Southern Region Engineering Conference
11-12 November 2010, Toowoomba, Australia
SREC2010-P2

Sustainable Materials Research at USQ

Hao Wang
Centre of Excellence in Engineered Fibre Composites (CEEFC)
Faculty of Engineering and Surveying, University of Southern Queensland (USQ)
Toowoomba, Queensland, 4350, Australia
wangh@usq.edu.au

Abstract— **Sustainability and environmental friendly are increasingly becoming two critical challenges to our materials' research community and industries. The first issue here is, when we make the engineered materials from the raw materials, does the usage of raw materials deplete the natural resources? In another word, do the materials sustainable? The second issue is how the utilisation of these materials impacts our environment? This includes energy input, waste generated, pollution emitted during all stages of the materials cycle. Therefore, do the materials green? USQ is actively engaged in the research and development sustainable and green materials. USQ's Materials and Manufacturing Group vigorously works in three areas: natural polymers and natural fibre composites; geopolymers; and wind turbine blades.**

Keywords- Sustainable material, green materials, natural polymers, natural fibres, geopolymers, wind turbine blades

I. INTRODUCTION

Sustainability and environmental friendly are increasingly becoming two critical challenges to our materials' research community and industries. First, our modern life and society are built on materials. Every item we see, we touch or we build is made of one material or another. Development and utilisation of materials have become the significant part of the advancement of our societies. The full materials cycle starts from raw materials, which are extracted from natural resources by mining, drilling, harvesting, etc. These raw materials are then purified, refined, and converted into bulk forms such as metals, ceramics, petroleum, rubber, fibres, etc. Further synthesis and processing results in engineered materials, including metal alloys, ceramic powders, glass, plastics, composites, semiconductors, elastomers. Finally these engineered materials are further shaped, treated, and assembled into products, devices, and appliances.

The first issue here is, when we make the engineered materials from the raw materials, does the usage of raw materials deplete the natural resources? In another word, do the materials sustainable? The second issue is how the utilisation of these materials impacts our environment? This includes energy input, waste generated, pollution emitted during all stages of the materials cycle. Therefore, do the materials green? USQ is actively engaged in the research and development sustainable and green materials. USQ's Materials and Manufacturing Group vigorously works in three areas: natural polymers and natural fibre composites; geopolymers; and wind turbine blades.

In the area of natural polymers and natural fibre composites, we use renewable vegetable oils as raw materials, and convert them into polymer resins. These resins can further combine with natural fibre, such as hemp, jute and agricultural residues to make natural fibre composites. In the area of geopolymers, industry by-products, such as fly ash and slag, are used as raw materials, and a low temperature geopolymerisation (less energy input) is employed to make the green alternative of Portland cement. In the area of wind turbine blades, we perform structural and materials design for large blades to capture the clean and renewable wind energy. In all these research areas, USQ closely collaborate with industries and other world leading research groups, and put itself in the forefront of the research and development of sustainable and green materials. .

II. CONCEPT OF SUSTAINABLE BIO-BASED MATERIALS

A bio-based product derived from renewable resources having recycling capability and triggered biode-gradability (i.e., stable in their intended lifetime but would biodegrade after disposal in composting conditions) with commercial viability and environmental acceptability is defined as a "sustainable" bio-based product. Bio-composites, or more specifically the "green composites," consist of biofiber and bioplastic from renewable resources and thus are expected be biodegradable. However, plastic derived from renewable resources may be nonbiodegradable, depending on the structure and curing nature of plastic during fabrication of bio-composites. Thermoplastic is having more environmental impact than thermosets because of its recyclibility. Again bio-based products obtained from renewable resources also maintain carbon dioxide neuntrality.

The "sustainability" issues of bioplastics, e.g., PLA, cellulosic plastics (cellulose esters), and PHA (bacterial polyesters) are undergoing considerable debate in scientific literature, providing divergent views. The susntainability issue of each specific bioplastic is a complex problem, and several parameters must be considered, including the raw materials from which the bioplastic is generated, the energy consumed during bioplastic conversion, and its life cycle assessment analysis from production to ultimate disposal or recycle, with due recognition to the design and engineering of the bioplastic. In comparing the sustainability of a newly emerging bioplastic with a petroleum-based plastic, the analysis should take in to account the technology development time gap between petrochemicals (say , 100 years old) and newly developing bioplastics (say from 5–10 years old or from now). The detailed descriptions of each of these factors are beyond the scope of this article. It is encouraging to derive cost-effective bio-based products or bio-composites from costly bioplastics through inexpensive natural/biofiber reinforcements. Most of the bioplastics cannot compete economically at their present state of technological development with the currently dominating petroleum-based plastics. The effective bio-composite formulations of such bioplastics from natural fiber reinforcements, through careful design and engineering, can result in new commercial attractions applications. The emergence of new applications of bio-composites would necessitate a large-scale demand of bioplastics, which would promote sustainability. A detailed understanding of natural/biofibers, bioplastic, and bio-composite formulations is necessary for the development of new and bio-based bio-composite materials. The following sections highlight issues in design and engineering of value-added bio-composite materials and the attainment of the sustainability of bio-based products to compete with petroleum-based products.

III. NATRUAL FIBRE COMPOSITES

Natural fibers may be classified by their origin as cellulosic(from plants), protein (from animals) and mineral. Plant fibers may be further classified a: seed hairs, such as cotton; bast (stem) fibers, such as linen from the flax plant; hard (leaf) fibers, such as sisal; husk fibers, such as coconut. However commercially important natural fibers can be obtained from the seed hairs, stems, and leaves of plants. The material properties of natural fibers are comparable those of synthetic ones. Cellulose is the main structural component that provides strength andstability to the plant cell walls andis one of the most abundant organic compounds on earth. The amount of cellulose in a fiber influences the properties, economics of fiber production and the utility of the fiber for various applications. In plant cell walls, stiff semi-crystalline cellulose microfibrils are embedded in a pliable amorphous matrix, which can be characterized along the lines of a fiber reinforced composite. In terms of primary walls, cellulose fibrils have been found to be preferentially deposited perpendicular to the axis of cells during their initial state of growing. Due to the great stiffness and strength of cellulose fibrils, it is much easier to expand the cell wall perpendicular to the orientation of cellulose. The secondary cell walls consist of different layers that are deposited on the primary cell wall in a characteristic manner (strictly parallel). Cellulose synthase enzymes are in the form of rosette complexes, which float in the plasma membrane inside strings of cellulose chains. Cellulose is a hydrophilic glucan polymer consist of a linear chain of b-1,4-bonded anhydroglucose units which contains alcoholic hydroxyl groups. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules, as well as with hydroxyl groups from the surrounding air. The modulus of elasticity of the homopolymer cellulose is approximately 134 GPa in the axial direction under moist conditions. The matrix polymers, hemicelluloses and lignin, have a modulus of elasticity of 40 MPa and 2 GPa, respectively. The interaction between the stiff cellulose fibrils and the plant matrix polymers in the cell wall is one of the key issues in understanding the mechanical performance of plants.

Because of the poor compatibility between natural fibers and the hydrophobic polymer matrices, the fibers must be suitably modified by either physical or chemical treatments. Generally, chemical coupling agents are molecules possessing two functions. Thefirst function is to reactwith hydroxyl groups of cellulose and the second is to react with functional groups of the matrix. Chemical processes, such as alkali treatment, silanisation, acetylation, benzoylation, acrylation, maleated coupling agents, isocyanates and permanganate, are frequently examined. Treatment methods like the esterification of hydroxyl groups of fibers are inexpensive, easy and effective in many cases. The ester linkages between the cellulose and polymer decrease the interfacial tension and increase the number of relaxed chains at the interphase, which facilitates the stress transfer in both phases. Isocyanate and silane have shown their high importance for fiber modification particularly to increase the water resistance of resulting composites. In the presence of moisture, the hydrolyzable alkoxy group of silane coupling agents leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface. Isocyanate treatment was more effective than silane in composites of wood fiber and polystyrene in terms of influencing the mechanical properties, which was attributed to the increased covalent and electrostatic bonding during isocyanate treatment. Stearic acid [CH3(CH2)16COOH], sodium chlorite (NaClO2), triazine (C3H3N3) derivatives (e.g., C3N3Cl3) and peroxide (a specific functional group or a molecule with the functional group ROOR containing the divalent ion O-O) are the other chemical treatments those can increase the interface adhesion between the fiber and matrix, and provide better moisture resistance of fibers by reducing surface energies.

IV. APPLICATIONS OF NATURAL FIBRE COMPOSITES

A. *Automobile Industry*

The use of natural fibers in automotive applications was initiated in the 1930s and 1940s when Henry Ford strongly advised the use of natural materials, such as hemp, in producing reinforced soy resin composites for the manufacture of exterior body panels. A relative weight reduction in parts, good mechanical and manufacturing properties, the possibility of forming complex components in a single machining operation, relatively good impact performance, and occupational health advantages in assembly and handling compared to glass fiber further highlight the importance of bio-based products. The automotive market is growing in terms of quantity, quality and product variety, where fuel efficiency is being considered as key factor for future growth. A 25% reduction in vehicle weight is equivalent to a saving of 250 million barrels of crude oil and a reduction in CO2 emissions of 220 billion pounds per year. European Union legislation implemented in 2006 has directed that 85% of a vehicle must be reused or recycled by 2015. Japan requires 95% of a vehicle to be recovered (which includes incineration of some components) by 2015. The energy consumption to produce a flax-fiber mat (9.55 MJ/kg), including cultivation, harvesting and fiber separation, amounts to approximately

17% of the energy needed to produce a glass-fiber mat (54.7 MJ/kg). Life cycle assessment (LCA) is a method that intends to evaluate the environmental impact and damage caused by a product over its entire lifecycle. It can also be used to promote improvements in products or processes. Astudy using the LCA of the replacement of glass fibers by jute fibers as reinforcement to produce automotive structural components was carried out, and demonstrated the better overview performance of jute composites than that of glass. A semi-quantitative overview comparison of all aspects of bonnets based on sustainable design procedure presented a decrease in fuel consumption of a small buggy by 0.029%, which means about 7.71 l for an expected life of 265 500km (the reduction in weight of thebonnetwasabout15%byusing jute fiber). Glass fibers present some advantages for industrial employment in comparison with natural fibers. Environmental aspects show that natural fiber implies an increase of about 15% of the performance of the composites, while focusing on economical aspects, jute fibers cost about seven times less than glass fibers.

Extensive research has been underway to study the potential of different natural fibers as reinforcement for a synthetic or renewable polymer matrix in order to develop the components for different body parts of automobiles. Natural fiber and non-biodegradable polymer composites are gaining market demand in every sector of human life, but still reports of selective consumption of the bio-part of composites by microbes, leaving behind intact probably equally harmful nonbiodegradable polymer fragments, forces the creation of compositesmadeof biodegradable polymer matrices due to their complete conversion to water and carbon dioxide during degradation without a leaving harmful residue for nature. Poly(lactic acid) (PLA) is one of the most important types of matrix for natural fillers because of its biodegradability and maintained mechanical properties without rapid hydrolysis during use. Nonetheless, the inherent brittleness of PLA has been the main obstacle to expanding its commercial use. Nina et al. described the production and the mechanical characteristics of composites (which maybe used for different componentsin automobiles as per equipment) of different types of natural fibers like cotton, hemp, kenaf and man-made cellulose fibers (Lyocell) with PLA at a fiber mass proportion of 40% (volume content =35.5%) by compression molding. Mechanical properties of different composites were studied, where each specimen was tested at 08 (MD) and 908 (CD) direction. Considering the composites measured in MD, cotton/PLA composites showed the lowest tensile strength with 41N/mm^2. Slightly better data could be achieved in composites reinforced with bast fiber bundles: kenaf/PLA (53 N/mm$^{2)}$, hemp/PLA (56 N/mm^2) and hemp/kenaf/PLA (61 N/mm^2). The highest tensile strength values were reached by adding man-made Lyocell fibers (82 N/mm^2), followed by hemp/Lyocell/PLA with 72 N/mm^2. While kenaf and hemp fiber bundles, as well as their mixtures, significantly increase the tensile strength and Young's modulus of composites, they markedly lower the impact strength of the pure host matrix. Flex/hemp fiber with epoxy matrix demonstrated the highest strength among all the composites, which could be beneficial in developingmany parts in a vehicle due to its resistance to environmental degradation. Cotton fibers cause a high impact strength but lower tensile strength and stiffnessand maybe applied for impact stressed components like interior parts in cars or safety helmets. A mixture of bast and cotton could combine the positive tensile characteristics of bast with the good impact properties of cotton and appears suitable not only for various car parts, but also for suitcases. Lyocell/PLA composites showed better tensile and impact characteristics therefore, could be used for almost all the above applications at the compromise of price. Cellulose acetate (CA), known for its properties such as biodegradability, wettability and liquid transport, is another biomaterial that has been applied for making interior parts. The thermoplastic nature of CA binder fiber makes it suitable for thermal calendaring, and non-woven material can be manufactured from blends of plasticized CA (PCA) fibers owing to its good thermal bonding ability, which can achieve acceptable tensile properties. PCA films appear to be a good option in terms of biodegradability because they experienced a significant weight loss of 20% within the first two weeks of degradation when evaluated by monitoring the percentage of carbon converted to CO2. CA bioplastic, citrate-based plasticizer and organically modified clay nanofillers have been studied as an eventual replacement composite for existing poly(propylene)/thermoplastic olefin based material in automotive applications. The interaction between the clay and the matrix was moderate, whereas the composite tensile strength and modulus was approximately 38 and 33% greater respectively after incorporating 5 wt.-% clay. A polymer composite composed of cellulose acetate butyrate and lyocell (a high modulus regenerated cellulose fiber with better interfacial adhesion between the fiber and the matrix) is an emerging candidate for automobile applications. Increased social awareness of the environmental problems posed by the non-degradable, nonrecyclable contents of salvaged automobiles is forcing manufacturers to enhance the biodegradable content. PTAT or EastarBio from Eastman Chemical Company, BioPET or Biomax from Dupont, Ecoflex from BASF, PLA from Dow-Cargill and PHBV from Metabolix are other examples of environmentally friendly material for automobiles. Most of this material contains biodegradable materials, tested under composting conditions, which can degrade in the natural condition leaving behind biomass and carbon dioxide.

Biobased structural composites for housing and infrastructure applications are of significant importance in the building materials of the next generation of construction in fencing, decking, siding, doors, windows, bridges, fiber cement and so on. Advantages associated with the use of natural fibers to reinforce cement, known as fiber cement, include the availability of raw material from renewable sources, high fiber tensile strength, high modulus of elasticity, relatively low cost and well-developed technology for fiber processing. Fiber cement presents improved toughness, ductility, flexural capacity and crack resistance compared to non-fiber reinforced cement based materials. Normally fiber plays two different roles. First, they increase the means of transferring stresses and loads across cracks and, second, fibers increase the toughness of cement composites by making energy absorbing mechanisms regarding cracks and debonding. The fiber reinforced composites may be developed by different processes, such as the formation of a thin laminate of dewatered fiber cement-water slurry and stacking of laminates in wet conditions followed by winding of the laminate around a cylindrical form (Hatschek process). Other popular processes include the formation of a well-mixed slurry of fiber in water and cement by high speed agitation mixing and vacuum removal of excess water. The resulting dewatered materialmaythen be pressed in the final shape. Another process called extrusion was used recently in making fiber-cement composites. The process involves the formation of a cohesive fiber-cement composite by forcing it through a die that can be adjusted to the desired shape. This method can produce composites with densified matrix and fiber packing, achieving low porosity and strengthening of the fiber matrix bond. In general, all the above-mentioned processes contain fiber concentrations ranging from 8–12% in the composites.

To improve the durability of the cement composites, additives such as fly ash, slag, silica fume, etc. are used, whereas artificial pozzolan addition causes a delay in degradation by lowering the pore solution pH. Silica fume, used in relatively large amounts (i.e., 30% or greater replacement of cement by weight), appears to significantly minimize composite degradation due to variation in wet/ dry cycling. The durability of fiber-cement composites may be controlled by the drying process (wet/dry cycling), volume fraction of fiber in the composites, the moisture percentage, fiber bleaching and beating, the type of fiber, curing conditions and overall matrix composition. There are many leading companies manufacturing fiber cement, including Cemplank, CertainTeed, GAF Materials, James Hardie, and Nichiha USA, that are developing many products applicable for roof, floor, insulation and building blocks for home construction.

C. Future Perspective

Natural fiber composites are regarded as a substitute for traditional materials and may hold the key to successfully tackling some of the challenges facing the automotive and aerospace industries in the context of the end-of-life vehicle laws. Today, perhaps more than ever, there is an increasing demand for fibers with improved properties and new functionality that can create added value for the final fiber based product. Biopolymers are now moving into mainstream use, and polymers that are biodegradable or based on renewable feedstock may soon be competing with commodity plastics as results of sale growth of more than 20–30% per year. Polymer composites with natural fibers have also been indicated as potential economically, viable alternatives for the fixation of carbon in nature, reducing CO2 emissions into the atmosphere during their cycle of production, processing and use, including the possibility of trading carbon credits for the production chain. It is estimated that polymer composites with plant fibers store on average 325 kg of carbon per metric ton during their service life. In August 2006, a ton of carbon was quoted at $15 to $18 (a year earlier the cost was $5), a value that is expected to rise to $30 or $40 between 2008 and2012, when the reduction of 5.2% of combined carbon emissions in the atmosphere (CO2 equivalent in relation to the 1990 emissions) comes into force, as established by the Kyoto Protocol.

Though natural fiber reinforced plastic parts offer many benefits compared to glass, several major technical considerations must be considered before the engineering, scientific and commercial communities gain the trust to enable wide scale acceptance of this, more particularly for the development of parts for higher applications, such as aerospace and automobile technology. Nanocomposites of cellulose microfibrils carry high potential for advanced engineering biocomposites of the future and better performance, durability, value, service life and utility, with maintained sustainability at very low filler concentration, may be expected. Cellulose nanocrystals may be successfully applied as templates to produce biosensors and catalysts.

Fiber cement is highly beneficial for construction whereas it undergoes an aging process in humid environments in which it suffers a reduction in strength and toughness. Durability problems are associated with an increase in fiber fracture and decrease in fiber pull-out due to a combination of weakening of the fibers by alkali attack, fiber mineralization by migration of hydration products to lumens and volume variations due to their high water absorption, which needs to be shorted out by adequate drying, mixing and modification. The development of conducting cellulose fibers by modification through polyelectrolyte multilayers based on polymers with desired functionalities is another advancing area of natural fiber based composites where an ecofriendly and easily disposable electronic material can be developed after tailoring stiffness and strength up to the level of traditional electronic parts.

An increase in thermal stability and hydrophobicity can be successfully achieved by chemical modification, but the degradability of these modified composites must be carefully evaluated. Performance during use is a key feature of any material composite and decides the real fate of products in several applications. Whatever the application, a natural concern often arises regarding the durability or degradability of polymeric materials, partly because of their useful lifetime and the requirement for maintenance and replacement. Literature in the area of natural fiber composites provide that the challenges are not new, such as 1) the issue of compatibility between cellulose fiber and the polymer matrix, 2) moisture sensitivity, 3) uniform dispersion, 4) thermal stability, 5) non-destructive processing of biobased material and 6) extreme agglomeration, which may be the cause of less of an increase in the application of natural fiber composites in commercial applications in comparison to glass fiber based materials. The design of an optimum model that can effectively balance biodegradability, mechanical properties and cost of resulting hybrids is an essential requirement for the future.

V. CONCLUSION

Cellulose-based materials are widely accepted in every aspect of society, and have challenged the limits of their traditional applications. Composites of polymers from natural fibers offer an answer to maintaining the sustainable development of economically and ecologically attractive technology. Renewable resource based composites have a major role to play in ‘‘green’’ packaging. Although these are emerging as alternatives to existing petroleumderived plastics, the present low level of production restricts their widespread application. The barrier properties of such degradable polymers can be improved through the introduction of nano-reinforcements. The incorporation of nanoparticles in a polymer matrix reduces the permeability of penetrate molecules and thus develops composites with high barrier properties. Conducting cellulose-based actuators have been fabricated in which conducting polymers can serve as an adhesive for cellulose particles. The surface modification of cellulose whiskers has been additionally advantageous to overcome compatibility challenges with synthetic polymer matrices. As most of the present polymers applied in manufacturing nano and microcomposites are synthetic materials, biocompatibility and biodegradability are much more limited than those of natural polymers; however, several critical issues, such as processability, moisture resistance, thermal stability and acceptable dispersion, remain to be solved in achieving the objective of producing an affordable alternative ecofriendly construction material for future composites.