

1 **Review on hygroscopic aging of cellulose fibres and their biocomposites**

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13  
14 **Abstract**

15  
16 This review presents critical literature on effects of humidity and temperature on the  
17 properties of natural fibres and its composites. The drawback of moisture absorption on the  
18 mechanical properties of natural fibre and its composites is evaluated. Numerous researchers  
19 have been working to address the moisture absorption issue, with specific attention paid to  
20 the surface treatment of fibres and refining the fibre-matrix interface. Because of the natural  
21 fibre's positive commercial and environmental outcomes, as well as their desirable properties  
22 such as high specific strength, natural fibre reinforced composites are displaying a good  
23 potential to be used in various applications such as automotive, aerospace and packaging.  
24 This review addresses a comprehensive survey on hygroscopic factors (long term  
25 environmental aging) affecting natural fibres and their performance as reinforcement in  
26 polymer composites. The effects of cellulose surface chemistry and topography on  
27 hydrophobicity are addressed. Furthermore, the review also addresses the progress in the  
28 development of superhydrophobic materials based on cellulose material for better moisture  
29 resistance. In addition, recent investigations dealing with bio-based coatings prepared from  
30 renewable resources are also discussed.

31  
32 **Keywords:** Humidity; Temperature; Superhydrophobic; Bio-based coatings, Natural fibre

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## 69 1. Introduction

70

71 The use of natural fibres as reinforcement in polymer composite materials is constantly  
72 growing, especially in the automotive and aerospace industries, because of a need to produce  
73 environmental friendly products. It is likely that application of natural fibres as reinforcement  
74 in polymer matrices could expand their usage in the near future due to their offered  
75 advantages, which include low weight, high strength, low maintenance cost and corrosion  
76 resistance (Azwa, Yousif, Manalo & Karunasena, 2013). Conversely, a major setback of  
77 natural fibres is their vulnerability to moisture absorption which results in poor mechanical  
78 performance when reinforced with polymers and therefore limits their application. Natural  
79 fibre composites undergo mechanical failure in humid conditions through water sorption  
80 resulting in delamination. When exposed to environmental conditions such as varying  
81 humidity and temperature, the composites are prone to moisture absorption leading to  
82 porosity, disbanding around filler, swelling, sorption in microcracks, and voids, which  
83 adversely affects the mechanical properties (Adroja, Koradiya & Parsania, 2013; Azwa &  
84 Yousif, 2013; Cristaldi, Latteri, Recca & Cicala, 2010; Sen & Reddy, 2013). Previous  
85 studies have reported that the factors such as, fibre volume fraction; temperature; humidity;  
86 matrix; fibre type and fibre-matrix adhesion influence the amount of moisture absorption, and  
87 therefore affect the composite properties. For instance, in wood fibre-polypropylene  
88 composites it was observed that the water absorption increases with increasing fibre content  
89 owing to the increased cellulose content (Bledzki & Faruk, 2004). The hydrophilic nature of  
90 natural fibres is obtained from lignocellulose, which contains strong polarized hydroxyl  
91 groups (Zafeiropoulos, 2011). This hydrophilic nature restricts compatibility with  
92 hydrophobic polymer matrix which results in poor interfacial interaction between a  
93 hydrophilic fibre and a hydrophobic polymer. In addition, the moisture absorption drawback  
94 could minimise the applications of natural fibres in advanced industrial sectors (aerospace  
95 and automotive); components in these sectors are exposed to a wide range of temperature and  
96 relative humidity and this affects the long-term strength and durability (Cristaldi, Latteri,  
97 Recca & Cicala, 2010; Zafeiropoulos, Williams, Baillie & Matthews, 2002) Dhakal, Zhang &  
98 Richardson, 2007; Zaki Abdullah, Dan-mallam & Megat Yusoff, 2013)

99

100 Surface modification of natural fibres has served as an essential tool to improve the  
101 compatibility with the polymer matrix. Studies on surface modification of natural fibres  
102 leading to moisture absorption have been reported in literature (Alawar, Hamed & Al-Kaabi,

103 2009; Cantero, Arbelaiz, Llano-Ponte & Mondragon, 2003; Dixit & Verma, 2012; Hashim,  
104 Roslan, Amin, Zaidi & Ariffin, 2012; John & Anandjiwala, 2008; Kalia, Kaith & Kaur, 2009;  
105 Keener, Stuart & Brown, 2004; Kumar, Obrai & Sharma, 2011; Rout, Misra, Tripathy, Nayak  
106 & Mohanty, 2001; Sgriccia, Hawley & Misra, 2008; Xie, Hill, Xiao, Militz & Mai, 2010;  
107 Zafeiropoulos, Williams, Baillie & Matthews, 2002). However, the long term effect of  
108 exposure of natural fibre composites to high relative humidity and temperature is  
109 problematic, further techniques such as nano-coatings, bio-based coatings and chemical  
110 modifications need to be exploited or optimised to enhance surface hydrophobicity of natural  
111 fibres. Emphasis has to be placed on the effects of cellulose surface chemistry and  
112 topography, both of which affect hydrophobicity. Interestingly, research on  
113 superhydrophobicity has stimulated much scientific and industrial interest because of  
114 applications in self-cleaning, friction reduction, water repellence and antifouling (Song &  
115 Rojas, 2013). In addition, bio-based polyurethane coatings with superior properties such as  
116 solvent resistance, hydrolytic stability, weatherability and acid-base resistance have been  
117 reported and show good moisture repellence properties. Another promising hydrophobic resin  
118 is poly(furfural alcohol) which holds excellent properties such as high heat distortion  
119 temperature, high chemical resistance, hydrophobicity and high chemical resistance (Deka,  
120 Misra & Mohanty, 2013; Kumar, Kumar & Anandjiwala, 2012). Reviews on effect of water  
121 sorption /diffusion on properties of natural fibres/ composites are present in literature.  
122 However, this review addresses issues of moisture absorption as a result of relative high  
123 humidity and temperature and focuses on significant effects on chemical and physical  
124 properties of natural fibres as well as on final performance of composite structures especially  
125 in long-term application. The review also discusses the drawbacks of mechanical fatigue  
126 associated with long-term durability of natural fibre reinforced composites especially when  
127 moisture sorption is accompanied by high environmental variations of temperature and  
128 humidity. Furthermore, the review also highlights research work done on chemical treatment  
129 to reduce the inherent hydrophilicity of lignocellulosic fibres and retard moisture absorption  
130 behaviour. Emphasis is placed on possible solutions to bridge the gap between chemical  
131 treatments, bio-based coatings and developing superhydrophobic materials using  
132 nanoparticles to improve the long-term utilization of fibre reinforced composites, especially  
133 when exposed to water absorption accompanied by high hygroscopic factors. Therefore, a  
134 comprehensive survey in the development of superhydrophobic materials based on cellulose  
135 material for better moisture resistance as well as the potential of bio-based coatings to be

136 used as suitable material for lowering moisture absorption in natural fibre composites is  
137 discussed

138

## 139 2. Natural fibres

140

### 141 2.1 Structure and properties of natural fibres

142

143 Natural fibres are divided based on their origins, coming from plants, animals or minerals.

144 All plant fibres are made-up of cellulose while animal fibres comprise of proteins (wool, hair,  
145 and silk). Natural fibres consist of bast fibres (or stem or soft sclerenchyma), hard or leaf

146 fibres, seed, cereal straw, wood, fruit, and other grass fibres. In their natural form, fibres are  
147 composites made up of hollow cellulose fibrils fused together by hemicellulose and lignin

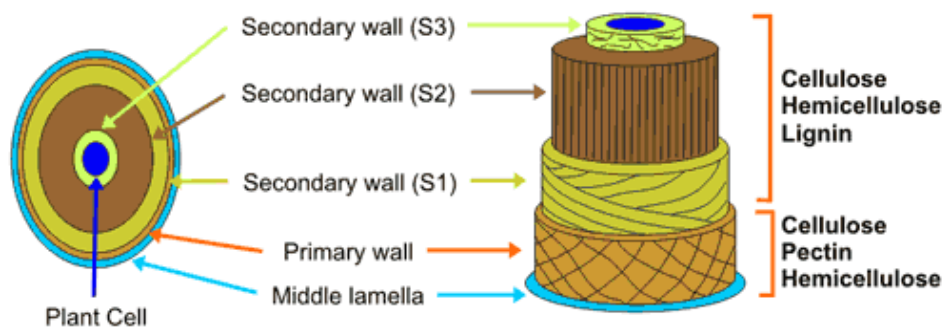
148 matrix (Jayaraman, 2003; John & Anandjiwala, 2008; John & Thomas, 2008) (see Figure 1).

149 Each fibril consists of complicated layered structure comprised of a thin primary wall  
150 surrounding a thick secondary wall. This secondary wall is comprised of three layers of

151 which the thick middle layer controls the mechanical properties of the fibre. The middle layer  
152 has a series of helically coiled cellular microfibrils created from long chain cellulose

153 molecules; between the microfibrils and the fibre axis a microfibrillar angle which varies  
154 from one fibre to another is found.

155



156

157 **Figure 1 Structure of natural fibre**

158 (<http://bioenergy.crc.uga.edu/Background/background.htm>)

159

160 The microfibrils are made up of 30-100 cellulose molecules with diameter of about 10-30 nm

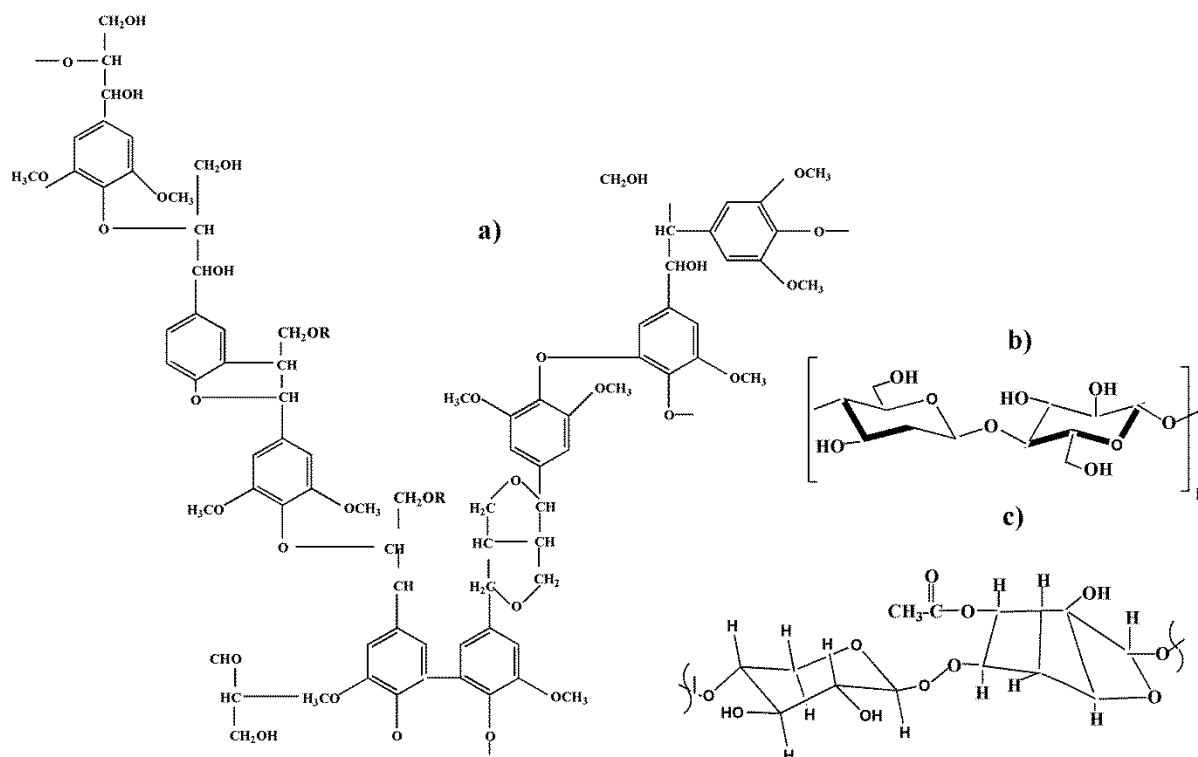
161 in extended chain conformation and offers mechanical strength to the fibre. The cell wall is

162 very complicated and made-up of hemicellulose, lignin and in some circumstances wax and

163 pectin. Hemicellulose molecules are held to cellulose by hydrogen bonds which act as

164 cementing matrix between the cellulose microfibrils, to form a hemicellulose-cellulose  
 165 network, which is seemingly the main structural constituent of the fibre. The stiffness of the  
 166 hemicellulose/cellulose composite is increased by a network of a hydrophobic lignin which acts  
 167 as a coupling agent in the fibre cell. The nature of cellulose and its crystallinity correlates to  
 168 the reinforcing efficiency of natural fibres. The main constituents of natural fibres are  
 169 hemicellulose; lignin; cellulose (Figure 2) while pectin; wax; fat and water soluble substances  
 170 are the minor components of the structure. These compositions may differ with test methods  
 171 and with growing conditions even for the same kind of fibre (see Table 1) (Mohanty, Misra &  
 172 Drzal, 2001; Singleton, Baillie, Beaumont & Peijs, 2003; Turmanova, Genieva, Dimitrova &  
 173 Vlaev, 2008).

174



175  
 176 **Figure 2** Chemical structures of (a) lignin (b) cellulose and (c) hemicellulose.  
 177 Reprinted from Kabir, Wang, Lau & Cardona, 2012, Copyright 2012,  
 178 with permission from Elsevier

179  
 180 Hemicelluloses are polysaccharides that comprise of several sugar moieties that are mostly  
 181 branched, and have a significantly lower molecular weight with a degree of polymerization  
 182 (DP) ranging from 50-200 compared to cellulose. The sugar moieties contain glucose but also  
 183 other monomers such as arabinose, xylose, mannose and galactose. Hemicellulose is partially

184 soluble in water and hygroscopic due to its open structure which contains of acetyl and  
185 hydroxyl groups (Mohanty, Misra & Hinrichsen, 2000).

186 The primary component of natural fibres is cellulose which characterized as a linear  
187 condensation polymer comprised of D-anhydro-glucopyranose units joined together by 1,4- $\beta$ -  
188 D-glycosidic linkages at C1 and C4 position. The overall structure of cellulose is made up of  
189 amorphous and crystalline regions. The cellulose content in the fibre, the microfibril angle  
190 and the degree of polymerization frequently determined the mechanical properties of the  
191 natural fibre (Mohanty, Misra & Hinrichsen, 2000).

192

193 Lignin is a randomly branched polyphenol, made up of phenylpropane (C<sub>9</sub>) units and it is the  
194 most complex polymer among naturally occurring high-molecular-weight materials. Owing  
195 to its hydrophobic character, lignin reduces the penetration of water across the cell walls,  
196 which is made up of amorphous hemicelluloses and cellulose fibres, and in that way assists  
197 the transport of aqueous solutions of metabolites in the conducting xylem tissue and nutrients.  
198 Lignin brings rigidity to the cell walls and works together with hemicellulose to join cells in  
199 woody parts of plants, producing a composite structure with outstanding elasticity and  
200 strength. Moreover, lignified materials successfully repel attacks by microorganisms by  
201 means of blocking penetration of various enzymes into the cell walls (Mohanty, Misra et al.  
202 2000). Heteropolysaccharides are a collective name of Pectins, and give flexibility to plants,  
203 while least part of natural fibres is made up waxes which consist of different types of  
204 alcohols.

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218 **Table 1** Chemical composition of various fibres. Reprinted from John & Thomas,  
 219 2008, Copyright 2007, with permission from Society of Plastics Engineers.  
 220 Reprinted from John & Anandjiwala, 2008, Copyright 2008, with  
 221 permission from Elsevier

Fibre	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Abaca	56-63	20-25	7-9	3
Alfa	45.5	38.5	14.9	2
Bagasse	55.2	16.8	25.3	-
Bamboo	26-43	30	21-31	-
Banana	63-64	19	5	-
Coir	32-43	0.15-0.25	40-45	-
Cotton	85-90	5.7	-	0.6
Curaua	73.6	9.9	7.5	-
Flax	71	18.6-20.6	2.2	1.5
Hemp	68	15	10	0.8
Henequen	60	28	8	0.5
Isora	74	-	23	1.09
Jute	61-71	14-20	12-13	0.5
Kenaf	72	20.3	9	
Kudzu	33	11.6	14	-
Nettle	86	10	-	4
Oil palm	65	-	29	-
Pissava	28.6	25.8	45	-
Pineapple	81	-	12.7	-
Ramie	68.6-76.2	13-16	0.6-0.7	0.3
Sisal	65	12	9.9	2
Sponge gourd	63	19,4	11.2	3
Straw (Wheat)	38-45	15-31	12-20	-
Sun hemp	41-48	8.3-13	22.7	-

222  
 223 Natural fibres possess desirable properties such as high specific strength, high toughness, low  
 224 density, ease of separation, good thermal properties, biodegradability, improved energy  
 225 recovery, low cost and a non-corrosive nature. Commonly, fibres with a lower microfibrillar



226 angle (MFA) (the angle between the fibre axis and cellulose microfibrils) and highest  
 227 cellulose content have better strength properties (see Table 2) (Eder & Burgert, 2010). The  
 228 spiral orientation of the fibre axis determines the ductile property in the plant fibre. If the  
 229 microfibrils are oriented parallel to the fibre axis, the fibres turn out to be stiff, inflexible, and  
 230 possess high tensile strength (John & Anandjiwala, 2008). Although natural fibres have  
 231 relatively lower strength properties compared to the synthetic fibres, the elongation at break  
 232 and specific modulus suggests the potentiality of these fibres to substitute synthetic fibres in  
 233 manufacturing of polymer composites (Kabir, Wang, Lau & Cardona, 2012).

234

235 **Table 2 Comparative properties of natural fibres with conventional manmade**  
 236 **fibres. Reprinted from Kabir, Wang, Lau & Cardona, 2012, Copyright 2012, with**  
 237 **permission from Elsevier**

Name of fibre	Density (g/cm <sup>3</sup> )	Micro-fibrillar angle (MFA) (°)	Tensile strength (MPa)	Young's modulus (GPa)	Specific strength (GPa/g/cm <sup>3</sup> )	Specific modulus (GPa/g/cm <sup>3</sup> )	Elongation at break (%)
<b>Jute</b>	1.3-1.4	7-9	393-773	13-26.5	0.3-0.5	10-18.3	1.16-1.5
<b>Flax</b>	1.50	10-11	345-1100	27.6	0.2-0.7	18.4	2.7-3.2
<b>Hemp</b>	1.14	6	690	30-60	0.6	26.3-52.6	1.6
<b>Ramie</b>	1.50	8; 7.5	400-938	61.4-128	0.3-0.6	40.9-85.3	1.2-3.8
<b>Sisal</b>	1.45	19.7	468-640	9.4-22.0	0.3-0.4	6.4-15.2	3-7
<b>PALF</b>	1.52	8-14	413-1627	34.5-82.51	0.3-1.1	22.7-54.3	1.6
<b>Cotton</b>	1.5-1.6	-	287-800	5.5-12.6	0.2-0.5	3.7-7.8	7.0-8.0
<b>E-glass</b>	2.5	-	2000-3500	70	0.8-1.4	28	2.5
<b>S-glass</b>	2.5	-	4570	86	1.8	34.4	2.8
<b>Aramid</b>	1.4	-	3000-3150	63-67	2.1-2.2	45-47.8	8 3.3-3.7

238

## 239 2.2 Advantages and disadvantages of plant fibres

240

241 The growing interest in using plant fibres or cellulosic fibres as reinforcement in polymeric  
242 based composites is mainly due to their abundance, diverse origin, modulus and  
243 comparatively high specific strength, lightweight, inexpensiveness (i.e. glass fibre having a  
244 density of  $2.6 \text{ g/cm}^3$  costs between \$1.30 and \$2.00/kg while flax fibre with a density of  $1.5$   
245  $\text{g/cm}^3$  cost between \$0.22 and \$1.10/kg) and affinity for biodegradable matrices when  
246 compared to glass fibre reinforced composites (Fakhrul & Islam, 2013; Joshi, Drzal, Mohanty  
247 & Arora, 2004). Cellulosic fibres as a completely renewable resource, they require little  
248 energy to be produced. Their carbon dioxide emissions are negligible to the atmosphere when  
249 they are composted or combusted and have a positive environmental impact. The processing  
250 atmosphere is user friendly allowing the fabric to breathe making working conditions better  
251 and as a result reducing the risk of allergic reactions and skin rashes. Plant fibres also display  
252 safer handling and working conditions unlike synthetic fibres. From a manufacturing  
253 viewpoint, car manufacturers find that the molding procedure for natural fibre composites  
254 consume less energy than that of fibreglass and yields less wear and tear on machinery, and  
255 as a result contribute to significant cost reductions  
256 (<http://bioenergy.cerc.uga.edu/Background/background.htm>). In addition they possess high  
257 electrical resistance and thermal reprocessing is also probable. They further provide good  
258 acoustic insulating properties owing to their hollow cellular structure and their worldwide  
259 accessibility is an added factor (John & Thomas, 2008).

260

261 Natural fibres are regarded as potential substitutes for manmade fibres in composite  
262 materials. Although natural fibres have benefits of being inexpensive and light weight, they  
263 are not totally immune to problems. One of the problems with natural fibres is their strong  
264 hydrophilic character which generates incompatibility with most polymer matrices as well as  
265 compounding difficulties. This leads to a heterogeneous dispersion of the fibres in the matrix  
266 and consequently impairs the properties of the resulting composite. One more setback of  
267 natural fibres is their low degradation temperatures ( $\sim 200 \text{ }^\circ\text{C}$ ), which make them unsuitable  
268 to process with thermoplastics above  $200 \text{ }^\circ\text{C}$  and this again limits the choice of polymer  
269 material. Another restraint to the successful utilization of natural fibres for tough composite  
270 application is low microbial resistance and vulnerability to rotting. These properties pose  
271 severe problems during transportation, storage, and composite processing. The  
272 inhomogeneity and variation of dimensions and of their mechanical properties (even between

273 individual plants in the same cultivation) creates another serious problem. Another serious  
274 drawback is the high moisture uptake of natural fibres leading to swelling and creating voids  
275 at the interface, which results in poor mechanical properties and decreases dimensional  
276 stability of composites. However, the recent literature revealed that, the moisture uptake of  
277 fibres can be diminished by modifying the hydrophilic hydroxyl groups from the fibre surface  
278 by means of different chemical modifications (alkali, silane, acetylation treatments and many  
279 more). These modifications are typically based on the use of reagent functional groups that  
280 are capable of reacting with the functional groups in the fibre structure and changing their  
281 composition. This would result to the reduction of moisture absorption tendency and simplify  
282 compatibility with the polymer matrix. Many studies, reports and reviews have been  
283 published on chemical modification of natural fibres in order to improve their compatibility  
284 with polymers matrices (Cantero, Arbelaiz, Llano-Ponte & Mondragon, 2003; Hashim,  
285 Roslan, Amin, Zaidi & Ariffin, 2012; John & Anandjiwala, 2008; Kalia, Kaith & Kaur, 2009;  
286 Keener, Stuart & Brown, 2004; Kumar, Obrai & Sharma, 2011; Xie, Hill, Xiao, Militz &  
287 Mai, 2010; Zafeiropoulos, Williams, Baillie & Matthews, 2002). Improved physical and  
288 mechanical properties have been reported and chemical treatment proved to reduce moisture  
289 absorption to a degree (Alawar, Hamed & Al-Kaabi, 2009; Dixit & Verma, 2012; Rout,  
290 Misra, Tripathy, Nayak & Mohanty, 2001; Sgriecchia, Hawley & Misra, 2008).

291

### 292 2.3 Moisture absorption behaviour of natural fibres

293

294 Natural fibres are characteristically hydrophilic in nature because of the existence of a large  
295 number of hydroxyl groups (-OH) in cellulose and hemicellulose. However, not all  
296 constituents contribute to the absorption of moisture. Cellulose, which forms the major part  
297 of the natural fibre, is hydrophilic in nature and it can absorb water molecules. Even though  
298 cellulose has a large -OH to carbon (C) ratio, a small amount -OH groups are exposed or  
299 accessible as cellulose is semicrystalline. The highly crystalline region of the cellulose is  
300 virtually inaccessible to water molecules but the water molecules are able to penetrate and  
301 gain access into the amorphous region of the cellulose. On the other hand, hemicellulose is  
302 predominantly amorphous with high -OH to C ratio making it highly accessible to water  
303 molecules. Lignin, however, is hydrophobic in nature and has low -OH to C ratio. When  
304 natural fibres absorb water molecules, they swell up due to water molecules occupying the  
305 space between the microfibrils. This space that the water molecules occupy is known as the  
306 temporary microcapillary network. The water molecules within the natural fibres can either

307 form a monolayer, which associate closely with the available –OH groups, or form a  
308 multilayer at which not all water molecules are in intimate contact with available –OH  
309 groups. (Zafeiropoulos, 2011).

310

311 In the case of natural fibre-reinforced composites, moisture absorption rest on factors for  
312 example fibre volume fraction, temperature, reinforcement alignment and diffusivity.  
313 Moisture diffusion into the composite materials is steered by one major mechanism, namely,  
314 diffusion. Diffusion can be defined as the process by which matter is transported from one  
315 part of a system to another as a result of random molecular motion. The diffusion mechanism  
316 consists of the direct penetration of water into the polymer and to a much less extent into the  
317 fibres. The capillarity and transport through microcracks and voids are most common  
318 mechanisms. The capillarity mechanism involves the flow of water molecules along the  
319 polymer-fibre interface, followed by diffusion from the interface into the greater part of  
320 matrix. The vehicle of moisture by microcracks and voids includes both storage and flow of  
321 water into the microcracks and other forms of micro damages. Moisture absorption behaviour  
322 is observed when the fibre-polymer composite is exposed to moisture, the polar nature of  
323 fibres, causes the fibre to absorb water and swell. As a result, the dilapidation process starts  
324 with the inflammation of the amorphous portion in the fibre that develops stress at the  
325 interface and causes micro-cracking of the matrix around the inflamed fibres. The cracks  
326 aggravate water uptake and its attack on the fibre-matrix boundary. The absorbed water  
327 begins to form intermolecular hydrogen bonding with the fibres and in so doing reduces the  
328 interfacial adhesion between the fibres and the polymer, and soluble constituents will start  
329 leaking from the fibres. These ultimately lead to the debonding between the fibre and the  
330 polymer (Alomayri, Assaedi, Shaikh & Low, 2014; Costa, Almeida & Rezende, 2005; Zhang,  
331 Milanovic, Zhang, Su & Miao, 2014).

332

### 333 **3. Hygroscopic aging of natural fibre and its composites**

334

335 Hygroscopy is the capability of a material to easily absorb moisture from the surrounding  
336 environment. This is mainly influenced by the environmental conditions such as humidity  
337 and temperature. The attraction of water molecules is achieved by either absorption or  
338 adsorption with the absorbing or adsorbing material somewhat becoming physically changed.  
339 This could be through a change in boiling point, increase in volume, physical characteristic or  
340 viscosity of the material, as water molecules can become suspended between the material's

341 molecules in the process. Hygroscopic material such as cellulose fibres exhibit different  
342 hygroscopic properties which lead to detrimental effects such as stress concentration in  
343 composite materials (<http://en.wikipedia.org/wiki/Hygroscopy>; Choi, Ahn, Nam & Chun,  
344 2001). Furthermore, the recurring changes of the internal stresses as a result of water  
345 absorption-desorption process may induce fatigue damage in the inter- and intralaminar  
346 region of the composite material and therefore influence the performance and long-term  
347 durability of the composite. In natural fibre reinforced composites the hygroscopic effect is  
348 usually experienced from repeated absorption and desorption of moisture in a wide range of  
349 humidity and temperature.

350

### 351 3.1 Natural fibres and composites

352

353 There is a growing importance in the automotive production to replace glass fibre with  
354 natural fibre as reinforcing material in thermoplastic composites, but one main concern for  
355 the use of natural fibres is their poor performance when subjected to wide variations in  
356 temperature and humidity. This can affect the long term durability and strength of the  
357 structures. The effects of moisture absorption on natural fibre reinforced polymer composites  
358 have been widely investigated and have taken much interest. Absorption of moisture or water  
359 by composites is governed by many factors including temperature, humidity, matrix, the  
360 nature of the fibre, difference in the water circulation within the composites and the response  
361 between water and the polymer (Dhakal, Zhang & Richardson, 2007; George, Bhagawan &  
362 Thomas, 1998; Ray, 2006; Zaki Abdullah, Dan-mallam & Megat Yusoff, 2013; Zhang,  
363 Milanovic, Zhang, Su & Miao, 2014). Absorbed moisture causes plasticization, hydrolysis,  
364 debonding at the interface and the formation of cracks through swelling. This results in poor  
365 interfacial bonding which could eventually reduce the efficiency at which the composite  
366 transfers load in components, therefore, resulting in lower mechanical properties. It is  
367 therefore crucial to study the long term effects of temperature and humidity on natural fibres  
368 and its composites.

369 Zaki Abdullah, Dan-mallam & Megat Yusoff, 2013 investigated the influence of  
370 environmental degradation on the mechanical properties of kenaf-PET hybrid fibre reinforced  
371 polyoxymethylene (POM) composites. The samples were exposed to moisture, water spray  
372 and ultraviolet penetration in accelerated weathering chamber for 672 hours. They reported  
373 that the tensile strength of long fibre kenaf/POM (20/80) composite dropped by 50% from

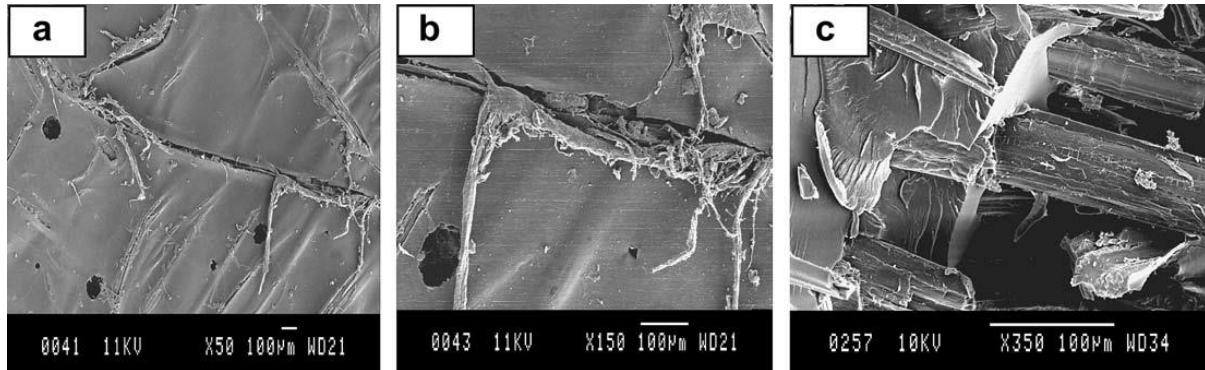
374 127.8 to 64.8 MPa while that of the hybrid (kenaf-PET/POM) composite dropped by only 2%  
375 from 73.8 to 72.5 MPa. This suggested that the hybrid had higher resistance to environmental  
376 degradation than the kenaf/POM composites, which was attributed to the hydrophobic  
377 characteristic of PET fibre in the composite and its high resistance to thermo-oxidative  
378 degradation. Unlike the hybrid composites, the kenaf/POM composites exposed to moisture  
379 and UV led to the degradation of lignin, hemicellulose and cellulose content in kenaf fibre  
380 resulting in a significant drop of the tensile strength. It was further observed that the flexural  
381 strength of hybrid samples for both short and long fibre composites had better retention of  
382 flexural strength than that of kenaf/POM composites. This was ascribed to high opposition of  
383 PET fibres to photodegradation compared to kenaf fibre.

384

385 The influence of water uptake on mechanical properties of hemp fibre reinforced unsaturated  
386 polyester composites were investigated (Dhakal, Zhang & Richardson, 2007). The reinforced  
387 composites were exposed to water absorption investigations by immersing the samples in  
388 water at 25 °C and 100 °C for different times. The water uptake of samples immersed in  
389 boiling water was higher than of samples immersed at room temperature. This was ascribed  
390 to the details that when the composites are subjected to moisture, the hemp fibre swells due to  
391 absorbed moisture and as a result micro-cracking of the composite occurs and this is more  
392 pronounced at high temperatures (see Figure 3 showing the micro cracking). It was also  
393 observed that absorption at room temperature took a longer period to attain equilibrium than  
394 absorption at high temperatures. Furthermore, the ratio of moisture absorption increased as  
395 the fibre volume fraction increased due to increased cellulose content. The mechanical  
396 properties of composites decreased with increase fraction of moisture absorption. However, it  
397 was noted that for hemp fibre reinforced samples (3 mm thickness from 5 layers); the  
398 ultimate tensile stress of the aged sample was higher than the dry samples. It was suggested  
399 that because of increased amount of absorbed water in the composites, this resulted to  
400 swelling of the fibres and filled the openings between the hemp fibre-polymer interfaces and  
401 eventually led to an increase in the mechanical properties of the composites. Improved  
402 Young's modulus was observed in the investigation of flax/PLA biocomposites immersed in  
403 seawater (Le Duigou, Bourmaud, Davies & Baley, 2014). The composite rigidity was  
404 evaluated between 0.025 and 0.1% range, and the Young's modulus of the composites  
405 immersed in seawater was found to increase until 0.5% range to 32 MPa. The reason behind  
406 the increase was attributed to a combined effect of fibre stiffness and water desorption during  
407 tensile testing. Similar observations have been reported on the influence of environmental

408 conditioning on physical and mechanical properties of flax fibres (Stamboulis, Baillie &  
409 Peijs, 2001). It was stated that after the flax fibre was exposure to humidified conditions (at  
410 90 % relative humidity (RH)), the fibres' tensile strength was increased by about 20%.

411



412

413 **Figure 3** Failure showing (a) matrix cracking, (b) fracture running along the  
414 interface and (c) fibre–matrix debonding due to attack by water  
415 molecules. Reprinted from Dhakal, Zhang & Richardson, 2007,  
416 Copyright 2007, with permission from Elsevier

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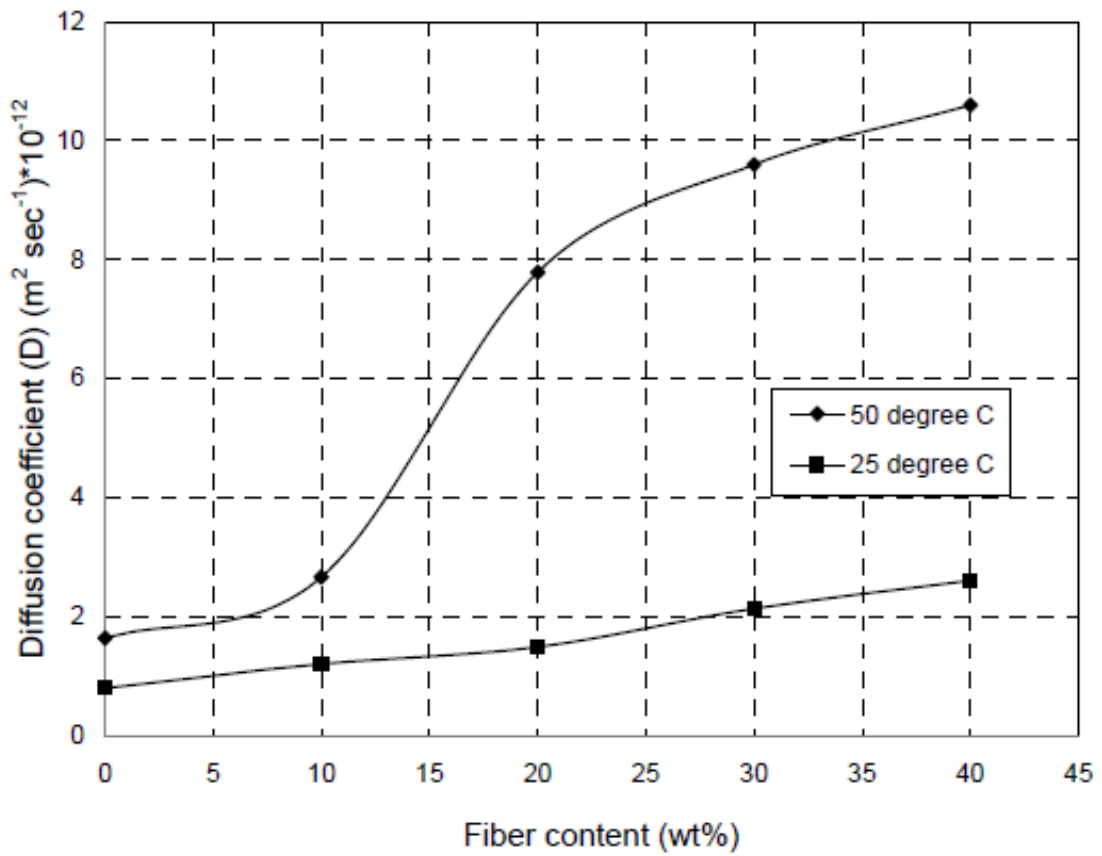
418 Chen, Miao & Ding, 2009 investigated the impact of moisture absorption on the interfacial  
419 strength of bamboo/vinyl ester composites. The bamboo strips were first conditioned at a  
420 constant temperature (20 °C) and at altered relative humidity stages (60, 70, 80 and 90%) till  
421 they reached equilibrium. It was reported that the rapid water uptake by bamboo strips at each  
422 RH stage firstly increased with the square root of time and then slowed down as water  
423 content came near equilibrium at 60% RH. The equilibrium moisture further increased  
424 sharply at 70% RH, and nearly doubled when the RH was increased from 80% to 90%. This  
425 was attributed to the large proportion of ground tissue (shaped like honeycomb structure)  
426 surrounding the cellulose fibres in the bamboo strips which have various capillary spaces that  
427 are ideal spots for keeping water. The interfacial shear strength (IFSS) reduced gradually with  
428 increasing RH during manufacturing contrast to composites manufactured at dry conditions.  
429 The IFSS value decreased by over a half when relative humidity increased to 70%, by more  
430 than 90% at 80% RH and almost zero at 90% RH. This was ascribed to poor interfacial  
431 bonding at high RH circumstances. The -OH groups found in the bamboo permits a large  
432 amount of hydrogen bonds to be formed between the matrix and the macromolecules of the  
433 cellulose. This result to a loss of compatibility between the polymer and the fibre bring about  
434 weakening and dilapidation of the interface.

435

436 Absorption of moisture in natural fibre composites is explained by three different major  
437 mechanisms. The first is the capillary action of water molecules into the openings and defects  
438 at the boundary between the fibres and the matrix because of incomplete bonding, followed  
439 by the flow of water molecules inside the microgaps amongst the polymer segments. Lastly  
440 the transportation of water molecules within microcracks in the polymer, made during the  
441 manufacturing process. Additionally, the moisture diffusion in polymer composites has been  
442 further classified to be non-Fickian or Fickian (Dhakal, Zhang & Richardson, 2007; Kim &  
443 Seo, 2006; Lin, Zhou & Dai, 2002; Osman, Vakhguelt, Sbarski & Mutasher, 2011). The  
444 Fickian flow denotes to the diffusion of water from a region of highest to lower  
445 concentrations generated by concentration gradient. The non-Fickian behaviour may be  
446 ascribed to the difference in absorption manner and state of water molecules present in the  
447 composites. At higher temperature, moisture uptake behaviour is accelerated due to an  
448 increase in the permeability coefficient and thereby greatly shortening the moisture saturation  
449 time. (Azwa, Yousif, Manalo & Karunasena, 2013; Joseph, Rabello, Mattoso, Joseph &  
450 Thomas, 2002; Osman, Vakhguelt, Sbarski & Mutasher, 2011). Kenaf fibre reinforced  
451 unsaturated polyester composites form different weight fractions (0, 10, 20, 30 and 40wt%)  
452 were prepared and assessed by dipping in tap water at different temperatures of 25 and 50 °C  
453 by Osman, Vakhguelt, Sbarski & Mutasher, (2011). The process of water absorption was  
454 found to approach the Fickian diffusion behaviour for both temperatures. This implied that  
455 water diffusion coefficients increased with increasing environmental temperature and fibre  
456 weight fraction as presented in Figure 4. The diffusion coefficient defines the rate of  
457 diffusion of particles, depending on the temperature, viscosity and particle size. It is a  
458 function of absolute temperature and has been shown to increase with increase in  
459 temperature. Furthermore, the flexural properties of the composites significantly decreased on  
460 exposure to moisture as presented in Figure 5a and b. This was ascribed to the creation of  
461 hydrogen bonding between the cellulosic fibre and water molecules and resulting in poor  
462 interfacial interaction between the kenaf fibre and polyester.

463



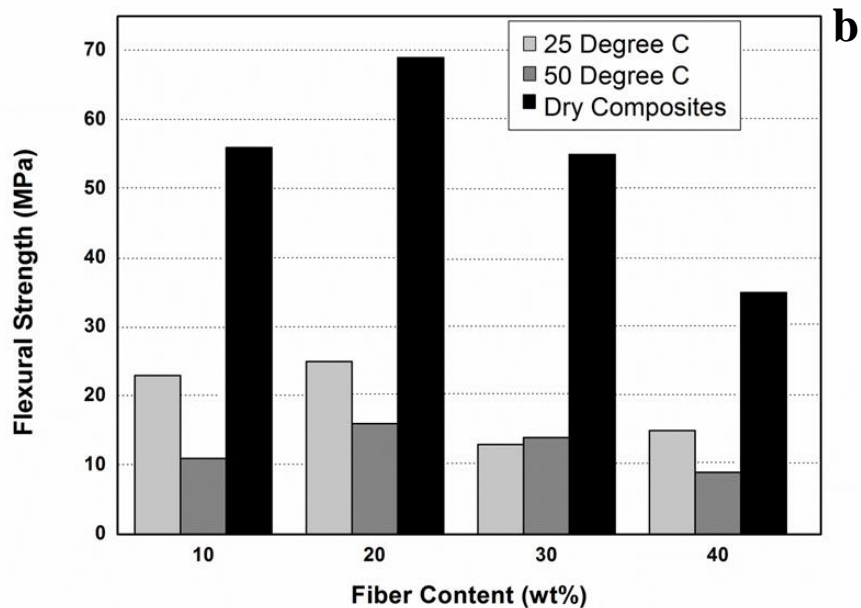
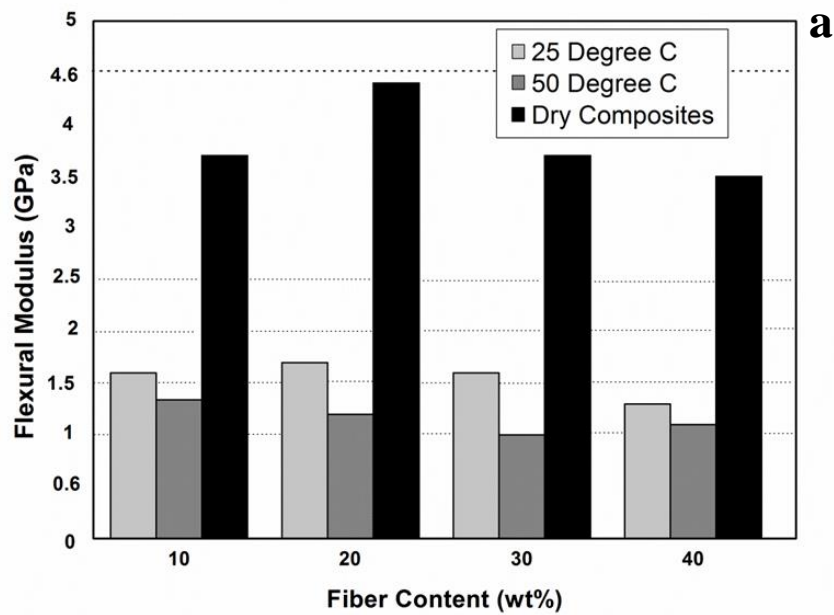


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465 **Figure 4** Diffusion coefficient for composites at various temperatures. Reprinted  
 466 from Osman, Vakhguelt, Sbarski & Mutasher, 2011, Open Access

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468



469 **Figure 5** Effect of moisture uptake on the (a) flexural Modulus and (b) flexural  
 470 strength. Reprinted from Osman, Vakhguel, Sbarski & Mutasher, 2011,  
 471 Open Access  
 472

473  
 474 3.2 Chemically modified natural fibre composites

475  
 476 Several studies have been reported on chemical modification to increase adhesion between  
 477 natural fibres and polymer matrices, in order to decrease moisture absorption and enhance the

478 mechanical properties. The moisture absorption of fibres which is due its hydrophilic  
479 character, affects some of the properties such as fracture toughness, flexural modulus, and  
480 flexural strength. Sreekala & Thomas, 2003 investigated the effects of surface modification  
481 on water-sorption characteristics of oil palm fibres. Different fibre modifications such as  
482 silane treatment, gamma irradiation, acetylation treatment, mercerization, isocyanate  
483 treatment and peroxide treatment were used. The water absorption behaviour of a palm fibre  
484 was evaluated in deionized water at varying temperatures conditions (30, 50, 70 and 90 °C) in  
485 a thermostatically controlled air oven. The increasing in the sample weights were recorded at  
486 precise time intervals until equilibrium was reached. The treatment considerably reduced the  
487 water absorption for all temperatures, but with observed irregularities for different modified  
488 system. The decline in the water absorption was ascribed to the chemical and physical  
489 changes brought by the modification onto the fibre. The treated fibre surfaces revealed  
490 changes in the porous structure of the fibre and different chemical bonds formed on the fibre  
491 surface during treatments. The permeability, sorption and diffusion coefficients decreased  
492 due to treatment. However, the mechanical properties (presented in Table 3) were found to  
493 decrease for swollen system compared to un-swollen. Nevertheless, enhancement in the  
494 Young's modulus was observed for mercerized and silane treatment and was ascribed to the  
495 modifications that happened at the cellulosic part of the fibres.

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511 **Table 3** Tensile properties of the treated OPEFB fibre. Reprinted from Sreekala  
 512 & Thomas, 2003, Copyright 2003, with permission from Elsevier

Treatment	Fibre	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Untreated	Unswollen	248 (12)	14 (0.8)	6700 (25)
	Swollen	224 (11)	40 (1)	2200 (20)
Mercerization	Unswollen	224 (11)	16 (0.9)	5000 (48)
	Swollen	170 (9)	35 (1)	265 (15)
Latex	Unswollen	98 (3)	23 (1)	1850 (14)
	Swollen	82 (2)	29 (1)	455 (10)
Irradiation	Unswollen	88 (4)	25 (0.9)	1600 (14)
	Swollen	41 (4)	33 (0.8)	190 (12)
Silane	Unswollen	273 (10)	16 (0.7)	5250 (60)
	Swollen	238 (9)	20 (0.8)	2500 (30)
TDIC	Unswollen	160 (4)	22 (1)	2000 (11)
	Swollen	84 (6)	37 (1)	341 (8)
Acetylated	Unswollen	143 (8)	28 (1)	2000 (25)
	Swollen	81 (7)	41 (1.1)	341 (10)
Peroxide	Unswollen	133 (5)	24 (1.1)	1100 (12)
	Swollen	84 (5)	30 (1)	190 (8)

513 Figures in parentheses = Standard deviation

514  
 515 The impact of fibre surface modification on the properties of sisal-polyester composites were  
 516 investigated by Singh, Gupta & Verma, 1996. Unsaturated polyester was reinforced with sisal  
 517 fibre modified with different chemical modifiers such as organotitanate, zirconate, silane and  
 518 N-substituted methacrylamide. The composite samples were subjected to 95% relative  
 519 humidity at 50 °C and immersed in water for 35 days. It was found that modified sisal  
 520 reinforced composites absorbed water at a slow rate compared to untreated sisal composites.  
 521 This was due the development of a reasonably more hydrophobic interface region by co-  
 522 reacting organofunctionality of the coupling agents with the matrix. A substantial reduction  
 523 in the flexural and tensile strength of 30% and 50% respectively was observed under humid  
 524 conditions. In the case of epoxy resin reinforced with jute fibre modified with an

525 epoxyfunctional- $\gamma$ -glycidoxypropyltrimethoxy-silane (Gassan & Bledzki, 1997), the moisture  
526 uptake was determined in deionized water (23 °C) for approximately six weeks. It was found  
527 that the moisture absorption of composites with silane treated fibres reduced by 10-20%. The  
528 equilibrium and kinetics of moisture absorption improved with increasing fibre loading. The  
529 tensile modulus and strength as well as the fatigue strength dropped by 30% as the moisture  
530 content increased.

531

532 Several investigations have been evaluated on polyester and epoxy reinforced with *Luffa*  
533 *cylindrical* fibre (Saw, Purwar, Nandy, Ghose & Sarkhel, 2013; Seki, Sever, Erden,  
534 Sarikanat, Nesar & Ozes, 2012; Tanobe, Flores-Sahagun, Amico, Muniz & Satyanarayana,  
535 2014) modified with sodium hydroxide (NaOH), methacrylamide and grafted with furfuryl  
536 alcohol (FA) respectively. In the case of Seki, Sever, Erden, Sarikanat, Nesar & Ozes, 2012,  
537 polyester/luffa fibre reinforced composite was exposed to water aging under a steam of  
538 seawater containing 5% sodium chloride for 170 h at 50°C. It was observed after aging, the  
539 elongation at break; tensile; inter-laminar and flexural strength values of the composite  
540 decreased by ~ 31%, 24%, 45% and 28% respectively. Nevertheless, in the case of Tanobe,  
541 Flores-Sahagun, Amico, Muniz & Satyanarayana, 2014, the surface treatment of *Luffa*  
542 *cylindrical* fibres with 2% NaOH for 90 min was found to be the best treatment with  
543 reference to the highest fracture energy observed. However, no significant increase in the  
544 tensile strength was detected for the modified composites compared to untreated fibre  
545 composites. It was further observed that treatment with methacrylamide efficiently decreased  
546 the water uptake of the composites. Investigations by Saw, Purwar, Nandy, Ghose & Sarkhel,  
547 2013, showed that the alkali modified and FA-grafted composites had a slow rate of water  
548 absorption contrary to unmodified luffa reinforced composites after 240 hours of being  
549 subjected in water. The water absorption rate was found to decrease from untreated fibre,  
550 alkali modified and FA-grafted respectively. This was attributed to reduced hydroxyl groups  
551 in the fibre which resulted in better fibre-matrix interaction and led to a hydrophobic  
552 composite. The alkali treated composites showed comparable water absorption of 7.32, 9.82  
553 and 11.21% at 23, 50 and 100°C respectively. The FA-grafted luffa composites showed the  
554 lowest diffusion rate as a result enhanced compatibility between the luffa fibre and the epoxy  
555 resin.

556

557 Spinace, Lambert, Fermoselli & De Paoli, 2009, characterized the properties of curaua fibres  
558 subjected to sodium hypochlorite and cold oxygen plasma modification. It was observed that

559 moisture absorption percentage of untreated fibre was 9.10 wt.% and changed for treated  
560 fibre to 8.30 wt.% at normal environmental conditions. The decrease indicated that the  
561 modification changed the hydrophilic property of the curaua fibres. Based on the above  
562 mentioned studies, chemical treatment of natural fibres has reduced moisture absorption.  
563 However, more investigations are required to induce a higher level of hydrophobicity in  
564 chemically modified natural fibre reinforced composites when subjected to long-term  
565 environmental/hygroscopic aging. There are other strategies to retard moisture absorption in  
566 natural fibres when exposed to long-term aging. This includes introduction of bio-based  
567 coatings on the composites. The advantage of using bio-based coatings is to ensure the  
568 biodegradable and environmentally friendly nature of fibres as opposed to using synthetic and  
569 toxic chemicals. In addition, bio-based coatings have superior hydrophobic properties and are  
570 produced from renewable resources. Another approach is the use of superhydrophobic  
571 materials in order to reduce the surface energy and enhance surface roughness on natural  
572 fibre surfaces.

573

## 574 **Bio-based coatings**

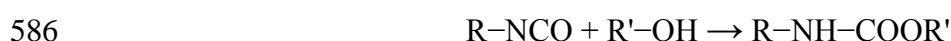
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### 576 4.1 Polyurethane coatings

577

578 In the 1950s polyurethanes (PU) were introduced as coating resins and subsequently  
579 expanded in their application (Awasthi & Agarwal, 2007). They have been used typically for  
580 aircraft top-coats, plastics, automotive top-coats and wood because of their excellent  
581 chemical and mechanical properties. Furthermore, polyurethane coatings show superior  
582 solvent resistance, hydrolytic stability, weatherability and acid-base resistance compared to  
583 other resins. Polyurethane resins are derived from reaction of an isocyanate with polyol or  
584 hydroxyl-functionalized oligomer according to the following reaction:

585



587

588 In general, very tough polyurethane films are produced from acrylics polyol and polyesters  
589 under suitable curing specifications and are commonly used for high performance coatings.  
590 In addition, polyols containing esters offer adhesion promotion and abrasion resistance, while  
591 polyether polyols offer low temperature and viscosity properties. The difference between the

592 polyether and polyester polyols is their industrial production which differ in their monomer  
593 compositions, for instance polyether polyols are limited to tetrahydrofuran, ethylene,  
594 propylene and butylene oxides. On the other hand, polyester polyols are products of alcohols  
595 and organic acids which can be produced from different combinations of monomers and this  
596 further adds a great value to the polyurethane products. (Awasthi & Agarwal, 2007, 2010). So  
597 far polyurethanes produced industrially are usually petroleum based polyol. Hence, there is  
598 now a growing request for renewable resources such as crude oil and low priced sustainable  
599 products (Kong, Liu, Qi & Curtis, 2013). Therefore, substitution of petroleum based products  
600 with bio-based products offers excellent advantages such as; easy availability, lower  
601 environmental impact, sustainability, structural integrity, affordability as well as their use  
602 benefits the agricultural sector.

603

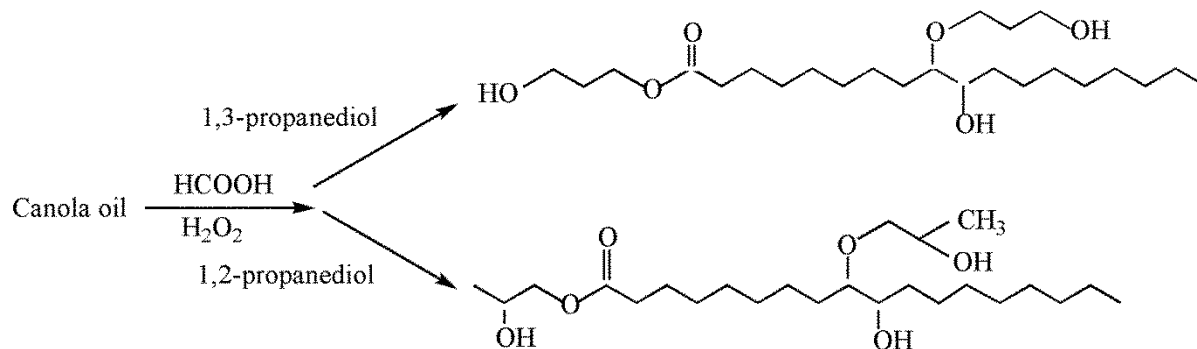
604 Vegetable oils based polyols have a great opportunity to be used in the production of PUs and  
605 expand their applications such as painting and surface coatings. Furthermore, vegetable oils  
606 have been used in many applications such as, lubrication, oil field, illumination, biomedical,  
607 and automotive (Deka & Karak, 2009). Vegetable oils are mainly composed of  
608 triacylglycerides, and when hydrolysed, they produce a variety of glycerol and fatty acids.  
609 Fatty acids have long hydrocarbon chains which promote hydrophobicity to the end product.  
610 Moreover, fatty acids known as dimerized fatty acids have established their use in areas such  
611 as polyurethanes, polyesteramide, polyamide and polyester coatings. This is because of their  
612 structure that consists of a combination of hydrocarbon molecules and non-crystallinity that  
613 provides flexibility and lubricity, even at very low temperatures (Lee, Tsai, Tsai & Chen,  
614 2007; Liu et al., 2011; Malshe & Waghoo, 2006). Survey has showed that the introduction of  
615 vegetable oils into polymers unlike physically mixed fatty acids with polymers provides  
616 superior properties such as low melting point; improved degradation to the polymer;  
617 flexibility and improved handling (Deka & Karak, 2009; Rajput, Hundiwale, Mahulikar &  
618 Gite, 2014).

619

620 Two Bio-based poly(ether ester) polyols (Liprol™ 270 and Liprol™ 320) (Figure 6) coatings  
621 were successfully synthesized and commercialized by Kong, Liu & Curtis, 2012. The polyols  
622 were produced from canola oil by epoxidation followed by acid catalysed ring opening and  
623 trans-esterification with 1,3-propanediol or 1,2-propanediol. It was observed that the  
624 mechanical properties of both Liprol PU samples improved upon exposure to alkali solution  
625 and water at 80°C for 7 days (Table 4). This was due to the removal of glycerol and the

626 introduction of an ether group during the ring opening reaction and as a result created highly  
627 crosslinked networks in Liprol PU samples, and further increased the glass transition  
628 temperature.

629



630

631

632 **Figure 6** Synthesis of poly(ether ester) polyols from canola oil. Reprinted from  
633 Kong, Liu & Curtis, 2012, Open Access

634



635 **Table 4** Hydrolytic stability and alkali resistance properties of polyurethane after exposure to 100 % relative humidity at 80 °C and  
 636 3.3% NaOH solution for 7 days. Reprinted from Kong, Liu & Curtis, 2012, Open Access

	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Hydrolytic stability		Alkali resistance	
				Tensile strength retaining (%)	Elongation at break retaining (%)	Tensile strength retaining (%)	Elongation at break retaining (%)
Liprol™ 270- MDI	61 ± 1	1430 ± 8	5.9 ± 0.7	93	95	94	93
Liprol™ 320- MDI	67 ± 2	1700 ± 10	4.6 ± 0.4	94	94	95	96
Castor oil-MDI	9.3 ± 0.3	8.3 ± 0.2	62.3 ± 0.6	81	80	67	68

637 A sequence of polyester polyols were synthesized from trimethylol propane (TMP), 1,4-  
638 cyclohexanedimethanol (1,4-CHDM) and 1,6-hexanediol (HDO), with a combination of 1,4-  
639 cyclohexanedicarboxylic acid and adipic acid (Zhang, Tu & Dai, 2013). It was found that the  
640 viscosity and glass transition temperatures of the polyester polyols were affected by the  
641 alcohol structure. But their values were increased by raising the molar ratio of 1,4-CHDM  
642 and/or TMP. The polyurethane coatings were found to have excellent impact resistance,  
643 optical properties, flexibility and hardness. Higher hardness was observed for diol CHDM  
644 derived PU and the PU derived from diol HDO had the lowest hardness. The chemical and  
645 water resistance improved with greater molar ratios of 1,4-CHDM or TMP. In the case of  
646 Awasthi & Agarwal, 2007 polyester polyols resin were synthesized with three diacids and  
647 further crosslinked with hexamethylene diisocyanate (HDI) to form polyurethane coating  
648 films. They found that the cycloaliphatic diacids provided the polyesters with better solubility  
649 in ethyl ketone compared to polyester prepared from linear and aromatic diacids. It was also  
650 confirmed that cycloaliphatic diacids provided polyurethane coatings with better mechanical  
651 properties. Improved chemical resistance and good water resistance was observed (see in  
652 Table 5 and 6).

653

654 **Table 5 Resistance to water<sup>a</sup> of polyurethane films. Reprinted from Awasthi &**  
655 **Agarwal, 2007, Open Access**

Sample	Water	
	Deionized water	Seawater
CS-1	5	5
CS-2	5	5
CS-3	5	5

656 <sup>a</sup> When dipped for 6 months; 5 = Film unaffected

657

658 **Table 6 Resistance to water<sup>a</sup> of polyurethane films. Reprinted from Awasthi &**  
659 **Agarwal, 2007, Open Access**

Sample	Acids					
	Acetic acid		Sulfuric acid		Hydrochloric acid	
	5% (v/v)	15% (v/v)	5% (v/v)	10% (v/v)	10% (v/v)	36% (v/v)
CS-1	5	5	5	4	5	5
CS-2	5	5	5	5	5	4
CS-3	5	5	4	2	4	3

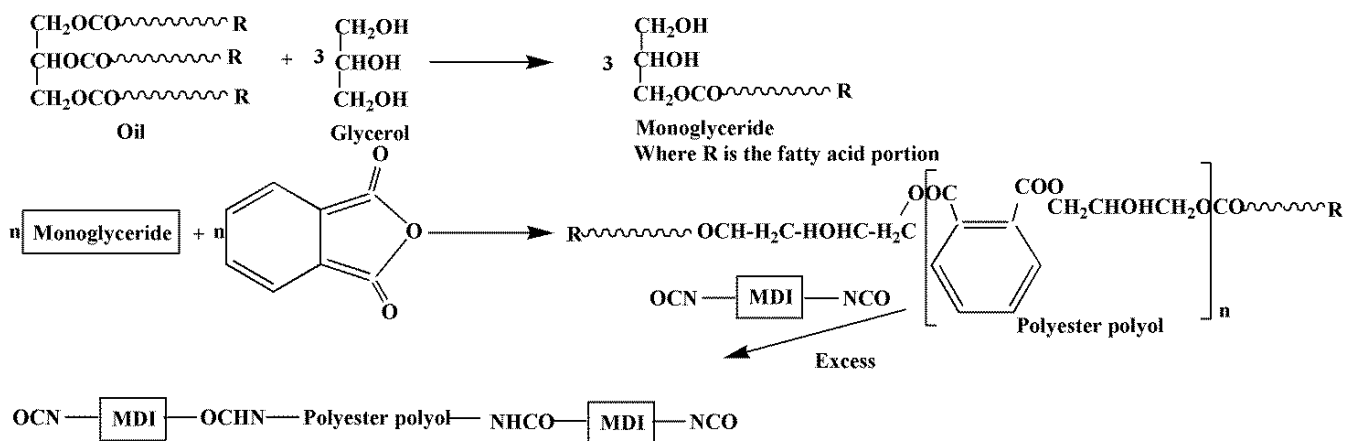
660 <sup>a</sup> When dipped for 6 months; 2= Softening of film; 3 = Blistering of film; 4 = Change in  
661 colour and loss in gloss; 5 = Film unaffected

662 Deka & Karak, 2009, investigated hyperbranched polyurethane (HBPU) for surface coating  
663 applications synthesized from monoglyceride of *Mesua ferrea* L. 2,4-toluene diisocyanate  
664 (TDI), poly( $\epsilon$ -caprolactone) (PCL), glycerol and seed oil in the absence of a catalyst. The  
665 mechanical properties improved with increase HBPU content as a result of enhanced  
666 molecular interactions brought by the amount of hydrogen bonding and aromatic molecules.  
667 An increase in flexural properties was observed due to PCL molecules, long hydrocarbon  
668 chains, ester linkages and ether groups. Furthermore, the mechanical properties of  
669 polyurethanes depended on; chemical linkages, entanglement, shape, size, molecular weight,  
670 and crystallinity of the polymer. The chemical resistance results of hyperbranched  
671 polyurethane after immersion in fresh water and in different chemical solutions (3% NaOH,  
672 5% HCl, 20% EtOH, and 10% NaCl) for 7 days was found to be chemically stable except for  
673 NaOH. This was attributed to alkali hydrolysable ester groups of monoglyceride segments  
674 and poly( $\epsilon$ -caprolactone) present in HBPU.

675

676 In another case, soy bean oil was esterified by glycerol (1:3) molar ratio to produce  
677 monoglycerides, and then reacted with phthalic anhydride (20, 40 and 60%) to produce  
678 polyester polyols (Ismail, Motawie & Sadek, 2011). Diphenylmethane diisocyanate (MDI)  
679 was reacted with the polyols at NCO/OH ratios 1.2, 1.4, 1.6 using toluene as a solvent to  
680 produce polyester-polyurethane coatings (Figure 7). The polyurethane coatings were  
681 successfully prepared from soy bean oil polyols and MDI and easily cured by atmospheric  
682 moisture. Drying times were lowered with increasing phthalic anhydride content in the  
683 samples. The samples with phthalic anhydride 60% and containing NCO/OH 1.4 and 1.6,  
684 exhibited brittle characters and failed in impact and flexibility resistance tests. On the other  
685 hand, as the NCO/OH ratio was increased in each category of phthalic anhydride, the  
686 mechanical, physical and chemical properties and anticorrosive characters of the coatings  
687 improved.

688

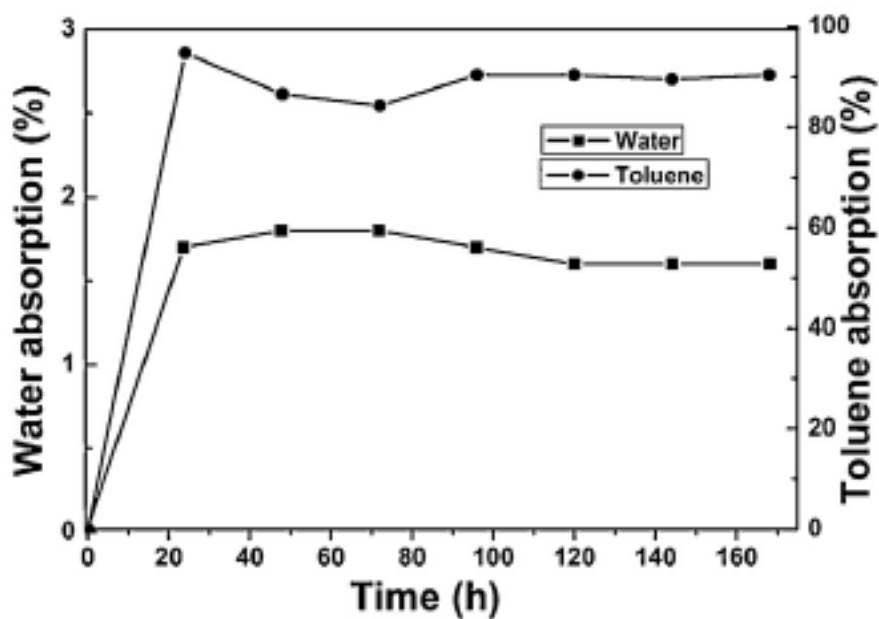


689

690 **Figure 7 Reaction sequence of the preparation of polyurethanes. Reprinted from**  
 691 **Ismail, Motawie & Sadek, 2011, Open Access**

692 novel route to obtain a hydrophilic chain extender and diisocyanate from castor oil and fatty  
 693 acid,

694 Fu, Zheng, Yang, Chen & Shen, 2014, studied a new way to prepare water borne  
 695 polyurethane dispersion (BPUD) using diisocyanate from castor oil and fatty acids. The  
 696 assessed BPUD mechanical properties showed that the bio-based PUs had fairly low  
 697 elongation at break, tensile strength and pendulum hardness. This was due to high flexibility  
 698 of the castor oil as a result of long hydrocarbon segments and its poly-functionality. The  
 699 BPUD film after immersion in water for 168 hours was found to be marginally swelled and  
 700 whitened with a water absorption value of 1.75%, which indicated that the castor oil based  
 701 PU, had improved water resistance properties (see Figure 8). Although a toxic undecylenic  
 702 acid was used as an intermediate to synthesis bio-based diisocyanate (BDI), the obtained bio-  
 703 based water borne polyurethane dispersion was suggested as suitable product to petroleum  
 704 based materials because of exhibiting better hydrophobic and thermal characteristics.



705  
 706 **Figure 8** Swelling-time diagram of BDUP film. Reprinted from Fu, Zheng, Yang,  
 707 **Chen & Shen, 2014, Copyright 2008, with permission from Elsevier**  
 708

709 Rajput, Hundiwale, Mahulikar & Gite, 2014, prepared wood finished polyurethane coatings  
 710 from a combination of renewable sources. The coatings were prepared from a reaction of  
 711 polyesteramide polyol and aromatic diisocyanate. The results showed that the oleic and dimer  
 712 fatty acids can be used to synthesize polyesteramide and wood finished polyurethane  
 713 coatings. The coatings were found to be thermally stable up to 220–250 °C when subjected to  
 714 thermal degradation. Moreover, the coatings were also capable of increasing shelf-life of  
 715 wood substrates because of better mechanical and weather resistance properties.

716 Based on the above mentioned studies, even though there's not work described in literature  
 717 on the application of polyurethane as coatings for natural fibre composites. There is potential  
 718 for PU to be used as coatings to reduce water uptake in composites.

719  
 720 4.2 Poly(furfuryl alcohol)

721  
 722 Poly(furfuryl alcohol) (PFA) is one of the most attractive biobased renewable resource  
 723 polymer that possess excellent properties such high heat distortion temperature, high  
 724 chemical resistance, hydrophobicity and high chemical resistance (Deka, Misra & Mohanty,  
 725 2013; Kumar, Kumar & Anandjiwala, 2012). PFA is derived from a furfuryl alcohol (FA)  
 726 precursor which is a main chemical product produced from furfural. Furfural is an aldehyde

727 which is obtained from hydrolysis of agricultural residue of sugar cane, rice hulls, hazelnut  
728 shells, wheat, corn, birch wood and oat. In addition, nearly 85-90% of the furfural produced  
729 globally is being transformed into furfuryl alcohol by an inexpensive derivation route, and a  
730 cationic condensation reaction is used to polymerize the furanic monomer. (Deka, Misra &  
731 Mohanty, 2013). Several studies have been reported on developing Poly(furfuryl alcohol) or  
732 FA biofilms with low water uptake and with potential environmental friendly applications  
733 (Baysal, Ozaki & Yalinkilic, 2004; Deka, Misra & Mohanty, 2013; Dong, Yan, Zhang & Li,  
734 2014; Hazarika & Maji, 2013; Kumar, Kumar & Anandjiwala, 2012).

735

736 Kumar, Kumar & Anandjiwala, 2012, prepared biofilms from soy protein isolate (SPI) and  
737 poly(furfuryl alcohol) as renewable materials for water resistance properties. It was found the  
738 mechanical properties of the biofilms at  $65 \pm 2\%$  RH cured at optimum curing time had a  
739 tensile strength ( $\sigma$ ) of  $\sim 20$  MPa, Young's modulus (E) of  $\sim 0.5$  GPa and maximum water  
740 uptake of  $\sim 50\%$  when immersed fully in water for 24 h with good dimensional stability.  
741 Additionally, the thermal degradation properties of the biofilms were found to improve  
742 because of the use of poly(furfuryl alcohol) on soy protein isolate. In another study on kenaf  
743 fibre/PFA composites (Deka *et al.*, 2013), moisture absorption behaviour was found to  
744 increase with increasing kenaf fibre content and deviated from the Fickian behaviour, but a  
745 non-Fickian with a maximum water uptake of 7.8% at saturation point. This was attributed to  
746 the high hydrophilic nature of natural fibres. The researchers found that the best properties of  
747 the green composites were achieved at 20 wt.% fibre loading and showed significant  
748 increases in the flexural (48%) and tensile (310%) strength as well as the storage modulus  
749 (123%). Interestingly, retention after moisture absorption of up 89% for flexural, 82% for  
750 impact and to 83% for tensile strength was observed after the composites were subjected to  
751 hot water. Similar observations were recorded by Dong, Yan, Zhang & Li, 2014 on the  
752 investigation of polymer-wood composites prepared through vacuum impregnation of FA and  
753 nano-SiO<sub>2</sub> into fast-growing poplar wood. In this case, the water uptake was reduced by  
754 about 60% when compared to untreated wood fibre composite (Table 7), and this was  
755 attributed to the hydrophobic nature of poly(furfuryl alcohol) which decreased the water  
756 absorption.

757 Recently Mokhothu & John, 2015, investigated the use of a furanic based coating on flax  
758 fabric reinforced phenolic panels. Samples with and without coating were conditioned at 90  
759 °C and relative humidity of 90% for three days and the water uptake and mechanical  
760 properties of samples before and after conditioning were analysed. Furanic based coated

761 samples exhibited improved moisture resistance and registered lower decrease in tensile  
 762 properties after conditioning when compared to polyurethane (PU) and a water resistant  
 763 market product coated samples.

764

765 From the above studies it is clear that there is high potential of polyurethane and  
 766 poly(furfuryl alcohol) coatings to be used as suitable material for lowering moisture  
 767 absorption in natural fibre reinforced composites. Furthermore, the coatings can be a possible  
 768 solution to enhance hydrophobicity in composites in order to improve their mechanical and  
 769 physical performance when exposed to long-term environmental aging.

770

771 **Table 7 Physical and mechanical properties of untreated and treated wood samples.**

772

**Reprinted from Dong, Yan, Zhang & Li, 2014, Open Access**

Wood samples	Bulk effect <sup>a</sup> (BE) (%)	Water uptake <sup>a</sup> (WU) (%)	Anti-swelling efficiency <sup>a</sup> (ASE) (%)	Hardness <sup>b</sup> (Shore D)
Untreated*	2.99 (± 0.40)	113.32 (± 7.88)	0 (± 2.99)	46.97 (± 4.25)
FA-treated	15.02 (± 1.08)	44.45 (± 5.55)	65.75 (± 0.86)	63.14 (± 4.35)
FA/SiO <sub>2</sub> -treated	15.28 (± 0.33)	41.38 (± 3.68)	68.67 (± 1.72)	69.28 (± 345)

773 <sup>a</sup>Each value represents the average of six samples ± standard deviation, <sup>b</sup>Each value  
 774 represents the average of twenty samples, \*Treated with water

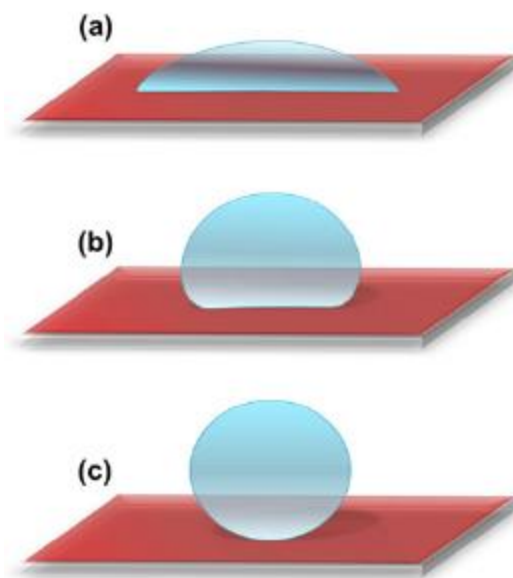
775

## 776 5. Fabrication of hydrophobic and superhydrophobic surfaces from organic- 777 inorganic hybrid material

778

779 Surface modification of cellulosic materials has stimulated much scientific interest to  
 780 improve durability and water repellent properties. This has been inspired by observing  
 781 biological tiny structures of several types of surfaces like fish scales as well as rice and lotus  
 782 leaves which display superb superhydrophobicity and/or hydrophobicity properties. A super-  
 783 or hydrophobic surface is a surface which does not absorb water instead forms water droplets  
 784 on a solid surface without being absorbed as shown in Figure 9. Additionally the solid  
 785 surface has to have a high water contact angle greater than 150° and a sliding angle lesser  
 786 than 10° to be hydrophobic. (Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Dong, Yao,

787 Yang, Jiang & Shen, 2013; Latthe, Terashima, Nakata & Fujishima, 2014; Song & Rojas,  
788 2013). Furthermore, the contact angle between a liquid and a solid surface differs with the  
789 surface roughness as well as the surface energy or chemistry (Ding, Li, Hotta, Kim, Kuwaki  
790 & Shiratori, 2006). Therefore, many studies and reviews have been reported on coating  
791 techniques to increase surface roughness such as sol-gel process, etching, electrospinning,  
792 chemical grafting, chemical vapour deposition and liquid flame spray (Berendjchi, Khajavi &  
793 Yazdanshenas, 2011; Gurav et al., 2014; Hu, Zen, Gong & Deng, 2009; Lee, An, Latthe, Lee,  
794 Hong & Yoon, 2013; Mahadik et al., 2013; Stepien et al., 2013; Stepien et al., 2011, 2012;  
795 Synytska, Khanum, Ionov, Cherif & Bellmann, 2011; Teisala et al., 2010) Important progress  
796 achieved in this field has also been reported in several review papers (Genzer & Efimenko,  
797 2006; Ma & Hill, 2006; Nakajima, Hashimoto & Watanabe, 2001; Sanjay, Annaso, Chavan  
798 & Rajiv, 2012; Song & Rojas, 2013).

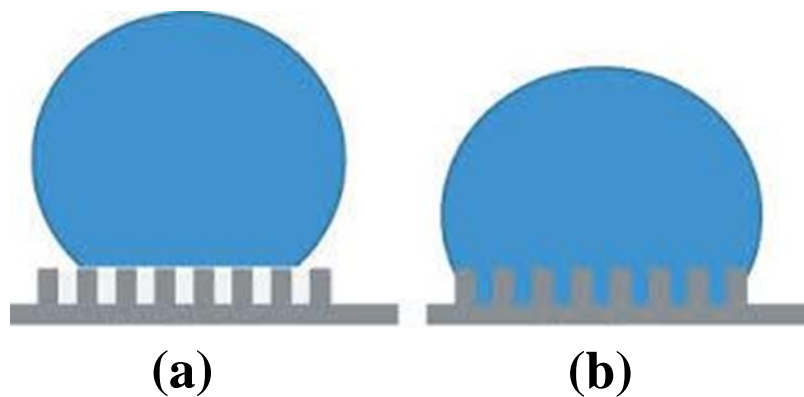


800  
801 **Figure 9** A schematic showing (a) hydrophilic surface with water contact angle less  
802 than  $90^\circ$ ; (b) hydrophobic surface with water contact angle greater than  
803  $90^\circ$  and (c) superhydrophobic surface with water contact angle larger than  
804  $150^\circ$ . Reprinted from Latthe, Terashima, Nakata & Fujishima, 2014, Open  
805 Access

806  
807 The relationship between the wettability and surface roughness has been elaborated by the  
808 Cassie-Baxter and Wenzel models and many studies have reported on these models (Celia,  
809 Darmanin, De Givenchy, Amigoni & Guittard, 2013; Genzer & Efimenko, 2006; Ma & Hill,



2006; Nakajima, Hashimoto & Watanabe, 2001; Nosonovsky & Bhushan, 2009; Sanjay, Annaso, Chavan & Rajiv, 2012; Song & Rojas, 2013; Wenzel, 1936; Zheng & Lü, 2014). The behaviour of a water droplet on a coarse solid surface in both Cassie-Baxter's and Wenzel's state are presented in Figure 10, and the water droplet can either fill or sit above the coarse surface. According to the Wenzel model, the droplet sustains contact with the rough surface and then fills the surface as a result to increased surface contact area (Figure 10b). Therefore, a surface will be more hydrophobic when the surface roughness is increased, while a hydrophilic surface will be more hydrophilic. On the other hand, according to the Cassie-Baxter model, the liquid droplet is suspended on the coarse surface and rests on a fused phase made of a solid-liquid and solid-vapour borders (Figure 10a).



**Figure 10 The wetting behaviour of a liquid droplet on rough solid surface: (a) Cassie's mode and (b) Wenzel's mode**

The Wenzel equation below take into account that water droplet sustains contact with the rough surface and then fills the surface. This will imply that the surface area associated with the contact angle will increase by the roughness factor  $r$ .

$$\cos \theta_w = r \cos \theta \quad (1)$$

where  $\theta_w$  is the contact angle of the rough surface, the influence of the surface interaction determined by  $\cos \theta$  is emphasized by the roughness factor  $r$ . When  $\theta < 90^\circ$ , a rise in roughness factor  $r$  reduces  $\theta_w$ , however if  $\theta > 90^\circ$ ,  $\theta_w$  increases with increasing roughness factor  $r$ .

In the Cassie-Baxter equation as shown below, the apparent contact angle determined from contributions of different phases

837

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2)$$

839

840 where  $\theta_{CB}$  is the apparent contact angle,  $f_1$  and  $f_2$  are the surface fraction while  $\theta_1$  and  $\theta_2$  are  
841 the contact angle of phase 1 and 2, respectively. This equation applies to both smooth and  
842 rough surfaces. When one of the surfaces is the liquid-air interface,  $f$  is defined as the fraction  
843 of the solid surface that is wetted by the liquid. Then the air fraction is  $(1 - f)$  with  $\theta = 180^\circ$   
844 for air, the resulting contact angle can be calculated by the following equation

845

$$\cos \theta_{CB} = f(1 + \cos \theta) - 1 \quad (3)$$

847 The parameter  $f$  ranges from 0 to 1, when  $f = 0$  the liquid droplet wet the surface at all and  
848 when  $f = 1$  the surface is completely wet, while in the Cassie- Baxter state, the water droplet  
849 will easily roll over the surface (Sanjay, Annaso, Chavan & Rajiv, 2012).

850

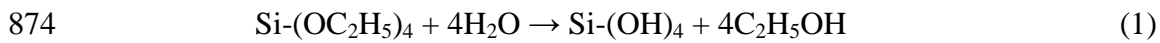
## 851 5.1 Sol-gel process

852

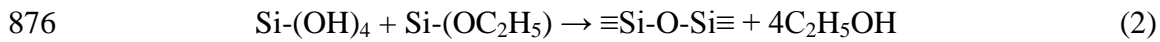
853 Sol-gel process is a wet process that is broadly employed in the textile field using a simple  
854 pad or dip coating (Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Landage, Kulkarni &  
855 Ubarhande, 2012; Rao, Latthe, Mahadik & Kappenstein, 2011; Xu, Zhuang, Xu & Cai,  
856 2011). Nano sol-gel method has been applied for preparing self-cleaning, antibacterial and  
857 water repellent finishes on fabrics (Gurav et al., 2014; Mahadik et al., 2013; Teisala et al.,  
858 2010; Verho, Bower, Andrew, Franssila, Ikkala & Ras, 2011). Sol-gel process is a chemical  
859 method used to synthesize typical metal oxides from a precursor (chemical solution) to form  
860 an integrated network of either discrete particle. The method has been used to produce  
861 superhydrophobic surfaces from a variety of alkylsilane precursors such as; tetraethyl  
862 orthosilicate or tetraethoxysilane (TEOS) (Colleoni, Donelli, Freddi, Guido, Migani &  
863 Rosace, 2013; Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Wang, Liu, Liu, Zhang, Li &  
864 Wang, 2011), methyltrimethoxysilane (MTMS) (Xu *et al.*, 2011), tetraethylorthotitanate or  
865 tetraethyl titanate (Alongi, Ciobanu & Malucelli, 2012), tetrabutyl titanate (TBT) (Chen et  
866 al., 2011), methyltriethoxysilane (METES) (Chen et al., 2011; Rao, Latthe, Mahadik &  
867 Kappenstein, 2011) and tetramethoxysilane (TMOS) (Alongi, Ciobanu & Malucelli, 2012).  
868 The sol-gel process involves the generation of organic-inorganic hybrid materials through  
869 hydrolysis and condensation reactions of organometallic compounds. Hydrolysis and  
870 condensation reactions of tetraethoxysilane (TEOS) are the mostly used to produce silica as

871 indicated in equation 1-3, in which hydrolysis of alkylsilane in acid or basic conditions,  
872 alcohol condensation and water condensation are presented respectively.

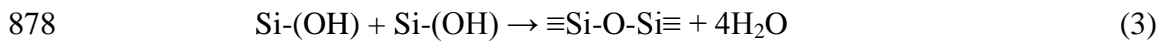
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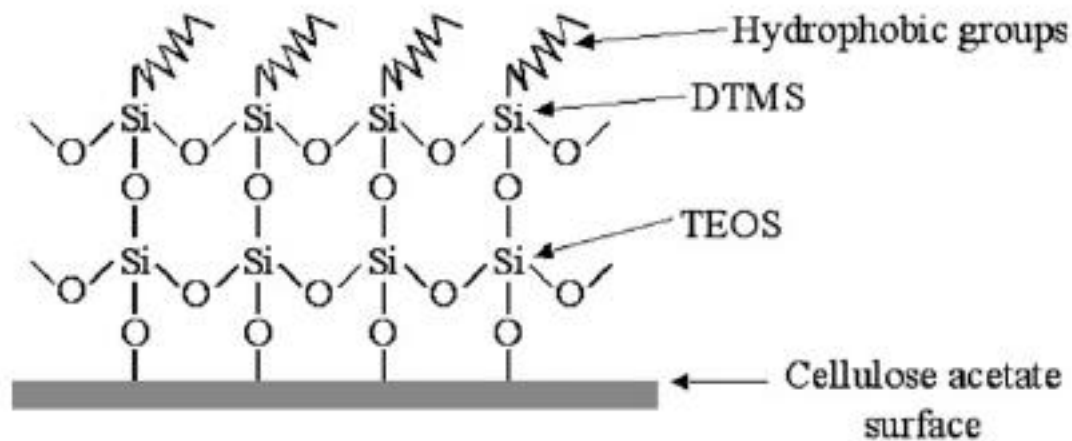
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880 According to the reactions, the alkylsilane initially hydrolyse in acid or basic conditions to  
881 form silicic acid which condensates with another alkylsilane or with itself to form a cross-  
882 linked polysiloxane network and then a gel is formed. The –OH groups on the fibre surface  
883 can react with –OH groups of polysiloxane and as a result the gel can be covalently bonded to  
884 the fibre surface. In some cases two or more precursors are used in the sol-gel process to  
885 create roughness and reduce surface energy (Stamboulis, Baillie & Peijs, 2001). In addition,  
886 post-treatment with long alkyl chains have also been used (Ding, Li, Hotta, Kim, Kuwaki &  
887 Shiratori, 2006).

888

889 Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006, converted electrospun nano-fibrous  
890 cellulose acetate mat surface from superhydrophilic to superhydrophobic surface by coating  
891 the nano-fibrous with silica particles prepared by sol-gel process. A sol-gel method was used  
892 prepared two coating solutions, first sol-gel (I) with decyltrimethoxysilane (DTMS) and  
893 second sol-gel (II) without DTMS according to these molar concentrations;  
894 0.5:0.1:20:11:0.008 of TEOS, DTMS, ethanol, H<sub>2</sub>O and HCl respectively. Samples of  
895 cellulose acetate secured on a glass substrate were submerged into a sol-gel solution for 5 s  
896 followed by drying in air for 1 hour, then oven dried at 120 °C to obtain the desired  
897 morphology as depicted in Figure 11.

898



899

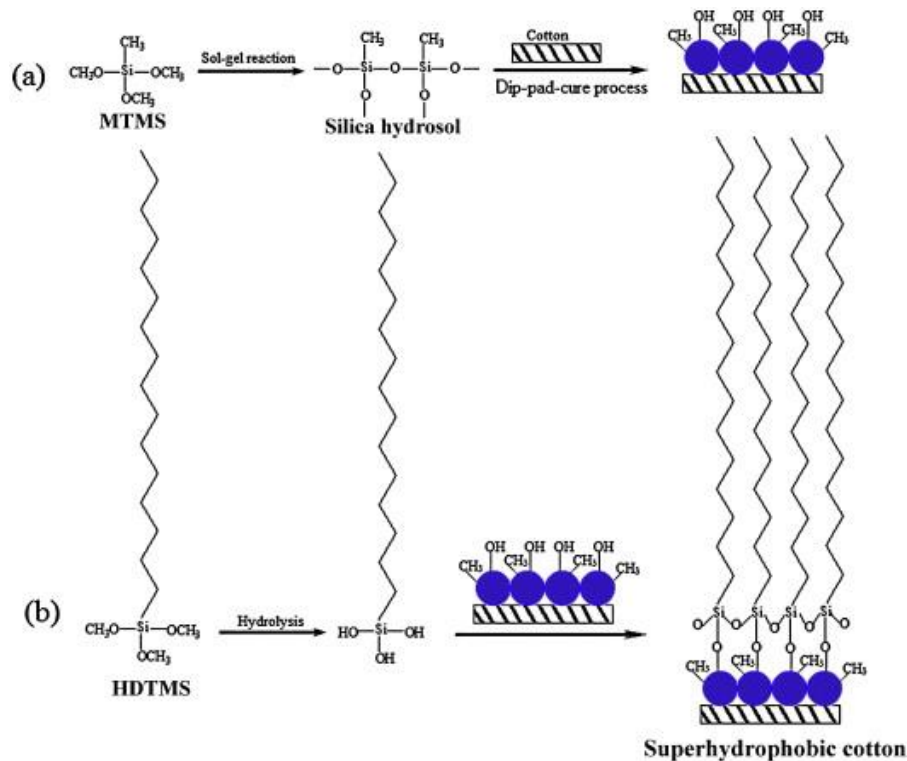
900 **Figure 11** A proposed schematic diagram of sol-gel (I) films on cellulose acetate  
 901 surface. Reprinted from Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006,  
 902 Open Access

903

904 It was reported that the superhydrophilic cellulose acetate nano-fibrous mats were  
 905 successfully prepared by dipping in a sol-gel solution. The sol-gel coated nano-fibrous mat  
 906 had the same atomic ratio of silicon to carbon on its surface and further displayed  
 907 hydrophobicity as a result of DTMS. Moreover, the hydrophobic cellulose acetate mats  
 908 coated with the sol-gel film were converted to superhydrophobic mats by increasing the  
 909 surface roughness of the cellulose acetate. It was further observed that cellulose acetate  
 910 coated (8 wt.%) with micro-sized particles coated with the sol-gel (I) had higher  
 911 hydrophobicity than that of fibrous 10 wt.% cellulose acetate mats without particles due to  
 912 increased surface roughness and area. In another study, silica nanoparticles together with  
 913 hexadecyltrimethoxysilane (HDTMS) were used to prepare superhydrophobic cotton fabrics  
 914 (Xu, Zhuang, Xu & Cai, 2011). The sol-gel reaction in the presence of a base catalyst and  
 915 surfactant was used to synthesize silica nanoparticles with methyltrimethoxysilane (MTMS)  
 916 as a precursor as shown in Figure 12. The treated fibre displayed improved water repellence  
 917 with a contact angle of  $151.9^\circ$  and water shedding angle of  $13^\circ$  for  $5\ \mu\text{L}$  water droplets. This  
 918 was attributed to a substantial contribution of  $\text{SiO}_2$  hydrosol coatings and HDTMS bonding  
 919 which decreased the surface energy of cotton fabric.

920

921

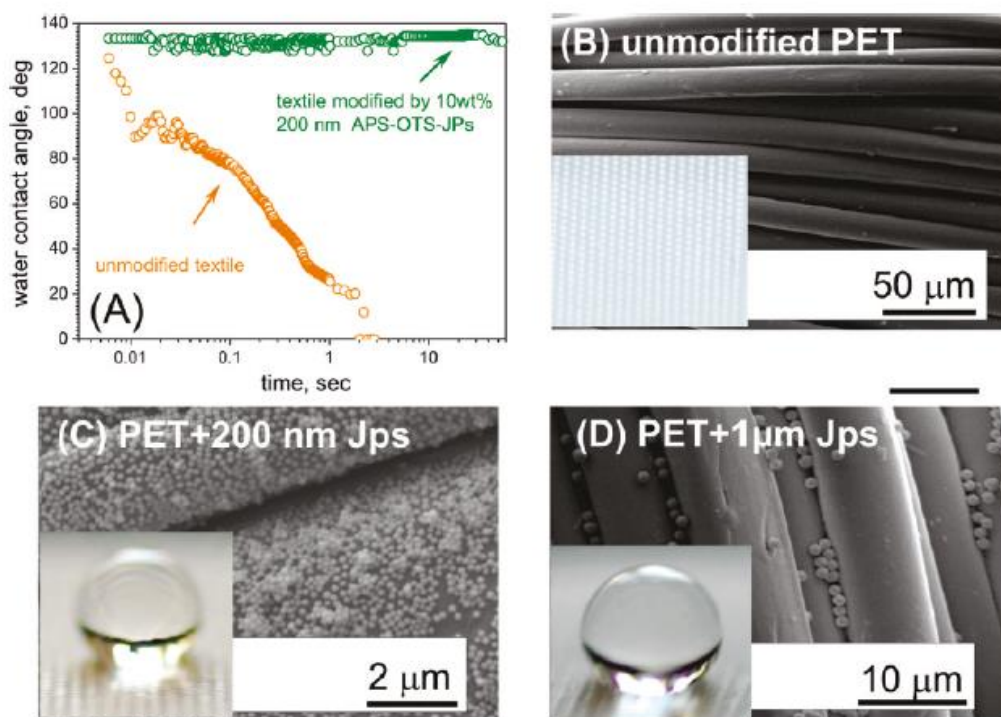


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926  
927

**Figure 12** Scheme showing (a) the cotton fabric coated by the silica hydrosol A2 and (b) the cotton fabric coated by the silica hydrosol A2 followed by HDTMS modification. Reprinted from Xu, Zhuang, Xu & Cai, 2011, Copyright 2011, with permission from Elsevier

928 Several researches have investigated silica coating to improve hydrophobicity of cellulose  
929 fibre (Berendjchi, Khajavi & Yazdanshenas, 2011; Synytska, Khanum, Ionov, Cherif &  
930 Bellmann, 2011) or solid surface (Wang, Liu, Liu, Zhang, Li & Wang, 2011) have been  
931 reported. Synytska, Khanum, Ionov, Cherif & Bellmann, 2011 studied the influence of Janus  
932 particles on the morphology and wetting properties of poly(ethylene terephthalate) (PET)  
933 textiles. Janus particles are silica particles with diverse properties (polarity, optical, magnetic  
934 and charge) at opposite sides. Janus particles were synthesized by hydrolysis-condensation of  
935 TOES. The obtained particles were modified with aminopropyltrimethoxy silane (APS) and  
936 octadecyltrichlorosilane (OTS). Particles of 1 and 200  $\mu\text{m}$  were found attached between  
937 fibres the fibre surface respectively and improved the textile surface from a hydrophilic  
938 surface to a hydrophobic surface. The textile material exhibited a high contact angle ( $\theta_{\text{ADV}} \approx$   
939  $140^\circ$ ) and a low tilt angle ( $\theta_{\text{TILT}} = 10^\circ$ ), making the surface of the textile to be water repellent  
940 (as show in Figure 13). In another study, the production of superhydrophobic wood surface  
941 through sol-gel method was investigated (Wang, Liu, Liu, Zhang, Li & Wang, 2011). The

942 wood surface coated with silica nanoparticles was modified with 1H, 1H, 2H, 2H-  
 943 perfluoroalkyltriethoxysilane (POTS). It was reported that the silica nanoparticles dispersed  
 944 homogeneously on the wood surface as a result of silica and POTS that offered a high surface  
 945 roughness and low surface energy respectively. The wood surface was improved to a  
 946 superhydrophobic surface with a sliding angle below 3° and water contact angle of 164°.  
 947

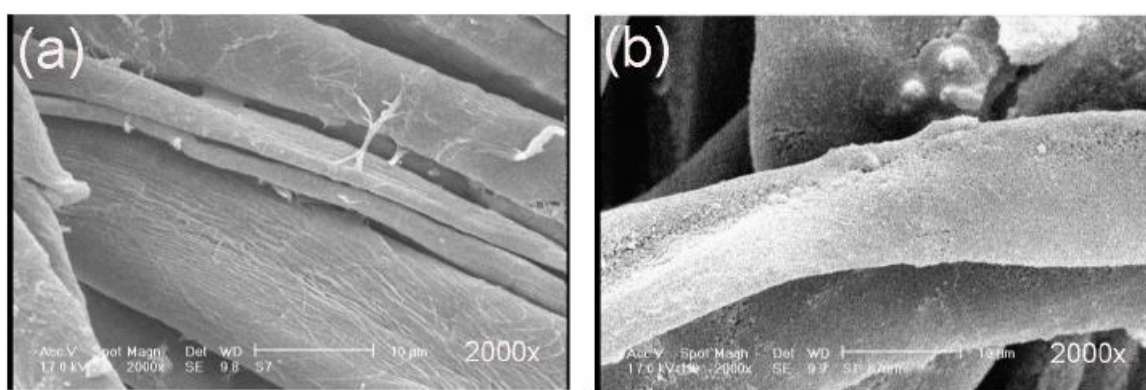


948  
 949 **Figure 13** Wetting properties of textiles modified with Janus particles (Jps). (A)  
 950 Time-resolved water contact angle on native textile (red) and textile  
 951 modified by Janus particles (green). (B,C,D) Morphology images and  
 952 optical images of water droplets on the native textile, textile modified by  
 953 200 nm, and 1 μm large Janus particles. Reprinted from Synytska,  
 954 Khanum, Ionov, Cherif & Bellmann, 2011, Copyright 2011, with  
 955 permission from American Chemical Society

956  
 957 Berendjchi, Khajavi & Yazdanshenas, 2011 prepared a superhydrophobic and antibacterial  
 958 cotton fibre surface using a sol-gel method, with different amounts of copper (Cu)  
 959 nanoparticles and some samples modified with hexadecyltrimethoxysilane (HDTMS). The  
 960 alkylsilane-treated SiO<sub>2</sub> cotton samples were found to have higher surface roughness  
 961 compared to the untreated cotton samples (see Figure 14). The cotton fabrics were found to  
 962 have a higher air trapping capability which resulted to high values of static water contact

963 angle ( $151.1^\circ$ ) and water shedding angle ( $30^\circ$ ). This was further seen when the Cu  
964 nanoparticles were increased by 0.5% (wt/wt) into silica sol-gel solution. The Cu  
965 nanoparticles agglomerate with the silica nanoparticles and as a result increased the static  
966 water angle to  $155^\circ$  for a 10- $\mu$ l droplet. However, at higher amounts of Cu nanoparticles (2%  
967 wt/wt) the cotton fabric surface was found to be smooth and slippery. All cotton fabrics  
968 doped with Cu nanoparticles showed the effective antibacterial activity against gram-negative  
969 and gram-positive bacteria. These studies showed that addition of aminopropyltrimethoxy  
970 silane, 1H, 1H, 2H, 2H-perfluoroalkyltriethoxysilane and hexadecyltrimethoxysilane resulted  
971 in a better adhesion of silica coating on both surfaces.

972



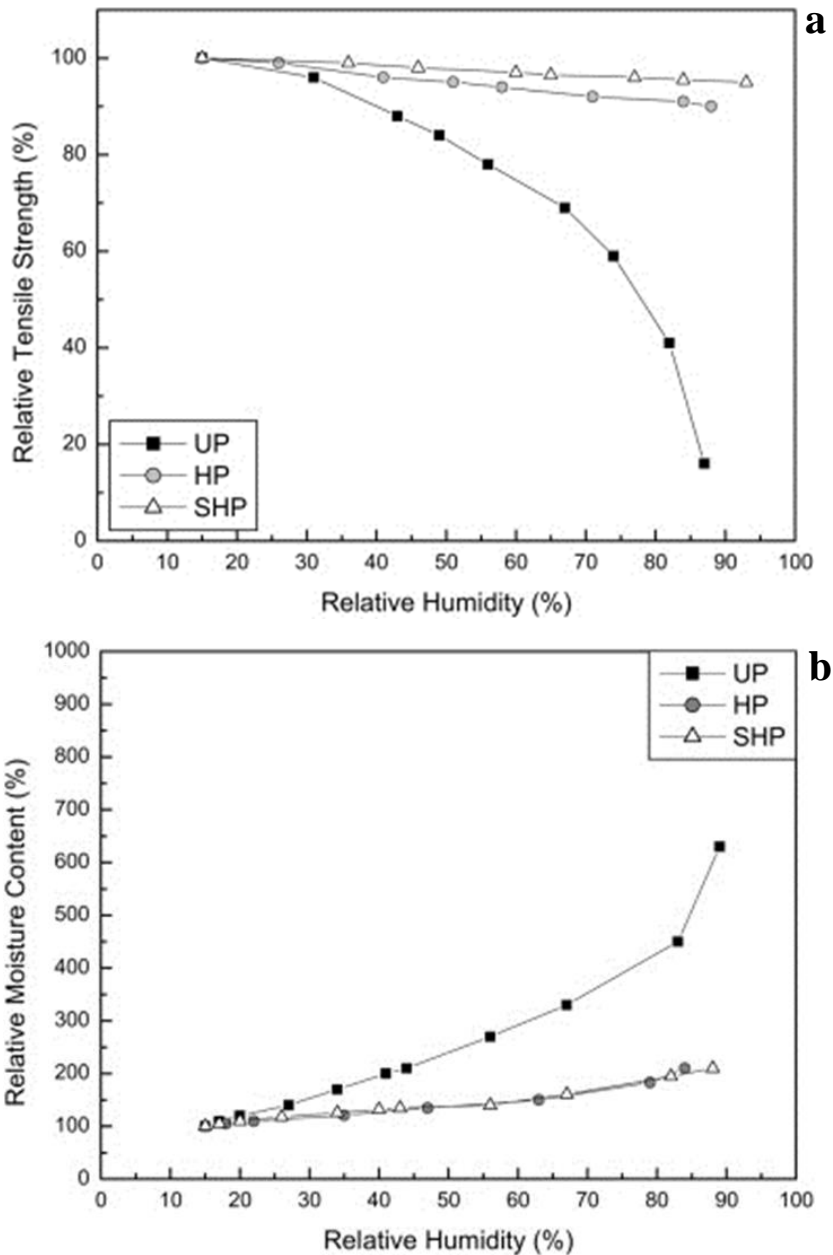
973

974 **Figure 14 SEM micrographs of different samples (a) Untreated. (b) Treated with**  
975 **SiO<sub>2</sub>. Reprinted from Berendjchi, Khajavi & Yazdanshenas, 2011, Open**  
976 **Access**

977

978 Yang & Deng, 2008, investigated the physical properties of superhydrophobic paper  
979 prepared from polydiallyldimethylammonium chloride (polyDADMAC) and silica particles  
980 (precursor TEOS), in the presents of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS,  
981  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ). The modified superhydrophobic paper prepared showed  
982 improved water resistance with a water contact angle greater than  $150^\circ$  and sliding angle less  
983 than  $5^\circ$ . This was attributed to the higher air trapping capability on paper surface as a results  
984 silica particle and POTS. Furthermore, the mechanical properties of the superhydrophobic  
985 paper were improved even at high relative humidity condition (shown from Figure 15a). The  
986 high tensile strength recommended that the fibre-fibre bonds were well protected in those  
987 surface modified linerboard specimens due to TEOS treatment. The results showed that the  
988 relative moisture content of untreated linerboard increased to 650% with increasing relative  
989 humidity (from 15 to 90%). In contrary, hydrophobic and superhydrophobic linerboard had

990 higher moisture resistance and their relative moisture resistance was almost the same (see  
991 Figure 15b).  
992

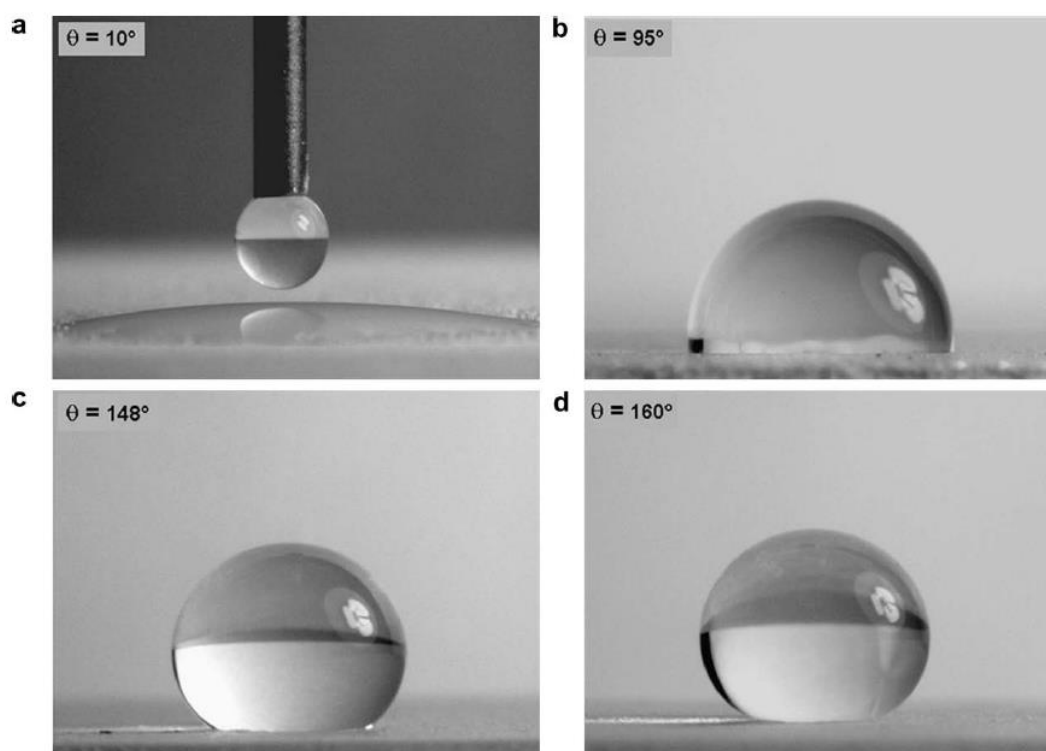


993  
994 **Figure 15 (a) Relative tensile strength and (b) Relative moisture content vs relative**  
995 **humidity of UP (untreated linerboard), HP (hydrophobic paper treated by**  
996 **POTS only), and SHP (superhydrophobic paper) specimens. Reprinted**  
997 **from Yang & Deng, 2008, Copyright 2008, with permission from Elsevier**  
998

999 In the investigation of superhydrophobic silica films prepared by sol-gel method,  
1000 methyltriethoxysilane was used as a hydrophobic reagent by Latthe, Imai, Ganesan & Rao,  
1001 2010). The coating was prepared from reaction series of tetraethoxysilane (TEOS), methanol



1002 (MeOH), water (H<sub>2</sub>O) constant at 1:22.09:6.25 molar ratios respectively, with ammonium  
1003 fluoride (NH<sub>4</sub>F) as a catalyst and the MTES/TEOS molar ratio (M) was varied from 0 to 0.43.  
1004 The static water angle increased with increasing molar ratio and the highest contact angle was  
1005 found at 160° and water sliding as low as 3° (see Figure 16). This was attributed to increasing  
1006 amount of M during so-gel, which reduced the hydroxyl and alkoxy groups responsible for  
1007 the hydrophobic property. Therefore, by increasing the molar ratio, the Si(CH<sub>3</sub>) groups also  
1008 increases the silica film surface which promotes hydrophobicity. It was further found that the  
1009 silica films (M= 0.43) maintained their superhydrophobicity when immersed in water for at  
1010 least two weeks and when exposed to relative high humidity (90%) and temperature (30 °C)  
1011 over 60 days.  
1012



1013  
1014 **Figure 16** Photographs of water droplet on the silica films prepared from (a) M = 0,  
1015 (b) M = 0.08, (c) M = 0.25 and (d) M = 0.43. Reprinted from  
1016 Latthe, Imai, Ganesan & Rao, 2010, Open Access

1017  
1018 From the above studies, the sol-gel produced silica particles were used to induce  
1019 hydrophobicity in textile substrates by reducing the surface energy which effectively  
1020 enhances hydrophobicity. The reduction in the surface energy was achieved by the ability to  
1021 alter the particle size distribution that helps to introducing nanoscale roughness to the textile

1022 substrate. Furthermore, the –OH groups from polysiloxane are able to react with the –OH  
1023 groups on the surface of fibres and form covalent bonds. In addition, the presence of methyl  
1024 groups and least number of hydroxyl groups is considered beneficial for the  
1025 superhydrophobicity.

1026

## 1027 5.2 Liquid flame spray (LFS) nanocoatings

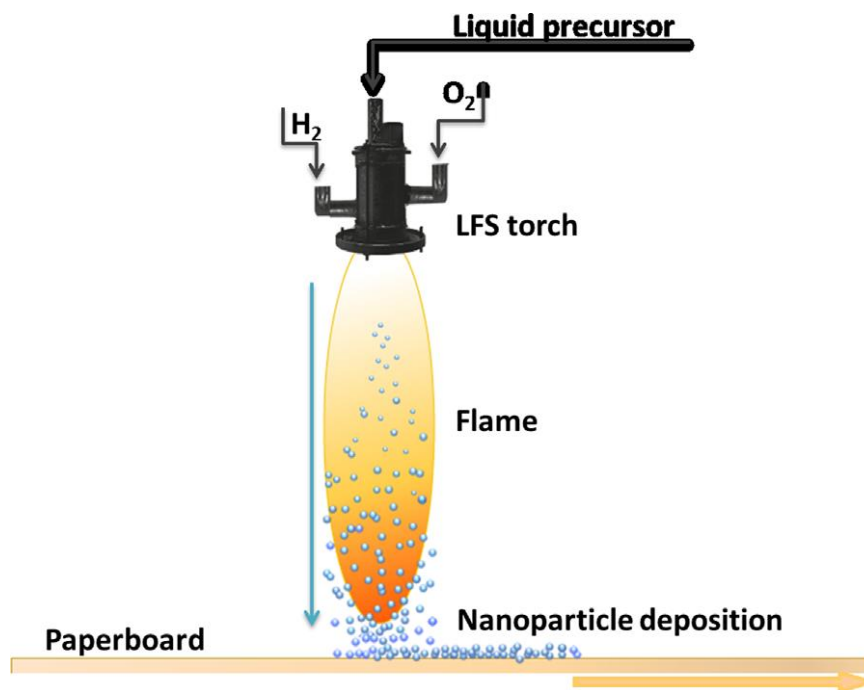
1028

1029 Liquid flame spray is a technique that is uses thermal spraying to generate and deposit  
1030 nanosized metal oxides. LFS is used for coating various substrates and for fibre doping and  
1031 normally water vapour and carbon dioxide are the by-products. Liquid feed stocks are  
1032 prepared by diluting the liquid precursor in alcohol or water and are together fed with  
1033 combustion gases into a specialized spray gun (see Figure 17). The precursor solution is  
1034 atomised to micron-sized droplets through a high-velocity gas flow after the burner nozzle  
1035 has being exited. The desired nanoparticles are deposited on a paperboard surface by a  
1036 subsequent reaction of precursor vapour and evaporation of liquid droplets from a hot and  
1037 turbulent flame. The nanoparticles can grow larger in the flame through agglomeration,  
1038 coalescence, coagulation and condensation. The size of the particle can be controlled, by  
1039 adjusting the collecting or depositing distance or by controlling the total mass flow rate of the  
1040 precursor.

1041

1042

1043



1044

1045 **Figure 17** Liquid flame spraying process. Reprinted from Stepien et al., 2012,  
 1046 Copyright 2008, with permission from Elsevier

1047

1048 The LFS process is comparatively cheap and environmentally friendly as a result of low  
 1049 amounts of waste produced and the use of relatively simple and inexpensive equipment  
 1050 (Teisala et al., 2010). The main advantage of this method is the wide spectrum of metal oxide  
 1051 nanoparticles that can be produced by using different types of precursors. For example,  
 1052 Stepien et al., 2011, 2012 dissolved titanium (IV) isopropoxide (TTIP) precursor or tetraethyl  
 1053 orthosilicate in isopropanol (IPA) to adjust the moisture properties of paperboard with TiO<sub>2</sub>  
 1054 and SiO<sub>2</sub> nanosized coatings produced by LFS process. In their studies, superhydrophobic  
 1055 paperboard surface with high water contact angle was fabricated by TiO<sub>2</sub> coatings. The TiO<sub>2</sub>  
 1056 particles replaced the –OH groups with aliphatic groups and resulted to a superhydrophobic  
 1057 coated paperboard surface. In the case of Teisala et al., 2013b, highly photoactive LFS TiO<sub>2</sub>  
 1058 nanoparticle coatings were found to be easily converted from superhydrophobic to  
 1059 superhydrophilic by natural daylight illumination, UV-illumination, and low-intensity  
 1060 artificial daylight illumination. Furthermore, superhydrophobic surface of the LFS TiO<sub>2</sub>  
 1061 coating was instantly achieved after the coating procedure. This was due to accumulated  
 1062 carbonaceous over-layer on TiO<sub>2</sub>, which ensured the suitable chemistry and the hierarchical  
 1063 roughness which further enhanced the hydrophobicity of the surface. In another study the  
 1064 group investigated the wetting phenomena on high- and low-adhesive superhydrophobic  
 1065 LFS-generated TiO<sub>2</sub> coatings on paperboard substrates using water–ethanol solution as a

1066 probe liquid Teisala et al., 2013a. It was found that the submicrometer scale air gaps, which  
1067 exist on superhydrophobic surfaces below the liquid droplets, were more stable with  
1068 increasing amount of ethanol than in the larger-scale micrometric air gaps. This was because  
1069 of the smoothening pigment layer below the nanoparticle coating, the LFS–TiO<sub>2</sub>-coated  
1070 board had the air entrapping surface structure predominantly at the submicrometer scale, and  
1071 thus, the surface had high resistance against wetting by water-ethanol solution. In addition,  
1072 contact angle of  $155^\circ \pm 2^\circ$  was measured on the LFS–TiO<sub>2</sub>-coated board with the ethanol  
1073 concentration of 15 wt%.

1074

### 1075 5.3 Dip coating and single-step deposition

1076

1077 Superhydrophobic materials have been produced from widely used nano-scaled surface  
1078 roughness with hydrophobically modified surface. However, complicated procedures with  
1079 high cost and harmful compounds to modify superhydrophobic surfaces have limited their  
1080 applications. Several methods such as, dip coating and single-step deposition have also been  
1081 used to achieve super-hydrophobic surfaces. Hu, Zen, Gong & Deng, 2009, investigated the  
1082 superhydrophobic improvement of paper by modifying the paper surface with micro-sized  
1083 CaCO<sub>3</sub> and fatty acid coating. The surface roughness was controlled by means of a surface  
1084 hydrophobic modification agent. Dip coating procedure was used to prepared water resistant  
1085 paper surface with improved water absorption and contact angle ( $150^\circ$ ). This was a result of  
1086 combined surface treatments with dipping coating technique. Furthermore, different coatings  
1087 thickness gave higher water resistance due to decreased water penetration rate.

1088

1089 Solid surfaces with well-controlled superhydrophobic and superoleophilic properties were  
1090 investigated due to their supreme importance to water-oil separation technology (Lee, An,  
1091 Latthe, Lee, Hong & Yoon, 2013). The superhydrophobic-superoleophilic membranes on  
1092 electrospun polystyrene nano-fibres were successfully prepared by single-step deposition  
1093 method. The diesel and water contact angle of polystyrene nano-fibre membrane were  $0^\circ$  and  
1094  $155^\circ \pm 3^\circ$ , respectively. The membrane exhibited excellent superhydrophobicity and simply  
1095 separated diesel oil from water even after many separation process.

1096

1097

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1099

1100 **6. Summary**

1101

1102 In summary natural fibres and fibre reinforced polymer composites have shown their  
1103 susceptibility moisture absorption and in the long term, will cause them to lose their  
1104 application. Furthermore, when exposed to high temperatures, the damages caused by  
1105 moisture are known to increase and therefore vital protections are required for natural fibre  
1106 based composites exposed to such condition. This calls for the production of super and/or  
1107 hydrophobic composites that can be used in humid environment. The selection of suitable  
1108 modification techniques is the key factor to ensure that the natural fibres will have the precise  
1109 characteristics for high moisture resistance. In literature, chemical modification of natural  
1110 fibres has the ability to reduce moisture absorption. However, more investigations are  
1111 required to induce a higher level of hydrophobicity in chemically modified natural fibres  
1112 reinforced polymer composites when subjected to long-term hygroscopic aging.

1113

1114 Literature review presented an area of interest on superhydrophobic nano-coatings and bio-  
1115 based coatings from polyurethane and poly(furfuryl alcohol). Materials subjected to coatings  
1116 showed better moisture absorption resistance. It is further reported that research on  
1117 superhydrophobicity has stimulated much scientific and industrial interest because of  
1118 applications in friction reduction, water repellence and antifouling. In addition bio-based  
1119 coatings with superior properties such as solvent resistance, hydrolytic stability,  
1120 weatherability and acid-base resistance reported show good moisture absorption properties.  
1121 Although there's not much work reported in literature on the use of polyurethane and furfural  
1122 coatings on fibre reinforced composites subjected to hygroscopic aging, there is a potential of  
1123 these types of coatings to be used as suitable material for lowering moisture absorption in  
1124 natural fibre composites. Therefore, further application and research needs to be exploited for  
1125 coating natural fibres and fibre reinforced composites with superhydrophobic nano-coating  
1126 and bio-based coatings. This will lead to the development of high moisture resistance  
1127 composites and improve their mechanical properties.

1128

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1130

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1133

1134 **8. References**

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1136 Adroja, P. P., Koradiya, S., & Parsania, P. (2013). Fabrication, mechanical and electrical  
1137 study of sandwich biocomposites of epoxy resin of 1, 1'-bis (3-methyl-4-  
1138 hydroxyphenyl) cyclohexane. *Indian Journal of Engineering and Materials Sciences*,  
1139 20(6), 568-572.

1140 Alawar, A., Hamed, A. M., & Al-Kaabi, K. (2009). Characterization of treated date palm tree  
1141 fiber as composite reinforcement. *Composites Part B: Engineering*, 40(7), 601-606.

1142 Alomayri, T., Assaedi, H., Shaikh, F., & Low, I. M. (2014). Effect of water absorption on the  
1143 mechanical properties of cotton fabric-reinforced geopolymer composites. *Journal of*  
1144 *Asian Ceramic Societies*, 2(3), 223-230.

1145 Alongi, J., Ciobanu, M., & Malucelli, G. (2012). Thermal stability, flame retardancy and  
1146 mechanical properties of cotton fabrics treated with inorganic coatings synthesized  
1147 through sol-gel processes. *Carbohydrate Polymers*, 87(3), 2093-2099.

1148 Awasthi, S., & Agarwal, D. (2007). Influence of cycloaliphatic compounds on the properties  
1149 of polyurethane coatings. *Journal of Coatings Technology and Research*, 4(1), 67-73.

1150 Awasthi, S., & Agarwal, D. (2010). Preparation and characterisation of polyurethane coatings  
1151 based on polyester polyol. *Pigment & Resin Technology*, 39(4), 208-213.

1152 Azwa, Z., Yousif, B., Manalo, A., & Karunasena, W. (2013). A review on the degradability  
1153 of polymeric composites based on natural fibres. *Materials & Design*, 47, 424-442.

1154 Baysal, E., Ozaki, S. K., & Yalinkilic, M. K. (2004). Dimensional stabilization of wood  
1155 treated with furfuryl alcohol catalysed by borates. *Wood science and technology*, 38(6),  
1156 405-415.

1157 Azwa, Z., & Yousif, B. (2013). Thermal degradation study of kenaf fibre/epoxy composites  
1158 using thermo gravimetric analysis. *Proceedings of the 3rd Malaysian Postgraduate*  
1159 *Conference (MPC 2013)* (pp. 256-264): Education Malaysia.

1160 Berendjchi, A., Khajavi, R., & Yazdanshenas, M. E. (2011). Fabrication of superhydrophobic  
1161 and antibacterial surface on cotton fabric by doped silica-based sols with nanoparticles  
1162 of copper. *Nanoscale Res. Lett*, 6(1), 1-8.

1163 Bledzki, A. K., & Faruk, O. (2004). Creep and impact properties of wood fibre-  
1164 polypropylene composites: influence of temperature and moisture content. *Composites*  
1165 *Science and Technology*, 64(5), 693-700.

1166 Cantero, G., Arbelaz, A., Llano-Ponte, R., & Mondragon, I. (2003). Effects of fibre

- 1167 treatment on wettability and mechanical behaviour of flax/polypropylene composites.  
1168 *Composites Science and Technology*, 63(9), 1247-1254.
- 1169 Celia, E., Darmanin, T., De Givenchy, E. T., Amigoni, S., & Guittard, F. (2013). Recent  
1170 advances in designing superhydrophobic surfaces. *Journal of colloid and interface*  
1171 *science*, 402, 1-18.
- 1172 Chen, H., Miao, M., & Ding, X. (2009). Influence of moisture absorption on the interfacial  
1173 strength of bamboo/vinyl ester composites. *Composites Part A: Applied Science and*  
1174 *Manufacturing*, 40(12), 2013-2019.
- 1175 Chen, Z., Pan, S., Yin, H., Zhang, L., Ou, E., Xiong, Y., & Xu, W. (2011). Facile synthesis of  
1176 superhydrophobic TiO<sub>2</sub>/polystyrene core-shell microspheres. *EXPRESS Polymer*  
1177 *Letters*, 5(1), 38-46.
- 1178 Choi, H., Ahn, K., Nam, J.-D., & Chun, H. (2001). Hygroscopic aspects of epoxy/carbon  
1179 fiber composite laminates in aircraft environments. *Composites Part A: Applied Science*  
1180 *and Manufacturing*, 32(5), 709-720.
- 1181 Colleoni, C., Donelli, I., Freddi, G., Guido, E., Migani, V., & Rosace, G. (2013). A novel sol-  
1182 gel multi-layer approach for cotton fabric finishing by tetraethoxysilane precursor.  
1183 *Surface and Coatings Technology*, 235, 192-203.
- 1184 Costa, M. L., Almeida, S. F. M. d., & Rezende, M. C. (2005). Hygrothermal effects on  
1185 dynamic mechanical analysis and fracture behavior of polymeric composites.  
1186 *Materials Research*, 8(3), 335-340.
- 1187 Cristaldi, G., Latteri, A., Recca, G., & Cicala, G. (2010). Composites based on natural fibre  
1188 fabrics. *Woven fabric engineering*, 317-342.
- 1189 Deka, H., & Karak, N. (2009). Bio-based hyperbranched polyurethanes for surface coating  
1190 applications. *Progress in Organic Coatings*, 66(3), 192-198.
- 1191 Deka, H., Misra, M., & Mohanty, A. (2013). Renewable resource based “all green  
1192 composites” from kenaf biofiber and poly (furfuryl alcohol) bioresin. *Industrial Crops*  
1193 *and Products*, 41, 94-101.
- 1194 Dhakal, H., Zhang, Z., & Richardson, M. (2007). Effect of water absorption on the  
1195 mechanical properties of hemp fibre reinforced unsaturated polyester composites.  
1196 *Composites Science and Technology*, 67(7), 1674-1683.
- 1197 Ding, B., Li, C., Hotta, Y., Kim, J., Kuwaki, O., & Shiratori, S. (2006). Conversion of an  
1198 electrospun nanofibrous cellulose acetate mat from a super-hydrophilic to super-  
1199 hydrophobic surface. *Nanotechnology*, 17(17), 4332.
- 1200 Dixit, S., & Verma, P. (2012). The effect of surface modification on the water absorption

1201 behavior of coir fibers. *Advances in Applied Science Research*, 3(3).

1202 Dong, J., Yao, Z., Yang, T., Jiang, L., & Shen, C. (2013). Control of superhydrophilic and  
1203 superhydrophobic graphene interface. *Scientific reports*, 3.

1204 Dong, Y., Yan, Y., Zhang, S., & Li, J. (2014). Wood/Polymer Nanocomposites Prepared by  
1205 Impregnation with Furfuryl Alcohol and Nano-SiO<sub>2</sub>. *BioResources*, 9(4), 6028-6040.

1206 Eder, M., & Burgert, I. (2010). Natural fibres—function in nature. *Industrial Applications of*  
1207 *Natural Fibres—Structure, Properties and Technical Applications*, John Wiley & Sons,  
1208 Chichester, 23-39.

1209 Fakhrol, T., & Islam, M. (2013). Degradation behavior of natural fiber reinforced polymer  
1210 matrix composites. *Procedia Engineering*, 56, 795-800.

1211 Fu, C., Zheng, Z., Yang, Z., Chen, Y., & Shen, L. (2014). A fully bio-based waterborne  
1212 polyurethane dispersion from vegetable oils: From synthesis of precursors by thiol-  
1213 ene reaction to study of final material. *Progress in Organic Coatings*, 77(1), 53-60.

1214 Gassan, J., & Bledzki, A. K. (1997). Effect of moisture content on the properties of silanized  
1215 jute-epoxy composites. *Polymer composites*, 18(2), 179-184.

1216 Genzer, J., & Efimenko, K. (2006). Recent developments in superhydrophobic surfaces and  
1217 their relevance to marine fouling: a review. *Biofouling*, 22(5), 339-360.

1218 George, J., Bhagawan, S., & Thomas, S. (1998). Effects of environment on the properties of  
1219 low-density polyethylene composites reinforced with pineapple-leaf fibre. *Composites*  
1220 *Science and Technology*, 58(9), 1471-1485.

1221 Gurav, A. B., Latthe, S. S., Vhatkar, R. S., Lee, J.-G., Kim, D.-Y., Park, J.-J., & Yoon, S. S.  
1222 (2014). Superhydrophobic surface decorated with vertical ZnO nanorods modified by  
1223 stearic acid. *Ceramics International*, 40(5), 7151-7160.

1224 Hashim, M. Y., Roslan, M. N., Amin, A. M., Zaidi, A. M. A., & Ariffin, S. (2012).  
1225 Mercerization Treatment Parameter Effect on Natural Fiber Reinforced Polymer Matrix  
1226 Composite: A Brief Review. *World Academy of Science, Engineering and Technology*,  
1227 68, 1638-1644.

1228 Hazarika, A., & Maji, T. K. (2013). Study on the properties of wood polymer  
1229 nanocomposites based on melamine formaldehyde-furfuryl alcohol copolymer and  
1230 modified clay. *Journal of Wood Chemistry and Technology*, 33(2), 103-124.

1231 <http://bioenergy.cerc.uga.edu/Background/background.htm> (04/08/2014).

1232 <http://en.wikipedia.org/wiki/Hygroscopy> (14/05/15)

1233 <http://www.naturalfibersforautomotive.com/?p=20> (13/05/15)

1234 Hu, Z., Zen, X., Gong, J., & Deng, Y. (2009). Water resistance improvement of paper by



1235 superhydrophobic modification with micro-sized CaCO<sub>3</sub> and fatty acid coating.  
1236 *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 351(1), 65-70.

1237 Ismail, E. A., Motawie, A., & Sadek, E. (2011). Synthesis and characterization of  
1238 polyurethane coatings based on soybean oil–polyester polyols. *Egyptian Journal of*  
1239 *Petroleum*, 20(2), 1-8.

1240 Jayaraman, K. (2003). Manufacturing sisal–polypropylene composites with minimum fibre  
1241 degradation. *Composites Science and Technology*, 63(3), 367-374.

1242 John, M. J., & Anandjiwala, R. D. (2008). Recent developments in chemical modification  
1243 and characterization of natural fiber-reinforced composites. *Polymer composites*, 29(2),  
1244 187-207.

1245 John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*,  
1246 71(3), 343-364.

1247 Joseph, P., Rabello, M. S., Mattoso, L., Joseph, K., & Thomas, S. (2002). Environmental  
1248 effects on the degradation behaviour of sisal fibre reinforced polypropylene composites.  
1249 *Composites Science and Technology*, 62(10), 1357-1372.

1250 Joshi, S. V., Drzal, L., Mohanty, A., & Arora, S. (2004). Are natural fiber composites  
1251 environmentally superior to glass fiber reinforced composites? *Composites Part A:*  
1252 *Applied Science and Manufacturing*, 35(3), 371-376.

1253 Kabir, M., Wang, H., Lau, K., & Cardona, F. (2012). Chemical treatments on plant-based  
1254 natural fibre reinforced polymer composites: An overview. *Composites Part B:*  
1255 *Engineering*, 43(7), 2883-2892.

1256 Kalia, S., Kaith, B., & Kaur, I. (2009). Pretreatments of natural fibers and their application as  
1257 reinforcing material in polymer composites—a review. *Polymer Engineering &*  
1258 *Science*, 49(7), 1253-1272.

1259 Keener, T., Stuart, R., & Brown, T. (2004). Maleated coupling agents for natural fibre  
1260 composites. *Composites Part A: Applied Science and Manufacturing*, 35(3), 357-362.

1261 Kim, H. J., & Seo, D. W. (2006). Effect of water absorption fatigue on mechanical properties  
1262 of sisal textile-reinforced composites. *International Journal of Fatigue*, 28(10), 1307-  
1263 1314.

1264 Kong, X., Liu, G., & Curtis, J. M. (2012). Novel polyurethane produced from canola oil  
1265 based poly (ether ester) polyols: Synthesis, characterization and properties. *European*  
1266 *Polymer Journal*, 48(12), 2097-2106.

1267 Kong, X., Liu, G., Qi, H., & Curtis, J. M. (2013). Preparation and characterization of high-  
1268 solid polyurethane coating systems based on vegetable oil derived polyols. *Progress in*

- 1269 *Organic Coatings*, 76(9), 1151-1160.
- 1270 Kumar, R., Kumar, R., & Anandjiwala, R. (2012). Biofilms from soy protein isolate and  
1271 polyfurfuryl alcohol. *Plastics, Rubber and Composites*, 41(1), 1-7.
- 1272 Kumar, R., Oubrai, S., & Sharma, A. (2011). Chemical modifications of natural fiber for  
1273 composite material. *Der Chemica Sinica*, 2(4).
- 1274 Landage, S., Kulkarni, S., & Ubarhande, D. (2012). Synthesis and application of Silica  
1275 Nanoparticles on Cotton to impart Superhydrophobicity. *International Journal of*  
1276 *Engineering Research and Technology* (Vol. 1): ESRSA Publications.
- 1277 Lathe, S. S., Imai, H., Ganesan, V., & Rao, A. V. (2010). Porous superhydrophobic silica  
1278 films by sol-gel process. *Microporous and Mesoporous Materials*, 130(1), 115-121.
- 1279 Lathe, S. S., Terashima, C., Nakata, K., & Fujishima, A. (2014). Superhydrophobic surfaces  
1280 developed by mimicking hierarchical surface morphology of lotus leaf. *Molecules*,  
1281 19(4), 4256-4283.
- 1282 Le Duigou, A., Bourmaud, A., Davies, P., & Baley, C. (2014). Long term immersion in  
1283 natural seawater of Flax/PLA biocomposite. *Ocean Engineering*, 90, 140-148.
- 1284 Lee, D. K., Tsai, H. B., Tsai, R. S., & Chen, P. H. (2007). Preparation and properties of  
1285 transparent thermoplastic segmented polyurethanes derived from different polyols.  
1286 *Polymer Engineering & Science*, 47(5), 695-701.
- 1287 Lee, M. W., An, S., Lathe, S. S., Lee, C., Hong, S., & Yoon, S. S. (2013). Electrospun  
1288 polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for  
1289 selective separation of water and low viscous oil. *ACS applied materials & interfaces*,  
1290 5(21), 10597-10604.
- 1291 Lin, Q., Zhou, X., & Dai, G. (2002). Effect of hydrothermal environment on moisture  
1292 absorption and mechanical properties of wood flour-filled polypropylene composites.  
1293 *Journal of Applied Polymer Science*, 85(14), 2824-2832.
- 1294 Liu, X., Xu, K., Liu, H., Cai, H., Su, J., Fu, Z., Guo, Y., & Chen, M. (2011). Preparation and  
1295 properties of waterborne polyurethanes with natural dimer fatty acids based polyester  
1296 polyol as soft segment. *Progress in Organic Coatings*, 72(4), 612-620.
- 1297 Ma, M., & Hill, R. M. (2006). Superhydrophobic surfaces. *Current opinion in colloid &*  
1298 *interface science*, 11(4), 193-202.
- 1299 Mahadik, S. A., Vhatkara, R. S., Mahadik, D. B., Kavale, M. S., Wagh, P. B., Gupta, S., &  
1300 Gurav, J. (2013). Superhydrophobic silica coating by dip coating method. *Applied*  
1301 *Surface Science*, 277, 67-72.
- 1302 Malshe, V., & Waghoo, G. (2006). Weathering study of dimer fatty acid cured epoxy paints.

- 1303 *Progress in Organic Coatings*, 56(2), 151-153.
- 1304 Mokhothu, T. H., & John, M. J. (2015). Bio-based coatings for reducing water sorption on  
1305 natural fibre reinforced composites 13<sup>th</sup> annual UNESCO/IUPAC workshop and  
1306 conference on functional polymeric materials & composites, 7-10 September 2015, Port  
1307 Elizabeth, South Africa
- 1308 Mohanty, A., Misra, M., & Drzal, L. (2001). Surface modifications of natural fibers and  
1309 performance of the resulting biocomposites: an overview. *Composite Interfaces*, 8(5),  
1310 313-343.
- 1311 Mohanty, A., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and  
1312 biocomposites: an overview. *Macromolecular Materials and Engineering*(276-277),  
1313 1-24.
- 1314 Nakajima, A., Hashimoto, K., & Watanabe, T. (2001). Recent studies on super-hydrophobic  
1315 films. *Monatshefte für Chemie/Chemical Monthly*, 132(1), 31-41.
- 1316 Nosonovsky, M., & Bhushan, B. (2009). Superhydrophobic surfaces and emerging  
1317 applications: non-adhesion, energy, green engineering. *Current opinion in colloid &*  
1318 *interface science*, 14(4), 270-280.
- 1319 Osman E., Vakhguel A., Sbarski I., Mutasher S. Water absorption behavior and its effect on  
1320 the mechanical properties of kenaf natural fiber unsaturated polyester composites. 18<sup>th</sup>  
1321 International conference on composite materials, 21-26 August 2011, Jeju Island,  
1322 Korea.
- 1323 Rajput, S. D., Hundiwale, D. G., Mahulikar, P. P., & Gite, V. V. (2014). Fatty acids based  
1324 transparent polyurethane films and coatings. *Progress in Organic Coatings*, 77(9),  
1325 1360-1368.
- 1326 Rao, A. V., Lathe, S. S., Mahadik, S. A., & Kappenstein, C. (2011). Mechanically stable and  
1327 corrosion resistant superhydrophobic sol-gel coatings on copper substrate. *Applied*  
1328 *Surface Science*, 257(13), 5772-5776.
- 1329 Ray, B. (2006). Effects of changing environment and loading speed on mechanical behavior  
1330 of FRP composites. *Journal of reinforced plastics and composites*, 25(12), 1227-1240.
- 1331 Rout, J., Misra, M., Tripathy, S., Nayak, S., & Mohanty, A. (2001). The influence of fibre  
1332 treatment on the performance of coir-polyester composites. *Composites Science and*  
1333 *Technology*, 61(9), 1303-1310.
- 1334 Sanjay, S. L., Annaso, B. G., Chavan, S. M., & Rajiv, S. V. (2012). Recent progress in  
1335 preparation of superhydrophobic surfaces: a review. *Journal of Surface Engineered*  
1336 *Materials and Advanced Technology*, 2012.

- 1337 Saw, S. K., Purwar, R., Nandy, S., Ghose, J., & Sarkhel, G. (2013). Fabrication,  
1338 Characterization, and Evaluation of Luffa cylindrica Fiber Reinforced Epoxy  
1339 Composites. *BioResources*, 8(4), 4805-4826.
- 1340 Seki, Y., Sever, K., Erden, S., Sarikanat, M., Neser, G., & Ozes, C. (2012). Characterization  
1341 of Luffa cylindrica fibers and the effect of water aging on the mechanical properties of  
1342 its composite with polyester. *Journal of Applied Polymer Science*, 123(4), 2330-2337.
- 1343 Sen, T., & Reddy, H. (2013). Pretreatment of Woven Jute FRP Composite and Its Use in  
1344 Strengthening of Reinforced Concrete Beams in Flexure. *Advances in Materials  
1345 Science and Engineering*, 2013.
- 1346 Sgriccia, N., Hawley, M., & Misra, M. (2008). Characterization of natural fiber surfaces and  
1347 natural fiber composites. *Composites Part A: Applied Science and Manufacturing*,  
1348 39(10), 1632-1637.
- 1349 Singh, B., Gupta, M., & Verma, A. (1996). Influence of fiber surface treatment on the  
1350 properties of sisal-polyester composites. *Polymer composites*, 17(6), 910-918.
- 1351 Singleton, A., Baillie, C., Beaumont, P., & Peijs, T. (2003). On the mechanical properties,  
1352 deformation and fracture of a natural fibre/recycled polymer composite. *Composites  
1353 Part B: Engineering*, 34(6), 519-526.
- 1354 Song, J., & Rojas, O. J. (2013). Approaching super-hydrophobicity from cellulosic materials:  
1355 a review. *Nord. Pulp Pap. Res. J*, 28, 216-238.
- 1356 Spinace, M. A., Lambert, C. S., Feroselli, K. K., & De Paoli, M.-A. (2009).  
1357 Characterization of lignocellulosic curaua fibres. *Carbohydrate Polymers*, 77(1), 47-53.
- 1358 Sreekala, M., & Thomas, S. (2003). Effect of fibre surface modification on water-sorption  
1359 characteristics of oil palm fibres. *Composites Science and Technology*, 63(6), 861-869.
- 1360 Stamboulis, A., Baillie, C., & Peijs, T. (2001). Effects of environmental conditions on  
1361 mechanical and physical properties of flax fibers. *Composites Part A: Applied Science  
1362 and Manufacturing*, 32(8), 1105-1115.
- 1363 Stepien, M., Chinga-Carrasco, G., Saarinen, J. J., Teisala, H., Tuominen, M., Aromaa, M.,  
1364 Haapanen, J., Kuusipalo, J., Mäkelä, J. M., & Toivakka, M. (2013). Wear resistance of  
1365 nanoparticle coatings on paperboard. *Wear*, 307(1), 112-118.
- 1366 Stepien, M., Saarinen, J. J., Teisala, H., Tuominen, M., Aromaa, M., Kuusipalo, J., Mäkelä, J.  
1367 M., & Toivakka, M. (2011). Adjustable wettability of paperboard by liquid flame spray  
1368 nanoparticle deposition. *Applied Surface Science*, 257(6), 1911-1917.
- 1369 Stepien, M., Saarinen, J. J., Teisala, H., Tuominen, M., Aromaa, M., Kuusipalo, J., Mäkelä, J.  
1370 M., & Toivakka, M. (2012). Surface chemical characterization of nanoparticle coated

1371 paperboard. *Applied Surface Science*, 258(7), 3119-3125.

1372 Synytska, A., Khanum, R., Ionov, L., Cherif, C., & Bellmann, C. (2011). Water-repellent  
1373 textile via decorating fibers with amphiphilic janus particles. *ACS applied materials &*  
1374 *interfaces*, 3(4), 1216-1220.

1375 Tanobe, V. O., Flores-Sahagun, T. H., Amico, S. C., Muniz, G. I., & Satyanarayana, K.  
1376 (2014). Sponge Gourd (*Luffa Cylindrica*) Reinforced Polyester Composites:  
1377 Preparation and Properties. *Defence Science Journal*, 64(3), 273-280.

1378 Teisala, H., Tuominen, M., Aromaa, M., Mäkelä, J., Stepien, M., Saarinen, J., Toivakka, M.,  
1379 & Kuusipalo, J. (2010). Development of superhydrophobic coating on paperboard  
1380 surface using the liquid flame spray. *Surface and Coatings Technology*, 205(2), 436-  
1381 445.

1382 Teisala, H., Tuominen, M., Aromaa, M., Stepien, M., Mäkelä, J. M., Saarinen, J. J.,  
1383 Toivakka, M., & Kuusipalo, J. (2013a). High-and low-adhesive superhydrophobicity on  
1384 the liquid flame spray-coated board and paper: structural effects on surface wetting and  
1385 transition between the low-and high-adhesive states. *Colloid and Polymer Science*,  
1386 291(2), 447-455.

1387 Teisala, H., Tuominen, M., Stepien, M., Haapanen, J., Mäkelä, J. M., Saarinen, J. J.,  
1388 Toivakka, M., & Kuusipalo, J. (2013b). Wettability conversion on the liquid flame  
1389 spray generated superhydrophobic TiO<sub>2</sub> nanoparticle coating on paper and board by  
1390 photocatalytic decomposition of spontaneously accumulated carbonaceous overlayer.  
1391 *Cellulose*, 20(1), 391-408.

1392 Turmanova, S. C., Genieva, S., Dimitrova, A., & Vlaev, L. (2008). Non-isothermal  
1393 degradation kinetics of filled with rice husk ash polypropylene composites. *EXPRESS*  
1394 *Polymer Letters*, 2(2), 133-146.

1395 Verho, T., Bower, C., Andrew, P., Franssila, S., Ikkala, O., & Ras, R. H. (2011).  
1396 Mechanically durable superhydrophobic surfaces. *Advanced Materials*, 23(5), 673-  
1397 678.

1398 Wang, S., Liu, C., Liu, G., Zhang, M., Li, J., & Wang, C. (2011). Fabrication of  
1399 superhydrophobic wood surface by a sol-gel process. *Applied Surface Science*,  
1400 258(2), 806-810.

1401 Wenzel, R. N. (1936). Resistance of solid surfaces to wetting by water. *Industrial &*  
1402 *Engineering Chemistry*, 28(8), 988-994.

1403 Xie, Y., Hill, C. A., Xiao, Z., Militz, H., & Mai, C. (2010). Silane coupling agents used for  
1404 natural fiber/polymer composites: A review. *Composites Part A: Applied Science and*

1405            *Manufacturing*, 41(7), 806-819.

1406 Xu, L., Zhuang, W., Xu, B., & Cai, Z. (2011). Fabrication of superhydrophobic cotton fabrics  
1407            by silica hydrosol and hydrophobization. *Applied Surface Science*, 257(13), 5491-5498.

1408 Yang, H., & Deng, Y. (2008). Preparation and physical properties of superhydrophobic  
1409            papers. *Journal of colloid and interface science*, 325(2), 588-593.

1410 Zafeiropoulos, N., Williams, D., Baillie, C., & Matthews, F. (2002). Engineering and  
1411            characterisation of the interface in flax fibre/polypropylene composite materials. Part I.  
1412            Development and investigation of surface treatments. *Composites Part A: Applied*  
1413            *Science and Manufacturing*, 33(8), 1083-1093.

1414 Zafeiropoulos, N. E. (2011). *Interface engineering of natural fibre composites for maximum*  
1415            *performance*. Elsevier.

1416 Zaki Abdullah, M., Dan-mallam, Y., & Megat Yusoff, P. S. M. (2013). Effect of  
1417            Environmental Degradation on Mechanical Properties of Kenaf/Polyethylene  
1418            Terephthalate Fiber Reinforced Polyoxymethylene Hybrid Composite. *Advances in*  
1419            *Materials Science and Engineering*, 2013.

1420 Zhang, D., Milanovic, N. R., Zhang, Y., Su, F., & Miao, M. (2014). Effects of humidity  
1421            conditions at fabrication on the interfacial shear strength of flax/unsaturated polyester  
1422            composites. *Composites Part B: Engineering*, 60, 186-192.

1423 Zhang, J., Tu, W., & Dai, Z. (2013). Transparent polyester polyol-based polyurethane  
1424            coatings: the effect of alcohols. *Journal of Coatings Technology and Research*, 10(6),  
1425            887-895.

1426 Zheng, Q., & Lü, C. (2014). Size Effects of Surface Roughness to Superhydrophobicity.  
1427            *Procedia IUTAM*, 10, 462-475.

1428

1429