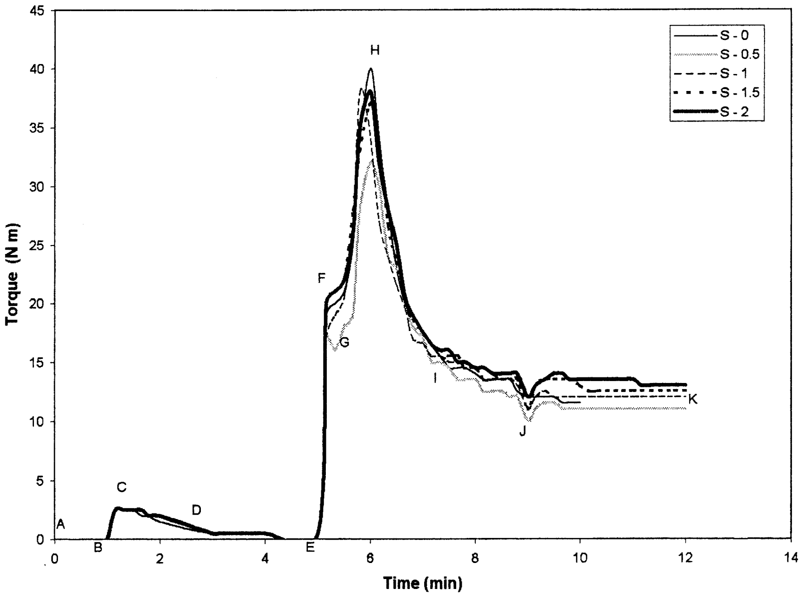

FIGURE 1 Brabender torque-time curves for silica and rubberwood filled PP/NR blends with different concentration of sulfur.

resistance created by unmelted NR. Upon melting of the NR, the viscosity decreases. This results in lowering the torque. When filler is added at third minute (at D) the torque dropped immediately. This is because rubberwood and silica powders are fine particles and they were covered by melted rubber, which acts as a lubricant (reduction in resistance to the rotor). The lower torque continued until cold and unmelted polypropylene was charged into the mixing chamber, at which time an abrupt increase in torque is registered (E–F). As the polypropylene melts viscosity again tends to decrease (G). Simultaneously free filler particles which incorporate in the polypropylene matrix, increase the viscosity of the melt (H). Upon completion of filler incorporation, viscosity of the melts begins to decrease due to higher temperature and shear (H–I). When curing agents are added, crosslinks were formed, which increase the viscosity (I–J). Higher crosslinking and a more stable network structure were formed with increasing sulfur content. Therefore, as sulfur concentration increases a higher resistance to the final equilibrium torque is registered (K). Figure 2 shows the relationship between stabilization torque and sulfur concentration. It can be seen that the stabilization torque increases with increase in sulfur concentration. This provides evidence

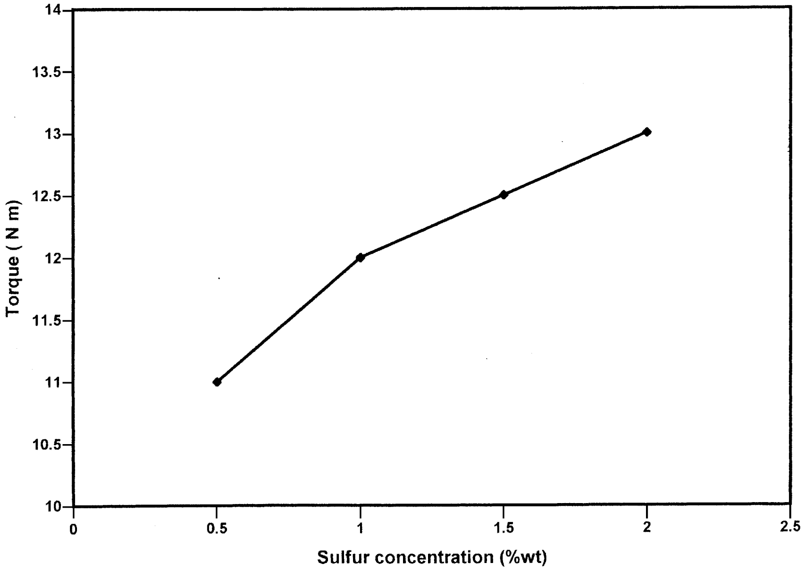

FIGURE 2 The relationship between stabilization torque and sulfur concentration.

of an increase in the crosslink formation with increasing concentration of sulfur.

3.2. Mechanical Properties

The effect of sulfur concentration on tensile strength of silica and rubberwood filled PP/NR composites is shown in Figure 3. It can be seen that the tensile strength increases with increasing sulfur concentration. This is due to the increased crosslink density at higher concentration of sulfur. The entangled rubber chains cannot slip past each other during strain, resulting in higher tensile strength. Only small portions of the crosslinked rubber chains can undergo deformation and hence relieve a portion of the applied stress. Consequently, dynamic vulcanised composites exhibit better ultimate strength. Saroop and Mathur [9] in their studies on dynamically vulcanized polypropylene/butadiene styrene block copolymer (SBS) blends, also reported that dynamic vulcanization of blends gave superior mechanical properties. However, Ha and Kim [10] reported that the tensile strength and modulus increased with increasing dicumyl peroxide (DCP) concentration in blends of EPDM (ethylene-propylene-diene terpolymer)-rich compositions but decreased with increasing

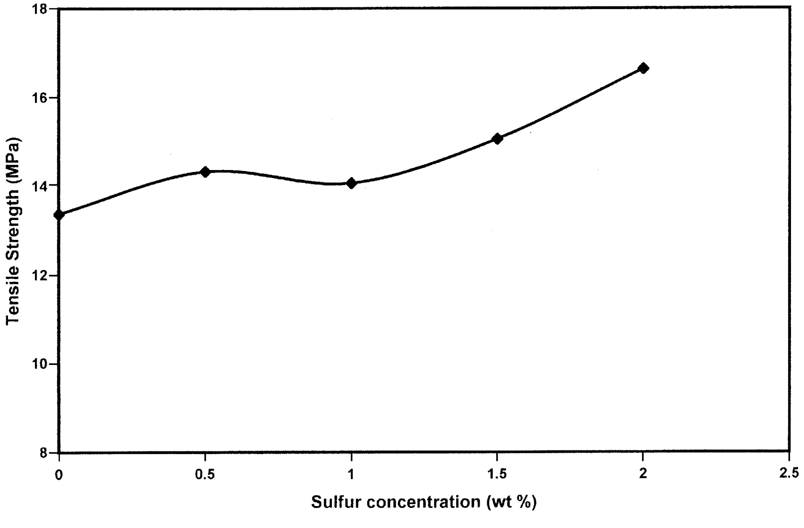

FIGURE 3 The effect of sulfur concentration on the tensile strength of silica and rubberwood filled PP/NR blend.

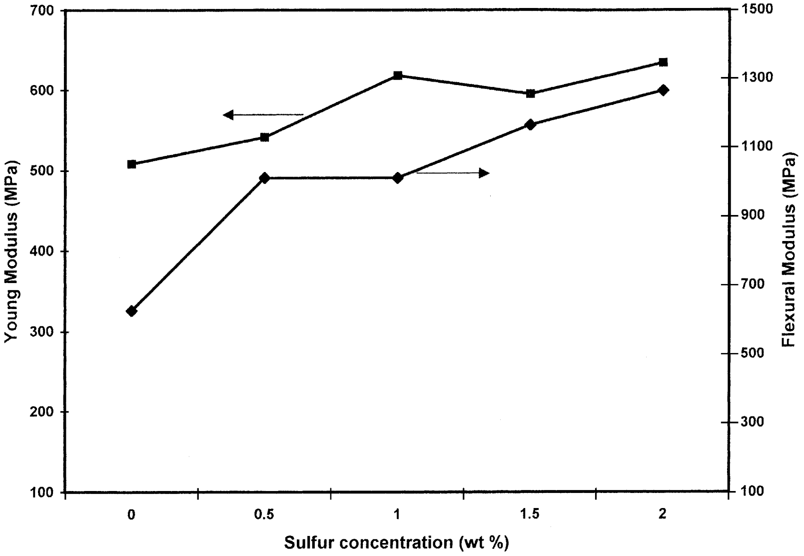

FIGURE 4 Variation of Young modulus and flexural modulus as a function of sulfur concentration.

DCP concentration in blends of PP-rich composites for dynamically cured EPDM and PP/HDPE ternary blends.

Variations of the Young modulus and flexural modulus as a function of sulfur concentration are shown in Figure 4. Both properties increase with increasing sulfur concentration, which may be due to the increased extent of crosslinking. As indicated by the water absorption data of the composites (next section) and the Brabender torque rheometer (previous section), the crosslink density increases with increasing sulfur concentration. Thus, the number of the individual macromolecular segments increases, albeit they become shorter and require a higher applied stress to cause rupture.

3.3. Water Absorption

The effect of sulfur concentration on the weight gain, Wg (water absorption), and weight loss, W_1, of silica and rubberwood filled PP/NR hybrid composites is shown in Figures 5 and 6. In Figure 5, all composites show a similar pattern of water absorption: that is, initial sharp uptake followed by gradual increase until equilibrium water content was achieved at about 25 days. However, at a similar absorption time, composites with higher concentration of sulfur show lower water absorption (weight gain, Wg). Figure 6 also exhibits that

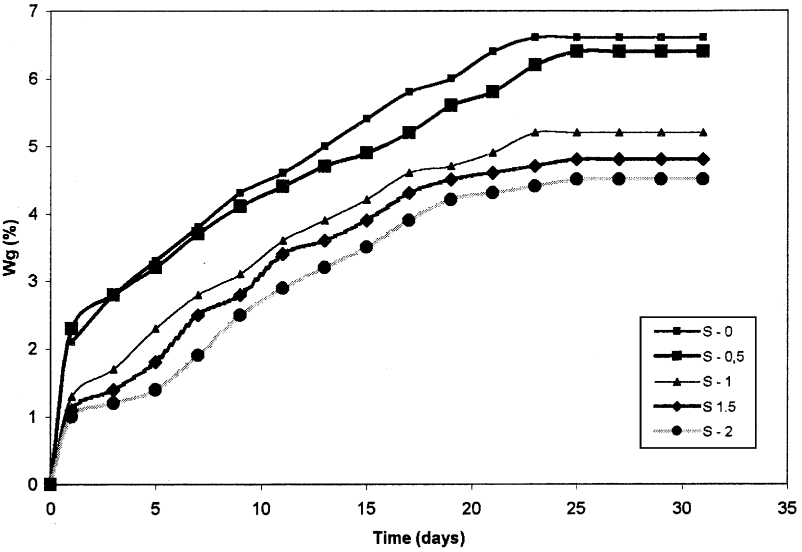

FIGURE 5 The effect of sulfur concentration on the weight gain of rubberwood filled PP/NR blend.

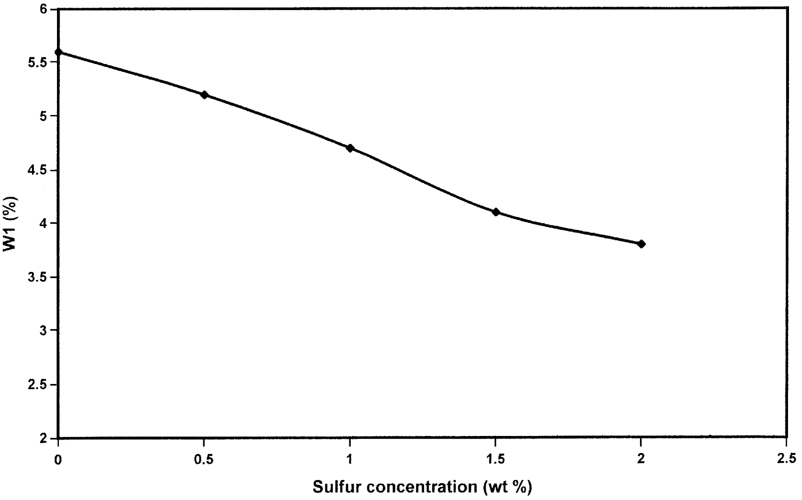

FIGURE 6 The effect of sulfur concentration on the weight loss of rubberwood filled PP/NR blend.

weight loss, W_1, decreases with increasing sulfur concentration. Both figures provide a clear indication of the increase in the crosslink density in the silica and rubberwood filled PP/NR composites. As the crosslink density increases within the NR phase, the composites become stiffer and less penetrable by the water molecules.

4. CONCLUSIONS

Mechanical properties, *viz.* tensile strength, stress at peak, Young modulus and flexural modulus of the silica and rubberwood filled PP/NR composites, were improved with the addition of sulfur, which leads to the formation of crosslinks. The increase in crosslink density was evident from the weight gain (water absorption), weight loss and Brabender plastograms. Water absorption and weight loss decrease with increasing sulfur concentration, whereas stabilization torque at the end of mixing stage exhibits an increasing trend.

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