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Interesting green elastomeric composites: silk textile reinforced natural rubber

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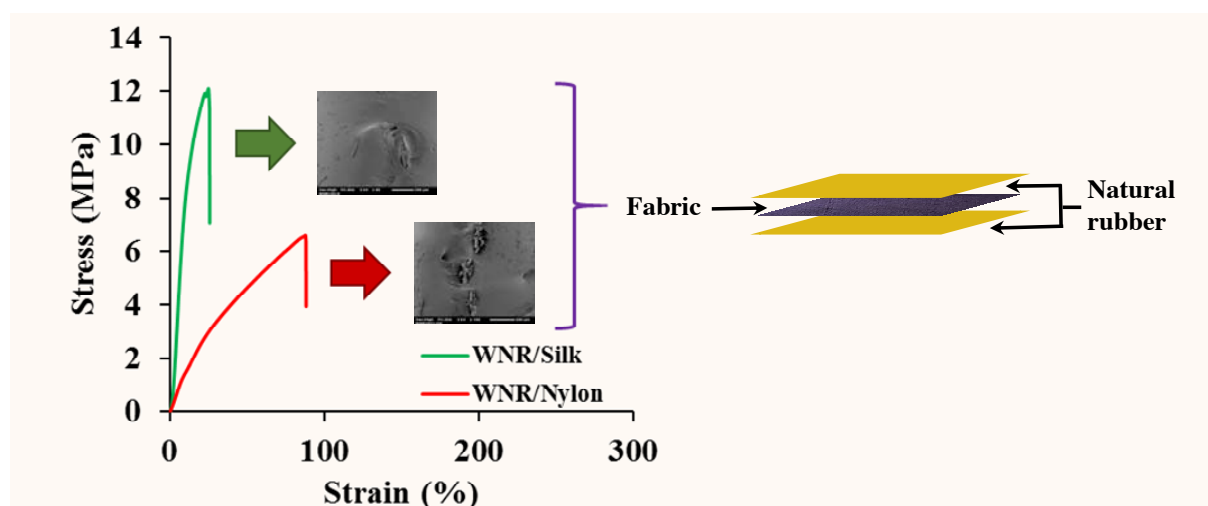
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Graphical abstract

The green composite samples were prepared by sandwiching a single layer of textile between layers of NR. NR/silk composites exhibited higher mechanical properties than NR/nylon composites which are in good agreement with the results from Scanning Electron Microscope.



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.

Keywords: elastomer, Polymer (textile) fibres, Mechanical testing, Silk natural rubber composites

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 build-up 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, 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.

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

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 hr.

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 hr.

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].

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	

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.



Fig. 1 Composite fabrication via hot-pressing of sandwich samples.

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 cut into 0.5 g pieces and placed in a Kjeldahl flask. Then, 0.8 g of catalyst mixture (K_2SO_4 : $CuSO_4 \cdot 5H_2O$ in 7:0.8 by mass) was added, followed by 15 mL of concentrated sulfuric acid. The mixture was boiled gently in the digestion unit at 420°C until the solution became colorless. The digested solution was cooled to room temperature, and then transferred into distillatory using 25 mL of 4% H_3BO_3 as the receiving solution. The distillation continued until 200 mL of distillate was collected. Thereafter, the distillate was titrated with 0.01 M HCl. Blank was determined by adding all the reagents but omitting the samples. Total nitrogen content was calculated as follows:

$$\% \text{Nitrogen} = [(B - C) \times N \times (14 / 1000)] / W \times 100 \quad \text{Eq. 1}$$

where B is mL of HCl required for titration of the receiving flask, C is mL of HCl required for titration of the blank, W is mass of sample (g) and N is concentration of HCl (N).

Lipid content of NR samples was assessed through extraction methods. For this, first, small pieces of rubber (2.8 g) were added to a vibratory miller machine with liquid nitrogen for grinding. The ground, frozen rubber was then extracted in chloroform:methanol (2:1) with agitation at 150 rpm for 6 hr. The extracted rubber was filtered and rinsed with the extracting solvent. The extracted rubber was then dried at 100°C for 1 hr and then weighed. The filtrate was evaporated using a rotary evaporator. The corrected residue was re-dissolved with 1 ml chloroform:methanol (2:1). The total extracted solution was then washed with 1 ml of 0.9% NaCl solution in order to separate water soluble components from lipids. Lipid component, separated at the bottom layer, was collected and the solvent was evaporated.

Fourier-transform infrared spectroscopy (FTIR) was conducted on a Nicolet Magna 850 in Attenuated Total Reflection (ATR) mode to qualitatively verify the difference in purity between WNR and PNR.

2.3.2 Composite characterisation

Thermogravimetric analysis (TGA) was carried out on a METTLER TGA/sDTA851e through a temperature ramp from 0 to 900°C at a rate of 10°C·min⁻¹. Nitrogen was used as an inert carrier gas.

The tensile mechanical properties of the composites were measured on an Instron 5944 universal testing machine equipped with a 50 N load-cell. Tests were carried out on dumb-bell shaped specimens at a crosshead speed of 100 mm·min⁻¹.

Dynamic mechanical thermal analysis (DMTA) was conducted using a TA Instruments DMTA Q800. Tests in single cantilever mode were carried out in temperature scanning mode from -110°C to 30°C, at a rate of 3°C·min⁻¹. In addition, measurements were performed in shear sandwich mode over a strain sweep from 0 to 25% at a constant temperature of 25°C.

Scanning electron microscopy (SEM) was used to investigate the morphology of cryo-fractured composite surfaces. The fractured surfaces were sputter-coated with Au/Pd and observed under a JEOL JSM-5310 SEM at an acceleration voltage of 10kV.

The surface energies of the different rubbers and fabrics were evaluated through contact angle measurements using various probing liquids [14]. Direct contact angle measurements with water, formamide, diiodomethane and tricresylphosphate were employed to determine the dispersive and polar components of surface energy.

3 Results and discussion

3.1 Chemical characterisation of natural rubber

The purity of WNR and PNR materials was assessed by determining their nitrogen and lipid content (Table 3). It was evident that the repeated centrifugation method used to produce PNR reduced the proportion of the non-rubber components significantly. In comparison to WNR, PNR had 98% lower nitrogen content and 38% lower lipid content. These observations were verified via FTIR-ATR analysis, where both WNR and PNR showed presence of the non-rubber constituents, albeit substantially reduced in PNR. Similar results were obtained in previous work [15].

Table 3 Nitrogen and lipid content of whole (WNR) and purified (PNR) natural rubber.

Content analysis	WNR	PNR
Nitrogen (wt. %)	0.97	0.02
Lipid (wt. %)	2.65	1.64

The nitrogen level of NR is directly indicative of its protein content (a factor of 6.25 is commonly used) [26]. As some of these proteins are potential allergens, deproteinisation of (natural and unnatural) rubbers is attractive where human contact with the materials, either during processing (*e.g.* during bicycle tire casing manufacture) or product use (*e.g.* gloves), is vital or unavoidable. However, the removal of non-rubber components has also shown to affect processing and mechanical properties of the natural rubber. For instance, PNR possesses better dynamic properties, including resistance to heat build-up, surface cracking from repeated bending (known as flex cracking), and cyclic loading, in comparison to WNR [25, 27].

3.2 Mechanical and thermal properties of the elastomeric composites

In the latter part of this study, we assessed property differences between silk and nylon reinforced WNR and PNR to examine potential effects of rubber purification on composite behaviour when subjected to mechanical and thermal stresses.

First, we used thermogravimetric analysis (TGA) to study the thermal properties of the unmixed materials (Fig. 2) and then the different composite samples (Fig. 3). There were no significant differences in the thermal properties between unreinforced WNR and PNR (Fig. 2A and 2B). Silk fabrics exhibited a 5-6% loss of mass below 100°C, unlike the rubbers and the nylon fabrics, which was associated with moisture evaporation (Fig. 2C and 2D) [23]. Silk fabrics also showed earlier onset of thermal degradation (around 250-300°C) in comparison to the unfilled rubbers (375-400°C) and nylon fabrics (400-425°C). A stark difference between the rubbers and nylon fabrics, and the silk fabric was that silk fibres exhibited a residual mass of around 18% at 900°C, whereas the other unmixed materials completely decomposed (almost 0% residual mass) as low as 500°C. The composite samples did not exhibit significant differences in thermal properties (Fig. 3), probably due to the only low volume fraction of fibre in the materials.

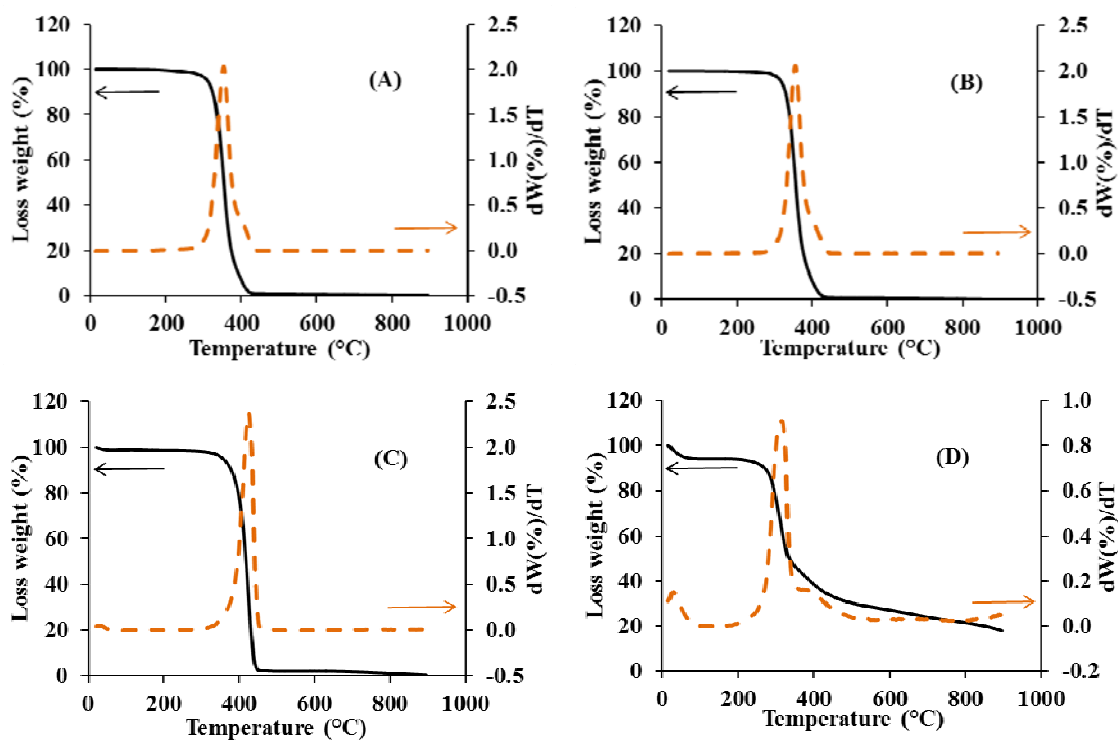


Fig. 2 TGA profiles of (A) WNR, (B) PNR, (C) nylon fabric and (D) silk fabric.

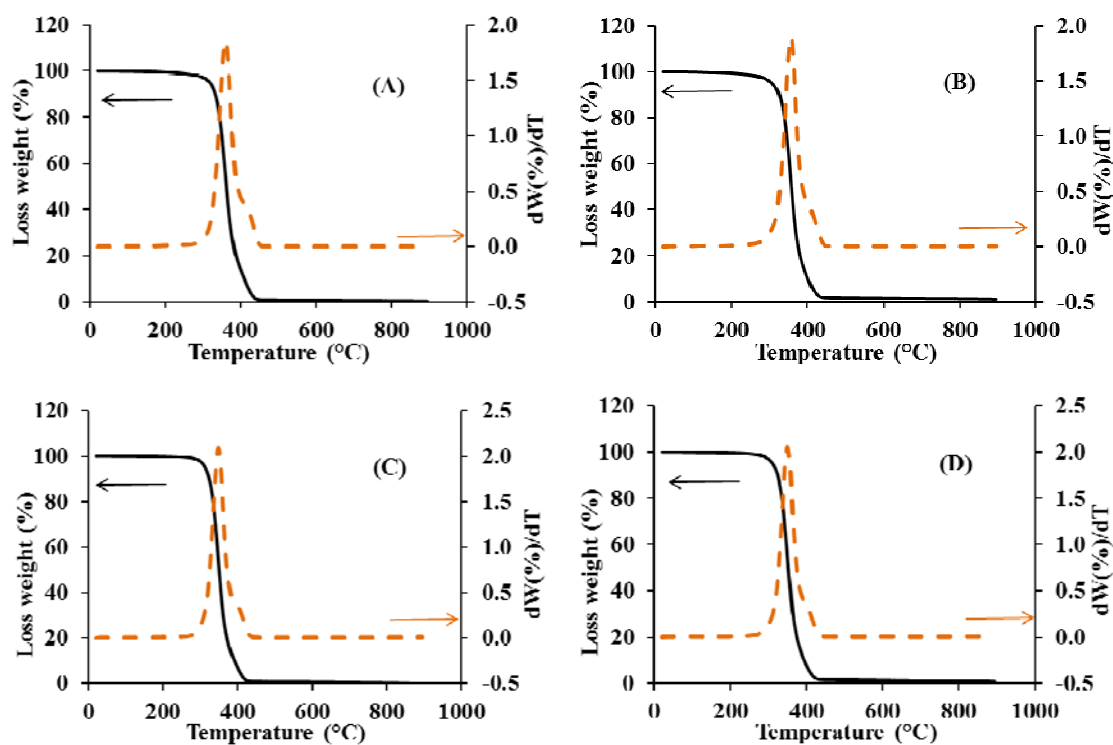


Fig. 3 TGA profiles of (A) WNR/nylon, (B) WNR/silk, (C) PNR/nylon and (D) PNR/silk.

The measured tensile properties of the various samples are presented in Table 4, with Fig. 4 showing typical stress-strain profiles. In general, the unreinforced rubbers were significantly weaker (by an order of magnitude) in strength, but substantially more extensible before failure (also by an order of magnitude. In addition, it was evident that nylon reinforced rubbers had tensile strengths 35-45% that of silk reinforced rubbers, although strains at failure around three times larger. These findings suggested that increases in strength of the reinforced rubbers were at a cost of ductility and toughness (area under the stress-strain curve).

While it was clear that silk textile reinforced natural rubbers had the highest strengths, the purity of the natural rubber also affected the tensile properties of the reinforced elastomeric composites. As a benchmark comparison, unreinforced PNR was statistically significantly stronger than unreinforced WNR (two-tailed t-test, $p = 0.0157$), but the latter exhibited a higher failure strain ($p = 0.0063$). This is in agreement with literature findings [25, 27]. However, interestingly, both nylon and silk reinforced WNR exhibited significantly higher tensile strengths than their PNR counterparts. The indicated that increased purity in rubber (*i.e.* reduced content of non-rubber constituents *e.g.* proteins and lipids) was detrimental to tensile properties of the reinforced materials. The effect was much greater for silk textile reinforcements with WNR reinforced materials demonstrating 40% higher strength than PNR reinforced materials; for nylon composites, the WNR reinforced materials were 20% stronger.

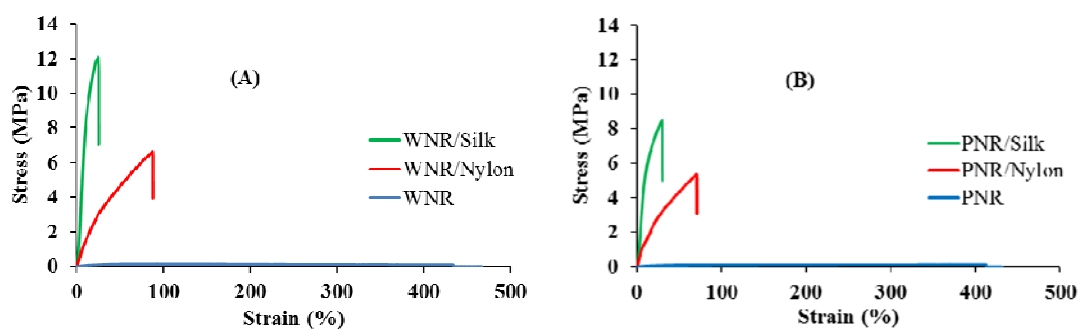


Fig. 4 Example tensile stress-strain profiles of (A) WNR and (B) PNR samples. The unreinforced rubbers have low strength, but high ductility (stress-strain curves along the *x*-axis).

Table 4 Tensile properties of WNR and PNR samples.

Samples	Tensile Strength (MPa)	Elongation at break (%)
Unreinforced WNR	0.12 ± 0.01	400 ± 20
WNR/Nylon	6.54 ± 0.17	76 ± 12
WNR/Silk	11.81 ± 0.31	21 ± 5
Unreinforced PNR	0.13 ± 0.01	388 ± 27
PNR/Nylon	5.48 ± 0.16	77 ± 10
PNR/Silk	8.49 ± 0.09	24 ± 5

DMTA in single cantilever mode was carried out to ascertain mechanical (stiffness and damping) behaviour over a larger temperature range (Fig. 5 and 6). The DMTA profile also enabled determination of glass transition temperatures of the materials (based on the peak in tan delta in Fig. 5B and Fig. 6B). The transition temperature was fairly constant at about -60°C , for both WNR and PNR, and also the silk and nylon reinforced rubbers. This suggested that the rubber component governed the transition temperature, possibly because the composite is matrix dominated; fibre volume fraction is around 5%. Comparing the evolution of tan delta (Fig. 5B and 6B), which corresponds to the dissipation energy of the materials, with temperature, no notable differences were observed below the transition temperature (-60°C) when the material is in ‘glassy phase’. At higher temperatures ($>-40^{\circ}\text{C}$), when the elastomeric material is in a ‘rubbery phase’, the composites, particularly the silk reinforced rubbers, exhibited lower dissipation energy. This may be particularly useful in possible uses as an energy-saving material, for example in bicycle tire applications.

Differences in storage modulus were more apparent below the transition temperature (Fig. 5A and 6A). Similar to the tensile properties observations, reinforced materials exhibited higher modulus than unreinforced rubber, and silk textile reinforced rubbers possessed higher storage modulus than nylon reinforced rubbers across a large temperature range.

Differences in modulus between the silk and nylon composites were less significant in PNR matrix than WNR matrix. In fact, the storage modulus of WNR/silk composites was almost twice that of PNR/silk composites (at low temperatures). This was in agreement with tensile test results, which showed significantly higher strength and

stiffness for WNR/silk composites than PNR/silk composites at ambient temperature. This suggested that WNR must have a better interfacial compatibility to silk fibres than PNR, and therefore the non-rubber constituents (*e.g.* proteins, and lipids) in WNR may have an important role in silk-fibre–rubber-matrix adhesion.

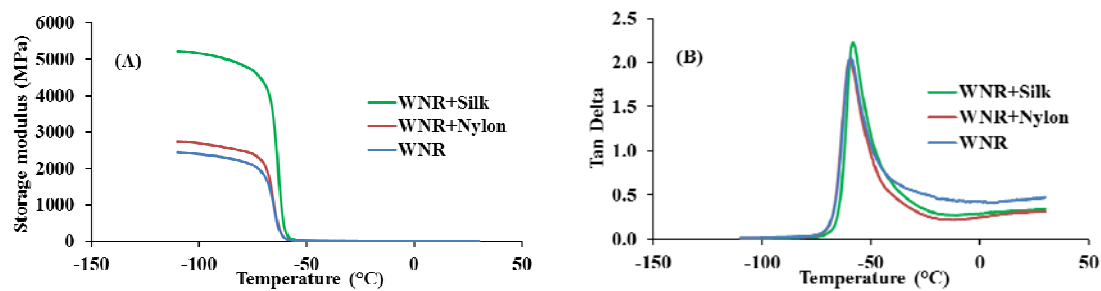


Fig. 5 DMTA (single cantilever mode) temperature scanning profiles of (A) storage modulus and (B) tan delta for WNR.

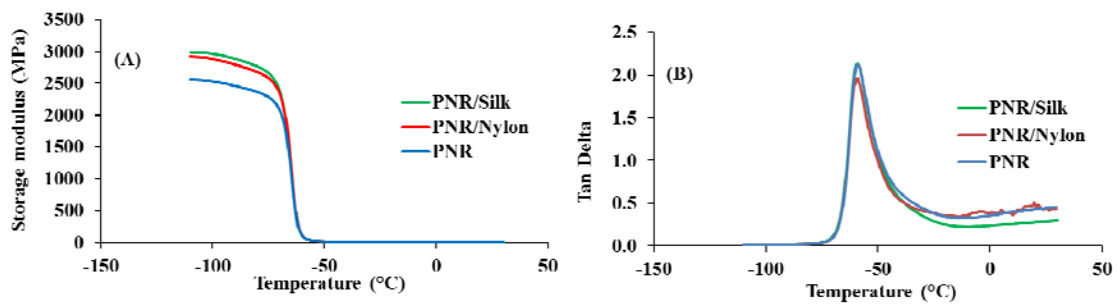


Fig. 6 DMTA (single cantilever mode) temperature scanning profiles of (A) storage modulus and (B) tan delta for PNR.

3.3 Interfacial properties of composite

Focussing on interfacial properties of the composites, and particularly the effect of rubber purity on composite properties, next, we examined the DMTA properties of the elastomeric composites in shear sandwich mode. Firstly, we found that the properties in shear mode (Fig. 7) were in good agreement to that in single cantilever mode (Fig. 5 and 6). Silk reinforced NR materials consistently exhibited the highest storage modulus. When we compared the effect of NR purity, we found that PNR presented less interaction with silk compared to WNR (by around 10-15% in modulus). This again could be explained by the presence of proteins and lipids in WNR, which may interact more readily and be more compatible with the silk proteins, resulting in better mechanical properties.

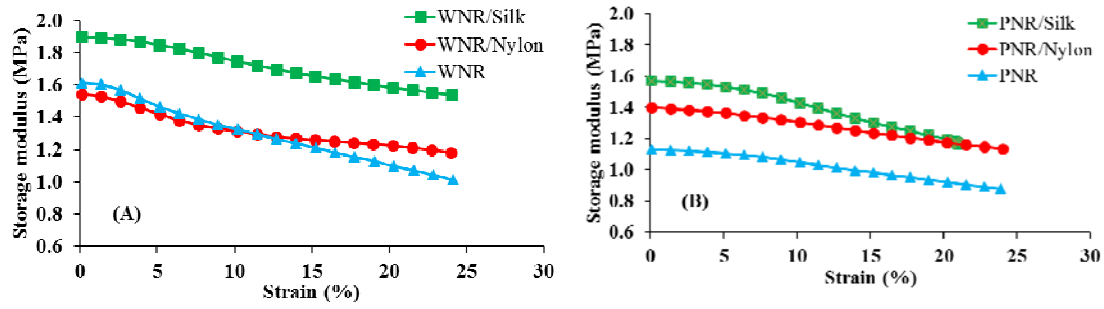


Fig. 7 DMA in shear sandwich mode at 25 °C with strain of (A) WNR samples and (B) PNR samples.

In any fibre reinforced composite, interaction between interfaces of materials would affect the mechanics of stress-transfer and therefore composite properties [28]. We found that silk/WNR composites performed significantly better in mechanical properties than silk/PNR composites, and smaller differences were also observed in the case of nylon reinforcement. We hypothesise this was most likely due to different interfacial interactions between the reinforcement and the whole or purified natural rubber.

To test our hypothesis, the surface energy of natural rubbers and fabrics was determined using contact angle measurements (Table 5). It is well-known that a better knowledge of adhesion phenomena is required for practical applications of multi-component materials [28]. Adhesion between two materials is due to interatomic and intermolecular forces established at the interface, provided that an intimate contact is achieved [16]. The most common interfacial forces result from van der Waals and Lewis acid–base interactions. The magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as surface free energies of both entities in contact [17-20]. Table 5 shows the calculated polar (γ^p) and dispersive (γ^d) components and their additive total (γ^t) of surface energy for the different types of natural rubbers and fabrics. Then, the work of adhesion (W) between two materials was calculated based on Eq. 2-4 [21-22]. The work of adhesion (W) for the composites is presented in Table 6.

$$W = 2(\gamma_r \cdot \gamma_f)^{0.5} \quad \text{Eq. 2}$$

$$\gamma_r = \gamma_r^p + \gamma_r^d \quad \text{Eq. 3}$$

$$\gamma_f = \gamma_f^p + \gamma_f^d \quad \text{Eq. 4}$$

where γ_r is the surface energy of rubber, γ_f is the surface energy of fabric, γ_r^p is the polar component of rubber, γ_r^d is the dispersive component of rubber, γ_f^p is the polar component of fabric and γ_f^d is the dispersive component of fabric.

Table 5 Surface energy of different materials.

Surface energy $\text{mJ}\cdot\text{m}^{-2} (\pm 5\%)$	WNR	PNR	Nylon fabric	Silk fabric
γ^p	3	1	40	46
γ^d	30	31	29	25
γ^t	33	32	69	71

Table 6 Work of adhesion for different composite samples.

Work of adhesion $W (\text{mJ}/\text{m}^2) \pm 5\%$	WNR/silk	WNR/nylon	PNR/silk	PNR/nylon
	96.8	95.4	95.3	94.0

We observed that the total surface energy ($32\text{--}33 \text{ mJ}\cdot\text{m}^{-2}$) of both rubbers was comparable, with the dispersive component dominating. While the reinforcements fabrics, nylon and silk, and comparable total surface energy ($69\text{--}71 \text{ mJ}\cdot\text{m}^{-2}$), the reinforcements had a relatively larger polar component, particularly in the case of silk. As the surface energy of the reinforcements is substantially higher than that of the rubber matrix, good wetting is expected, however the differences in polarity may influence spreading and penetration [16]. We also found that the work of adhesion was fairly similar for all the composites, indicating that from a wetting analysis perspective, WNR and PNR had comparable affinity with both silk and nylon.

However, SEM micrographs of the cryo-fractured composite samples (Fig. 8) revealed contrary yet interesting evidence. There were almost no voids between WNR and silk fabric, suggesting good interaction and wetting of the silk fabric materials. In contrast, PNR/silk composites exhibited some voids within yarn bundles suggesting inadequate impregnation. In the case of nylon fabric, we noticed substantial interfacial voids around the yarn bundles for both rubber matrices. Therefore, while surface energies do not explain the difference in mechanical properties of WNR and PNR silk composites, the SEM micrographs suggest that wetting and protein-protein interactions are likely sources of the observed difference.

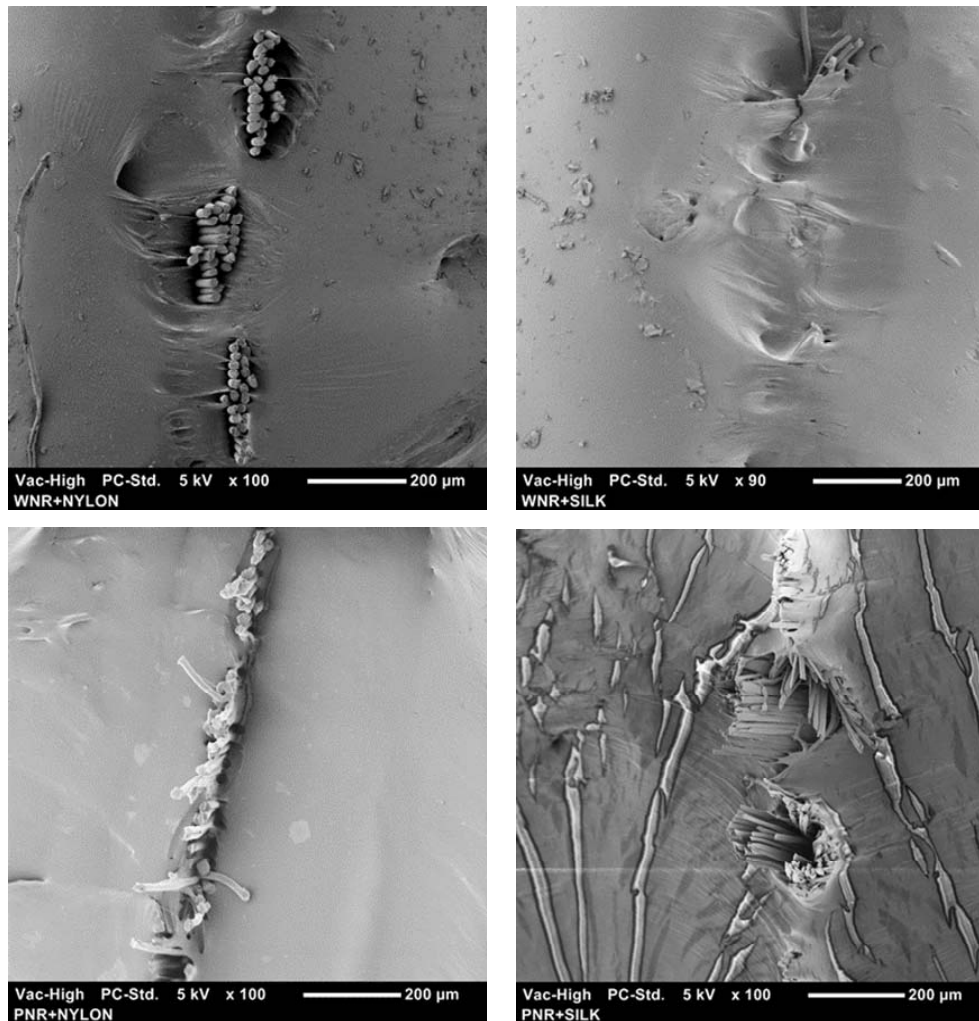


Fig. 8 SEM micrographs of the cryo-fracture composite samples using liquid nitrogen.

4 Conclusions

Fully-green silk textile reinforced natural rubber composites were fabricated and evaluated against similar nylon composites. We found that renewably-sourced natural silk fibres offered better enhancement opportunities to mechanical properties, particularly strength and storage modulus, than synthetic nylon textiles.

By studying two different types of natural rubber matrices, whole (non-purified) and purified, we were able to examine the effects of non-rubber constituents on properties of silk and nylon reinforced natural rubber composites. We found that while non-rubber constituents did not greatly alter the surface energies of the resulting composites, they did affect the wetting and impregnation of the fibrous materials. Specifically, whole natural

rubber impregnated far better in the textiles than purified natural rubber. Furthermore, the presence of protein impurities in whole rubber implied the possibility of protein-protein interactions in WNR/silk composites. Both these aspects contributed to the higher mechanical properties of WNR/silk composites.

The developed materials may be suitable for applications where damping, water-proofing, or high-pressure capacities in elastomeric tubing (such as in high-end bicycle tires), alongside high mechanical properties is required. The added advantage of these materials is that they are fully-green.

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