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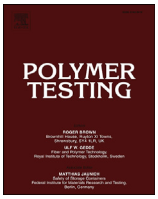

Material properties

Interesting green elastomeric composites: Silk textile reinforced natural rubber

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ABSTRACT

The reinforcement of natural rubber (NR) with particles and fibres enables their use in even high performance applications, such as in road-racing bicycle tire casings. Here, for the first time, we examine the potential of silk textiles as reinforcements in NR to produce a fully-green, flexible yet strengthened elastomeric composite material. Various material properties were evaluated and compared with similar nylon textile reinforced NR composites. Two types of NR were used: whole and purified natural rubbers. The composite samples were prepared by sandwiching a single layer of textile between layers of NR. NR/silk composites exhibited higher static and dynamic mechanical properties than NR/nylon composites. In addition, silk textiles in whole NR composites performed significantly better than purified NR composites, due to stronger fibre/matrix adhesion and better wettability in the former, as indicated by surface energy measurements and scanning electron microscopy micrographs. Such bio-based natural rubber/silk composites might find interesting applications in soft robotics and as flexible, inflatable tubes.

1. Introduction

Natural rubber (NR) is a very useful elastomer because it possesses properties such as high green strength, high tensile strength, low heat hysteresis and high damping [1–3]. Moreover, in contrast to synthetic elastomers, NR is a renewable product. Fresh NR latex from *Hevea brasiliensis* normally consists of 30–40% rubber, 50–60% water and 5–6% non-rubber components (*e.g.* proteins, lipids) [4]. A molecular chain of NR is composed of two or three units of *trans*-1,4 polyisoprene and a long sequence of *cis*-1,4 polyisoprene. At the initiating terminal, ω-terminal, the NR molecule associates with protein, while the chain end, α-terminal, associates with phospholipid. NR molecules can form gel fractions through reactions between functional terminal groups at the end of the NR molecules and proteins at the ω-terminal or phospholipids at the α-terminal [5]. The proposed new model for the structure of the rubber latex particle surface consists of a mixed layer of proteins and phospholipids around the latex particle [6].

For structural applications, such as in vehicular tires, the NR formulation requires optimisation. An important science of compounding is the reinforcement of NR because in its unreinforced form it presents a low resistance to tearing and abrasion. Typically, fillers are used to enhance these mechanical properties of NR. Two conventional fillers for reinforcing vulcanised rubber are carbon black and silica. Carbon black is a hydrophobic filler that is compatible with NR. On the other hand, silica is a hydrophilic filler; silane is often used as a coupling agent between silica and NR molecules [2]. The advantage of silica is the reduction of heat buildup in the rubber compound (during tyre rolling, for example), which saves a lot of energy compared to carbon black filler. However, silica is comparatively expensive and presents some problems in the rubber compounding process, including long curing times, non-conductivity, and rigidification upon cooling [3]. New types of fillers and reinforcements would be interesting to investigate for high-performance rubber compounding.

Bio-based composites which provide a good compromise between their final performance and environmental impact are becoming preferred materials for use. In the last two decades,

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natural fibers have been considered to reinforce rubber composites [7,8]. Bombyx mori silk is a natural polymer fibre that has been used in textile production for millennia. Silk in its natural form is composed of a filament core protein, silk fibroin, and a glue-like coating consisting of a family of sericin proteins. Silk has superb mechanical properties in comparison to other common technical and textile fibres (Table 1), specifically the combination of strength and ductility leading to its high toughness. Their properties have been translated in silk fibre reinforced polymer composites as well [9,10]. However, there has been limited work on silk reinforced elastomeric composites. While silk fiber reinforced NR composites were investigated several decades ago, including assessing the effects of rubber formulations, bonding agents, and fibre filler loading levels on processing characteristics and mechanical properties [15], the studies were based on short, discontinuous fibre reinforcements. In contrast, there are no studies in literature on silk textile reinforced NR composites.

An example application where such green materials are of increasing interest is in the sports and leisure industry. For example, high-performance bicycle tubular tire casings are commonly made from textile reinforced uncured (*i.e.* non-vulcanised) rubber, both NR latex and butyl-based rubber. In passing, while vulcanisation of rubber makes the material more durable (and therefore is a pre-requisite for most industrial applications), uncrosslinked rubber is preferred for tubulars for a range of reasons. Non-vulcanised tubulars are more flexible (offering reduced rolling resistance and a more comfortable ride) and less prone to flats (through punctures and crack-propagation). The reinforcement of the uncrosslinked rubber offers improved mechanical properties. While nylon and cotton textiles are commonly used, tubulars with silk textile based casings are preferred by some professional athletes. Importantly, silks are the only natural fibre to exist as fine filaments (Table 1) implying that high strength, fine yarns (of low tex or denier) can be produced with ease. For casings, these strong yet flexible and fine silk threads are then used to produce high thread count (*i.e.* high areal density) fabrics. Casings with a high thread per inch count fabric generally translate to a thinner, flexible and lighter material that allows for higher pressure capacities and decreased rolling resistance and consequently faster speeds, improved grip and a more comfortable ride (due to absorption of micro-impacts).

In the present paper, we examine fully-green elastomeric composites based on silk textiles and natural rubber. Two types of natural rubber are used: whole natural rubber (WNR: contains all non-rubber components) and purified natural rubber (PNR: contains less non-rubber components following removal through repeated centrifugation). Moreover, nylon fabric reinforced NR is studied as a benchmark. The study is an attempt to better understand the role of silk fabric reinforcements in NR and also to examine whether treatment and purification of natural rubber leads to any changes in properties of the composite. This is extremely relevant as the production of NR-based tubular tires for road-racing, for example, is often by hand. Workers may have allergic reactions to whole natural rubber, while purified natural rubber, free from allergen non-rubber constituents such as proteins, is more worker-friendly [25].

2. Experimental

2.1. Materials

2.1.1. Preparation of whole and purified natural rubber

Whole natural rubber (WNR), from *Hevea brasiliensis*, was prepared by casting fresh natural rubber latex on glass plates, and air-drying for a day at room temperature. The rubber samples were then oven-dried at 50 °C for 24 h.

To prepare purified natural rubber (PNR), fresh natural rubber latex was centrifuged at 10,000 rpm for 30 min at 25 °C. The cream fraction was dispersed in 1%w/v SDS and re-centrifuged at 10,000 rpm for 30 min at 25 °C. Then the cream fraction was washed in deionized water and re-centrifuged at 10,000 rpm for 30 min at 25 °C. The resulting PNR was casted into thin film, and dried at 50 °C for 24 h.

2.1.2. Reinforcement materials

Silk textiles were obtained from Chul Thai Silk Co., Ltd. Nylon fabric was obtained from Asia Fiber Co., Ltd. Both types of plain woven fabrics were sourced to have similar yarn count (Table 2). However, the silk fabric had a higher areal density than the nylon fabric, due to the higher density of silk fibre (*ca.* 1.3 g cm^{-3}) [11] in comparison to nylon fibre (*ca.* 1.15 g cm^{-3}) [12].

2.2. Composite manufacture

To fabricate the elastomeric composites, first, NR samples were compressed at 70 °C for 10 min in order to obtain 1 mm thick sheets. Thereafter, reinforcement fabric was sandwiched between two rubber sheets for a target fibre volume fraction of 5% (Fig. 1). Finally, the sandwich sample was compressed at 70 °C for 10 min, allowing the rubber to impregnate the fabric, and obtain a 2 mm thick composite sheet. For this study, we produced four different types of composite samples: WNR/Nylon, WNR/Silk, PNR/Nylon, and PNR/Silk.

2.3. Property analysis

2.3.1. Chemical characterisation of NRs

Nitrogen content of NR samples (WNR and PNR) was determined using the Kjeldahl method [13]. Dried rubber sheets were

Table 2
Properties of the nylon and silk reinforcement fabrics.

Fabric	Yarn count		Areal density (g m^{-2})
Nylon	Warp yarn	110 ± 10 per inch	57.5
	Weft yarn	80 ± 7 per inch	
	Total yarn	190 per inch^2	
Silk	Warp yarn	100 ± 9 per inch	66.5
	Weft yarn	90 ± 9 per inch	
	Total yarn	190 per inch^2	

Table 1
Properties of silk fibres in comparison to other technical and textile fibres. Data from Ref. [24].

Fibre	Density [g cm^{-3}]	Diameter [μm]	Tensile modulus [GPa]	Tensile strength [MPa]	Failure strain [%]
Silk (silkworm)	1.25–1.35	8–15	5–15	300–600	15–25
Cotton	1.50–1.60	15–25	5–10	300–600	6–8
Flax	1.45–1.55	15–30	50–80	500–900	2–4
Nylon (polyamide)	1.10–1.20	10–30	3–5	400–600	20–30
E-glass	2.50–2.60	10–20	70–80	2000–2500	2–4
Carbon	1.70–1.80	5–8	230–250	3000–4000	1–2