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# Preparation of spent coffee grounds-rubber composites using natural rubber latex as binder

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**Abstract**

The aim of this work was to explore the use of natural rubber latex (NRL) as a natural binder (according to the BCG concept) to replace commercial synthetic binders such as polyurethane resin. A composite sheet of spent coffee ground (SCG) and natural rubber (NR) was prepared by mixing of SCG in NRL compounds having concentrations of 30% and 60% dry rubber content (DRC). The amount of SCG in the composites was varied from 33 to 167 part per hundred rubber (phr). The mixture was cast in a mold to form a thin sheet then left drying at room temperature for 24 h. TGA thermogram shows 3 decomposition stages composed of moisture (including volatile matters), polysaccharide and lipid at 44%, 42% and 13% weight, respectively. Hardness (Shore A) increases gradually with increasing the amount of SCG, while tensile strength and elongation at break tend to decrease. Tensile strength decreases from 2.6 MPa to 1.2 MPa for the composites containing 33 phr and 133 phr of SCG, respectively. Alkaline surface treatment of SCG could improve the adhesion between SCG and NR as evidenced by the increase in tensile strength, elongation at break and compression set properties.

## 1. Introduction

Nowadays, ecological concerns and issues such as recycling and environmental care have gained much attention from global researchers. Because of such environmental awareness, the use of environmentally friendly fillers is on the rise. Usage of natural fillers offers some advantages over the traditional filler, i.e., lower cost, lower density, no toxicity and a considerably positive environmental impact [1,2].

Natural rubber which is a biopolymer with high molecular weight, obtained from *Hevea brasiliensis* trees abundantly cultivated in Thailand possesses outstanding properties, including flexibility, high tensile strength, toughness, resistance to high abrasion and can prevent the penetration of water and air as well [3]. Many researchers have been trying to find ways to use natural rubber as a raw material in the manufacturing of various products in order to increase the demand for natural rubber, which gives it a higher price [4]. Up to now the use of NR as binder for composite materials is never found elsewhere. Fiber-reinforced polymer composite (FRPC) has been established since the 1970s, in various industrial sectors (eg. aerospace, automotive, energy) due to their superior properties [5]. Most of binders are synthetic resin such as polyester resin, vinyl ester resin, polyurethane resin, phenolic resin as well as UV-curable monomers, for binding glass mats together.

Coffee is one of the most consumed beverages and plays an important role in many countries. Spent coffee ground (SCG) could be considered a pollutant, given the high contents of organic substances that demand great quantities of oxygen to decompose [4]. SCG is lignocellulosic nature that main chemical composition consists of cellulose and hemicellulose 51.5% and 40.4% by weight respectively [6]. Most attempts towards finding alternative uses for SCG have been concentrated on applications such as fertilizers, solid fuels and supplements for animal feed [7,8]. There are a few reports about using SCG as a filler in green bio-composites. Chin-San Wu investigated the mechanical properties and biodegradability of a polylactide (PLA)/SCG composite, as well as maleic-anhydride-grafted polylactide (PLA-g-MA) and treated SCG (TSCG). The PLA-g-MA/TSCG composite exhibited lower melt viscosity and desirable mechanical properties relative to PLA/SCG [9]. Pechurai *et al*. have studied the effect of SCG content on NR foam. The result showed that because of the presence of metal oxide in SCG, the hardness and tensile strength, as well as the elastic behavior, were reduced [10]. Siriwong *et al*. studied the effect of surface treatment *via* the addition of bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) and liquid epoxidized natural rubber (LENR) on the properties of SCG-filled NR. TESPT-treated SCG showed the highest mechanical properties, followed by LENR-treated SCG and untreated SCG, respectively [1]. The influence

of SCG and surface modified SCG with potassium hydroxide (KOH) as fillers on the properties of epoxidized natural rubber bio-composites had been studied by Raju *et al.* [11]. The results showed that the composites of modified SCG had enhanced tensile strength, 100% modulus and elongation at break.

Although SCG/NR composites have been studied, most works were prepared from solid NR in which the mixing and compounding stages require appropriate mixing machines. To benefit for wider area of applications, such as rubber flooring sheet for animal farms in rural area, composite preparation without such machines is explored. This novel technique will use NRL and require no machinery and tooling. Therefore, the main objective of this study is to investigate the possibility to use NRL as a natural and new binder for SCG/NR composites preparation. The effects of NRL concentration, size and amount of SCG, as well as the influence of surface treatment of SCG *via* alkaline treatment on their properties were planned, investigated and discussed.

## 2. Experimental

### 2.1 Materials

High ammonia natural rubber latex (NRL) 60% dry rubber content (DRC) was obtained from Thai Rubber Latex Group Public Company Limited. The 30% DRC NRL was then prepared by dilution the 60% DRC NRL with water. Spent coffee ground was supplied from the local coffee shops from Chiang Mai province (northern Thailand) without further purification. All ingredients for vulcanization of NRL (sulphur, ZnO, ZDEC and CPL) were purchased from Lucky Four Co., Ltd. in dispersion form.

### 2.2 Sieving and surface alkaline treatment of SCG

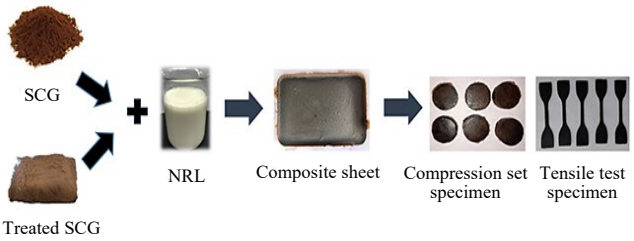
Received SCG was sieved into 2 sizes (size 1 and 2) to remove the impurities and measured by Master-sizer 2000 in dry mode. The surface of SCG was alkaline treated by soaking the SCG in sodium hydroxide solution (0.2 mol·L$^{-1}$ NaOH) for 10 min. The ratio of SCG:NaOH solution was 1:1 by weight. The treated SCG was dried at 40°C for 24 h, and kept in a desiccator before use.

### 2.3 Preparation of SCG filled NR composite

The NRL compound was pre-mixed with vulcanizing dispersion solution, described in Table 1, for 10 min prior to mix manually with SCG. The mixture was stirred until homogeneity was observed, then cast on a mold to form a sheet and left for drying at room temperature for 24 h. The drying step was monitored until the total weight of the sample became constant. SCG/NR composites were vulcanized at 120°C at 20 MPa of pressure in compression molding with optimum cure time ($T_{90}$) derived from moving die rheometer (MDR).

### 2.4 Characterization

Thermogravimetric analysis (TGA) was used to determine the compositions under thermal weight loss. The test was conducted using nitrogen gas from 40°C to 600°C and switched to oxygen gas from 600°C to 800°C. The heating rate of 20°C·min$^{-1}$ and flow rate of 60 mL·min$^{-1}$ were controlled the whole experiment. Tensile strength and elongation at break were determined with an Instron Universal Tester Model 5566, according to ASTM D-412. The dumbbell specimen (type C die) at 2 mm thickness was prepared. The cross-head speed 500 mm·min$^{-1}$ with the force of 1 kN was used. The compression set test was performed following ASTM D395 method B type A under constant deflection in air. The specimen was pressed 25% of their original thickness at 70°C for 22 h. The final thickness of samples was measured after releasing to stabilized thickness for 24 h. Hardness (Shore A)of SCG/NR composites was determined by using Wallace hardness tester (Shore A) based on ASTM D2240-91. A specimen at least 6 mm thickness was used for the test. An average value was derived from 6 measurements at different position of specimens. Morphology of SCG and fracture surface of composites from tensile test specimen were analyzed using FE-SEM Hitachi SU8010.




**Scheme 1.** Preparation of SCG/NR or treated SCG/NR composite sheet and test specimen.

**Table 1.** Formulation of NRL solution.

| Ingredients | Composition (part per hundred of rubber, phr) |
|---|---|
| NRL | 100* |
| Sulphur | 1.2 |
| ZDEC | 1.5 |
| ZnO | 0.5 |
| CPL | 1.0 |

*with respect to %DRC

## 3. Results and discussion

In general, the SCG obtained from coffee shops is an irregular shape with porous structure and relatively large particle size in the range of 100 µm to 500 µm [1]. The SCG for our study was purchased from Chiang Mai, northern part of Thailand, as fine power with brown color shown in Figure 1. It was then sieved into 2 different sizes and characterized as size 1 (374 µm) and size 2 (166 µm), as shown in Table 2. The surface area of size 1 and size 2 were found to be 0.023 m$^2$·g$^{-1}$ and 0.077 m$^2$·g$^{-1}$, respectively. TGA thermogram of SCG sample (freshly collected from Starbucks coffee shop, as shown in Figure 2) reveals three different decomposition stages. The first stage occurs at 30°C to 150°C with a weight loss of 43.54%, corresponding to the removal of water and volatile compounds. The second stage is found between 150°C to 600°C with a weight loss of 42.22%, attributing to the loss of polysaccharides, hemicellulose and cellulose [1,11]. Finally, the weight loss at 600°C arises from the oxidation decomposition of the carbon containing structure from previous steps. Therefore, TGA thermogram reveals that the composition of SCG is very complex containing a variety of organic compounds as a major component with small quantities of inorganic substances [6,12].

**Table 2.** Particle size and surface area of SCG.

| SCG | Particle size (μm) | Surface area ($m^2 \cdot g^{-1}$) |
|---|---|---|
| size 1 | 374 | 0.023 |
| size 2 | 166 | 0.077 |

**Figure 1.** Appearance of SCG as received.

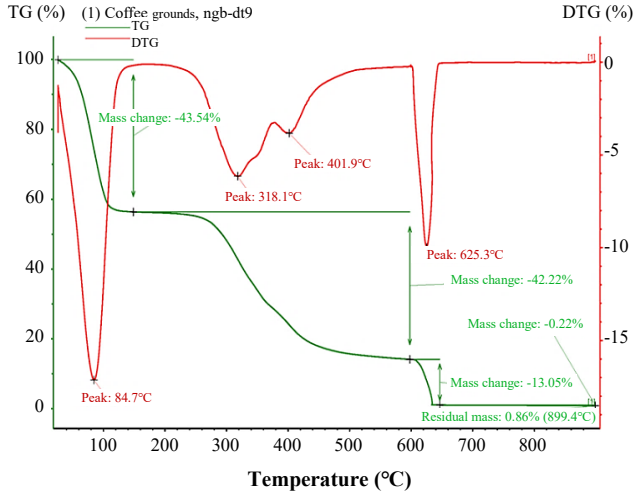



**Figure 2.** TGA thermogram of SCG

To study the use of SCG as a filler in rubber composite, each size of SCG was incorporated into NRL 30% and 60% DRC. Mechanical properties of rubber composites were investigated. Figure 3 represents the effect of SCG loading on hardness (Shore A) at 30% and 60% DRC of NRL, comparing the SCG of size 1 and size 2. It was found that the NRL 30% DRC SCG could incorporate high amount loading (100, 133 and 167 phr) due to it contains high water content related to low viscosity. In the contrary for NRL 60% DRC, the amount of SCG is loaded at 33, 50 and 67 phr. The limitation of SCG loading is controlled by the observation on the point before coagulation of SCG in NRL. The value of hardness increases gradually with respect to the amount of SCG as expected. At 30% DRC, it increases significantly with size 2 (smaller) higher than size 1 (bigger). On the contrary, at 60% DRC of NRL, the hardness decreased with decreasing of the particle size of SCG. From Figure 2, it is seen that at low SCG content, Shore A hardness does not depend on SCG content. However, at high SCG content, the hardness increases with increasing SCG content. SCG with a smaller particle size has a greater effect than that of the larger one (see Table 2). This should be related to the structure and surface area of the filler. The smaller the size the greater the effect is [13]. Moreover, hardness increased with SCG loading as expected. It is due to SCG is much stiffer than rubber, hence it could behave as filler to increase rubber stiffness [13]. No previous works were reported the effect of SCG particle size on the hardness of SCG/NR composite. Anyway, some works had reported that nanofillers enhanced the mechanical properties much more than those of microfillers in dental application [14,15]. An effort was also made on the influence of filler size and shape on polymeric composites properties, but the mechanisms remain unclear [16].

The tensile strength at 60%DRC decreases gradually with increasing the amount of SCG size 1, but it shows uncertain (no tendency / value is not related to amount of SCG) tensile strength value for SCG size 2 that superior to size 1 composites. It might due to random dispersion of packing structure of SCG during drying process. For 30%DRC, tensile strength decreases in size 1, but it increases surprisingly in size 2 as function of loading, with inferior values than size 1. It could be implied that smaller particle size of SCG imparts better dispersion and higher interaction of filler- rubber in high NRL concentration rather than low concentrated NRL. The irregular shape and low specific area of SCG particles which have inability to support stress transferred from the rubber matrix might also be the reasons of uncertain tensile strength trend [14]. Considering the elongation at break in Figure 5, it slightly decreases with the addition of SCG in the composites. The increment of filler content causes the reduction of the deformability of interfaces between the filler and the rubber matrix. At higher filler content, the degree of filler-filler interaction also became more prominent [17]. As compared to concentration of NRL, elongation at break decreases with SCG loading for size 1, but it slightly increases for size 2 in both NRL concentrations. The results reveal that elongation at break is proportional to amount of dry rubber content [18], as evidenced in low loading contents SCG especially for size 1.

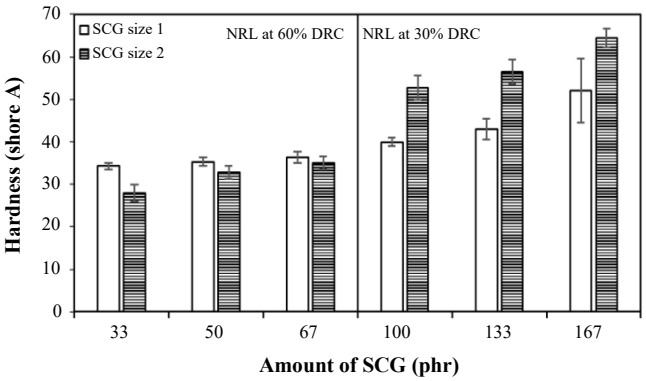



**Figure 3.** Effect of particle size and loading of SCG on hardness (Shore A) of the composites at 30% and 60% DRC of NRL.

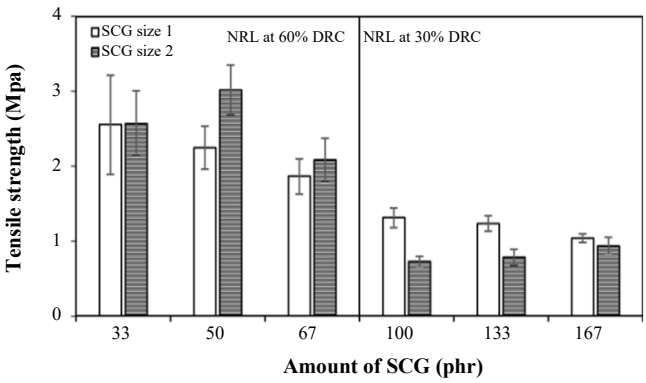



**Figure 4.** Effect of particle size and loading of SCG on tensile strength at 30% and 60% DRC of NRL.

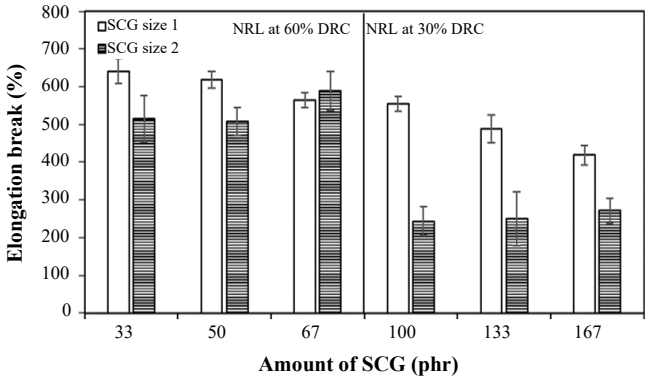



**Figure 5.** Influence of particle size and loading of SCG on elongation at break at 30% and 60% DRC of NRL.

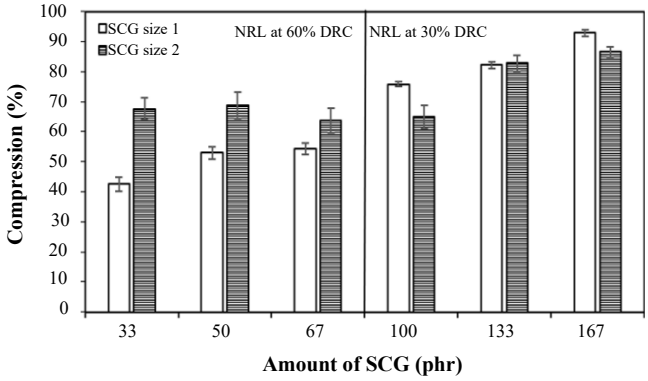



**Figure 6.** Effect of particle size and loading of SCG on compression set at 30% and 60% DRC of NRC.

The elastic behavior of the SCG/NR composite is expressed by the measurement of compression set, shown in Figure 6. It seems that the compression set tends to increase with increasing content of SCG, which indicates the poor recoverability of the composites. This could attribute to a deformation of the large cell structure under the compressive load, resulting in loss of the elastic recovery [17]. Also, the percentage of compression set decreases with increasing %DRC of NRL as expected. These results indicate that high concentration of NRL provided high dry rubber content that exhibits good elasticity and resistance to permanent deformation.

Based on the different chemical surface properties between SCG and NR, SCG is highly polar due to their lignocellulosic- based structure. The attempt to increase their compatibility was obtained *via* alkaline treatment of SCG. Their measured properties are shown in Table 3. This clearly shows that hardness, tensile strength, elongation at break as well as compression set of the composites after alkaline treatment exhibit greater properties than those of untreated SCG specimens. Alkaline treatment uncovered hydroxyl groups on the SCG surface, creating more hydrogen bonding and promotes physical interaction with NR, resulting in the increase in adhesion between SCG and NR [11]. In addition, the treatment eliminates impurities such as lignin and hemicellulose, promoting their better interaction [D]. Practically, treated SCG exhibits better dispersion in NRL, no aggregation of filler is occurred during film formation. The elimination circumstance transforms brown color of starting SCG into pale brown color.

Figure 7 displays morphology of SCG and fracture surfaces of composite specimen (30% DRC, 167 phr) from tensile measurement. SCG particle Figure 7(a) has irregular shape, rough surface and contains porous structure. Alkaline treatment of SCG removes the hemicellulose [19,20], and causes the surface to have more opened structure and higher porosity Figure 7(b). When SEM photographs of SCG/NR composite fracture surfaces are compared, it is clearly seen that treated SCG has better dispersion and more homogeneity with NR matrix as shown in Figure 7(c-d). The fracture surfaces at higher magnification expose the aggregation of SCG in the composites Figure 7(e) as compared to treated SCG composite Figure 7(f). Naturally SCG surface contains various free fatty acid molecules such as hydroxycinnamic acids and quinic acid, collectively recognized as chlorogenic acids [21]. Their acidified surface causes aggregation of SCG. Alkaline treatment could neutralize and provide hydroxyl functional group promoting the good dispersion of SCG particle in the composite [20]. The alkaline treatment is widely accepted to implement for enhancing the interaction of polymer and cellulosic fibrous composites [22].

**Table 3**. Properties of untreated- and alkaline treated SCG/NR composites.

| NRL (%DRC) | SCG (phr) | Properties | | | |
|---|---|---|---|---|---|
| | | Hardness (shore A) | Tensile strength (MPa) | Elongation at break (%) | Compression set (%) |
| Untreated SCG | | | | | |
| 30 | 100 | 53 ± 3 | 0.73 ± 0.07 | 243 ± 38 | 65 ± 4 |
| | 133 | 57 ± 3 | 0.78 ± 0.11 | 249 ± 71 | 83 ± 3 |
| | 167 | 64 ± 2 | 0.94 ± 0.10 | 271 ± 33 | 87 ± 2 |
| 60 | 33 | 28 ± 2 | 2.57 ± 0.44 | 515 ± 61 | 68 ± 4 |
| | 50 | 33 ± 2 | 3.02 ± 0.34 | 508 ± 37 | 69 ± 4 |
| | 67 | 35 ± 2 | 2.08 ± 0.29 | 589 ± 52 | 63 ± 4 |
| Alkaline treated SCG | | | | | |
| 30 | 100 | 50 ± 8 | 1.43 ± 0.57 | 702 ± 92 | 62 ± 3 |
| | 133 | 53 ± 2 | 2.35 ± 0.29 | 456 ± 60 | 69 ± 2 |
| | 167 | 55± 1 | 2.92 ± 0.17 | 487 ± 20 | 54 ± 1 |
| 60 | 33 | 34 ± 1 | 5.10 ± 1.07 | 674 ± 16 | 43 ± 0 |
| | 50 | 36 ± 1 | 5.62 ± 0.26 | 634 ± 26 | 51 ± 4 |
| | 67 | 37 ± 2 | 2.39 ± 0.69 | 489 ± 55 | 55 ± 2 |

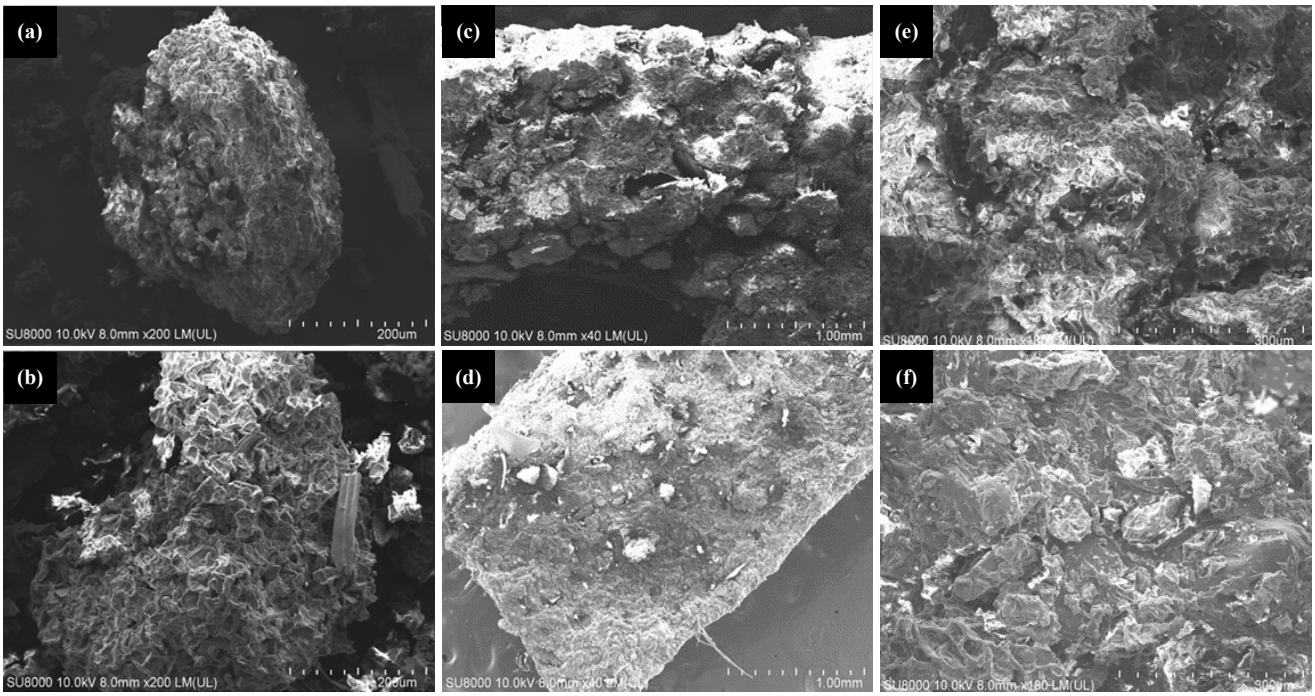



**Figure 7.** SEM micrographs of crude SCG (a), treated SCG (b), fracture surfaces of SCG/NR composite (c and e), treated SCG/NR composite (d and f), (30% DRC, 167 phr).

## 4. Conclusions

The use of NRL as a new binder for preparation of SCG/NR composite is possible, simple, easy and successful, without any complicated machines. Smaller size of SCG shows greater hardness, tensile strength and elongation at break, implying better dispersion and interaction. Alkaline surface treatment of SCG helps improve these properties due to the increase in hydrogen bonding and physical surface interaction. Moreover, alkaline treatment could eliminate the impurities on SCG surface, promoting better interaction between SCG and NR and properties enhancement is resulted.

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