

1 **Interesting green elastomeric composites: silk textile reinforced**  
2 **natural rubber**

3 Wirasak Smitthipong<sup>\*,a,b</sup>, Sukontip Suethao<sup>b</sup>, Darshil U. Shah<sup>\*,c</sup>, Fritz Vollrath<sup>\*,d</sup>

4 <sup>a</sup> Department of Materials Science, Faculty of Science, Kasetsart University, 50 Ngam Wong Wan  
5 Rd., Chatuchak, Bangkok 10900 Thailand.

6 corresponding author e-mail\*: fsciwssm@ku.ac.th

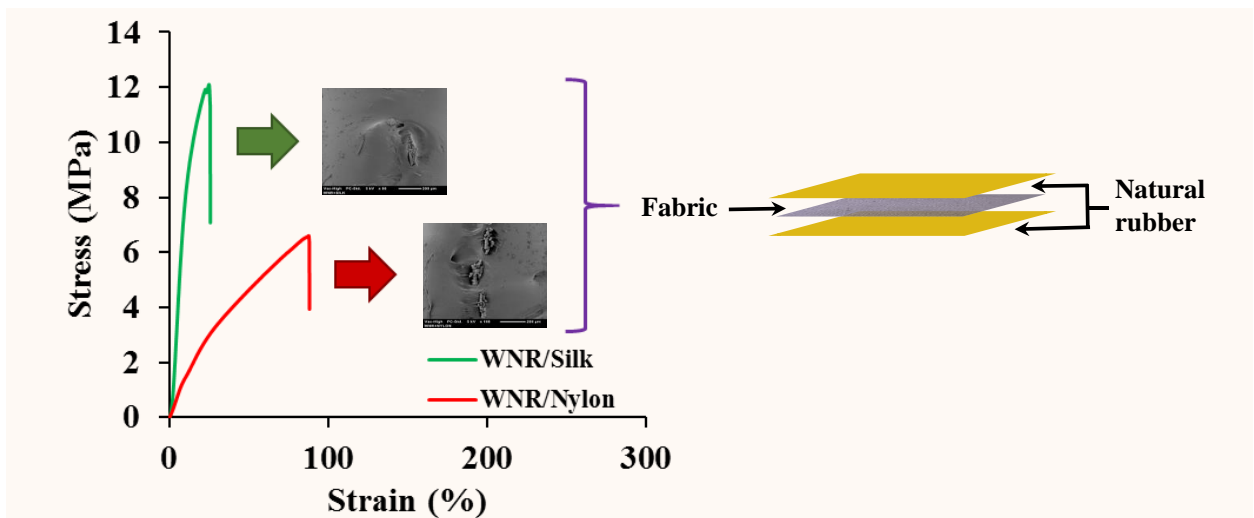
7 <sup>b</sup> Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart  
8 University, 50 Ngam Wong Wan Rd., Chatuchak, Bangkok 10900, Thailand.

9 <sup>c</sup> Centre for Natural Material Innovation, Faculty of Architecture, University of Cambridge,  
10 Cambridge CB2 1PX, UK., corresponding author: dus20@cam.ac.uk

11 <sup>d</sup> Oxford Silk group, Department of Zoology, University of Oxford, Oxford OX1 3PS, UK,  
12 corresponding author: fritz.vollrath@zoo.ox.ac.uk

13  
14 **Graphical abstract**

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



18 Electron Microscope.

19

20

21 **Abstract**

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

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

38

## 39 **1 Introduction**

40 Natural rubber (NR) is a very useful elastomer because it possesses properties  
41 such as high green strength, high tensile strength, low heat hysteresis and high damping  
42 [1-3]. Moreover, in contrast to synthetic elastomers, NR is a renewable product. Fresh  
43 NR latex from *Hevea brasiliensis* normally consists of 30-40% rubber, 50-60% water and  
44 5-6% non-rubber components (*e.g.* proteins, lipids) [4]. A molecular chain of NR is  
45 composed of two or three units of *trans*-1,4 polyisoprene and a long sequence of *cis*-1,4  
46 polyisoprene. At the initiating terminal,  $\omega$ -terminal, the NR molecule associates with  
47 protein, while the chain end,  $\alpha$ -terminal, associates with phospholipid. NR molecules can  
48 form gel fractions through reactions between functional terminal groups at the end of the  
49 NR molecules and proteins at the  $\omega$ -terminal or phospholipids at the  $\alpha$ -terminal [5]. The  
50 proposed new model for the structure of the rubber latex particle surface consists of a  
51 mixed layer of proteins and phospholipids around the latex particle [6].

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

65 Bio-based composites which provide a good compromise between their final  
66 performance and environmental impact are becoming preferred materials for use. In the  
67 last two decades, natural fibers have been considered to reinforce rubber composites [7-  
68 8]. Bombyx mori silk is a natural polymer fibre that has been used in textile production

69 for millennia. Silk in its natural form is composed of a filament core protein, silk fibroin,  
 70 and a glue-like coating consisting of a family of sericin proteins. Silk has superb  
 71 mechanical properties in comparison to other common technical and textile fibres (Table  
 72 1), specifically the combination of strength and ductility leading to its high toughness.  
 73 Their properties have been translated in silk fibre reinforced polymer composites as well  
 74 [9-10]. However, there has been limited work on silk reinforced elastomeric composites.  
 75 While silk fiber reinforced NR composites were investigated several decades ago,  
 76 including assessing the effects of rubber formulations, bonding agents, and fibre filler  
 77 loading levels on processing characteristics and mechanical properties [15], the studies  
 78 were based on short, discontinuous fibre reinforcements. In contrast, there are no studies  
 79 in literature on silk textile reinforced NR composites.

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

Fibre	Density [g·cm <sup>-3</sup> ]	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

82

83 An example application where such green materials are of increasing interest is in  
 84 the sports and leisure industry. For example, high-performance bicycle tubular tire  
 85 casings are commonly made from textile reinforced uncured (*i.e.* non-vulcanised) rubber,  
 86 both NR latex and butyl-based rubber. In passing, while vulcanisation of rubber makes  
 87 the material more durable (and therefore is a pre-requisite for most industrial  
 88 applications), uncrosslinked rubber is preferred for tubulars for a range of reasons. Non-  
 89 vulcanised tubulars are more flexible (offering reduced rolling resistance and a more  
 90 comfortable ride) and less prone to flats (through punctures and crack-propagation). The  
 91 reinforcement of the uncrosslinked rubber offers improved mechanical properties. While  
 92 nylon and cotton textiles are commonly used, tubulars with silk textile based casings are

93 preferred by some professional athletes. Importantly, silks are the only natural fibre to  
94 exist as fine filaments (Table 1) implying that high strength, fine yarns (of low tex or  
95 denier) can be produced with ease. For casings, these strong yet flexible and fine silk  
96 threads are then used to produce high thread count (*i.e.* high areal density) fabrics.  
97 Casings with a high thread per inch count fabric generally translate to a thinner, flexible  
98 and lighter material that allows for higher pressure capacities and decreased rolling  
99 resistance and consequently faster speeds, improved grip and a more comfortable ride  
100 (due to absorption of micro-impacts).

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

## 112 **2 Experimental**

### 113 **2.1 Materials**

#### 114 **2.1.1 Preparation of whole and purified natural rubber**

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

118 To prepare purified natural rubber (PNR), fresh natural rubber latex was  
119 centrifuged at 10,000 rpm for 30 min at 25°C. The cream fraction was dispersed in  
120 1% w/v SDS and re-centrifuged at 10,000 rpm for 30 min at 25°C. Then the cream

121 fraction was washed in deionized water and re-centrifuged at 10,000 rpm for 30 min at  
122 25°C. The resulting PNR was casted into thin film, and dried at 50°C for 24 hr.

### 123 2.1.2 Reinforcement materials

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

129 *Table 2 Properties of the nylon and silk reinforcement fabrics.*

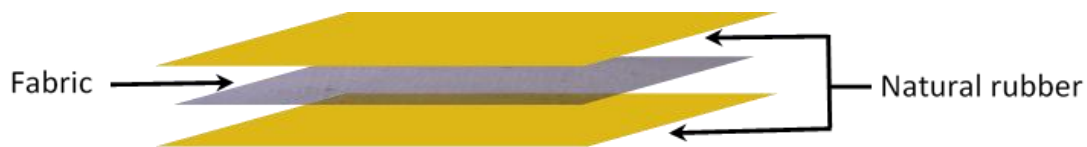
Fabric	Yarn count		Areal density (g·m <sup>-2</sup> )
Nylon	Warp yarn	110 ± 10 per inch	57.5
	Weft yarn	80 ± 7 per inch	
	Total yarn	190 per inch <sup>2</sup>	
Silk	Warp yarn	100 ± 9 per inch	66.5
	Weft yarn	90 ± 9 per inch	
	Total yarn	190 per inch <sup>2</sup>	

130

### 131 2.2 Composite manufacture

132 To fabricate the elastomeric composites, first, NR samples were compressed at  
133 70°C for 10 min in order to obtain 1 mm thick sheets. Thereafter, reinforcement fabric  
134 was sandwiched between two rubber sheets for a target fibre volume fraction of 5% (Fig.  
135 1). Finally, the sandwich sample was compressed at 70°C for 10 min, allowing the rubber  
136 to impregnate the fabric, and obtain a 2 mm thick composite sheet. For this study, we  
137 produced four different types of composite samples: WNR/Nylon, WNR/Silk,  
138 PNR/Nylon, and PNR/Silk.

139



140

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

## 142 2.3 Property analysis

### 143 2.3.1 Chemical characterisation of NRs

144 Nitrogen content of NR samples (WNR and PNR) was determined using the  
145 Kjeldahl method [13]. Dried rubber sheets were cut into 0.5 g pieces and placed in a  
146 Kjeldahl flask. Then, 0.8 g of catalyst mixture ( $K_2SO_4$ : $CuSO_4 \cdot 5H_2O$  in 7:0.8 by mass)  
147 was added, followed by 15 mL of concentrated sulfuric acid. The mixture was boiled  
148 gently in the digestion unit at 420°C until the solution became colorless. The digested  
149 solution was cooled to room temperature, and then transferred into distillatory using 25  
150 mL of 4%  $H_3BO_3$  as the receiving solution. The distillation continued until 200 mL of  
151 distillate was collected. Thereafter, the distillate was titrated with 0.01 M HCl. Blank was  
152 determined by adding all the reagents but omitting the samples. Total nitrogen content  
153 was calculated as follows:

$$154 \quad \% \text{Nitrogen} = [(B - C) \times N \times (14 / 1000)] / W \times 100 \quad \text{Eq. 1}$$

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

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

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

### 171 **2.3.2 Composite characterisation**

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

175 The tensile mechanical properties of the composites were measured on an Instron  
176 5944 universal testing machine equipped with a 50 N load-cell. Tests were carried out on  
177 dumb-bell shaped specimens at a crosshead speed of 100 mm·min<sup>-1</sup>.

178 Dynamic mechanical thermal analysis (DMTA) was conducted using a TA  
179 Instruments DMTA Q800. Tests in single cantilever mode were carried out in  
180 temperature scanning mode from -110°C to 30°C, at a rate of 3°C·min<sup>-1</sup>. In addition,  
181 measurements were performed in shear sandwich mode over a strain sweep from 0 to  
182 25% at a constant temperature of 25°C.

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

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

## 190 **3 Results and discussion**

### 191 **3.1 Chemical characterisation of natural rubber**

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



199 **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

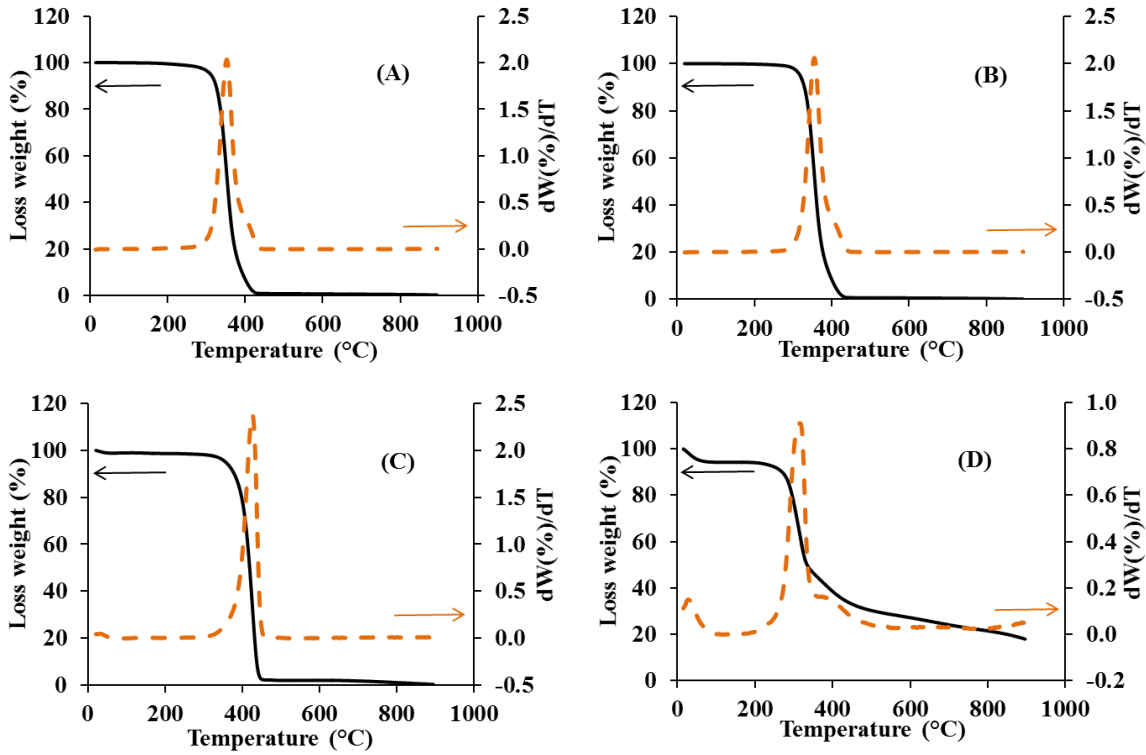
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201 The nitrogen level of NR is directly indicative of its protein content (a factor of  
202 6.25 is commonly used) [26]. As some of these proteins are potential allergens,  
203 deproteinisation of (natural and unnatural) rubbers is attractive where human contact with  
204 the materials, either during processing (*e.g.* during bicycle tire casing manufacture) or  
205 product use (*e.g.* gloves), is vital or unavoidable. However, the removal of non-rubber  
206 components has also shown to affect processing and mechanical properties of the natural  
207 rubber. For instance, PNR possesses better dynamic properties, including resistance to  
208 heat build-up, surface cracking from repeated bending (known as flex cracking), and  
209 cyclic loading, in comparison to WNR [25, 27].

### 210 **3.2 Mechanical and thermal properties of the elastomeric composites**

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

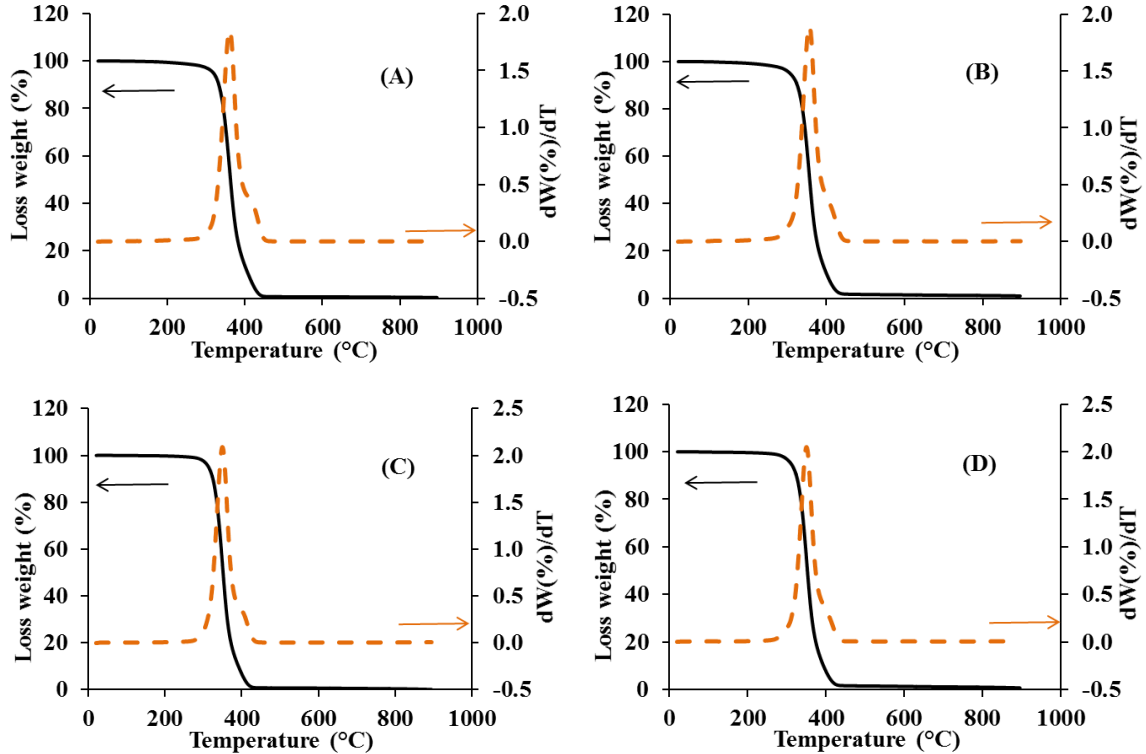
214 First, we used thermogravimetric analysis (TGA) to study the thermal properties  
215 of the unmixed materials (Fig. 2) and then the different composite samples (Fig. 3). There  
216 were no significant differences in the thermal properties between unreinforced WNR and  
217 PNR (Fig. 2A and 2B). Silk fabrics exhibited a 5-6% loss of mass below 100°C, unlike  
218 the rubbers and the nylon fabrics, which was associated with moisture evaporation (Fig.  
219 2C and 2D) [23]. Silk fabrics also showed earlier onset of thermal degradation (around  
220 250-300°C) in comparison to the unfilled rubbers (375-400°C) and nylon fabrics (400-  
221 425°C). A stark difference between the rubbers and nylon fabrics, and the silk fabric was  
222 that silk fibres exhibited a residual mass of around 18% at 900°C, whereas the other  
223 unmixed materials completely decomposed (almost 0% residual mass) as low as 500°C.  
224 The composite samples did not exhibit significant differences in thermal properties (Fig.  
225 3), probably due to the only low volume fraction of fibre in the materials.



226

227

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



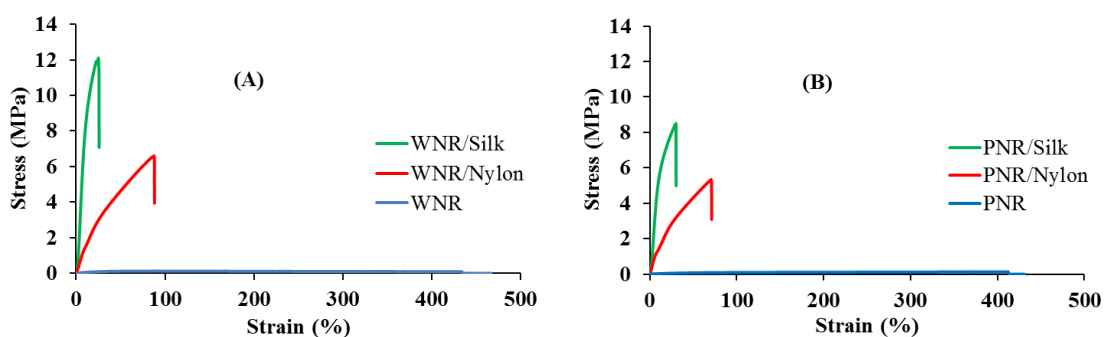
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**Fig. 3** TGA profiles of (A) WNR/nylon, (B) WNR/silk, (C) PNR/nylon and (D) PNR/silk.

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

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



250

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

254

255

**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

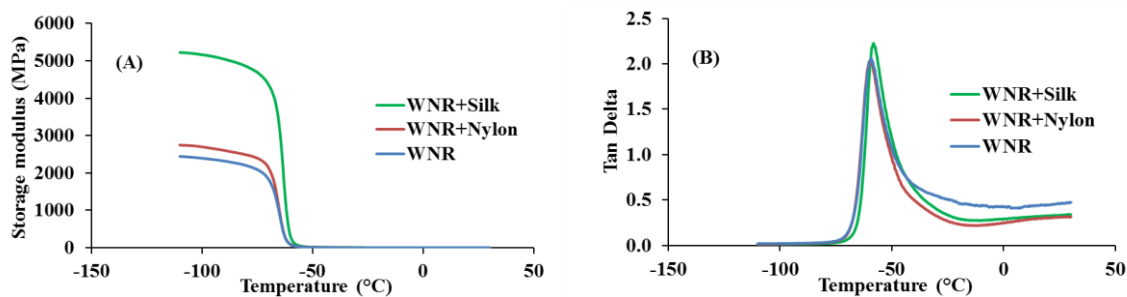
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257 DMTA in single cantilever mode was carried out to ascertain mechanical  
 258 (stiffness and damping) behaviour over a larger temperature range (Fig. 5 and 6). The  
 259 DMTA profile also enabled determination of glass transition temperatures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

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

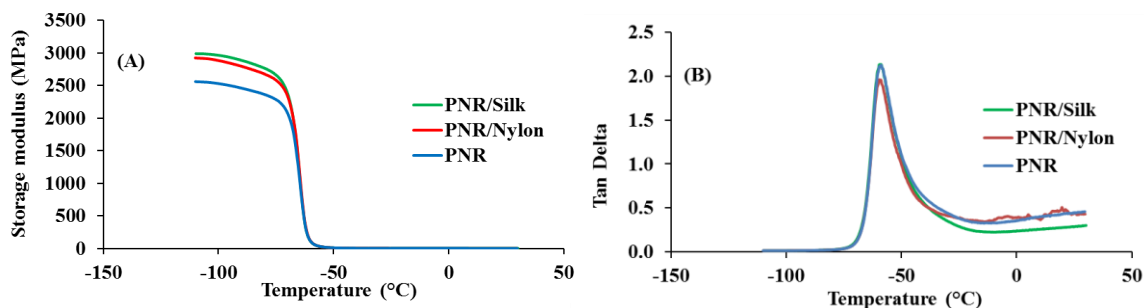
276 Differences in modulus between the silk and nylon composites were less  
 277 significant in PNR matrix than WNR matrix. In fact, the storage modulus of WNR/silk  
 278 composites was almost twice that of PNR/silk composites (at low temperatures). This was  
 279 in agreement with tensile test results,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

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



284

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

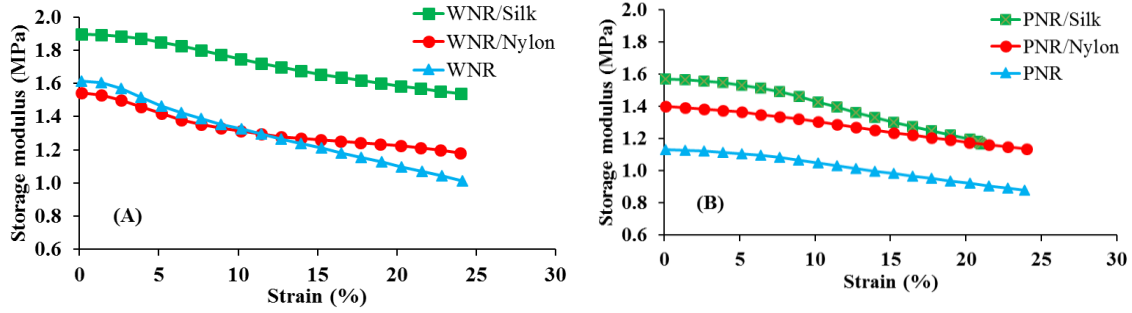


287

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

### 290 3.3 Interfacial properties of composite

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



301

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

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

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

322 
$$W = 2(\gamma_r \cdot \gamma_f)^{0.5} \quad \text{Eq. 2}$$

323 
$$\gamma_r = \gamma_r^p + \gamma_r^d \quad \text{Eq. 3}$$

324 
$$\gamma_f = \gamma_f^p + \gamma_f^d \quad \text{Eq. 4}$$

325 where  $\gamma_r$  is the surface energy of rubber,  $\gamma_f$  is the surface energy of fabric,  $\gamma_r^p$  is the polar  
 326 component of rubber,  $\gamma_r^d$  is the dispersive component of rubber,  $\gamma_f^p$  is the polar  
 327 component of fabric and  $\gamma_f^d$  is the dispersive component of fabric.

328 **Table 5** Surface energy of different materials.

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

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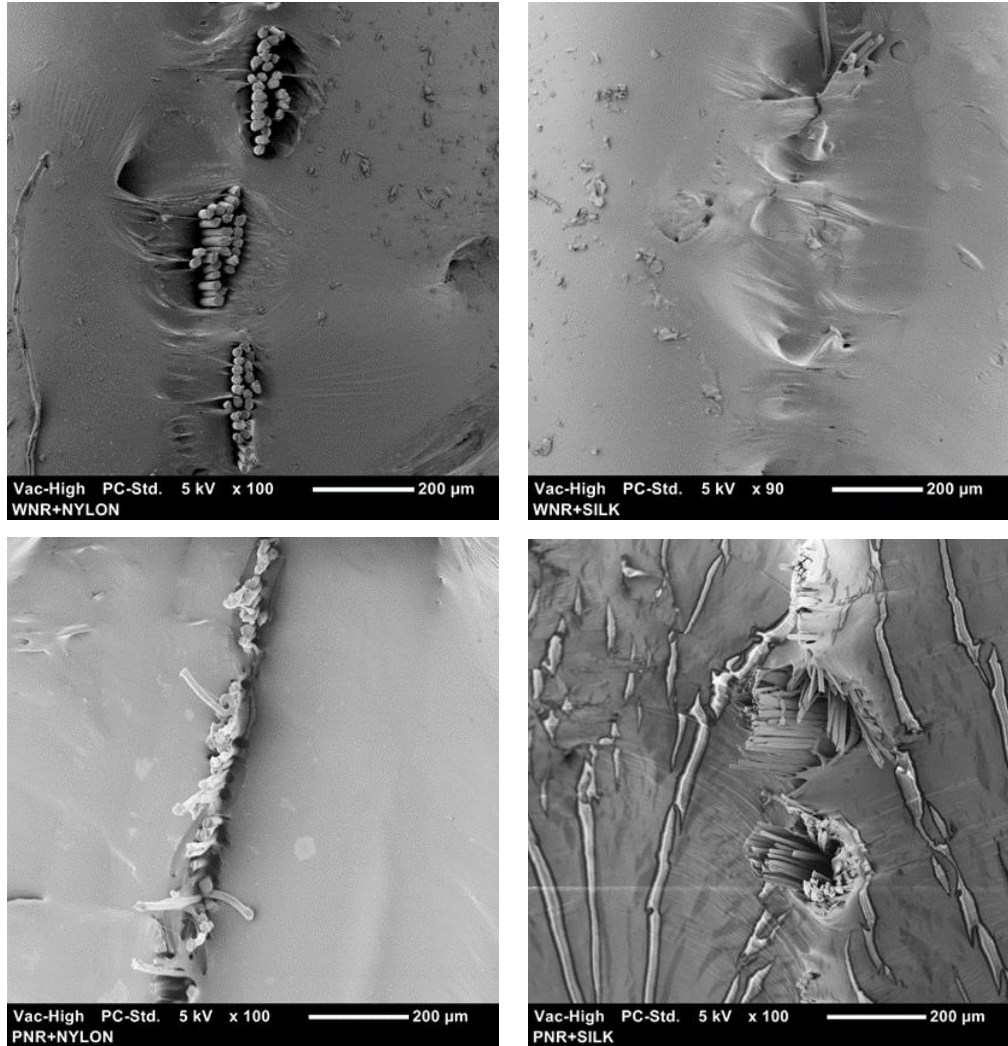
330 **Table 6** Work of adhesion for different composite samples.

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

331

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

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



350

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

352 **4 Conclusions**

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

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



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

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

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