Protective Coatings for Bio-Composites – A Review

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Abstract. Even though Bio-based composites are eco-friendly, they are susceptible to degradation owing to both mechanical as well as biological factors. While it is evident that moisture affects the composites considerably, there are other factors such as heat and abrasion that could further accelerate the degradation. This article aims to encapsulate a few techniques for protection of the natural fibre-based composites. The reasons of thermal degradation and efforts to minimize the combustibility of substrates by application of aqueous, organic as well as intumescent coatings along with chemical treatments is discussed in brief. An account on the methods of applying a barrier coat and its subsequent curing is given. The need of gel coats, their advantages and several treatments to enhance the fibres to combat against degradation are outlined.

1. Introduction
Composites made of natural fibres have several advantages such as lower density, better thermal insulation and mechanical properties when compared to composites reinforced with synthetic fibres. Further, unlike synthetic fibres, natural fibres are broken down by bacteria once they are no longer in use. To enhance the life of the natural fibre composites a top layer called coating is applied on them that acts as a barrier against the external factors. The use of natural fibres in composites is beneficial because of its relatively high strength, hardness, and low density. They are eco-friendly, less abrasive to the tool and less irritating to the skin and respiratory system of the people who use them. Also, their properties vary significantly based on the chemical composition and structure of the fibres.

Natural fibre reinforced composites (NFRC) are gaining a lot of attention and importance due to the concept of sustainable development. Also, a life cycle assessment study by S. Joshi shows that NFRCs are superior than Glass Fibre Reinforced composites [1]. Although the sensitivity of such composites towards moisture is a cause of concern. This paper intends to review the different kinds of coatings for protection and enhancement of properties of composites.

Coating is the process of covering the surface of the object by applying a protective top film on it. The purpose of applying the coating may be decorative, functional, or both. From a surface engineering point of view, a coat is a layer of material deposited onto a substrate to enhance the surface properties and protect the substrate from external attacks. There is a wide range of coating processes ranging from just
a few microns, up to several millimetres depositing upon different types of material. Even though there are a few wood preservatives, ultraviolet radiation absorbers, water repellents, fire retardants, paints and coatings, that are developed to shield bio-based composites from environmental degradation, all these solutions still pollute the environment in some way; therefore, it is essential that novel technologies are developed.

1.1. Reasons for degradation of Natural Fibre based composites: [2]
- Biological Degradation due to natural Enzymatic and Chemical Reactions by Fungi, Bacteria, Insects, Termites.
- Mechanical and Thermal Degradation due to factors such as abrasion and external heat leading to cracks and fracture of the top layer which in turn expose interior of composite.
- Weather Degradation in the form of shrinking, cracking, swelling due to the Sun, Rain and cycling temperature changes.

These fibres have several advantages over synthetic fibre composites in terms of mechanical properties along with lower densities, and biodegradability. However, their hydrophilic nature is a major disadvantage. Natural weathering is often a cause of changes in the properties of bio composites. Generally, shallow cracks appear on the surface after a few months of natural exposure. Several different formulations of coating as well as their application methods, along with their outcomes have been outlined in this paper.

2. Hydrophobic Coatings
The best of inventions accredited to humans are simply through manifestation and thorough observation of nature and its essence. Therefore, it seems quite logical to draw inspiration from nature itself even for development of protective coatings. The epidermis of a lotus leaf acts as a super-hydrophobic layer due to its unique surface roughness. Several efforts have been made to emulate this property. A surface is often considered as super hydrophobic when it exhibits a contact angle above 150° [3]. Fluor-containing compounds work as excellent hydrophilizing agents due to their low surface energy. Their high reactivity also enables a relatively high bonding strength of the coat towards the sample surface [4]. Also, it was seen that moisture sorption is reduced significantly with the increase in cross-linking of the fibre cell wall.

A mixture of epoxy resin and silica nano particles could be used to coat over glass slides using dip coating. Upon curing, when the polymer coating is exposed to oxygen plasma, it imparts a distinct surface roughness that mimics the roughness on a lotus leaf. Similarly, Ke et al. [5] have fabricated a super hydrophobic surface by sequential drop coating of silane-modified-silica solutions onto glass substrates. Thin super hydrophobic films were developed by assembling silica nanoparticles on glass substrates by C. Sun, L. Ge and Z. Gu. They employed two methods to create the lotus effect. In the first method, a template of 8 µm sized silica was coated with smaller particles by electrostatic deposition. The other method was by casting a Poly-dimethyl-silohexane mould on the template particles array.

The fibre-based composites must be subjected to a pre-treatment called silanization to form silane groups that act as a fibre-matrix coupling agent. Silanol (Si-OH) groups react with -OH groups of the fibres and the matrix functional groups which facilitates the adhesion of the coating on to the composite substrate. Zhidong Ma et al. developed a composite organic coating using Polyvinyl butyral, polymethyl-hydrosiloxane (PHMS) and chitosan, for use as a protective barrier for fibre-based composites [6]. However, these methods were not suitable and scalable for industrial applications. An industrially applicable, robust system for creating super hydrophobic surfaces on biobased composites has been developed at Chalmers University. A silica nanoparticle / polymer binder dispersion technique was devised for simplifying the application of hydrophobic barrier coat by spraying onto the composite surface like paint.
3. UV Curable Coatings

UV curable epoxy films were developed by M M. Aung using Jatropha seed oil. The acrylation process was reported to be slower and during the curing a thin film would be formed which further deterred the curing process as well as decreased the gel content [7]. Liang et al. developed an organic UV treatable coating using Tung oil-based derivative - Tung Maleic Anhydride. Challenges experienced in the curing of bio-based UV treatable coatings such as insufficient reactivity to UV radiation (which is paramount in achieving high crosslinking) and volume shrinkage were overcome. The high crosslinking density lead to improvement in thermal stability and enhanced the hydrophobicity and gel content.

Polyurethane coatings are majorly applied in the areas of rigid foams, elastomers, and sealants, but majorly used as adhesives. The surface properties such as pencil hardness, adhesion and flexibility of the coatings are especially important. Renewable cardanol can be used to prepare highly branched UV-curable oligomers that have a pencil hardness of 3H. Coatings based on Cardanol exhibited excellent adhesion, glass transition temperatures and hardness. Gaikwad et al. developed polyurethane coatings from Karanja and Cotton seed oils and their resulting mar hardness and pencil hardness was comparable to that of synthetically produced acrylic polyurethane 4H [8]. In addition, a coating with a hardness of 5H was developed by the use of hyperbranched polyurethane acrylate.

The hydrophobic property of PU coating was further improved upon by Zhang et al. by mixing the PU with Poly-dimethyl-siloxyhexane (PDMS) and Aluminium flakes. The coating also had self-cleaning properties owing to its high Water Contact Angle (WCA) of about 117°. Upon further modification with nano SiO$_2$ they achieved super hydrophobicity (WCA 151.5°) and lowered glossiness. This makes the method suitable for stealth applications. Acrylated epoxidized soybean oil (AESO) is also good barrier against moisture when polymerized by UV light initiator. The physical, mechanical and water resistance properties of coated composites were found to improve in comparison with untreated samples [9].

4. Fire Retardant Coatings

Coatings have been developed to reduce fire hazards, prevent combustion of materials and reduce the heat evolved or emitted during their combustion, while also meeting regulations of fire-safety. They do so by interfering with the polymer combustion process [10]. Mineral flame retardants such as aluminium tri-hydroxide are very effective in reducing the risk of fire.

Treatment of cellulose fibres with a strong acid produces cellulose nanocrystals. The regions rich in cellulose are crystallized, while the amorphous regions of low order are easily penetrated by the acid and are hydrolysed. This method has been reported to be an effective way to encourage the formation of char during thermal degradation. It is interesting to note that chemical modifications like these can enhance properties and improve fire proofing. Hemicellulose, when subjected to thermal degradation, releases the water adsorbed by it. Further, there is rupture of its weak side branches, along with a decrease in mass. Notable causes of weight loss are dehydration and decarboxylation reactions that lead to release of gases like Carbon monoxide, Carbon dioxide, water vapour, furfural and acetic acid. Thermal degradation of hemicellulose is less affected by other biomass because its decomposition takes place at lower temperatures. The presence of minerals favours ring scission and produces volatile products due to the prevailing dehydration reactions and formation of furans. However, a notable disadvantage of hemicellulose is that it has a low initial thermal decomposition temperature which endangers its use as a filler in polymeric matrices.

Owing to the fact that the properties of substances are a result of their structure and composition, the stability and thermal decomposition rate of starch also depends on the same factors. Thermal stability of corn starch decreases as the ratio of amylose increases. Parallely, due to presence of hydroxyl groups in Chitosan, the possibility of its usage in flame proofing applications is examined. The presence of
carbohydrates promotes char formation [11]. Clay combined with chitosan has been used as a barrier coating on poly lactic acid (PLA) and poly urethane (PU) for high-performance insulation and packaging applications. Resistance to inflammation and burn spread on composite fibre can be induced by a coat of alumina trihydrate which is aqueous in nature, calcium carbonate and antimony trioxide in combination with Vinlylidene-chloride acrylate which acts as a binder [12]. Another method of reducing the net heat evolved is by addition of low porosity and low melting inorganic Ceepree glass in combination with epoxy composites, where an inorganic carbonaceous layer is formed that acts as a flame inhibitor. This additive coating technology finds application in protection of the layers of composites from intense flames. The coated matter burns down, thus protecting the internal parts. Protection of metals from corrosion and fire is achieved by a fine coating of ethylene-chloro-trifluoro-ethylene copolymer (Solvay Solexis Halar) which has also been found to be effective with very thin coating [13].

Another method of barrier protection is intumescent coatings. Intumescent coating is a fire retardant and fire resistant material, which swells when heated, thus protecting the material underneath. Alcoa Corporation has patented an intrusive powder blend that contains fibrous or vitreous calcium magnesium silicate which finds applications as a mastic when mixed with a binder like polyvinyl acetate or acrylic resin. Additionally, an intumescent firestop or sealant can be made using the Expantrol 4BW commercialised by 3M along with hydrated sodium silicate-borate and a terpolymer of acrylate-vinyl acetate-ethylene, zinc borate, polyol, organic phosphate plasticizer and glass fibre. Dispersed carbon nanotubes are employed in silicon coatings in order to make surfaces such as textiles, foams, cables, metals and wood to be flame proof [14]. The barrier coat on the surface can be as thin as 10 mm. The coatings are made from unsaturated polyester resins and are subsequently cured. Glass reinforced polyester laminates can be coated with this material with a thickness of as little as 0.4 to 0.5 mm, the applied coat also provides a smooth surface. Commonly, formulations of ordinary unsaturated polyester resins and curing catalysts like peroxides are alternatively combined with thixotropic agents in order to control the flow properties. Flame retardancy of composites is quite useful in construction, marine and railway applications.

Different chemical treatments alkalinization, salinization, and combination of both (alkalinization & salinization) done on jute, ramie, sisal, and curaua fibres exhibit an improvement in the durability of the composites that are subjected to heat. Furthermore, the treatments also improved the adhesion of the natural fibres to the polymer matrix. An US patent avows that, including highly water-resistant resin components in an emulsion of polyvinylidene fluoride (like Arkema’s Kynar Aquatec), enhances the water resistance of intumescent coatings that are otherwise hydrophilic. Although, intumescent coatings swell up to protect the substrate when heated, some intumescent coatings applied on wooden panels are susceptible to cracking upon exposure to flames and burst open fully, thereby losing ability to protect the inner substrate. A study by N Amir [15] shows that the addition of rockwool fibres to an ammonium poly phosphate – melamine – pentaerythritol formulation, inclination to cracking is controlled. Another intumescent coating was developed using Chicken Egg Shells, ammonium polyphosphate, pentaerythritol and melamine [16]. The coating was found to enhance the barrier properties by forming a multicellular insulating foam reducing the conduction of heat into the underlying substrate. It was observed that the coating had acquired a thermal stability superior adhesion along with water repellence.

5. Gel Coats
Multiple properties like resistance to thermal degradation, conductivity to heat and electricity can be effectively brought out through polymer coatings, as it requires the application of different additives. While there is always a possibility of negatively affecting other properties of the composite structure, the additives can be applied in separate layers on the substrate. However, by the means of gel coats, this can be done in a single layer. Gel coats prove to be functional barriers that have versatile properties along with a superior surface finish. M Landowski developed a technique for the protection of glass fibre reinforced composites. Studies on both Macro and microstructural damages a typical Glass Fibre
Reinforced Polymer laminates was done using gel coat based on isophthalic acid and urethane modified vinyl ester [17]. They proposed that protection against blistering and degradation of the laminate due to water absorption could be done using a combination of nanoparticles reinforced gel coat (10 % nano particles). This is due to tortuosity of diffusion paths and resin rich boundary coating that prevents water diffusion inside laminate and subsequently its mechanical degradation. Multifunctional gelcoats are discussed extensively in a study by Pomázi et al. based on their functionalities; primarily flame retardancy, electric conductivity and hydrophilicity. Several methods of gelcoat preparation, application by spraying, rolling, in-mould coating, curing by exposure to ultraviolet radiation are discussed. Also, common defects occurring over the course of gel coating and testing methods are outlined [18].

6. Organic Coatings
Several eco-friendly and non-polluting plastic products have been developed by utilization of polymers made from spent sugarcane, apple, and oranges. Composite blends of poly vinyl alcohol and lignocellulosic fibres are derived from these spent fruits. Hexa-methoxy-methylamine which is a crosslinking agent, could be used for reducing water sorption on composites as they show a promising water repellent characteristic along with good binding properties. Bio-based coatings were used by T.H Mokhothu et al. for reducing the amount of water absorbed by composites containing phenolic resin. Polyurethane (PU) and Polyfurufuryl alcohol (PFA) resin were the two kinds of coatings examined. Results showed that samples coated with PFA had better mechanical performance and higher shielding against moisture in comparison with other bio-based coatings [19]. It was also observed that high crosslinking density caused higher hydrophobicity. It is evident that moisture diffusion is the reason for hydrolysis and the consequential plasticization of the matrix. Le Duigou et al. tried using Poly (L-Lactic Acid) as an extra layer over the flax based composites to protect them from degradation from saline sea water in order to overcome the degraded mechanical properties of the composite due to wet ageing. The outcomes show that PFA serves as a good bio-based coating for fire proofing of treated natural fibre reinforced composites [20]. Sodium silicate extracted from rice husk also has the potential to be used as thermal insulator. Water absorption increases when a coat of Cellulose Nano Fibrils (CNF) was applied onto a cardboard. The hydrophilicity of CNF film and coatings can be reduced by incorporating alkyd resins. Higher water content results in increased drying costs, which is unacceptable unless it can be compensated by improved product properties.

7. Fibre Treatments to Combat Degradation
A super hydrophobic cotton fabric was made by low pressure, plasma enhanced, chemical vapor enhanced deposition technology. Lauryl methacrylate was used as a functional monomer for treating the fabric. The properties like washing stability, hydrophobicity, permeability of water vapor and mechanical tensile strength of the resulting fabric are given in the study by L Xu et al. A stable and highly breathable, hydrophobic cotton fabric was successfully prepared without affecting its tensile strength. Due to the nano structure cells and grooves that are formed after the plasma treatment, the fraction of wetting area was diminished. Generally, water drops rapidly wet the surface of untreated cotton samples, but it was seen that water drops rounded on the treated surfaces and were non-wetting. To give a quantitative account, the contact angles improved from 87.73° to 163.65°, which explains the non-wettable property [21]. Increasing the temperature of water accelerates the rate of degradation, this is because of the combined effect of both increased absorption and accelerated enzymatic reactions due to the hot water. E. Rodriguez and G. Francucci discovered a novel method to treat plant fibres and they analysed its influence on the water absorption and mechanical properties of composites made of vinyl ester matrix. Jute fibres were treated with an alkali and polyhydroxy butyrate and the treatment enhanced the resistance against water absorption [22].

Protective coat of TiO2 nanoparticles in combination with a fatty acid, can increase hydrophobic property of nonwovens prepared from recycled jute. It was seen that the samples that were coated showed superior hydrophilicity in response to the TiO2 nanoparticle pre-treatment. Subsequent treatment with steric acid
(even at a low concentration), further improved the water repellence [23]. Further another sol–gel treatment was employed that helped in minimizing the fibre swelling. Seepage of water and its constituents corrupts the dimensional stability and also degrades mechanical properties and eventually creates a suitable environment for fungus attack. The reduction in swelling of the fibres is another aspect of importance so as to not deteriorate the original thickness and mechanical performance. Another noticeable feature of this coating is that the recycled fibres do not need initial cleaning; hence fibre strength is not affected.

Epoxy coating is another effective way to simultaneously increase the resistance of bamboo composite material against acid attack and improve its bond strength with concrete for the application of concrete reinforcement [24]. This paves a way to use coatings for not only external protection of the composites but also as a protective layer over reinforcements. Addition of Sodium silicate into PLA retards the fire propagation to half the rate in comparison to that of neat PLA and about 10% compared to fibre mat composites without sodium silicate coating [25]. When applied to fibre composite made of abaca, the rate of fire propagation was found to decrease by about 40%. Among abaca, jute and sisal fibres, abaca absorbs sodium silicate highly, due to the high degree of network structure found in abaca fibres. The silicate coating applied on the Abaca mat also increases the Elastic modulus of the composites, meaning that the silicate coat boosts the overall stiffness.

8. Conclusions and Scope for Further Research

It is conspicuous that interfacial adhesion between natural fibres and matrix resin decreases over time, which weakens the capacity of the composite to carry loads. The compatibility between fibre and the polymer matrix could be improved. Adhesion to substrates, especially in the case of natural fibres, requires a primer coat or a pre-treatment, but this can be avoided by self-priming formulas. Adhesion of the barrier coats to fibre or elastomer surfaces provides an R&D opportunity. Furthermore, there is a need for single coat barriers that are feasible in terms of cost and are easier in application. Some intumescent coatings on wooden panels are susceptible to cracking when exposed to flames and they open at the full extent of their expansion, thereby losing ability to protect the inner substrate. Flame retardant coatings are usually prone to water damage, whereas coatings that impart hydrophobic properties are advertently susceptible to flame damage. Materials that can heal themselves when damaged can be designed to sense failure and as a result, respond automatically to restore structural function. Possibly, nanocomposites can be used in coatings to impart self-healing properties.

References

[1] Joshi S, Drzal L, Mohanty A and Arora S 2004 Are natural fibre composites environmentally superior to glass fibre reinforced composites? Composites Part A: Applied Science and Manufacturing 35 371–376
[2] Rowell R 2012 Handbook Of Wood Chemistry And Wood Composites (Boca Raton: CRC Press)
[3] Nosonovsky M and Bhushan B 2009 Superhydrophobic surfaces and emerging applications: Non-adhesion energy green engineering Current Opinion in Colloid & Interface Science 14 270–280
[4] Ma M and Hill R 2006 Superhydrophobic surfaces Current Opinion in Colloid & Interface Science 11, 193-202 Available: 101016/jcocis200606002
[5] Ke Q, Fu W, Jin H, Zhang L, Tang T and Zhang J 2011 Fabrication of mechanically robust superhydrophobic surfaces based on silica micro-nanoparticles and polydimethylsiloxane Surface and Coatings Technology 205 4910–4914
[6] Ma Z, Sun M, Li A, Zhu G and Zhang Y 2020 Anticorrosion behavior of polyvinyl butyral (PVB) / polymethylhydrosiloxane (PMHS) / chitosan (Ch) environment-friendly assembled coatings Progress in Organic Coatings 144 105662
[7] Aung MM, Yaakob Z, Abdullah LC, Rayung M and Li WJ 2015 A comparative study of acrylate oligomer on Jatropha and Palm oil-based UV-curable surface coating Industrial Crops and Products 77 1047–1052

[8] Gaikwad MS, Gite VV, Mahulikar PP, Hundiwale DG and Yemul OS 2015 Eco-friendly polyurethane coatings from cottonseed and karanja oil Progress in Organic Coatings 86 164–172

[9] Zhang W, Jiang S and Lv D 2020 Fabrication and characterization of a PDMS modified polyurethane/Al composite coating with super-hydrophobicity and low infrared emissivity Progress in Organic Coatings 143 105622

[10] Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM and Dubois P 2009 New prospects in flame retardant polymer materials: From fundamentals to nanocomposites Materials Science and Engineering: R: Reports 63 100–125

[11] Laufer G, Kirkland C, Cain A A and Grunlan JC 2012 Clay–chitosan nanobrick walls: completely renewable gas barrier and flame-retardant nanocoatings ACS Applied Materials & Interfaces, 4 1643–1649

[12] Laufer G, Kirkland C, Cain AA and Grunlan JC 2012 Clay–chitosan nanobrick walls: completely renewable gas barrier and flame-retardant nanocoatings ACS Applied Materials & Interfaces 4 1643–1649

[13] Chandrasekaran S, Kundel N K, Garg B and Chin H B 1990 US Patent No 4957961 Washington DC: US Patent and Trademark Office

[14] Weil ED 2011 Fire-Protective and Flame-Retardant Coatings - A State-of-the-Art Review Journal of Fire Sciences 29 259–296

[15] Amir N, Othman SW and Ahmad F 2015 Fire resistance properties of ceramic wool fibre reinforced intumescent coatings

[16] Yew MC, Sulon NHR, Yew MK, Amalina MA and Johan MR 2014 Fire Propagation Performance of Intumescent Fire Protective Coatings Using Eggshells as a Novel Biofiller The Scientific World Journal 2014 1–9

[17] Landowski M, Budzik M and Imielińska K 2013 Water absorption and blistering of glass fibre-reinforced polymer marine laminates with nanoparticle-modified coatings Journal of Composite Materials 48 2805–2813

[18] Pomázi Á and Toldy A 2019 Multifunctional Gelcoats for Fibre Reinforced Composites Coatings 9 173

[19] Mokhothu TH and John MJ 2017 Bio-based coatings for reducing water sorption in natural fibre reinforced composites Scientific Reports 7

[20] Duigou AL, Deux JM, Davies P and Baley C 2010 PLLA/Flax Mat/Balsa Bio-Sandwich Manufacture and Mechanical Properties Applied Composite Materials 18 421–438

[21] Xu L, Deng J, Guo Y, Wang W, Zhang R and Yu J 2018 Fabrication of super-hydrophobic cotton fabric by low-pressure plasma-enhanced chemical vapor deposition Textile Research Journal 89 1853–1862

[22] Rodríguez E and Francucci G 2015 PHB coating on jute fibres and its effect on natural fibre composites performance Journal of Composite Materials 50 2047–2058

[23] Arfaoui MA, Dolez PI, Dubé M and David É 2018 Preparation of a hydrophobic recycled jute-based nonwoven using a titanium dioxide/stearic acid coating The Journal of The Textile Institute 110 16–25

[24] Rahman N, Shing LW, Simon L, Philipp M, Alireza J, Ling CS, Wuan LH and Nee SS Enhanced bamboo composite with protective coating for structural concrete application Energy Procedia 143 167–172 2017

[25] Thongpin C, Srimuk J, Hipkam N and Wachirapong P 2015 Effect of natural fibre types and sodium silicate coated on natural fibre mat/PLA composites: Tensile properties and rate of fire propagation IOP Conference Series: Materials Science and Engineering 87 012078