Review on hygroscopic aging of cellulose fibres and their biocomposites

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Abstract

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

Keywords: Humidity; Temperature; Superhydrophobic; Bio-based coatings, Natural fibre
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1. Introduction

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

Surface modification of natural fibres has served as an essential tool to improve the compatibility with the polymer matrix. Studies on surface modification of natural fibres leading to moisture absorption have been reported in literature (Alawar, Hamed & Al-Kaabi,
However, the long term effect of exposure of natural fibre composites to high relative humidity and temperature is problematic, further techniques such as nano-coatings, bio-based coatings and chemical modifications need to be exploited or optimised to enhance surface hydrophobicity of natural fibres. Emphasis has to be placed on the effects of cellulose surface chemistry and topography, both of which affect hydrophobicity. Interestingly, research on superhydrophobicity has stimulated much scientific and industrial interest because of applications in self-cleaning, friction reduction, water repellence and antifouling (Song & Rojas, 2013). In addition, bio-based polyurethane coatings with superior properties such as solvent resistance, hydrolytic stability, weatherability and acid-base resistance have been reported and show good moisture repellence properties. Another promising hydrophobic resin is poly(furfural alcohol) which holds excellent properties such as high heat distortion temperature, high chemical resistance, hydrophobicity and high chemical resistance (Deka, Misra & Mohanty, 2013; Kumar, Kumar & Anandjiwala, 2012). Reviews on effect of water sorption /diffusion on properties of natural fibres/ composites are present in literature. However, this review addresses issues of moisture absorption as a result of relative high humidity and temperature and focuses on significant effects on chemical and physical properties of natural fibres as well as on final performance of composite structures especially in long-term application. The review also discusses the drawbacks of mechanical fatigue associated with long-term durability of natural fibre reinforced composites especially when moisture sorption is accompanied by high environmental variations of temperature and humidity. Furthermore, the review also highlights research work done on chemical treatment to reduce the inherent hydrophilicity of lignocellulosic fibres and retard moisture absorption behaviour. Emphasis is placed on possible solutions to bridge the gap between chemical treatments, bio-based coatings and developing superhydrophobic materials using nanoparticles to improve the long-term utilization of fibre reinforced composites, especially when exposed to water absorption accompanied by high hygroscopic factors. Therefore, a comprehensive survey in the development of superhydrophobic materials based on cellulose material for better moisture resistance as well as the potential of bio-based coatings to be
used as suitable material for lowering moisture absorption in natural fibre composites is discussed.

2. Natural Fibres

2.1 Structure and properties of natural fibres

Natural fibres are divided based on their origins, coming from plants, animals or minerals. All plant fibres are made-up of cellulose while animal fibres comprise of proteins (wool, hair, and silk). Natural fibres consist of bast fibres (or stem or soft sclerenchyma), hard or leaf fibres, seed, cereal straw, wood, fruit, and other grass fibres. In their natural form, fibres are composites made up of hollow cellulose fibrils fused together by hemicellulose and lignin matrix (Jayaraman, 2003; John & Anandjiwala, 2008; John & Thomas, 2008) (see Figure 1). Each fibril consists of complicated layered structure comprised of a thin primary wall surrounding a thick secondary wall. This secondary wall is comprised of three layers of which the thick middle layer controls the mechanical properties of the fibre. The middle layer has a series of helically coiled cellular microfibrils created from long chain cellulose molecules; between the microfibrils and the fibre axis a microfibrillar angle which varies from one fibre to another is found.

![Figure 1: Structure of natural fibre](http://bioenergy.ccrcc.uga.edu/Background/background.htm)

The microfibrils are made up of 30-100 cellulose molecules with diameter of about 10-30 nm in extended chain conformation and offers mechanical strength to the fibre. The cell wall is very complicated and made-up of hemicellulose, lignin and in some circumstances wax and pectin. Hemicellulose molecules are held to cellulose by hydrogen bonds which act as
cementing matrix between the cellulose microfibrils, to form a hemicellulose-cellulose network, which is seemingly the main structural constituent of the fibre. The stiffness of the hemicellulose/cellulose composite is increased by a network of a hydrophobic lignin which acts as a coupling agent in the fibre cell. The nature of cellulose and its crystallinity correlates to the reinforcing efficiency of natural fibres. The main constituents of natural fibres are hemicellulose; lignin; cellulose (Figure 2) while pectin; wax; fat and water soluble substances are the minor components of the structure. These compositions may differ with test methods and with growing conditions even for the same kind of fibre (see Table 1) (Mohanty, Misra & Drzal, 2001; Singleton, Baillie, Beaumont & Peijs, 2003; Turmanova, Genieva, Dimitrova & Vlaev, 2008).

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

Hemicellulose is polysaccharides that comprise of several sugar moieties that are mostly branched, and have a significantly lower molecular weight with a degree of polymerization (DP) ranging from 50-200 compared to cellulose. The sugar moieties contain glucose but also other monomers such as arabinose, xylose, mannose and galactose. Hemicellulose is partially
soluble in water and hygroscopic due to its open structure which contains of acetyl and hydroxyl groups (Mohanty, Misra & Hinrichsen, 2000).

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

Lignin is a randomly branched polyphenol, made up of phenylpropane (C9) units and it is the most complex polymer among naturally occurring high-molecular-weight materials. Owing to its hydrophobic character, lignin reduces the penetration of water across the cell walls, which is made up of amorphous hemicelluloses and cellulose fibres, and in that way assists the transport of aqueous solutions of metabolites in the conducting xylem tissue and nutrients. Lignin brings rigidity to the cell walls and works together with hemicellulose to join cells in woody parts of plants, producing a composite structure with outstanding elasticity and strength. Moreover, lignified materials successfully repel attacks by microorganisms by means of blocking penetration of vicious enzymes into the cell walls (Mohanty, Misra et al. 2000). Heteropolysaccarides are a collective name of Pectins, and give flexibility to plants, while least part of natural fibres is made up waxes which consist of different types of alcohols.
Table 1  Chemical composition of various fibres. Reprinted from John & Thomas, 2008, Copyright 2007, with permission from Society of Plastics Engineers. Reprinted from John & Anandjiwala, 2008, Copyright 2008, with permission from Elsevier.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Cellulose (wt%)</th>
<th>Hemicellulose (wt%)</th>
<th>Lignin (wt%)</th>
<th>Waxes (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abaca</td>
<td>56-63</td>
<td>20-25</td>
<td>7-9</td>
<td>3</td>
</tr>
<tr>
<td>Alfa</td>
<td>45.5</td>
<td>38.5</td>
<td>14.9</td>
<td>2</td>
</tr>
<tr>
<td>Bagasse</td>
<td>55.2</td>
<td>16.8</td>
<td>25.3</td>
<td>-</td>
</tr>
<tr>
<td>Bamboo</td>
<td>26-43</td>
<td>30</td>
<td>21-31</td>
<td>-</td>
</tr>
<tr>
<td>Banana</td>
<td>63-64</td>
<td>19</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Coir</td>
<td>32-43</td>
<td>0.15-0.25</td>
<td>40-45</td>
<td>-</td>
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<tr>
<td>Cotton</td>
<td>85-90</td>
<td>5.7</td>
<td>-</td>
<td>0.6</td>
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<tr>
<td>Curaua</td>
<td>73.6</td>
<td>9.9</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td>Flax</td>
<td>71</td>
<td>18.6-20.6</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Hemp</td>
<td>68</td>
<td>15</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>Henequen</td>
<td>60</td>
<td>28</td>
<td>8</td>
<td>0.5</td>
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<tr>
<td>Isora</td>
<td>74</td>
<td>-</td>
<td>23</td>
<td>1.09</td>
</tr>
<tr>
<td>Jute</td>
<td>61-71</td>
<td>14-20</td>
<td>12-13</td>
<td>0.5</td>
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<tr>
<td>Kenaf</td>
<td>72</td>
<td>20.3</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>Kudzu</td>
<td>33</td>
<td>11.6</td>
<td>14</td>
<td>-</td>
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<tr>
<td>Nettle</td>
<td>86</td>
<td>10</td>
<td>-</td>
<td>4</td>
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<tr>
<td>Oil palm</td>
<td>65</td>
<td>-</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>Pissava</td>
<td>28.6</td>
<td>25.8</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>Pineapple</td>
<td>81</td>
<td>-</td>
<td>12.7</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>68.6-76.2</td>
<td>13-16</td>
<td>0.6-0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Sisal</td>
<td>65</td>
<td>12</td>
<td>9.9</td>
<td>2</td>
</tr>
<tr>
<td>Sponge gourd</td>
<td>63</td>
<td>19.4</td>
<td>11.2</td>
<td>3</td>
</tr>
<tr>
<td>Straw (Wheat)</td>
<td>38-45</td>
<td>15-31</td>
<td>12-20</td>
<td>-</td>
</tr>
<tr>
<td>Sun hemp</td>
<td>41-48</td>
<td>8.3-13</td>
<td>22.7</td>
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</table>

Natural fibres possess desirable properties such as high specific strength, high toughness, low density, ease of separation, good thermal properties, biodegradability, improved energy recovery, low cost and a non-corrosive nature. Commonly, fibres with a lower microfibrillar
angle (MFA) (the angle between the fibre axis and cellulose microfibrils) and highest cellulose content have better strength properties (see Table 2) (Eder & Burgert, 2010). The spiral orientation of the fibre axis determines the ductile property in the plant fibre. If the microfibrils are oriented parallel to the fibre axis, the fibres turn out to be stiff, inflexible, and possess high tensile strength (John & Anandjiwala, 2008). Although natural fibres have relatively lower strength properties compared to the synthetic fibres, the elongation at break and specific modulus suggests the potentiality of these fibres to substitute synthetic fibres in manufacturing of polymer composites (Kabir, Wang, Lau & Cardona, 2012).

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

<table>
<thead>
<tr>
<th>Name of fibre</th>
<th>Density (g/cm³)</th>
<th>Microfibrillar angle (MFA) (°)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Specific strength (GPa/g/cm³)</th>
<th>Specific modulus (GPa/g/cm³)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute</td>
<td>1.3–1.4</td>
<td>7–9</td>
<td>393–773</td>
<td>13–26.5</td>
<td>0.3–0.5</td>
<td>10–18.3</td>
<td>1.16–1.5</td>
</tr>
<tr>
<td>Flax</td>
<td>1.50</td>
<td>10–11</td>
<td>345–1100</td>
<td>27.6</td>
<td>0.2–0.7</td>
<td>18.4</td>
<td>2.7–3.2</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.14</td>
<td>6</td>
<td>690</td>
<td>30–60</td>
<td>0.6</td>
<td>26.3–52.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.50</td>
<td>8; 7.5</td>
<td>400–938</td>
<td>61.4–128</td>
<td>0.3–0.6</td>
<td>40.9–85.3</td>
<td>1.2–3.8</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.45</td>
<td>19.7</td>
<td>468–640</td>
<td>9.4–22.0</td>
<td>0.3–0.4</td>
<td>6.4–15.2</td>
<td>3–7</td>
</tr>
<tr>
<td>PALF</td>
<td>1.52</td>
<td>8–14</td>
<td>413–1627</td>
<td>34.5–82.5</td>
<td>0.3–1.1</td>
<td>22.7–54.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.5–1.6</td>
<td>-</td>
<td>287–800</td>
<td>5.5–12.6</td>
<td>0.2–0.5</td>
<td>3.7–7.8</td>
<td>7.0–8.0</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.5</td>
<td>-</td>
<td>2000–3500</td>
<td>70</td>
<td>0.8–1.4</td>
<td>28</td>
<td>2.5</td>
</tr>
<tr>
<td>S-glass</td>
<td>2.5</td>
<td>-</td>
<td>4570</td>
<td>86</td>
<td>1.8</td>
<td>34.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.4</td>
<td>-</td>
<td>3000–3150</td>
<td>63–67</td>
<td>2.1–2.2</td>
<td>45–47.8</td>
<td>8.3–3.7</td>
</tr>
</tbody>
</table>
2.2 Advantages and disadvantages of plant fibres

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

Natural fibres are regarded as potential substitutes for manmade fibres in composite materials. Although natural fibres have benefits of being inexpensive and light weight, they are not totally immune to problems. One of the problems with natural fibres is their strong hydrophilic character which generates incompatibility with most polymer matrices as well as compounding difficulties. This leads to a heterogeneous dispersion of the fibres in the matrix and consequently impairs the properties of the resulting composite. One more setback of natural fibres is their low degradation temperatures (~200 °C), which make them unsuitable to process with thermoplastics above 200 °C and this again limits the choice of polymer material. Another restraint to the successful utilization of natural fibres for tough composite application is low microbial resistance and vulnerability to rotting. These properties pose severe problems during transportation, storage, and composite processing. The inhomogeneity and variation of dimensions and of their mechanical properties (even between
individual plants in the same cultivation) creates another serious problem. Another serious drawback is the high moisture uptake of natural fibres leading to swelling and creating voids at the interface, which results in poor mechanical properties and decreases dimensional stability of composites. However, the recent literature revealed that, the moisture uptake of fibres can be diminished by modifying the hydrophilic hydroxyl groups from the fibre surface by means of different chemical modifications (alkali, silane, acetylation treatments and many more). These modifications are typically based on the use of reagent functional groups that are capable of reacting with the functional groups in the fibre structure and changing their composition. This would result to the reduction of moisture absorption tendency and simplify compatibility with the polymer matrix. Many studies, reports and reviews have been published on chemical modification of natural fibres in order to improve their compatibility with polymers matrices (Cantero, Arbelaitz, Llano-Ponte & Mondragon, 2003; Hashim, Roslan, Amin, Zaidi & Ariffin, 2012; John & Anandjiwala, 2008; Kalia, Kaith & Kaur, 2009; Keener, Stuart & Brown, 2004; Kumar, Obrai & Sharma, 2011; Xie, Hill, Xiao, Militz & Mai, 2010; Zafeiropoulos, Williams, Baillie & Matthews, 2002). Improved physical and mechanical properties have been reported and chemical treatment proved to reduce moisture absorption to a degree (Alawar, Hamed & Al-Kaabi, 2009; Dixit & Verma, 2012; Rout, Misra, Tripathy, Nayak & Mohanty, 2001; Sgriccia, Hawley & Misra, 2008).

2.3 Moisture absorption behaviour of natural fibres

Natural fibres are characteristically hydrophilic in nature because of the existence of a large number of hydroxyl groups (-OH) in cellulose and hemicellulose. However, not all constituents contribute to the absorption of moisture. Cellulose, which forms the major part of the natural fibre, is hydrophilic in nature and it can absorb water molecules. Even though cellulose has a large –OH to carbon (C) ratio, a small amount –OH groups are exposed or accessible as cellulose is semicrystalline. The highly crystalline region of the cellulose is virtually inaccessible to water molecules but the water molecules are able to penetrate and gain access into the amorphous region of the cellulose. On the other hand, hemicellulose is predominantly amorphous with high –OH to C ratio making it highly accessible to water molecules. Lignin, however, is hydrophobic in nature and has low –OH to C ratio. When natural fibres absorb water molecules, they swell up due to water molecules occupying the space between the microfibrils. This space that the water molecules occupy is known as the temporary microcapillary network. The water molecules within the natural fibres can either
form a monolayer, which associate closely with the available –OH groups, or form a multilayer at which not all water molecules are in intimate contact with available –OH groups. (Zafeiropoulos, 2011).

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

3. Hygroscopic aging of natural fibre and its composites

Hygroscopy is the capability of a material to easily absorb moisture from the surrounding environment. This is mainly influenced by the environmental conditions such as humidity and temperature. The attraction of water molecules is achieved by either absorption or adsorption with the absorbing or adsorbing material somewhat becoming physically changed. This could be through a change in boiling point, increase in volume, physical characteristic or viscosity of the material, as water molecules can become suspended between the material’s
molecules in the process. Hygroscopic material such as cellulose fibres exhibit different hygroscopic properties which lead to detrimental effects such as stress concentration in composite materials (http://en.wikipedia.org/wiki/Hygroscopy; Choi, Ahn, Nam & Chun, 2001). Furthermore, the recurring changes of the internal stresses as a result of water absorption-desorption process may induce fatigue damage in the inter- and intralaminar region of the composite material and therefore influence the performance and long-term durability of the composite. In natural fibre reinforced composites the hygroscopic effect is usually experienced from repeated absorption and desorption of moisture in a wide range of humidity and temperature.

3.1 Natural fibres and composites

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

Zaki Abdullah, Dan-mallam & Megat Yusoff, 2013 investigated the influence of environmental degradation on the mechanical properties of kenaf-PET hybrid fibre reinforced polyoxymethylene (POM) composites. The samples were exposed to moisture, water spray and ultraviolet penetration in accelerated weathering chamber for 672 hours. They reported that the tensile strength of long fibre kenaf/POM (20/80) composite dropped by 50% from
127.8 to 64.8 MPa while that of the hybrid (kenaf-PET/POM) composite dropped by only 2% from 73.8 to 72.5 MPa. This suggested that the hybrid had higher resistance to environmental degradation than the kenaf/POM composites, which was attributed to the hydrophobic characteristic of PET fibre in the composite and its high resistance to thermo-oxidative degradation. Unlike the hybrid composites, the kenaf/POM composites exposed to moisture and UV led to the degradation of lignin, hemicellulose and cellulose content in kenaf fibre resulting in a significant drop of the tensile strength. It was further observed that the flexural strength of hybrid samples for both short and long fibre composites had better retention of flexural strength than that of kenaf/POM composites. This was ascribed to high opposition of PET fibres to photodegradation compared to kenaf fibre.

The influence of water uptake on mechanical properties of hemp fibre reinforced unsaturated polyester composites were investigated (Dhakal, Zhang & Richardson, 2007). The reinforced composites were exposed to water absorption investigations by immersing the samples in water at 25 °C and 100 °C for different times. The water uptake of samples immersed in boiling water was higher than of samples immersed at room temperature. This was ascribed to the details that when the composites are subjected to moisture, the hemp fibre swells due to absorbed moisture and as a result micro-cracking of the composite occurs and this is more pronounced at high temperatures (see Figure 3 showing the micro cracking). It was also observed that absorption at room temperature took a longer period to attain equilibrium than absorption at high temperatures. Furthermore, the ratio of moisture absorption increased as the fibre volume fraction increased due to increased cellulose content. The mechanical properties of composites decreased with increase fraction of moisture absorption. However, it was noted that for hemp fibre reinforced samples (3 mm thickness from 5 layers); the ultimate tensile stress of the aged sample was higher than the dry samples. It was suggested that because of increased amount of absorbed water in the composites, this resulted to swelling of the fibres and filled the openings between the hemp fibre-polymer interfaces and eventually led to an increase in the mechanical properties of the composites. Improved Young’s modulus was observed in the investigation of flax/PLA biocomposites immersed in seawater (Le Duigou, Bourmaud, Davies & Baley, 2014). The composite rigidity was evaluated between 0.025 and 0.1% range, and the Young’s modulus of the composites immersed in seawater was found to increase until 0.5% range to 32 MPa. The reason behind the increase was attributed to a combined effect of fibre stiffness and water desorption during tensile testing. Similar observations have been reported on the influence of environmental
conditioning on physical and mechanical properties of flax fibres (Stamboulis, Baillie & Peijs, 2001). It was stated that after the flax fibre was exposure to humidified conditions (at 90% relative humidity (RH)), the fibres’ tensile strength was increased by about 20%.

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

Chen, Miao & Ding, 2009 investigated the impact of moisture absorption on the interfacial strength of bamboo/vinyl ester composites. The bamboo strips were first conditioned at a constant temperature (20 °C) and at altered relative humidity stages (60, 70, 80 and 90%) till they reached equilibrium. It was reported that the rapid water uptake by bamboo strips at each RH stage firstly increased with the square root of time and then slowed down as water content came near equilibrium at 60% RH. The equilibrium moisture further increased sharply at 70% RH, and nearly doubled when the RH was increased from 80% to 90%. This was attributed to the large proportion of ground tissue (shaped like honeycomb structure) surrounding the cellulose fibres in the bamboo strips which have various capillary spaces that are ideal spots for keeping water. The interfacial shear strength (IFSS) reduced gradually with increasing RH during manufacturing contrast to composites manufactured at dry conditions. The IFSS value decreased by over a half when relative humidity increased to 70%, by more than 90% at 80% RH and almost zero at 90% RH. This was ascribed to poor interfacial bonding at high RH circumstances. The -OH groups found in the bamboo permits a large amount of hydrogen bonds to be formed between the matrix and the macromolecules of the cellulose. This result to a loss of compatibility between the polymer and the fibre bring about weakening and dilapidation of the interface.
Absorption of moisture in natural fibre composites is explained by three different major mechanisms. The first is the capillary action of water molecules into the openings and defects at the boundary between the fibres and the matrix because of incomplete bonding, followed by the flow of water molecules inside the microgaps amongst the polymer segments. Lastly the transportation of water molecules within microcracks in the polymer, made during the manufacturing process. Additionally, the moisture diffusion in polymer composites has been further classified to be non-Fickian or Fickian (Dhakal, Zhang & Richardson, 2007; Kim & Seo, 2006; Lin, Zhou & Dai, 2002; Osman, Vakhguelt, Sbarski & Mutasher, 2011). The Fickian flow denotes to the diffusion of water from a region of highest to lower concentrations generated by concentration gradient. The non-Fickian behaviour may be ascribed to the difference in absorption manner and state of water molecules present in the composites. At higher temperature, moisture uptake behaviour is accelerated due to an increase in the permeability coefficient and thereby greatly shortening the moisture saturation time. (Azwa, Yousif, Manalo & Karunasena, 2013; Joseph, Rabello, Mattoso, Joseph & Thomas, 2002; Osman, Vakhguelt, Sbarski & Mutasher, 2011). Kenaf fibre reinforced unsaturated polyester composites form different weight fractions (0, 10, 20, 30 and 40wt%) were prepared and assessed by dipping in tap water at different temperatures of 25 and 50 °C by Osman, Vakhguelt, Sbarski & Mutasher, (2011). The process of water absorption was found to approach the Fickian diffusion behaviour for both temperatures. This implied that water diffusion coefficients increased with increasing environmental temperature and fibre weight fraction as presented in Figure 4. The diffusion coefficient defines the rate of diffusion of particles, depending on the temperature, viscosity and particle size. It is a function of absolute temperature and has been shown to increase with increase in temperature. Furthermore, the flexural properties of the composites significantly decreased on exposure to moisture as presented in Figure 5a and b. This was ascribed to the creation of hydrogen bonding between the cellulosic fibre and water molecules and resulting in poor interfacial interaction between the kenaf fibre and polyester.
Figure 4  Diffusion coefficient for composites at various temperatures. Reprinted from Osman, Vakhguelt, Sbarski & Mutasher, 2011, Open Access
Figure 5  Effect of moisture uptake on the (a) flexural Modulus and (b) flexural strength. Reprinted from Osman, Vakhguelt, Sbarski & Mutasher, 2011, Open Access

3.2 Chemically modified natural fibre composites

Several studies have been reported on chemical modification to increase adhesion between natural fibres and polymer matrices, in order to decrease moisture absorption and enhance the
mechanical properties. The moisture absorption of fibres which is due its hydrophilic character, affects some of the properties such as fracture toughness, flexural modulus, and flexural strength. Sreekala & Thomas, 2003 investigated the effects of surface modification on water-sorption characteristics of oil palm fibres. Different fibre modifications such as silane treatment, gamma irradiation, acetylation treatment, mercerization, isocyanate treatment and peroxide treatment were used. The water absorption behaviour of a palm fibre was evaluated in deionized water at varying temperatures conditions (30, 50, 70 and 90 °C) in a thermostatically controlled air oven. The increasing in the sample weights were recorded at precise time intervals until equilibrium was reached. The treatment considerably reduced the water absorption for all temperatures, but with observed irregularities for different modified system. The decline in the water absorption was ascribed to the chemical and physical changes brought by the modification onto the fibre. The treated fibre surfaces revealed changes in the porous structure of the fibre and different chemical bonds formed on the fibre surface during treatments. The permeability, sorption and diffusion coefficients decreased due to treatment. However, the mechanical properties (presented in Table 3) were found to decrease for swollen system compared to un-swollen. Nevertheless, enhancement in the Young’s modulus was observed for mercerized and silane treatment and was ascribed to the modifications that happened at the cellulosic part of the fibres.
Table 3  Tensile properties of the treated OPEFB fibre. Reprinted from Sreekala & Thomas, 2003, Copyright 2003, with permission from Elsevier

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

Figures in parentheses = Standard deviation

The impact of fibre surface modification on the properties of sisal-polyester composites were investigated by Singh, Gupta & Verma, 1996. Unsaturated polyester was reinforced with sisal fibre modified with different chemical modifiers such as organotitanate, zirconate, silane and N-substituted methacrylamide. The composite samples were subjected to 95% relative humidity at 50 °C and immersed in water for 35 days. It was found that modified sisal reinforced composites absorbed water at a slow rate compared to untreated sisal composites. This was due the development of a reasonably more hydrophobic interface region by co-reacting organofunctionality of the coupling agents with the matrix. A substantial reduction in the flexural and tensile strength of 30% and 50% respectively was observed under humid conditions. In the case of epoxy resin reinforced with jute fibre modified with an
epoxyfunctional-γ-glycidoxypropyltrimethoxy-silane (Gassan & Bledzki, 1997), the moisture uptake was determined in deionized water (23 °C) for approximately six weeks. It was found that the moisture absorption of composites with silane treated fibres reduced by 10-20%. The equilibrium and kinetics of moisture absorption improved with increasing fibre loading. The tensile modulus and strength as well as the fatigue strength dropped by 30% as the moisture content increased.

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

Spinace, Lambert, Fermoselli & De Paoli, 2009, characterized the properties of curaua fibres subjected to sodium hypochlorite and cold oxygen plasma modification. It was observed that
moisture absorption percentage of untreated fibre was 9.10 wt.% and changed for treated fibre to 8.30 wt.% at normal environmental conditions. The decrease indicated that the modification changed the hydrophilic property of the curaua fibres. Based on the above mentioned studies, chemical treatment of natural fibres has reduced moisture absorption. However, more investigations are required to induce a higher level of hydrophobicity in chemically modified natural fibre reinforced composites when subjected to long-term environmental/hygroscopic aging. There are other strategies to retard moisture absorption in natural fibres when exposed to long-term aging. This includes introduction of bio-based coatings on the composites. The advantage of using bio-based coatings is to ensure the biodegradable and environmentally friendly nature of fibres as opposed to using synthetic and toxic chemicals. In addition, bio-based coatings have superior hydrophobic properties and are produced from renewable resources. Another approach is the use of superhydrophobic materials in order to reduce the surface energy and enhance surface roughness on natural fibre surfaces.

**Bio-based coatings**

4.1 Polyurethane coatings

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

\[
R\text--NCO + R'\text--OH \rightarrow R\text--NH\text--COOR'
\]

In general, very tough polyurethane films are produced from acrylics polyl and polyesters under suitable curing specifications and are commonly used for high performance coatings. In addition, polyols containing esters offer adhesion promotion and abrasion resistance, while polyether polyols offer low temperature and viscosity properties. The difference between the
polyether and polyester polyols is their industrial production which differ in their monomer compositions, for instance polyether polyols are limited to tetrahydrofuran, ethylene, propylene and butylene oxides. On the other hand, polyester polyols are products of alcohols and organic acids which can be produced from different combinations of monomers and this further adds a great value to the polyurethane products. (Awasthi & Agarwal, 2007, 2010). So far polyurethanes produced industrially are usually petroleum based polyol. Hence, there is now a growing request for renewable resources such as crude oil and low priced sustainable products (Kong, Liu, Qi & Curtis, 2013). Therefore, substitution of petroleum based products with bio-based products offers excellent advantages such as; easy availability, lower environmental impact, sustainability, structural integrity, affordability as well as their use benefits the agricultural sector.

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

Two Bio-based poly(ether ester) polyols (Liprol™ 270 and Liprol™ 320) (Figure 6) coatings were successfully synthesized and commercialized by Kong, Liu & Curtis, 2012. The polyols were produced from canola oil by epoxidation followed by acid catalysed ring opening and trans-esterification with 1,3-propanediol or 1,2-propanediol. It was observed that the mechanical properties of both Liprol PU samples improved upon exposure to alkali solution and water at 80°C for 7 days (Table 4). This was due to the removal of glycerol and the
introduction of an ether group during the ring opening reaction and as a result created highly crosslinked networks in Liprol PU samples, and further increased the glass transition temperature.

Figure 6 Synthesis of poly(ether ester) polyols from canola oil. Reprinted from Kong, Liu & Curtis, 2012, Open Access
Table 4  Hydrolytic stability and alkali resistance properties of polyurethane after exposure to 100 % relative humidity at 80 °C and 3.3% NaOH solution for 7 days. Reprinted from Kong, Liu & Curtis, 2012, Open Access

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hydrolytic stability</th>
<th>Alkali resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tensile strength retaining (%)</td>
<td>Elongation at break retaining (%)</td>
</tr>
<tr>
<td>Liprol™ 270- MDI</td>
<td>61 ± 1</td>
<td>1430 ± 8</td>
<td>5.9 ± 0.7</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>Liprol™ 320- MDI</td>
<td>67 ± 2</td>
<td>1700 ± 10</td>
<td>4.6 ± 0.4</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Castor oil-MDI</td>
<td>9.3 ± 0.3</td>
<td>8.3 ± 0.2</td>
<td>62.3 ± 0.6</td>
<td>81</td>
<td>80</td>
</tr>
</tbody>
</table>
A sequence of polyester polyols were synthesized from trimethylol propane (TMP), 1,4-cyclohexanediol (1,4-CHDM) and 1,6-hexanediol (HDO), with a combination of 1,4-cyclohexanedicarboxylic acid and adipic acid (Zhang, Tu & Dai, 2013). It was found that the viscosity and glass transition temperatures of the polyester polyols were affected by the alcohol structure. But their values were increased by raising the molar ratio of 1,4-CHDM and/or TMP. The polyurethane coatings were found to have excellent impact resistance, optical properties, flexibility and hardness. Higher hardness was observed for diol CHDM derived PU and the PU derived from diol HDO had the lowest hardness. The chemical and water resistance improved with greater molar ratios of 1,4-CHDM or TMP. In the case of Awasthi & Agarwal, 2007 polyester polyols resin were synthesized with three diacids and further crosslinked with hexamethylene disiocynate (HDI) to form polyurethane coating films. They found that the cycloaliphatic diacids provided the polyesters with better solubility in ethyl ketone compared to polyester prepared from linear and aromatic diacids. It was also confirmed that cycloaliphatic diacids provided polyurethane coatings with better mechanical properties. Improved chemical resistance and good water resistance was observed (see in Table 5 and 6).

Table 5  Resistance to water\textsuperscript{a} of polyurethane films. Reprinted from Awasthi & Agarwal, 2007, Open Access

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deionized water</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CS-2</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CS-3</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}When dipped for 6 months; 5 = Film unaffected

Table 6  Resistance to water\textsuperscript{a} of polyurethane films. Reprinted from Awasthi & Agarwal, 2007, Open Access

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetic acid</th>
<th>Sulfuric acid</th>
<th>Hydrochloric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5% (v/v)</td>
<td>15% (v/v)</td>
<td>5% (v/v)</td>
</tr>
<tr>
<td>CS-1</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CS-2</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CS-3</td>
<td>5</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}When dipped for 6 months; 2= Softening of film; 3 = Blistering of film; 4 = Change in colour and loss in gloss; 5 = Film unaffected
Deka & Karak, 2009, investigated hyperbranched polyurethane (HBPU) for surface coating applications synthesized from monoglyceride of *Mesua ferrea* L. 2,4-toluene diisocyanate (TDI), poly(ε-caprolactone) (PCL), glycerol and seed oil in the absence of a catalyst. The mechanical properties improved with increase HBPU content as a result of enhanced molecular interactions brought by the amount of hydrogen bonding and aromatic molecules. An increase in flexural properties was observed due to PCL molecules, long hydrocarbon chains, ester linkages and ether groups. Furthermore, the mechanical properties of polyurethanes depended on; chemical linkages, entanglement, shape, size, molecular weight, and crystallinity of the polymer. The chemical resistance results of hyperbranched polyurethane after immersion in fresh water and in different chemical solutions (3% NaOH, 5% HCl, 20% EtOH, and 10% NaCl) for 7 days was found to be chemically stable except for NaOH. This was attributed to alkali hydrolysable ester groups of monoglyceride segments and poly(ε-caprolactone) present in HBPU.

In another case, soy bean oil was esterified by glycerol (1:3) molar ratio to produce monoglycerides, and then reacted with phthalic anhydride (20, 40 and 60%) to produce polyester polyols (Ismail, Motawie & Sadek, 2011). Diphenylmethane diisocyanate (MDI) was reacted with the polyols at NCO/OH ratios 1.2, 1.4, 1.6 using toluene as a solvent to produce polyester-polyurethane coatings (Figure 7). The polyurethane coatings were successfully prepared from soy bean oil polyols and MDI and easily cured by atmospheric moisture. Drying times were lowered with increasing phthalic anhydride content in the samples. The samples with phthalic anhydride 60% and containing NCO/OH 1.4 and 1.6, exhibited brittle characters and failed in impact and flexibility resistance tests. On the other hand, as the NCO/OH ratio was increased in each category of phthalic anhydride, the mechanical, physical and chemical properties and anticorrosive characters of the coatings improved.
novel route to obtain a hydrophilic chain extender and diisocyanate from castor oil and fatty acid, Fu, Zheng, Yang, Chen & Shen, 2014, studied a new way to prepare water borne polyurethane dispersion (BPUD) using diisocyanate from castor oil and fatty acids. The assessed BPUD mechanical properties showed that the bio-based PUs had fairly low elongation at break, tensile strength and pendulum hardness. This was due to high flexibility of the castor oil as a result of long hydrocarbon segments and its poly-functionality. The BPUD film after immersion in water for 168 hours was found to be marginally swelled and whitened with a water absorption value of 1.75%, which indicated that the castor oil based PU, had improved water resistance properties (see Figure 8). Although a toxic undecylenic acid was used as an intermediate to synthesis bio-based diisocyanate (BDI), the obtained bio-based water borne polyurethane dispersion was suggested as suitable product to petroleum based materials because of exhibiting better hydrophobic and thermal characteristics.

**Figure 7  Reaction sequence of the preparation of polyurethanes. Reprinted from Ismail, Motawie & Sadek, 2011, Open Access**
Rajput, Hundiwale, Mahulikar & Gite, 2014, prepared wood finished polyurethane coatings from a combination of renewable sources. The coatings were prepared from a reaction of polyesteramide polyol and aromatic diisocyanate. The results showed that the oleic and dimer fatty acids can be used to synthesize polyesteramide and wood finished polyurethane coatings. The coatings were found to be thermally stable up to 220–250 °C when subjected to thermal degradation. Moreover, the coatings were also capable of increasing shelf-life of wood substrates because of better mechanical and weather resistance properties.

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

4.2 Poly(furfuryl alcohol)

Poly(furfuryl alcohol) (PFA) is one of the most attractive biobased renewable resource polymer that possess excellent properties such high heat distortion temperature, high chemical resistance, hydrophobicity and high chemical resistance (Deka, Misra & Mohanty, 2013; Kumar, Kumar & Anandjiwala, 2012). PFA is derived from a furfuryl alcohol (FA) precursor which is a main chemical product produced from furfural. Furfural is an aldehyde...
which is obtained from hydrolysis of agricultural residue of sugar cane, rice hulls, hazelnut shells, wheat, corn, birch wood and oat. In addition, nearly 85-90% of the furfural produced globally is being transformed into furfuryl alcohol by an inexpensive derivation route, and a cationic condensation reaction is used to polymerize the furanic monomer. (Deka, Misra & Mohanty, 2013). Several studies have been reported on developing Poly(furfuryl alcohol) or FA biofilms with low water uptake and with potential environmental friendly applications (Baysal, Ozaki & Yalinkilic, 2004; Deka, Misra & Mohanty, 2013; Dong, Yan, Zhang & Li, 2014; Hazarika & Maji, 2013; Kumar, Kumar & Anandjiwala, 2012).

Kumar, Kumar & Anandjiwala, 2012, prepared biofilms from soy protein isolate (SPI) and poly(furfuryl alcohol) as renewable materials for water resistance properties. It was found the mechanical properties of the biofilms at 65 ± 2% RH cured at optimum curing time had a tensile strength (σ) of ~20 MPa, Young’s modulus (E) of ~0.5 GPa and maximum water uptake of ~50% when immersed fully in water for 24 h with good dimensional stability. Additionally, the thermal degradation properties of the biofilms were found to improve because of the use of poly(furfuryl alcohol) on soy protein isolate. In another study on kenaf fibre/PFA composites (Deka et al., 2013), moisture absorption behaviour was found to increase with increasing kenaf fibre content and deviated from the Fickian behaviour, but a non-Fickian with a maximum water uptake of 7.8% at saturation point. This was attributed to the high hydrophilic nature of natural fibres. The researchers found that the best properties of the green composites were achieved at 20 wt.% fibre loading and showed significant increases in the flexural (48%) and tensile (310%) strength as well as the storage modulus (123%). Interestingly, retention after moisture absorption of up 89% for flexural, 82% for impact and to 83% for tensile strength was observed after the composites were subjected to hot water. Similar observations were recorded by Dong, Yan, Zhang & Li, 2014 on the investigation of polymer-wood composites prepared through vacuum impregnation of FA and nano-SiO₂ into fast-growing poplar wood. In this case, the water uptake was reduced by about 60% when compared to untreated wood fibre composite (Table 7), and this was attributed to the hydrophobic nature of poly(furfuryl alcohol) which decreased the water absorption.

Recently Mokhothu & John, 2015, investigated the use of a furanic based coating on flax fabric reinforced phenolic panels. Samples with and without coating were conditioned at 90 °C and relative humidity of 90% for three days and the water uptake and mechanical properties of samples before and after conditioning were analysed. Furanic based coated
samples exhibited improved moisture resistance and registered lower decrease in tensile properties after conditioning when compared to polyurethane (PU) and a water resistant market product coated samples.

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

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

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

<table>
<thead>
<tr>
<th>Wood samples</th>
<th>Bulk effect$^a$ (BE) (%)</th>
<th>Water uptake$^a$ (WU) (%)</th>
<th>Anti-swelling efficiency$^a$ (ASE) (%)</th>
<th>Hardness$^b$ (Shore D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>2.99 (± 0.40)</td>
<td>113.32 (± 7.88)</td>
<td>0 (± 2.99)</td>
<td>46.97 (± 4.25)</td>
</tr>
<tr>
<td>FA-treated</td>
<td>15.02 (± 1.08)</td>
<td>44.45 (± 5.55)</td>
<td>65.75 (± 0.86)</td>
<td>63.14 (± 4.35)</td>
</tr>
<tr>
<td>FA/SiO$_2$-treated</td>
<td>15.28 (± 0.33)</td>
<td>41.38 (± 3.68)</td>
<td>68.67 (± 1.72)</td>
<td>69.28 (± 345)</td>
</tr>
</tbody>
</table>

*a*Each value represents the average of six samples ± standard deviation, *b*Each value represents the average of twenty samples, *Treated with water

5. **Fabrication of hydrophobic and superhydrophobic surfaces from organic-inorganic hybrid material**

Surface modification of cellulosic materials has stimulated much scientific interest to improve durability and water repellent properties. This has been inspired by observing biological tiny structures of several types of surfaces like fish scales as well as rice and lotus leaves which display superb superhydrophobicity and/or hydrophobicity properties. A super- or hydrophobic surface is a surface which does not absorb water instead forms water droplets on a solid surface without being absorbed as shown in Figure 9. Additionally the solid surface has to have a high water contact angle greater than 150° and a sliding angle lesser than 10° to be hydrophobic. (Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Dong, Yao,
Yang, Jiang & Shen, 2013; Latthe, Terashima, Nakata & Fujishima, 2014; Song & Rojas, 2013). Furthermore, the contact angle between a liquid and a solid surface differs with the surface roughness as well as the surface energy or chemistry (Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006). Therefore, many studies and reviews have been reported on coating techniques to increase surface roughness such as sol-gel process, etching, electrospinning, chemical grafting, chemical vapour deposition and liquid flame spray (Berendjchi, Khajavi & Yazdanshenas, 2011; Gurav et al., 2014; Hu, Zen, Gong & Deng, 2009; Lee, An, Latthe, Lee, Hong & Yoon, 2013; Mahadik et al., 2013; Stepien et al., 2013; Stepien et al., 2011, 2012; Synytska, Khanum, Ionov, Cherif & Bellmann, 2011; Teisala et al., 2010) Important progress achieved in this field has also been reported in several review papers (Genzer & Efimenko, 2006; Ma & Hill, 2006; Nakajima, Hashimoto & Watanabe, 2001; Sanjay, Anaso, Chavan & Rajiv, 2012; Song & Rojas, 2013).

![Schematic Diagram](image)

**Figure 9** A schematic showing (a) hydrophilic surface with water contact angle less than 90°; (b) hydrophobic surface with water contact angle greater than 90° and (c) superhydrophobic surface with water contact angle larger than 150°. Reprinted from Latthe, Terashima, Nakata & Fujishima, 2014, Open Access

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

\[
\cos \theta_w = r \cos \theta
\]

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

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

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

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

5.1 Sol-gel process

Sol-gel process is a wet process that is broadly employed in the textile field using a simple pad or dip coating (Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Landage, Kulkarni & Ubarhande, 2012; Rao, Latthe, Mahadik & Kappenstein, 2011; Xu, Zhuang, Xu & Cai, 2011). Nano sol-gel method has been applied for preparing self-cleaning, antibacterial and water repellent finishes on fabrics (Gurav et al., 2014; Mahadik et al., 2013; Teisala et al., 2010; Verho, Bower, Andrew, Franssila, Ikkala & Ras, 2011). Sol-gel process is a chemical method used to synthesize typical metal oxides from a precursor (chemical solution) to form an integrated network of either discrete particle. The method has been used to produce superhydrophobic surfaces from a variety of alkylsilane precursors such as; tetraethyl orthosilicate or tetraethoxysilane (TEOS) (Colleoni, Donelli, Freddi, Guido, Migani & Rosace, 2013; Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006; Wang, Liu, Liu, Zhang, Li & Wang, 2011), methyltrimethoxysilane (MTMS) (Xu et al., 2011), tetraethylorthotitanate or tetraethyl titanate (Alongi, Ciobanu & Malucelli, 2012), tetrabutyl titanate (TBT) (Chen et al., 2011), methyltrithoxysilane (METES) (Chen et al., 2011; Rao, Latthe, Mahadik & Kappenstein, 2011) and tetramethoxysilane (TMOS) (Alongi, Ciobanu & Malucelli, 2012). The sol-gel process involves the generation of organic-inorganic hybrid materials through hydrolysis and condensation reactions of organometallic compounds. Hydrolysis and condensation reactions of tetraethoxysilane (TEOS) are the mostly used to produce silica as
indicated in equation 1-3, in which hydrolysis of alkylsilane in acid or basic conditions, alcohol condensation and water condensation are presented respectively.

\[
\text{Si-(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si-(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH} \tag{1}
\]

\[
\text{Si-(OH)}_4 + \text{Si-(OC}_2\text{H}_5) \rightarrow \equiv\text{Si-O-Si≡} + 4\text{C}_2\text{H}_5\text{OH} \tag{2}
\]

\[
\text{Si-(OH)} + \text{Si-(OH)} \rightarrow \equiv\text{Si-O-Si≡} + 4\text{H}_2\text{O} \tag{3}
\]

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

Ding, Li, Hotta, Kim, Kuwaki & Shiratori, 2006, converted electrospun nano-fibrous cellulose acetate mat surface from superhydrophilic to superhydrophobic surface by coating the nano-fibrous with silica particles prepared by sol-gel process. A sol-gel method was used prepared two coating solutions, first sol-gel (I) with decyltrimethoxysilane (DTMS) and second sol-gel (II) without DTMS according to these molar concentrations; 0.5:0.1:20:11:0.008 of TEOS, DTMS, ethanol, H\textsubscript{2}O and HCl respectively. Samples of cellulose acetate secured on a glass substrate were submerged into a sol-gel solution for 5 s followed by drying in air for 1 hour, then oven dried at 120 °C to obtain the desired morphology as depicted in Figure 11.
It was reported that the superhydrophilic cellulose acetate nano-fibrous mats were successfully prepared by dipping in a sol–gel solution. The sol-gel coated nano-fibrous mat had the same atomic ratio of silicon to carbon on its surface and further displayed hydrophobicity as a result of DTMS. Moreover, the hydrophobic cellulose acetate mats coated with the sol-gel film were converted to superhydrophobic mats by increasing the surface roughness of the cellulose acetate. It was further observed that cellulose acetate coated (8 wt.%) with micro-sized particles coated with the sol–gel (I) had higher hydrophobicity than that of fibrous 10 wt.% cellulose acetate mats without particles due to increased surface roughness and area. In another study, silica nanoparticles together with hexadecyltrimethoxysilane (HDTMS) were used to prepare superhydrophobic cotton fabrics (Xu, Zhuang, Xu & Cai, 2011). The sol-gel reaction in the presence of a base catalyst and surfactant was used to synthesize silica nanoparticles with methyltrimethoxysilane (MTMS) as a precursor as shown in Figure 12. The treated fibre displayed improved water repellence with a contact angle of 151.9° and water shedding angle of 13° for 5 μL water droplets. This was attributed to a substantial contribution of SiO₂ hydrosol coatings and HDTMS bonding which decreased the surface energy of cotton fabric.
Several researches have investigated silica coating to improve hydrophobicity of cellulose fibre (Berendjchi, Khajavi & Yazdanshenas, 2011; Synytska, Khanum, Ionov, Cherif & Bellmann, 2011) or solid surface (Wang, Liu, Liu, Zhang, Li & Wang, 2011) have been reported. Synytska, Khanum, Ionov, Cherif & Bellmann, 2011 studied the influence of Janus particles on the morphology and wetting properties of poly(ethylene terephthalate) (PET) textiles. Janus particles are silica particles with diverse properties (polarity, optical, magnetic and charge) at opposite sides. Janus particles were synthesized by hydrolysis-condensation of TOES. The obtained particles were modified with aminopropyltrimethoxy silane (APS) and octadecyltrichlorosilane (OTS). Particles of 1 and 200 μm were found attached between fibres the fibre surface respectively and improved the textile surface from a hydrophilic surface to a hydrophobic surface. The textile material exhibited a high contact angle (θ_{ADV} ≈ 140°) and a low tilt angle (θ_{TILT} = 10°), making the surface of the textile to be water repellent (as shown in Figure 13). In another study, the production of superhydrophobic wood surface through sol-gel method was investigated (Wang, Liu, Liu, Zhang, Li & Wang, 2011). The
wood surface coated with silica nanoparticles was modified with 1H, 1H, 2H, 2H-perfluoroalkyltriethoxysilane (POTS). It was reported that the silica nanoparticles dispersed homogeneously on the wood surface as a result of silica and POTS that offered a high surface roughness and low surface energy respectively. The wood surface was improved to a superhydrophobic surface with a sliding angle below 3° and water contact angle of 164°.

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

Berendjchi, Khajavi & Yazdanshenas, 2011 prepared a superhydrophobic and antibacterial cotton fibre surface using a sol-gel method, with different amounts of copper (Cu) nanoparticles and some samples modified with hexadecyltrimethoxysilane (HDTMS). The alkylsilane-treated SiO₂ cotton samples were found to have higher surface roughness compared to the untreated cotton samples (see Figure 14). The cotton fabrics were found to have a higher air trapping capability which resulted to high values of static water contact
angle (151.1°) and water shedding angle (30°). This was further seen when the Cu nanoparticles were increased by 0.5% (wt/wt) into silica sol-gel solution. The Cu nanoparticles agglomerate with the silica nanoparticles and as a result increased the static water angle to 155° for a 10-μl droplet. However, at higher amounts of Cu nanoparticles (2% wt/wt) the cotton fabric surface was found to be smooth and slippery. All cotton fabrics doped with Cu nanoparticles showed the effective antibacterial activity against gram-negative and gram-positive bacteria. These studies showed that addition of aminopropyltrimethoxy silane, 1H, 1H, 2H, 2H-perfluoroalkyltriethoxysilane and hexadecyltrimethoxysilane resulted in a better adhesion of silica coating on both surfaces.

![Figure 14 SEM micrographs of different samples (a) Untreated. (b) Treated with SiO₂. Reprinted from Berendjchi, Khajavi & Yazdanshenas, 2011, Open Access](image)

Yang & Deng, 2008, investigated the physical properties of superhydrophobic paper prepared from polydiallyldimethylammonium chloride (polyDADMAC) and silica particles (precursor TEOS), in the presents of 1H,1H,2H,2H-perfluoroctyltriethoxysilane (POTS, CF₃(CF₂)₃CH₂CH₂Si(OH)₅). The modified superhydrophobic paper prepared showed improved water resistance with a water contact angle greater than 150° and sliding angle less than 5°. This was attributed to the higher air trapping capability on paper surface as a results of silica particle and POTS. Furthermore, the mechanical properties of the superhydrophobic paper were improved even at high relative humidity condition (shown from Figure 15a). The high tensile strength recommended that the fibre-fibre bonds were well protected in those surface modified linerboard specimens due to TEOS treatment. The results showed that the relative moisture content of untreated linerboard increased to 650% with increasing relative humidity (from 15 to 90%). In contrary, hydrophobic and superhydrophobic linerboard had
higher moisture resistance and their relative moisture resistance was almost the same (see Figure 15b).

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

In the investigation of superhydrophobic silica films prepared by sol-gel method, methyltriethoxysilane was used as a hydrophobic reagent by Latthe, Imai, Ganesan & Rao, 2010). The coating was prepared from reaction series of tetraethoxysilane (TEOS), methanol
(MeOH), water (H₂O) constant at 1:22.09:6.25 molar ratios respectively, with ammonium fluoride (NH₄F) as a catalyst and the MTES/TEOS molar ratio (M) was varied from 0 to 0.43. The static water angle increased with increasing molar ratio and the highest contact angle was found at 160° and water sliding as low as 3° (see Figure 16). This was attributed to increasing amount of M during so-gel, which reduced the hydroxyl and alkoxy groups responsible for the hydrophobic property. Therefore, by increasing the molar ratio, the Si(CH₃) groups also increases the silica film surface which promotes hydrophobicity. It was further found that the silica films (M= 0.43) maintained their superhydrophobicity when immersed in water for at least two weeks and when exposed to relative high humidity (90%) and temperature (30 °C) over 60 days.

![Photographs of water droplet on the silica films prepared from (a) M = 0, (b) M = 0.08, (c) M = 0.25 and (d) M = 0.43. Reprinted from Latthe, Imai, Ganesan & Rao, 2010, Open Access](image)

From the above studies, the sol-gel produced silica particles were used to induce hydrophobicity in textile substrates by reducing the surface energy which effectively enhances hydrophobicity. The reduction in the surface energy was achieved by the ability to alter the particle size distribution that helps to introducing nanoscale roughness to the textile.
substrate. Furthermore, the –OH groups from polysiloxane are able to react with the –OH groups on the surface of fibres and form covalent bonds. In addition, the presence of methyl groups and least number of hydroxyl groups is considered beneficial for the superhydrophobicity.

5.2 Liquid flame spray (LFS) nanocoatings

Liquid flame spray is a technique that uses thermal spraying to generate and deposit nanosized metal oxides. LFS is used for coating various substrates and for fibre doping and normally water vapour and carbon dioxide are the by-products. Liquid feed stocks are prepared by diluting the liquid precursor in alcohol or water and are together fed with combustion gases into a specialized spray gun (see Figure 17). The precursor solution is atomised to micron-sized droplets through a high-velocity gas flow after the burner nozzle has been exited. The desired nanoparticles are deposited on a paperboard surface by a subsequent reaction of precursor vapour and evaporation of liquid droplets from a hot and turbulent flame. The nanoparticles can grow larger in the flame through agglomeration, coalescence, coagulation and condensation. The size of the particle can be controlled, by adjusting the collecting or depositing distance or by controlling the total mass flow rate of the precursor.
The LFS process is comparatively cheap and environmentally friendly as a result of low amounts of waste produced and the use of relatively simple and inexpensive equipment (Teisala et al., 2010). The main advantage of this method is the wide spectrum of metal oxide nanoparticles that can be produced by using different types of precursors. For example, Stepien et al., 2011, 2012 dissolved titanium (IV) isopropoxide (TTIP) precursor or tetraethyl orthosilicate in isopropanol (IPA) to adjust the moisture properties of paperboard with TiO$_2$ and SiO$_2$ nanosized coatings produced by LFS process. In their studies, superhydrophobic paperboard surface with high water contact angle was fabricated by TiO$_2$ coatings. The TiO$_2$ particles replaced the –OH groups with aliphatic groups and resulted to a superhydrophobic coated paperboard surface. In the case of Teisala et al., 2013b, highly photoactive LFS TiO$_2$ nanoparticle coatings were found to be easily converted from superhydrophobic to superhydrophilic by natural daylight illumination, UV-illumination, and low-intensity artificial daylight illumination. Furthermore, superhydrophobic surface of the LFS TiO$_2$ coating was instantly achieved after the coating procedure. This was due to accumulated carbonaceous over-layer on TiO$_2$, which ensured the suitable chemistry and the hierarchical roughness which further enhanced the hydrophobicity of the surface. In another study the group investigated the wetting phenomena on high- and low-adhesive superhydrophobic LFS-generated TiO$_2$ coatings on paperboard substrates using water–ethanol solution as a
probe liquid Teisala et al., 2013a. It was found that the submicrometer scale air gaps, which exist on superhydrophobic surfaces below the liquid droplets, were more stable with increasing amount of ethanol than in the larger-scale micrometric air gaps. This was because of the smoothening pigment layer below the nanoparticle coating, the LFS–TiO$_2$-coated board had the air entrapping surface structure predominantly at the submicrometer scale, and thus, the surface had high resistance against wetting by water-ethanol solution. In addition, contact angle of 155° ± 2° was measured on the LFS–TiO$_2$-coated board with the ethanol concentration of 15 wt%.

5.3 Dip coating and single-step deposition

Superhydrophobic materials have been produced from widely used nano-scaled surface roughness with hydrophobically modified surface. However, complicated procedures with high cost and harmful compounds to modify superhydrophobic surfaces have limited their applications. Several methods such as, dip coating and single-step deposition have also been used to achieve super-hydrophobic surfaces. Hu, Zen, Gong & Deng, 2009, investigated the superhydrophobic improvement of paper by modifying the paper surface with micro-sized CaCO$_3$ and fatty acid coating. The surface roughness was controlled by means of a surface hydrophobic modification agent. Dip coating procedure was used to prepared water resistant paper surface with improved water absorption and contact angle (150°). This was a result of combined surface treatments with dipping coating technique. Furthermore, different coatings thickness gave higher water resistance due to decreased water penetration rate.

Solid surfaces with well-controlled superhydrophobic and superoleophilic properties were investigated due to their supreme importance to water-oil separation technology (Lee, An, Latthe, Lee, Hong & Yoon, 2013). The superhydrophobic-superoleophilic membranes on electrospun polystyrene nano-fibres were successfully prepared by single-step deposition method. The diesel and water contact angle of polystyrene nano-fibre membrane were 0° and 155° ± 3°, respectively. The membrane exhibited excellent superhydrophobicity and simply separated diesel oil from water even after many separation process.
6. **Summary**

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

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

7. **Acknowledgements**

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