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Effect of reinforcements on polymer matrix bio-composites – an overview

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Abstract: The inherent properties of bio-composites such as biodegradability, environment friendly, low cost of production, high strength and durability make them a suitable replacement to traditional materials such as glass and nylon. Bio-polymers are finding wide applications due to their intrinsic properties such as low density, low thermal conductivity, corrosion resistance and ease of manufacturing complex shapes. This paper aims toward a comprehensive study on polymer bio-composites. The review mainly focuses on types of reinforcements such as natural fibers, seed shells, animal fibers, cellulose, bio-polymers, bio-chemicals and bioceramics which enhance the mechanical properties, such as tensile strength, compressive strength, flexural strength, Young's modulus and creep behavior, of the composites. The pertinent study carried out in this review explores an enormous potentiality of the composites toward a wide variety of applications.

Keywords: bio-composites; biodegradability; mechanical properties.

1 Introduction

Composites are developed by combining two or more materials which are different in form and essentially insoluble with each other. Traditional materials are replaced by composite materials because of their inherent properties such as tensile strength (TS), low thermal expansion and high strength to weight ratio. But composites are mostly developed by reinforcing synthetic fibers which are in general non-biodegradable. Considering the environmental impact, researchers are developing

environment-friendly bio-composites using natural fillers without compromising on the quality of the product.

Bio-composites are developed using natural fillers as the reinforcing material. Natural fillers are renewable, easily available, environmental friendly, have low cost, are lightweight and show good mechanical properties [1]. In case of artificial medical implants, natural-fiber-reinforced composites are preferred due to their biocompatibility and resorbability with the physical living system. Scientists and technologists have a growing interest in banana, cotton, coir, sisal and jute for application in consumer goods, low-cost housing and other civil structures as they show better electrical resistance, good thermal and acoustic insulating properties and higher resistance to fracture when reinforced in the composites [2]. The properties of bio-composites mainly depend on number of variables, including the fiber type, environmental conditions, processing methods and pre-treatment of the fiber [3].

Polymers are macromolecules developed from singular repeating units called monomers and show excellent properties such as corrosion and water resistant, flexibility and ease of manufacturing, which make them a promising candidate for replacing traditional materials. Polymers can be biodegradable and non-biodegradable. Concerning the environmental impact, researchers are developing composites from biodegradable polymers which have almost zero effect on the environment. The objective of this study is to exemplify the effect of reinforcements such as natural fibers, seed shells, animal fibers and cellulose on the mechanical properties of polymer matrix composites (PMCs).

The recent trend toward environmentally friendly polymer composites has been developed using lignocellulosic fibers such as flax, hemp, ramie or sisal as a replacement for glass fibers [4, 5]. The reason is that the material characteristics are comparable to conventional materials [6]. Natural fillers are generally hydrophilic in nature. When the fillers are reinforced in the hydrophobic matrix, they show poor interfacial bonding. Thus, various pre-treatment processes are carried out on the natural fillers to ensure enhanced fiber-matrix adhesion. Alkali treatment is one of the most important methods to clean and modify the fiber surface to lower surface tension and enhance interfacial adhesion between natural fiber and polymeric matrix [7]. Another disadvantage of natural-fiber-reinforced

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thermosetting PMCs is poor toughness. However, the drawback is overcome by fiber treatment [8] such as alkali treatment, silane treatment, acrylic acid (AA) treatment and benzoylation. The review is intended to illustrate the effect of reinforcement on different properties of PMCs, such as TS, compressive strength, impact strength, flexural strength, tensile modulus, flexural modulus, stiffness, creep behavior, interfacial shear strength (IFSS), fracture toughness, water absorption, crystallinity, electrical conductivity, elongation at break, heat release rate (HRR), consistency indices, thermal stability and damping index of the composite. The work emphasizes on the different pre-treatments of fibers, such as degumming, sodium hydroxide (NaOH) treatment, AA treatment, steam explosion, silane treatment, butyric anhydride and pyridine treatment, and the addition of compatibilizers, coupling agents (CAs), and diisocyanates to improve the fiber-matrix interaction. The review further explores possible applications of bio-composites addressing key issues of natural fillers that need to be resolved. The review will comprehend the possibility of bio-composites as a replacement to synthetic materials, metals and alloys.

2 Polymer matrix composites

PMCs are developed by reinforcing continuous or short fibers, whiskers and fillers in the polymer matrix. Natural

fillers such as natural fibers, seed shells, cellulose, animal fibers, biochemicals and bio-polymers are mostly reinforced in PMCs. Lee and Mariatti [9], Conzatti et al. [10], Song et al. [11] and Jia et al. [12] used natural fibers, animal fibers, cellulose fibers (CFs) and polymer fibers as reinforcements in PMCs. These are mostly used where TS is a major concern because the fibers when aligned unidirectionally offer maximum TS. Such types of composites find wide applications in developing structures of high strength and stiffness. However, Xu et al. [13], Elanthikkal et al. [14] and Chen and Wang [15] incorporated seed shells, cellulose whiskers, biochemicals and bioceramics in PMCs where TS and stiffness are not the key issues to be taken care of such as lightweight structures and automobile panel body. The schematic diagram of different reinforcements that can be incorporated in the polymer matrix is shown in Figure 1.

2.1 Natural fibers

These are generally by-products of plants in fiber forms used significantly for developing biodegradable composites. The fibers can be extracted from fruit fibers or crop fibers. Natural fiber plastic composites have earned a great interest and broader application during the past decade due to their inherent properties [16]. Bagasse is the by-product of sugarcane industry. It is a fibrous matter that remains after the extraction of sugarcane juice. Lee

Figure 1: Different reinforcements in polymer matrix composites.

and Mariatti [9] developed a composite by reinforcing the inner (pith) and outer (rind) part of the bagasse fiber in unsaturated polyester. The researchers observed that the outer part of the bagasse-fiber-reinforced polyester composite shows better flexural strength. It increases from 13 MPa for the unfilled resin to 30 MPa for the outer part of bagasse fiber composites against 22.4 MPa for the inner part of bagasse fiber composites at 15 vol.% of fiber contents. The reason for the improved behavior of the outer part is that the pith contains small fibers consisting mainly of sucrose whereas the rind contains longer and finer fiber arranged throughout the stem and bound together by lignin and hemicelluloses providing better strength. The reinforced composites were stiffer and have high strength compared to pure resin. But the composite shows higher water content due to the incorporation of bagasse fiber which is attributed to its hydrophilic nature.

Attempts are being made to carry out the pre-treatment of bagasse fibers with chemicals to remove moisture and obtain better bonding with the matrix. Cao et al. [17] observed that polyester-reinforced bagasse fibers treated with 1% alkali (NaOH) solution show improvement by 13% in TS, 14% in flexural strength and 30% in impact strength after alkali treatment of fibers. Scanning electron microscopy (SEM) observations show better surface modification and improved fiber-matrix adhesion of alkali-treated fibers. Goulart et al. [18] investigated the effect on the mechanical properties of sugarcane-bagasse-fiber-reinforced polypropylene (PP) composites due to the chemical treatment of the fibers. The fibers were pre-treated with 10% sulfuric acid solution and delignified with 1% NaOH solution. The investigators observed an improvement in the TS by 16%, flexural modulus by 51% and impact strength by 45% compared to pure polymers. The reason for the improvement of properties is the pre-treatment process carried out on the fibers, which removes considerable amount of moisture and other materials such as cellulose lignin, hemicelluloses and lignin from fibers, thus increasing fiber matrix adhesion. Luz et al. [19] reported that the best process for composite manufacturing is injection molding as it induces the better mixer method for the fiber and matrix. The researchers developed a bagasse-fiber-reinforced PP composite and observed a decrease in TS by 50% and 42% for the bagasse and benzylated bagasse fiber composite as compared to pure PP. It is due to the agglomeration of reinforcement in the composites. But better flexural modulus was observed for the developed composite. Bagasse-fiber-reinforced unsaturated polyester resin was developed by Vilay et al. [20] after treating the fibers with NaOH and AA. The investigators reported improved properties for AA-treated fibers

compared to NaOH-treated fiber composites. The storage moduli for pure polymer and untreated fiber composites were 1800 and 2750 MPa, respectively, at 35°C, which is quite low compared to NaOH- and AA-treated fibers with storage moduli of 2900 and 2780 MPa, respectively. It is accredited to the fact that treatment improves the fiber surface adhesives characteristics by the fibrillation process enhancing fiber matrix interaction. Jute fibers are soft shiny vegetable fibers which can be used as strong threads. The fibers were reinforced in polylactic acid (PLA) by Plackett et al. [21] using the stacking technique. The investigators observed a degradation of polylactide after the composite production, but the TS and tensile stiffness of composites at 210°C can be doubled to those of the polylactide by incorporating jute fibers. The result is attributed to the reduced viscosity of polylactide at higher temperatures, which induces better wettability of the fiber and matrix. Apart from these, other factors such as changes in PLA crystallinity, composite porosity and jute fiber surface chemistry played a significant role for improving the properties of composites. Electron microscope observation revealed formation of voids in composites. A jute-fabric-reinforced green epoxy composite was fabricated using hand layup and compression molding by Militký and Jabbar [22]. The researchers found that creep strain for treated composites was lower than that for untreated fibers. The improved performance of treated composites is accredited to the increase in mechanical interlocking between the fiber and matrix due to formation of micropores on the fiber surface. However, bonding between the fiber and matrix was enhanced as observed from laser-treated composites. Doan et al. [23] investigated the effect of the addition of the CA maleic anhydride grafted polypropylene (MAHgPP) on the properties of jute fiber/PP composites. The results show that the addition of 2 wt.% MAH to the PP matrix improves the interaction with jute fibers, enhancing the mechanical properties of composites. IFSS was increased to 91% and 68%, respectively, and TS was 41% and 28% using 2 wt.% MAHgPP for PP1 (low melt flow rate) and PP2 (high melt flow rate), respectively, because without the addition of CAs, the fiber acts as the included filler in the resin matrix not being properly wetted by the resin. It results in poor interfacial bonding between the fiber and the matrix. Acha et al. [24] investigated the creep and dynamic behavior of jute-PP composites. Two different surface treatments such as the addition of CAs and chemical modification of fibers were compared in their study. The researchers observed that creep deformation decreases with the increase of jute content, which is due to the addition of rigid reinforcement into a viscoelastic matrix. The results from the creep test and SEM

confirm that the interaction between the matrix and the jute fibers was enhanced when maleated PP was used as a compatibilizer. It is due to the esterification reaction between cellulosic jute fiber hydroxyl groups and anhydride functionality of maleated PP. However, dynamic mechanical tests confirm improvement in the fiber matrix interaction by both the pre-treatment processes. In order to improve the strength and fracture toughness of natural-fiber-based composites (NFCs) for bearing loads, surface treatments and flock-fiber-based Z-axis reinforcement technology were utilized by Pinto et al. [25]. The results showed that NFCs (primarily jute fibers) would replace traditional resin-reinforced glass or carbon fibers and provide higher sustainability, environment-friendly and low-cost material. The incorporation of reinforcement improves the toughness by 81% for plain weave reinforcement and by 65% for unidirectional reinforcement. The increase in toughness is attributed to energy consumed by the flock fiber pull-out and fiber breaking corresponding to the dominating modes of failure. Thus, NFCs find applications in automotive, housing or construction industries. Akil et al. [26] investigated the effect of water absorption by three different mediums, such as distilled water, seawater and acidic solution, on the mechanical properties of jute-fiber-reinforced unsaturated polyester composites. The researchers observed a decrease in flexural and compression properties and an increase in maximum strain due to water absorption of the composites, which is attributed to the inherent property of jute fibers which have a tendency to absorb high amount of moisture when exposed to the aqueous environment, which leads to higher degradation rate. Moisture absorption is lower in seawater and acidic solution compared to distilled water. The presence of large salt molecules in seawater reduces the diffusion process into the matrix of the composite materials which results in a lower absorption. Considerable interest has been shown in the past few years toward the potential use of bast fibers such as hemp to act as reinforcement in PMCs [27]. Hemp fibers are the fastest growing fibers and can be easily spun into fibers. These fibers were preferred in textile and paper clothing industries. However, these fibers have not been promisingly addressed in the literature for manufacturing of composites because of their tendency to roll up easily. The fibers can be effectively used after different pre-treatment processes. Dhakal et al. [28] prepared hemp-fiber-reinforced unsaturated polyester composites using fiber volume fractions of 0, 0.10, 0.15, 0.21 and 0.26. The composites were subjected to water immersion tests to investigate the effects of water absorption on their mechanical properties. The investigators observed that with increasing fiber

content, there was an increase in the water intake of the composites resulting in a decrease of mechanical properties compared to dry samples. The TS for unsaturated polyester and two-layer hemp polyester composites show no significant improvement and a 22% increase in TS, respectively, after being immersed in water. However, at three- and four-layered composite, the strength decreases to 38% and 15%, respectively. The fact is that at higher fiber volume there is a decrease in tensile properties. In addition, the decrease in TS is greater for wet composite samples immersed in water as compared to dry samples. But five-layer hemp-reinforced samples show higher values of the ultimate tensile stress for wet samples as compared to dry samples. It is attributed to high amounts of water that causes swelling of the fibers filling the gaps between the fiber and the polymer matrix and thus could lead to an increase in the mechanical properties of the composites. Keller [29] developed a composite by incorporating hemp fibers in the brittle poly(3-hydroxybutyrate-co-hydroxyvalerate) matrix and ductile co-polyester amide matrix after degumming with biological processes and steam explosion. The composite fabrication was carried out using a co-rotating twin-screw extruder. The TS and Young's modulus were doubled and quadrupled, respectively, to 30 MPa and 3.5 GPa with 32% fiber weight. Scarponi [30] replaced woven glass with woven hemp in epoxy laminate and found similar mechanical properties for both the fibers, but woven hemp was more eco-friendly as compared to the synthetic counterpart for glass along with better semi-structural properties. It is because the tensile properties of the natural fibers were almost comparable to glass fibers. Baghaei et al. [31] developed a composite by reinforcing hemp co-wrapped hybrid yarns in PLA using compression molding. The researchers observed that with 45 mass% fiber content, the impact, tensile and flexural strength of the developed composites were 26.3 kJ/m², 59.3 MPa and 124.2 MPa, respectively, which corresponds to 2 and 3.3 times more than neat PLA. The results are attributed to the incorporation of fibers in the polymer matrix and good interaction between the fibers and the matrix. Thus, the fibers can be effectively used to enhance the properties of the polymer after pre-treatment processes. Ramie fiber (RF) is a bast fiber and is effectively utilized in fabric production. Yu and Li [32] investigated that the addition of poly butylenesadipateco-terephthalate (PBAT) increases the impact toughness and thermal stability of the ramie/PLA composite but decreases the glass transition temperature and percentage crystallinity. The incorporation of ramie in the neat PLA increased the TS from 45.2 MPa for neat polymer to 59.3 MPa for the composite. There was also an increase in

flexural strength from 94.1 MPa for neat polymer to 136.8 MPa for the composite. This is due to the high strength of RF. But the values decrease with increasing fiber content which is related to the presence of a soft elastomeric phase. However, at higher PBAT content, the phase separation of PLA and PBAT occurs, causing higher chances for fiber agglomeration at the interface. A similar approach was adopted by Yu et al. [33] with the addition of isophorone diisocyanate (IPDI) on the ramie/PLA composite. The researchers observed an improvement in the interfacial bonding between the RFs and PLA matrix. The TS of the composite without diisocyanates was 52.5 MPa. The TS of the composites with the addition of the different diisocyanates such as 1,6-hexane diisocyanate, 4,4'-diphenylmethane diisocyanate and IPDI was increased to 61.4, 62.0 and 60.1 MPa, respectively. This is due to the crosslinking reaction that occurred when the addition of diisocyanate was at a low concentration. But excess diisocyanate content resulted in a decrease in the mechanical properties of the composites. This is because with the increase of diisocyanate, the isocyanate group tends to aggregate resulting in the less contact area with the RF and the matrix, which decreases interfacial adhesion between the fiber and matrix. The incorporation of RF in PLA increases composite crystallinity, higher electrical conductivity and lower percolation threshold as observed by Li et al. [34]. But better shape stability and excellent reversibility for good and poor solvent respectively were observed in RF-reinforced conductive polymer composites. Doum fibers are eco-friendly with improved mechanical properties. The investigation was carried out by Essabir et al. [35] on both the tensile and rheological properties of the doum-fiber-reinforced PP composite. CAs such as styrene-(ethylene-butene)-styrene three-block copolymer grafted with maleic anhydride (SEBS-g-MA) were used for better wettability. The results revealed a 7% improvement in tensile properties due to the addition of fibers which increased more up to 18% with the use of a CA as compared to neat polymer. Furthermore, the binary and ternary composites showed a gain of 70% and 77% in Young's modulus value at 30 wt.% fiber content. There was also an increase in 18% in TS at 10 wt.% fiber content for ternary composites. The results are ascribed to the fact that the OH groups present on the surface of fibers make strong ester bonds with MA function and the PP chains resulting in improvement of properties. Pothan et al. [36] investigated the effect of surface treatment on the banana-fiber-reinforced polyester composites and observed improvement in the storage modulus of the composites. Treatments using silane A174 and NaOH result in a maximum increase of modulus value which is accredited

to the change in the molecular structure of the polymer by interaction with the organofunctional group of the silane-treated fiber. There is also an improvement in glass transition temperature due to silane treatment. Coconut fibers obtained as a by-product of coconut find wide applications in industries because of high TS. Fernandes et al. [37] developed composite materials by introducing cork powder and coconut short fibers in high-density polythene in two different weight ratios. Better fiber-matrix interaction was observed by adding a CA. The researchers observed improvement in the elastic modulus by 27% and TS by 46% due to the addition of 10% weight coconut fibers. The increase in the tensile properties is justified due to the enhancement of the interfacial adhesion between the matrix and the fibers promoted by the CA based on MA. It increases the ability to transfer stresses across the interface resulting in an increase in the mechanical properties of the composite. Coir fibers extracted from the husk of coconut were used extensively in industries due to their highest elongation at break. Nam et al. [38] introduced coir fibers in polybutylene succinate (PBS) after the alkali treatment of the fibers and found that the IFSS value for treated fibers was 55.6% higher than untreated fibers with better interfacial adhesion. There was an increase of TS by 54.5%, tensile modulus by 141.9%, flexural strength by 45.7% and flexural modulus by 97.4% as compared to pure PBS resin. This is due to the fact that alkali treatment enhances the fiber-matrix adhesion because it removes natural and artificial impurities from the fiber surface as well as changes the arrangement of units in the cellulose macromolecule. Furthermore, it increases the surface roughness and the amount of cellulose exposed on the fiber surface resulting in better mechanical interlocking. Thus, the development of a rough surface topography and improvement in aspect ratio results in a better fiber-matrix interfacial bond increasing the mechanical properties of the composite. Kenaf which is mostly found in Southern Asia shows characteristics similar to jute fibers. Zampaloni et al. [39] developed a kenaf-fiber-reinforced PP composite using the compression molding process. The researchers observed that kenaf-PP composites developed using the compression molding technique show better TS compared to other compression-molded natural fiber composites such as sisal-, coir-, hemp-, flax-reinforced thermoplastics. The flexural strength of the composite at 40% fiber weight was almost double the value for sisal and coir but almost equal to hemp and flax. This is because bast fibers such as kenaf, hemp and flax have high tensile and flexural properties compared to leaf fibers of coir and sisal. A unidirectional bio-degradable composite was developed

by Ochi [40] by reinforcing kenaf fibers in emulsion-type PLA resin. The composite developed shows an increment in the TS, flexural strength and elastic modulus with 50% fiber content. The tensile and flexural strength of the composite was 223 and 254 MPa, respectively, for 70% fiber content. The results are attributed to the best molding conditions preventing the reduction of strength due to thermal degradation of the composite. Moreover, the fabrication with emulsion-type biodegradable resin results in the reduction in voids and fiber contacts in the composites enhancing their mechanical properties. The researchers also observed the reduction of the composite weight by 38% after 4 weeks of composting. A comparative study was carried out by Shibata et al. [41] between abaca fibers and glass fibers both reinforced in poly 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) based on fiber content, fiber length as well as surface treatment of natural fibers. Composite fabrication involved melt mixing and injection molding processes. The researchers observed that tensile properties were high at a fiber length of 5 mm. The abaca fiber surface treated with butyric anhydride and pyridine for about 5 h provides better flexural properties. The flexural strength and modulus were 27 and 900 MPa, respectively, for pure PHBV, which increased to 40 and 2240 MPa after the introduction of abaca fiber. The reason for such behavior is better interfacial bonding between the fiber and matrix resulting in the enhanced properties of the composite. However, surface treatment of abaca fibers did not have a significant effect on the tensile properties of the composites. A comparative study was carried out by Feng et al. [42] by reinforcing sisal fibers (SFs), steam-exploded SFs and steam-exploded bagasse fibers in PBS to investigate the rheological properties of the three different composites. The researchers observed that the consistency indices in case of fibrous filler-reinforced composites were higher than powder-filled composites with similar fiber content (e.g. 10 and 30 wt.%). The reason is that consistency indices depend mainly on the surface area. The larger the filler surface area, the greater is the consistency index of the composite. Zierdt et al. [43] combined bio-based polyamide 11 (PA11) and NaOH-modified beech fibers which improved the thermal stability, elastic modulus and storage modulus of the composite with increased onset temperature of thermogravimetric analysis from 290 to 330°C. The reason is removal of hemicellulose from the fibers which is lowest thermally stable component in the fiber. The highest value of the elastic modulus of 5049 MPa was observed at 50% modified fiber content, which is four times higher than neat PA11 and 8% higher than unmodified fiber composites. But water uptake decreases the modulus value which

is accredited to softening of the matrix. A TS of about 65 MPa was observed for the developed composite at 50% fiber content with no significant difference between modified and unmodified fibers. The developed composite finds application as construction material due to its improved mechanical properties. Bledzki et al. [44] observed that composites developed from natural vegetable fibers (NVF) show superior mechanical properties with a low specific mass. The major problem associated with NVF is debonding with the matrix due to its higher moisture absorption and poor wettability. The researchers found that the addition of CAs enhances Young's modulus and the TS of the composite. Ramanaiah and Ratna Prasad [45] reinforced sansevieria fiber in polyester and observed that the tensile and impact strength reached about 2.55 and 4.2 times of the pure resin at the highest value of fiber content. The TS of sansevieria fiber composites is 41.37% and 52% higher than that of sisal and banana fiber composites, respectively. The tensile modulus of sansevieria fiber composites is higher by 67.5% compared to banana fiber composites and little lower than SF composites. The impact strength of the sansevieria/polyester composite is 1.98 and 1.45 times more than that of jute/polyester and banana/polyester composites. The increase in the amount of fiber introduction reduces thermal conductivity, but with temperature the trend was completely opposite. Furthermore, there was a reduction in HRR and peak HRR of the matrix by 10.4% and 25.7%, respectively, due to the introduction of sansevieria fibers. The major drawback was that developed composites ignite earlier, release maximum carbon dioxide and total smoke during combustion as high as pure resin. The properties are attributed to the good mechanical and thermal insulation properties of sansevieria fibers. The composite developed from natural fiber (*Hildegardia populifolia*)-reinforced polypropylene carbonate (PPC) was studied by Li et al. [46]. The fabrication process involved melt mixing followed by compression molding. Increasing fiber content resulted in increasing composite TS and stiffness. The yield strength at 20% fiber weight for treated and untreated fibers was about 30.4 and 32.4 MPa, respectively, which increased to 35.2 and 34.5 MPa for 40 wt.% of fiber. This is due to the fact that alkali treatment on the fiber removes -CO- containing hemicellulose from the fiber obtaining a lighter color and better properties of the PPC/*Hildegardia* fiber composite. The introduction of short fibers decreased the elongation at break and energy to break but provided better thermo-oxidative stability. Agricultural by-products such as wheat husk and corn husk have found their way as reinforcing materials in recent times. Microfibers of wheat husk were reinforced into PLA and PP by Mamun

and Bledzki [47] in a high-speed mixer followed by injection molding. Wheat husk-PP composites show TS 15% higher compared to rye husk-PP composites, but 30% lower than wood-PP composites. However, enzyme modification improves the property by 30% for wheat husk-PP composites and 25% for rye husk-PP composites, respectively. This is attributed to the reduction of the fiber particle size, improved interface and the increase of the average molecular weight of the fiber by the removal of the unwanted materials. The addition of a CA (MA-PP) increases the TS by 30% and 35% for wheat husk-PP and rye husk-PP composites, respectively, compared to unmodified composites, which is due to the formation of ester linkage via MA-PP between the cellulosic filler and the PP molecule. Youssef et al. [48] developed a low-density polyethylene (R-LDPE)-reinforced corn husk composite and observed that with increasing fiber load, there was an increase in TS and reduction in hardness with no change in the characteristic peak position of the composite. The TS increases from 13.5 to 24.3 MPa from 0% to 10% fiber weight. The increase in strength is ascribed to the flow and film formation of the R-LDPE in the composite structure. The value of TS decreases above 10 wt.% and up to 20 wt.%. The decrease in strength above 10% fiber weight is due to the decrease of the flow of melted R-LDPE in the composite. However, there is a decrease in hardness values from 8.13 to 3.02 kP/mm² from 0 to 20 wt.% fiber content. Thus, it can be suitably used as a packaging material. Tensile, flexural, and impact strengths of hybrid Roselle and SF/polyester composite were investigated in both dry and wet conditions by Athijayamani et al. [49]. The investigators reported that TS for 50 mm fiber length at 10, 20 and 30 wt.% was found to be 32.4, 41.7 and 48.8 MPa, whereas for 100 mm fiber length, the value increases to 48.1, 50.9 and 58.7 MPa, respectively, in the dry condition. However, the values decrease to 30.1 and 43.1 MPa for 10 and 30 wt.% fiber volume at 50 mm fiber length when subjected to the moisture environment. This is due to the fact that the soaking of composite samples in water affects the interaction of the fiber and matrix and creates debonding, resulting in the decrease in the mechanical properties of the composites. The flexural strength also increased by 23.4% and 11.2% for 10 and 30 wt.% fiber volume at 50 and 100 mm fiber length, respectively. However, the maximum impact strength of the composite was found to be 1.41 and 1.39 kJ/m² with fiber content of 20 wt.% at 150 mm fiber length in both dry and wet conditions, respectively. The tensile and flexural tests of the jowar-fiber-reinforced polyester composite were investigated by Ratna Prasad and Mohana Rao [50] and properties were compared to sisal and bamboo fiber

composites. Jowar fiber shows a TS of 302 MPa, a modulus of 6.99 GPa and an effective density of 922 kg/m³. The researchers observed that at 0.40 volume fraction of fiber, the TS of the jowar fiber composite is almost equivalent to that of the bamboo composite and 1.89 times that of the sisal composite. Furthermore, the tensile modulus is 11% and 45% greater than those of bamboo and sisal composites. The jowar fiber reinforced polyester composite shows an increase in flexural strength by 4% and 35% whereas flexural modulus shows 1.12 and 2.16 times enhancement as compared to bamboo and sisal composites respectively. The improvement in the properties of the composite is due to the strength of jowar fiber compared to that of sisal and stronger bonding with the polyester matrix. This implies that jowar-fiber-reinforced composites can be a suitable replacement to sisal and bamboo composites in lightweight applications. Bettini et al. [51] developed a PP-reinforced sawdust composite to observe the effect of compatibilizer and lubricant concentrations on both mechanical and rheological properties of the composite. Maleic-anhydride-grafted PP (PP-g-MA) and Struktol TPW 113 were being used as a compatibilizer and lubricant, respectively. The researchers found that TS was improved and reached a maximum value with increasing compatibilizer concentration but decreased in the presence of the lubricant. There is also a reduction in strength due to its low molecular weight and incompatibility with the PP matrix. The increase of strength due to the compatibilizer addition is attributed to the interaction of maleic-anhydride-grafted chains with the sawdust hydroxyls, achieving appropriate interfacial adhesion between these phases. Furthermore, the presence of both the additives decreased the TS, complex viscosity, storage modulus and melt flow index of the composites, which is due to the interaction between lubricant and compatibilizer decreasing the efficiency of the composite. Wood fibers have recently gained huge interest in the present market for their enhanced creep resistance properties. Bledzki and Faruk [52] developed wood-fiber-reinforced PP composites at 40, 50 and 60 wt.% fiber content. The researchers observed that the addition of MAH-PP decreases the damping index to about 145% for hard wood fiber-PP composites at 60 wt.% fiber content and increases the creep modulus. The creep resistance was found to increase with increasing wood fiber content. Ashori and Nourbakhsh [53] studied the effects of wood species, particle sizes and hot-water treatment on the physical and mechanical properties of wood-plastic composites. Two different composites with oak and pine wood were developed with PP and MA as a matrix material and CA. The researchers reported that pine fibers show better properties than oak fibers,

which is due to the higher fiber length and aspect ratio of pine compared to oak fiber. Moreover, hot-water-treated fibers show high tensile, flexural and impact properties with increased water absorption. Tensile modulus was found to be 2613 MPa for the extracted PP/PF sample, which is 210% higher than that of the pure PP matrix. However, the flexural strength and flexural modulus were found to be 43.8 and 2943 MPa, respectively, for the extracted PP/PF sample. The results are accredited to the better fiber matrix interaction. The lignocellulosic materials can thus be used in the form of both fibers and flour in reinforcing the PP matrix. Zhang et al. [54] reported that wood floor can be converted into thermoplastics through benzylation treatment. The researchers developed a composite by reinforcing discontinuous and continuous SFs in plasticized China fir sawdust. The developed composite can be a potential replacement to petro based materials due to its competent mechanical properties and biodegradability. The highest values of tensile, flexural, impact strength and Young's modulus were found to be 17.5 MPa, 36.8 MPa, 5.6 kJ/m² and 2.39 GPa, respectively, at 72.8% weight gain of the fibers with 15 vol% of fiber. This is because of improved thermal flowability of benzylated wood, resulting in better mold packing. However, above 15 vol% of fiber, the matrix coverage is insufficient to wet the fibers. It leads to void formation and poor interfacial adhesion which results in the reduction of mechanical properties. Georgiopoulos et al. [55] developed wood fiber reinforced with PBAT copolyester and PLA using the melt mixing process and compression molding, which shows a significant improvement in the creep resistance of the composites at around 20% fiber content, which decreases with 30% fiber wt. Wu [56] observed that spent coffee ground (SCG)-reinforced polylactide grafted maleic anhydride (PLA-g-MA/SCG) shows better water-resistant behaviors and low melt viscosity and is much more biodegradable as compared to only PLA/SCG. For PLA/SCG composites, the TS at failure decreased markedly as SCG content increases due to the poor dispersal of SCG in the PLA matrix. The TS at failure was 44.3 MPa for neat PLA, which further decreased to 42.1 MPa on grafting with MA. But treated spent coffee grounds (TSCG) show a TS of about 8–20 MPa greater than that of the PLA/SCG composites. The result is accredited to the improved dispersion of TSCG in the PLA-g-MA matrix as a result of formation of branched or cross-linked macromolecules. Arib et al. [57] investigated the tensile and flexural properties of pineapple-fiber-reinforced PP composites and found that the tensile modulus and TS of the developed composites were 687.02 and 37.28 MPa, respectively, at a volume fraction of 10.8%. The flexural strength and modulus was 5.1% and

5.6% higher than pure PP, but the properties of the composite were lower than other natural-fiber-reinforced polymer composites, which is due to the fiber-to-fiber interaction, voids and dispersion problems. Liu et al. [58] investigated the effect of the polyester amide grafted glycidyl methacrylate (PEA-g-GMA) compatibilizer on the thermal properties, mechanical properties and morphology of the pineapple-fiber-reinforced soy-based bio-composite. The researchers reported that the TS and modulus of the bio-composites increased by 2 and 18 times and flexural strength and modulus improved by 3 and 15 times at 30 wt.% fiber content, which further increases with the presence of a compatibilizer as compared to soy-based bioplastics, which is due to the successful transmission of stress from the matrix to fiber. The rate of water absorption increases for the bio-composite in comparison to bioplastics which further decreases due to the addition of a compatibilizer. Espert et al. [59] investigated the water absorption properties of natural fibers such as cellulose fiber, SF, coir fiber and luffa sponge fiber reinforced PP composites at 23°C, 50°C and 70°C. The investigators noticed reduction of TS of the wet samples than dry samples due to moisture absorption by the fibres. But the addition of ethyl vinyl acetate (EVA) can improve the interaction between the fibers and the matrix. This is because EVA, which is a copolymer of ethylene, adheres to the PP matrix and vinyl acetate can bond due to its acetate groups to the hydroxyl groups of the fibers. Murali Mohan Rao et al. [60] developed a composite by reinforcing the vakka fiber in the polyester matrix and its tensile, flexural and dielectric properties were compared with sisal, bamboo and banana fiber composites. The TS and tensile modulus for the vakka composite were about 32%, 8%, and 12%, 66% higher than sisal and banana composites respectively and comparable to bamboo composites. This improvement is accredited to the strength and stronger bonding of the vakka fiber with the polyester matrix compared to sisal and banana. Above 0.27 volume fraction of vakka fiber content, the flexural strength is found to be increased more than banana fiber composites. The flexural modulus is around 63% and 35% higher than banana and SF composites due to the higher flexural stiffness of the vakka fiber composite as compared to banana and SF composites. However, the dielectric strength of the vakka fiber composite was found to be more at higher fiber content unlike sisal, bamboo and banana composites. Pothan et al. [61] investigated the dynamic mechanical analysis of banana-fiber-reinforced polyester composites focusing mainly on fiber loading, frequency and temperature. The researchers observed that the value of storage modulus is maximum for the neat polyester at low

temperature and becomes maximum for the composites at 40% fiber loading above glass transition temperature (T_g). The value of T_g increased with increasing fiber content, but the loss modulus and damping peaks were lowered with the addition of fibers. The apparent activation energy was highest for the developed composites at 40% fiber content. Pothan and Thomas [62] investigated the dynamic mechanical properties of chemically modified banana-fiber-reinforced polyester composites. The researchers reported that the overall polarity parameter and storage modulus were found to be maximum for the silane A151 (vinyl triethoxy silane)-treated fiber composites. The result is attributed to the change in the molecular structure of the polymer due to interaction with the organofunctional group of the silane-treated fiber. Idicula et al. [63] developed short banana/sisal-hybrid-fiber-reinforced polyester composites keeping the volume fraction of two fibers in the ratio 1:1 and observed that at a volume fraction of 0.40, the storage modulus was maximum above the glass transition temperature. The storage modulus was 178 MPa for neat polyester resin, which increased to 2818 MPa after incorporation of 0.40 volume fraction of fibers. The researchers also observed high tensile and flexural strength values at a volume fraction of 0.40. The ratio of the volume of banana and sisal at 3:1 gives the maximum TS. The increase of volume fraction of fibers from 0.19 to 0.40 increases the TS by 46% and flexural strength by 30% of the composite. This is due to the higher fiber content of around 0.40 volume fraction, which results in close packing of the fibers. The adjacent fibers prevent crack propagation in the composite. Thus, effective stress transfer takes place between the fiber and matrix leading to better properties of the composite. But above 0.4 volume fraction weak fiber-matrix interaction is observed due to agglomeration of fibers. However, compared to banana/polyester and hybrid composites, the sisal/polyester composite showed maximum damping behavior and highest impact strength due to the improved properties of the SF. Sapuan and Bachtiar [64] investigated the tensile properties of sugar palm fiber (SPF)-reinforced polystyrene composites and found that short SPF-reinforced composites show improved TS and modulus. The TS increases with the increase in fiber content for the composite. At lower fiber content 10–30% by weight, the average TS is 19.3 MPa, which is 35.5% lower than neat polymer. But at higher fiber content of around 40–50%, the TS increases. The highest value of tensile modulus 1706 MPa is obtained at a fiber content of 30 wt.%. The result is accredited to better dispersion and interaction with the polystyrene matrix resulting in good bonding between the fiber and matrix. Liu et al. [65] observed that sugar beet pulp (SBP) reinforced in PLA

shows an improvement in the TS of 37.5 ± 0.5 MPa for 10 wt.% fiber content as compared to 30.5 ± 1.7 MPa for pure PLA specimens. However, with increasing SBP content of up to 20 and 40 wt.%, the TS decreases to 28.9 ± 3.0 and 11.9 ± 1.6 , respectively. The reason for this is attributed to poor wettability of the fibers and the matrix.

Thus, incorporation of natural fibers has a significant effect in enhancing the mechanical properties of the composite. It is being observed that the highest TS of 302 MPa and Young's modulus of 6.99 GPa are observed for jowar-fiber-reinforced PMCs. But SF shows the lowest TS of 17.5 MPa. However, kenaf fiber shows a maximum flexural strength of 254 MPa when introduced in the matrix phase. Moreover, the pre-treatment of natural fibers plays a significant role in improving fiber matrix interaction by removing cellulose, hemicellulose and moisture from the fibers thereby enhancing the properties of the composite.

2.2 Seed shells

Seed shells are gaining huge interest in the field of composites because they are biodegradable and contain essential ingredients which can be effectively utilized in the development of composite materials. Essabir et al. [66] introduced an alkali-treated argan-nut shell (ANS) in high-density polyethylene (HDPE), which improved the adhesion between the fiber and matrix along with an increase in Young's modulus of the composite. When the filler content reached 25 wt.%, the TS decreased to a lower value of 27.17 MPa. There was an increase in 2.3% in tensile at 5 wt.% filler content. This is due to removal of the non-cellulosic compound, impurities and waxy substances from the surface of fibers and also the reduction of content of hemi-cellulose and lignin leading to improved interaction between the matrix and the hydroxyl groups of bio-fillers. The work was further extended by Essabir et al. [67] by adding SEBS-g-MA, which reduces fiber pull-out, micro-spaces and voids in the developed composite. The investigators observed a decrease of 36% in the TS with ANS particles as compared to neat PP at 30% fiber wt. The result is attributed to weak interfacial adhesion due to decohesion between the matrix and the bio-filler under stress. There was an improvement in Young's modulus of the composite by 62% due to fiber addition which further decreases due to the addition of a CA. The decrease in Young's modulus is due to the use of rubber copolymer as the sustenance of MA which has a low elastic modulus of around 7.2 MPa, thus decreasing Young's modulus of the bio-composite. The addition of a CA reduces the water absorption of the composite from 4.3% to 3%. But

their addition did not have a significant improvement on the thermal stability of the composite. Essabir et al. [68] developed a composite by combining PP with nut shells of argan to investigate the effect on both the mechanical and thermal properties of the developed composite due to the size of the particle and the load on the particle. Three different particle sizes were considered and the PP matrix was grafted with 8 wt.% of a linear copolymer, which were based on the CAs styrene and butadiene. The investigators observed that Young's modulus was improved due to the addition of particles as compared to only PP, which is due to the good interaction between the matrix and the reinforcement. Furthermore, there was a gain of Young's modulus to about 42.65%, 26.7% and 2.9% at 20 wt.% with three particle ranges, respectively. However, Young's modulus was reduced with the decrease of particle size. The TS decreases with the increase of particle size and particle content, which can be explained by two different possibilities. First, small particles have a comparatively higher total surface area for a given particle loading indicating higher TS with increasing surface area of filled particles. Secondly, decohesion between the matrix and particles under stress results in stress concentration which accelerates the sample break. There was also a reduction in the thermal stability of developed composites (256–230°C) as compared to only PP (258°C) due to the loading of particle from 10 to 25 wt.%. Xu et al. [13] introduced rubber seed shell (RSS) in HDPE which shows highest interfacial bonding ability, thermal stability, water resistance, flexural and TS of the developed composite. The flexural strength and modulus of HDPE/RSS200 (RSS powder modified at the optimum super-heated vapor temperature of 200°C group) increased by 10.26% and 15.99%, 21.27% and 7.31%, and 7.98% and 11.12% corresponding to the particle sizes of 60–80, 80–100 and 100–120 mesh. The TS for the samples increased from 16.67, 15.81 and 15.09 MPa to 17.29, 16.07 and 17.04 MPa, respectively. The enhancement in the TS is due to the greater interfacial compatibility between the RSS and the polymer after being modified with 200°C superheated vapor. The flexural and TS of modified samples increased by 21.27% and 12.92% compared to unmodified samples. The storage modulus also increases from 3370 to 3819 MPa. The improvement of the matrix and the particle generates more restriction of the deformation of the resin matrix in the elastic zone resulting in a higher modulus value. El Mechtali et al. [69] developed a composite by chemically treated almond shell (AS) particles reinforced in the PP matrix with and without the addition of a compatibilizer (PP-g-MA). Alkali treatment and etherification was carried out on the ASs to improve the interfacial adhesion between the filler and matrix. The treated filler particles show an

improvement in 14% in Young's modulus as compared to unmodified samples. Thermal stability also increased by etherification up to 385°C compared to neat PP 362°C. The increase in the thermal stability can be explained by the formation of an ether bond after C_{12} treatment which is stable at this temperature. But TS for alkali-treated fiber with and without a CA was reduced to 26 and 27 MPa as compared to ternary and binary untreated particle composites (28.14 and 29 MPa), respectively. This is attributed to the fact that alkali treatment changes the fine structure of the native cellulose I to cellulose II by a process known as alkalization which negatively affected the stress transfer in the particles.

Composite developed by incorporating seed shells shows lower values of TS compared to most of the natural fiber PMCs. The highest TS of 29 MPa was observed for the AS particle composite. The improvement in the properties of the developed composite is accredited to the pre-treatment of the seed shells and the matrix.

2.3 Animal fibers

Composite materials are also developed by reinforcing animal fibers in the polymer matrix. The fibers contain proteins in high amount. Composite materials are developed either by reinforcing the fibers directly or by the protein extracted from the fibers. Conzatti et al. [10] incorporated a maleinized PP compatibilizer in the wool fiber/isotropic PP composite. The results revealed an improvement in the thermal and thermo-oxidative stabilities, which is due to the suitable adhesion between the fiber and matrix in the presence of a compatibilizer. The stress and strain values are 30 MPa and 0.05, respectively, which are lower than neat PP. Bertini et al. [70] synthesized a keratin-reinforced PP composite after expulsion of free amino acids, peptides and low-molecular-weight proteins from keratin fillers. Hydrolysis of keratin was done, which showed a significant effect on the crystallization behavior and thermo-oxidative degradation of PP. MA was combined with PP to have a uniform distribution of keratin. Mechanical properties are observed to be better due to the addition of the MA functional group which transfers the stresses effectively from the polymer matrix to the bio-filler resulting in improved mechanical properties. The researchers noticed better properties of the composite along with improved crystallization rate and thermal stability due to the addition of keratin. Saiwaew et al. [71] developed fish water soluble protein (FWSP)-reinforced PLA and FWSP/oleic acid composite using a screw extruder and observed that tensile strength (TS),

percentage elongation (%E) and Young's modulus (Y) of 5FWSP-ole composite sheets decrease by about 84.53%, 76.37% and 57.71%, respectively. The result is attributed to the relatively rigid parts of the FWSP-ole granules which induce cracks and result in low TS, %E and Y compared with neat PLA. The researchers noticed an improvement in TS from 5.33 ± 0.95 MPa for the 5FWSP-ole composite to 11.88 ± 1.82 MPa for the 10FWSP-ole composite although the elongation at break was the same. This is because of crosslinking during the compounding process which induces partial adhesion. But an increase in the elongation of break at 462.96% with a generation of pinhole was observed due to mixing of oleic acid during the extrusion process. There was also an enhancement in TS, %E and Y of 5FWSP-ole/ole composite sheets by 294.00%, 462.96% and 49.50%, respectively, compared to 5FWSP-ole composite sheets because ole acted as a lubricant. MA reduced the size and stretching phase of FWSP along with good interfacial bonding and reduced pinholes and water vapor permeability. Investigation by Ameer et al. [72] showed that composites developed from pig chondrocytes reinforced in a fibrin gel phase and dispersed in the volume of polyglycolic acid (PGA) show no significant change in collagen content compared to only PGA having 40% of native cartilage value. The reason for selection of fibrin gel as the matrix is that fibrin gel is FDA-approved material and used extensively in the clinical setting as a tissue adhesive and can be collected from a patients' own blood. The content of glycosaminoglycan per cell in the composite scaffolds was 2.6 times that of the PGA and 88% that of native pig cartilage. Polyvinylpyrrolidone reinforced with silk fibroin was fabricated by Kim et al. [73], which are generally biodegradable and are used in case of implantable devices for lifelong powering. Ag nanowires enhanced dispersion of the nanoparticles, whereas polyvinyl pyrrolidone prevents the contact between two Ag nanowires. The researchers found that if 30 wt.% fillers are uniformly dispersed in the solution, then highest output voltages and current densities of 2.2 V and 0.12 mA/cm² in case of films and 1.8 V and 0.1 mA/cm² in wires can be obtained.

Thus, animal fibers and proteins have emerged as excellent reinforcement in PMCs. The FWSP shows a TS of 11.88 ± 1.82 MPa at 10 wt.% of FWSP. The composite developed using animal proteins can find promising applications as implants and scaffolds in biomedical sciences.

2.4 Cellulose

Composites are developed by reinforcing biodegradable polymers in the polymer matrix. Cellulose is an organic

polymer found in abundance in the environment and forms the major ingredient of the plant cell wall. Cellulose is one the most promising molecules in addressing the depletion of non-renewable resources and replacing fossil-based polymer materials [74]. Cellulose either in the form of fibers or whiskers is used in the development of composite materials. Cellulose whiskers obtained from banana fibers were reinforced in polyethylene-co-vinyl acetate (EVA) by Elanthikkal et al. [14]. The researchers observed improved properties as compared to only EVA copolymer due to the addition of cellulose whiskers having higher stiffness. Cellulose extracted from the bamboo fibers was reinforced with poly(2-hydroxy ethyl methacrylate) solution and electrospun by Rao et al. [75]. The researchers observed 96% cell viability and 74% cancer cell viability with paclitaxel addition in the developed nano-composite fibers. Thus, the developed nano-composite finds wide application as a fiber mesh for covering the area of skin cancer and healing of wounds. The bamboo-fiber-reinforced PP composite was developed by Chen et al. [76]. MA at 24% was used as a compatibilizer which improves the mechanical properties of the composite such as the tensile modulus, tensile strength and impact strength. The reason for this is the improved interaction of the bamboo fiber and PP due to the strong association of MA with the hydroxyl groups on the bamboo surface. The TS of the composite developed with the addition of a compatibilizer was found to be 32–36 MPa and tensile modulus was 5–6 GPa, which is higher than a commercial wood pulp composite. Liu et al. [77] synthesized a CF-reinforced millable polyurethane (MPU-20) composite. The composites had apparent specific gravity lower than 100 kg/m³ with 20–200 mm thickness and cushion factor <4. Higher steam injection pressures and higher MPU-20 dosages resulted in improving the cushioning properties of the composite. Cellulose nanofibers (CNF) were reinforced in PLA by Ding et al. [78], which increases the overall crystallization kinetics of the polymer, thereby decreasing the crystallization about half time. However, the crystallization rate of PLA/CNF composites depends mainly on the presence of CNF. The degree of crystallinity for PLA materials increased from 16.39% to as high as 27.89% and 25.72% with 0.5 and 1.0 wt.% of CNF content, respectively, which is due to the nucleation of crystallites for PLA and increased nucleation power with increasing CNF content. A composite material was developed by Song et al. [11], introducing modified nano-cellulose fibers (NCF) in PLA. NCF was grafted with hydrophobic monomer resulting in the reduction of water vapor transmission rate (WVTR). The lowest value of WVTR was found to be 34 g/m²/day obtained by the addition of 1% of modified NCF to PLA. This is due to the improvement in

hydrophobic characteristics of the fibers leading to better interaction with the matrix reducing WVTR. The composite plays a significant role as green-based packing material. Compatibility between the matrix and reinforcement enhanced the properties of the composite. Hu et al. [79] introduced acetylated cellulose nanocrystals (CNCs) in PBS, which improved compatibility between nanoparticles and polyester matrix. It also increases the specific flexural strength and the specific flexural modulus to 75.7% and 57.2%, respectively. The yield strength and Young's modulus increase from 14 to 44 MPa and 660 to 1502 MPa, respectively, with the addition of 1.5 wt.% CNCs. The improvement of the mechanical properties is due to the reinforcing effect of CNCs. Glyoxal was used by Qiu and Netravali [80] for crosslinking of polyvinyl alcohol (PVA) to improve the mechanical and thermal properties of microfibrillated cellulose (MFC)-PVA composites. The researchers observed that crosslinking of MFC-PVA by glyoxal results in acetal linkage formation which decreased the swelling ability, melting temperature and solubility of PVA but increased the glass transition temperature of the composite. Young's modulus of the neat PVA was 248 MPa, which increased up to 687, 1033 and 3898 MPa for 5, 10 and 50 wt.% MFC content, respectively. The fracture stress value was 43.3 and 53.5 MPa for MFC content of 5 and 10 wt.%, respectively. It further increases to 89.9 and 84.9 MPa when MFC content was increased to 40 and 50 wt.%, respectively. The fracture stress of neat PVA was only 34.1 MPa. The moisture absorption for the neat PVA was 9.1%, which decreases with the addition of MFC from 7.1% to 8.1%. However, the crosslinked PVA and MFC/PVA show Young's modulus values of 666 and 1404 MPa, which are higher than only PVA and MFC/PVA values of 248 and 1033 MPa without crosslinking, respectively. It is due to the rigid structure formed after the crosslinking of PVA. The composite finds its application to replace traditional non-biodegradable plastics. Three different composite materials were developed by Gårdebjer et al. [81] with PLA, poly(lactide-co-glycolide) and poly3-hydroxybutyrate (PHB), which were reinforced with both modified and unmodified CNCs. Modified CNCs showed better polymer and filler interaction than the unmodified ones. Crystallinity was induced in the PLA and PHB film due to the addition of modified CNC. It is due to better dispersion and fewer aggregates of modified CNC in the matrix. Liu et al. [82] developed a water-induced shape-memory composite with poly-DL-lactide (PDLLA) and microcrystalline cellulose (MCC). The composite showed good shape-memory effect, biodegradability and cytocompatibility. The water absorption for pure PDLLA was almost zero, which increases with increasing MCC content and its highest

value is 5.32% at 35 wt.% MCC content. The reason behind is the hydrophilic nature of MCC and increased wettability of the PDLLA matrix by the introduction of MCC. The storage modulus of pure PDLLA was 2711 MPa at 30°C, which shows an increment of up to 95% to 5275 MPa for the PDLLA-MCC composite at 35% fiber wt. The composite also exhibits a higher value of stiffness than pure PDLLA with the increase in MCC content, which is due to the lower deformation capacity of the PDLLA-MCC composite. The composite can be effectively utilized in different biomedical applications. Hu et al. [83] developed a composite by reinforcing CNCs into PPC. Mechanical properties were improved with the addition of CNC. The researchers observed that 0.1 wt.% CNC addition causes a 10-fold increase in TS and a 7-fold increase in Young's modulus. A significant improvement in yield strength from 1.8 to 37 MPa and Young's modulus from 207 to 2192 MPa, respectively, was observed with the increase of CNC content from 0 to 1.5 wt.%. The results are attributed to reinforcing effects of CNC. Thermal stability decreases with increasing CNC content, which is due to aggregation of CNC particles during the preparation of composites. Thus, it could be used as an alternative in the field of commercial plastics as an eco-friendly material. Voronova et al. [84] investigated the thermal stability of the CNC-reinforced polyvinyl chloride composite. The results revealed that PVA/CNC composites degrade at much higher temperature due to the presence of CNC nanoparticles than PVA alone. The maximum value of thermal stability for PVA/CNC composites was observed at 8–12 wt.% CNC content which is due to strong interactions of hydroxyl groups of PVA macromolecules and surface hydroxyl groups of CNC particles. But thermal stability decreased with CNC content above 12% where CNCs degraded first followed by PVA degradation. The reason behind this is agglomeration of particles at higher CNC content resulting in the reduction of thermal stability. Soykeabkaew et al. [85] developed a biodegradable composite using lignocellulosic fibers and lithium chloride/N,N-dimethylacetamide as a solvent and observed the effect of the immersion time of the aligned fibers in the solvent. The researchers observed high longitudinal TS and Young's modulus of 460 MPa and 28 GPa, respectively, for the developed composite on the optimization of the immersion time which can be a replacement to glass fiber composites. The immersion time for 2 h reveals best properties as the amount of the outer layer of the fibers which is dissolved to create a matrix phase is adequate to bond the remaining core fibers efficiently together. This leads to a good interfacial bonding and stress transfer in the composite reducing the formation of voids. A composite material was developed by reinforcing cellulose and cellulignin

fibers attained from sugarcane bagasse in PP by Luz et al. [19]. Although chemically modified, the fibers show lower TS compared to neat PP, which is due to the decrease of fiber dimension after the chemical treatment. The TS lies between 20.1 and 26.2 MPa for the composite, which is lower than pure PP (27 MPa). The highest and lowest TS values were observed at 10 and 20 wt.% fiber content for cellulose/PP composites and cellulignin/PP composites. High elongation at break of 10% at 10 wt.% of fiber for the acetylated cellulignin/PP composite and lowest of 6% for cellulose/PP at 20 wt.% of fiber was observed. However, the composite shows the improved flexural property compared to neat polymer, which is due to the fiber content in the composite. Differential scanning calorimetry analysis reveals that composites reinforced with untreated fibers were more crystalline than treated fibers, which is due to the more nucleating ability of untreated fibers as after treatment each fiber behaves differently. Soykeabkaew et al. [86] developed composites of Lyocell and Bo-cell fibers and observed superior mechanical and thermal properties which can be further improved based on fiber selection and preparation parameters. The Bo-cell fibers show an average TS of 910 MPa and a Young's modulus of 23 GPa with 8% elongation at break, which are high compared to the Lyocell composites. This enhancement in properties is attributed to the high mechanical strength of Bo-cell fibers. Duchemin et al. [87] developed a novel all-cellulose composite from MCC powder in 8% LiCl/DMAc solution. Cellulose solutions were precipitated in the composite solution for producing 0.2- to 0.3-mm-thick films. The researchers concluded that all-cellulose composites were controlled by the rate of precipitation, initial cellulose concentration and dissolution time. All-cellulose composites can have a maximum TS of up to 106 MPa and a tensile modulus of up to 7.6 GPa. Du et al. [88] observed that the introduction of hardwood high yield pulp (HWHYP), softwood high yield pulp (SWHYP) and bleached kraft softwood pulp fibers in PLA increases the storage moduli, tensile moduli, strength and elasticity with the highest value of TS of 121 MPa. The enhancement in the tensile properties is around 1-fold higher as compared to neat PLA. The tensile moduli for the kraft were highest followed by SWHYP and then HWHYP, which is due to the differences in cellulose content and aspect ratio of three pulp fibers. However, the TS of the HWHYP/PLA composite starts to decrease as the fiber loading increases from 40% to 50% due to the shortest fiber length and highest surface area of the HWHYP, which was not sufficient to fully wet fibers by the polymer at a fiber loading of 50%. The non-uniform wetting decreased the strength of the HWHYP/PLA composite. Prachayawarakorn and Pomdage [89]

introduced low-density polyethylene with thermoplastic starch (TPSC) to improve the properties of the composite. Carrageenans and cotton fibers were then introduced in the TPSC/LDPE combination for further modification of the composite. The composites were prepared using internal mixture and injection molding machines. The researchers found that incorporation of both the fibers in the composite improved the mechanical properties significantly along with the increase of stress at the maximum level. The enhancement in the stress at maximum load, Young's modulus and hardness was observed to be approximately 27.5%, 320% and 31.0%, respectively, for the modified fibers as compared to unmodified ones. The reason behind this is the formation of a new hydrogen bond between the TPCS and the carrageenan, resulting in the difficulty of the movement of the polymer chains. But the water intake ability remained unchanged for the composite. Degradation of the modified composite was also found to be higher than the non-modified ones. In order to increase the interfacial bonding between starch granules and PLA matrix, Yang et al. [90] grafted starch with PLA in the starch/PLA composite, which showed a significant improvement in the strain at failure but reduced water resistance. The researchers further observed that St-g-PLA had a uniform distribution in the PLA matrix, showing rapid leaching while aging in water. The unmodified starch granules when blended with PLA show a considerable reduction of the strain at failure which is due to poor interfacial adhesion between starch granules and PLA. However, PLA grafting on the surface of starch granules improves the strain at failure of St-g-PLA/PLA to a great extent close to pure PLA. Various models such as the Halpin-Tsai model, the Kerner model and the Nicolais-Narkis model were utilized to carry out the comparison of results with the tensile test observations.

Thus, the study reveals that cellulose-based fibers are promisingly reinforced in PMCs. Man-made fibers extracted from cellulose show considerable mechanical properties. Bo-cell-fiber-incorporated PMCs show the highest TS and modulus of 910 MPa and 23 GPa, respectively. The properties of Bo-cell fibers are comparable to conventional glass fibers.

2.5 Bio-polymers

Polymers are materials developed by combining repeated single monomers. They are either biodegradable or non-biodegradable. Bio-polymers are a class of polymers extracted from natural resources and are completely biodegradable. In order to decrease the adverse effect of

long-lasting plastic composites on the environment, a biodegradable composite was developed with PLA fibers reinforced in both PLA and PBS matrices by Jia et al. [12]. Film stacking and hot pressing were used for composite fabrication. The investigators reported that the TS and Young's modulus of the PLA-PLA composite were higher than those of the PLA-PBS composite by 12–40% and 39–54%, respectively, which is due to the high chemical similarity of the PLA-PLA composite resulting in better interfacial bonding than the PLA-PBS composite. Mai et al. [91] developed self-reinforced PLA (SR-PLA) and found that the tensile modulus of SR-PLA composites increased by 2.5 times, the TS by 2 times, the impact energy by 14 times along with heat deflection temperature by 26°C in comparison to only PLA, which is due to the reinforcing of the PLA matrix. The developed composite was bio-based and recyclable. Lim et al. [92] developed the PLA-reinforced poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHB-HHx) composite by the direct melt compounding process. Both the PLA and PHB-HHx were found to be unmixed in that composition range. The researchers observed that increasing PHB-HHx content reduced the crystallinity of the PLA, which is accredited to the chain length of PHB-HHx affecting entanglement of PLA. However, stiffness of the composite was improved in comparison to the only PLA due to the ductile nature of PHB-HHx. The addition of PHB-HHx resulted in better ductility of the PLA/PHB-HHx composite along with higher plastic deformation and better toughness. Thus, PHB-HHx-added PLA can be used in various applications such as flexible films and food packaging. But the TS and Young's modulus for neat PLA were around 62.2 (± 3.5) and 1603.0 (± 7.0) MPa, which decreased to about 40.1 (± 2.4) and 1093.0 (± 7.0) MPa, respectively, for the PLA/PHB-HHx composite at 6/4 combination. Chitosan is a natural polymer obtained from amino polysaccharides and has exclusive properties. Magnetic chitosan composites (MCCs) have higher adsorption rate and higher adsorption efficiency and can efficiently remove pollutants in an aqueous solution, as reported by Reddy and Lee [93]. It is due to the presence of amine and hydroxyl groups of chitosan which are predominantly responsible for binding inorganic and organic pollutants. Thus, MCCs can be effectively used for treating of polluted water. The investigators observed that a wide variety of materials such as chelating ligands, nanomaterials, inorganic oxides and biomaterials have been used to enhance the adsorption performance of MCCs because the materials offer a wide range of advantages including no secondary pollution, easy separation and recovery and strong chelating capabilities. Amri et al. [94] modified chitosan/PP composites with organosolv lignin and AA, which resulted in a reduction in TS but an

improvement in Young's modulus and impact strength due to chitosan addition. The researchers noticed that treated fibers show better mechanical and thermal properties than untreated ones. The TS, Young's modulus and impact strength were 26.37 MPa, 1513.48 MPa and 48.5 J/m, respectively, for untreated composites, which increased maximum up to 35.40 MPa, 2296.94 MPa and 65.8 J/m upon treatments of fibers. It is because organosolv lignin reacts with AA through a nucleophilic addition reaction between the aromatic group of organosolv lignin and the carbon-carbon double bond (C=C) of AA. The product then adheres to the surface of chitosan forming ester linkage between the hydroxyl group of chitosan and the carboxylic group of AA. The bonding reduces the hydrophilic character of the chitosan leading to better interfacial adhesion with the PP matrix. But increasing fiber loading decreases the TS of the composites, which is due to the lack of interaction at the chitosan and PP matrix interface.

Thus, recent trends toward the development of PMCs have incorporated self-reinforced polymers which show considerable mechanical properties. The homogeneity of both the matrix and reinforcement phase enables us to attain superior properties for the developed composite. SR-PLA shows a maximum TS and modulus of 40.1 (± 2.4) and 1093.0 (± 7.0) MPa, respectively.

2.6 Bio-chemicals and bioceramics

Composites developed by particulate-reinforced biodegradable polylactic acid (PDLLA) and hydroxyapatite (HA) with a second reinforcement unidirectional PLA fiber were investigated by Nazhat et al. [95]. The investigators observed an increase in the Tg-PDLLA value but a reduction in the damping value due to the addition of both the filler materials. The first transition temperature for unfilled PDLLA was found to be around 45.8°C, which increases up to 51.4°C due to the addition of filler materials because the fibers were able to withstand applied load compared to unfilled PLA. Chen and Wang [15] developed a composite using the two bioactive ceramics HA and tricalcium phosphate (TCP), which were introduced into polyhydroxybutyrate-polyhydroxyvalerate (PHB-PHV) up to 30% by volume. Bioceramic particles were evenly distributed in the polymer. The researchers found that storage modulus, loss modulus and stiffness were highly increased with increasing HA/TCP content, which is due to the reinforcing of the polymer resulting in the improved properties of the composite. The micro hardness value was found to be increased from around 8.56 to 15.73 Vickers hardness number (VHN) for the increasing

Table 1: Mechanical properties of composites.

S.no	Reinforcements	Mechanical properties							
		Tensile strength	Elastic modulus	Flexural strength	Flexural modulus	Storage modulus	Impact strength	Yield strength	Hardness
1	Sugar beet pulp	37.5 ± 0.5 MPa	—	—	—	—	—	—	—
2	Bagasse	—	—	30 MPa (outer) 22.4 MPa (inner)	—	2750 MPa (untreated fibers) 2900 MPa (NaOH treated) 2780 MPa (acrylic acid treated)	—	—	—
3	Hemp	30 MPa 59.3 MPa with PLA matrix	3.5 GPa (for poly(3-hydroxybutyrate-co-hydroxyvalerate) matrix) 6 GPa for copolyester amide matrix	124.2 MPa with PLA matrix	—	—	26.3 kJ/m² PLA matrix	—	—
4	Ramie	59.3 MPa 61.4 MPa, for 1,6-hexane diisocyanate (HDI) 62.0 MPa for 4,40-diphenyl methane diisocyanate (MDI) 60.1 MPa for isophorone diisocyanate (IPDI)	—	136.8 MPa	—	—	—	—	—
5	Kenaf	223 MPa	—	254 MPa	—	—	—	—	—
6	Abaca	—	—	40 MPa	2240 MPa	—	—	—	—
7	Beech fibers	65 MPa	5049 MPa	—	—	—	—	—	—
8	<i>Hildegardia populifolia</i>	—	—	—	—	—	—	30.4 MPa (treated) 32.4 MPa (untreated) fibers at 20% fiber weight 35.2 MPa (treated) 34.5 MPa (untreated) fibers at 40% fiber weight	— — — — — 3.02 kP/mm²
9	Corn husk	24.3 MPa	—	—	—	—	—	—	—
10	Roselle and sisal	32.4 MPa (10 wt.%) 41.7 MPa (20 wt.%) and 48.8 MPa (30 wt.%) 50 mm fiber length, respectively 48.1 MPa (10 wt.%), 50.9 MPa (20 wt.%), 58.7 MPa 30 wt.% at 100 mm fiber length	—	—	—	—	1.41 kJ/m² at 150 mm fiber length	—	—
11	Jowar	302 MPa	6.99 GPa	—	—	—	—	—	—

Table 1 (continued)

S.no	Reinforcements	Mechanical properties							
		Tensile strength	Elastic modulus	Flexural strength	Flexural modulus	Storage modulus	Impact strength	Yield strength	Hardness
12	Pine fiber	–	2613 MPa	43.8 MPa	2943 MPa	–	–	–	–
13	Sisal fibers	17.5 MPa	2.39 GPa	36.8 MPa	–	–	5.6 kJ/m ²	–	–
14	Pineapple	37.28 MPa	687.02 MPa	–	–	–	–	–	–
15	Banana/sisal hybrid fiber	–	–	–	–	2818 MPa	–	–	–
16	Sugar palm fiber	19.3 MPa	1706 MPa	–	–	–	–	–	–
17	Argan-nut shell	27.17 MPa	–	–	–	–	–	–	–
18	Rubber seed shell	17.29 (60–80 mesh) 16.07 (80–100 mesh) 17.04 MPa (100–120 mesh)	–	–	–	3819 MPa	–	–	–
19	Almond shell	26 MPa (with coupling agent) 27 MPa (without coupling agent) 28.14 MPa (binary untreated) 29 MPa (ternary untreated)	–	–	–	–	–	–	–
20	Fish water soluble protein (FWSP)	5.33 ± 0.9 5 MPa for 5 FWSP 11.88 ± 1.82 MPa for 10 FWSP	–	–	–	–	–	–	–
21	Bamboo fiber	32 MPa (without compatibilizer) 36 MPa (addition of compatibilizer)	5 GPa (without compatibilizer) 6 GPa (addition of compatibilizer)	–	–	–	–	–	–
22	Acetylated cellulose nanocrystals	–	1502 MPa	–	–	–	–	44 MPa	–
23	Micro fibrillated cellulose (MFC)	–	687 MPa for 5 wt.% MFC 1033 MPa for 10 wt.% MFC 3898 MPa for 50 wt.% MFC	–	–	–	–	–	–
24	Microcrystalline cellulose (MCC)	106 MPa	7.6 GPa	–	–	5275 MPa at 35% fiber wt	–	–	–
25	Cellulose nanocrystal (CNC)	–	2192 MPa at 1.5 wt.% CNC	–	–	–	–	37 MPa at 1.5 wt.% CNC	–
26	Lignocellulosic fibers	460 MPa	28 GPa	–	–	–	–	–	–

Table 1 (continued)

S.no	Reinforcements	Mechanical properties							
		Tensile strength	Elastic modulus	Flexural strength	Flexural modulus	Storage modulus	Impact strength	Yield strength	Hardness
27	Cellulose and cellulignin fibers from sugarcane bagasse	20.1–26.2 MPa (in between)	–	–	–	–	–	–	–
28	Bo-cell fibers	910 MPa	23 GPa	–	–	–	–	–	–
29	Poly(lactic acid)	40.1 (±2.4) MPa	1093.0 (±7.0) MPa	–	–	–	–	–	–
30	Chitosan	26.37 MPa (for non-treated fibers) 35.40 MPa (for treated fibers)	1513.48 MPa (for non-treated fibers) 2296.94 MPa (for treated fibers)	–	–	–	48.5 J/m (for nontreated fibers) 65.8 J/m (for treated fibers)	–	–

value of HA in the HA/PHB-PHV composite and 0.56 to 10.18 VHN for the increasing value of TCP in the TCP/PHB-PHV composite. Liang et al. [96] reinforced nano-calcium carbonate (CaCO_3) in PLA using a twin extruder. Stearate treatment was performed on the nano- CaCO_3 , which revealed improvement in the crystallization onset temperature, crystallization temperature and crystallization end temperature as well as the crystalline degree at a particle weight fraction of 1%, which further increases up to 3%. The researchers also concluded that heterogeneous nucleation of the nano- CaCO_3 in the PLA matrix causes the improvement in the degree of crystallinity of the composite. Two different bio-composites were developed with gallic acid (GA) and thymol (T) grafted with P(3HB)-g-EC, i.e. GA-g-P(3HB)-g-EC and T-g-P(3HB)-g-EC by Iqbal et al. [97]. The composites were fabricated using surface dipping and incorporation techniques. The composites with 15GA, 15T and 20T show highest bacteriostatic and bactericidal activities. The investigators also observed that both the composites have 100% viability and have no adverse effect on skin cells. Moreover, both the composites showed increased degradation rates and play a significant role in biomedical applications such as skin regeneration, multiphasic tissue engineering and medical implants. In order to overcome the low heat deflection and brittleness of the bioplastic, Patil et al. [98] developed a composite from polyethyleneoxide-polycaprolactone-polyethyleneoxide and silica, which are both biodegradable and biocompatible. The researchers observed that with the increase of silica content, the storage modulus increases. There has been a continuous development in commercially available green composites which are basically obtained from the natural resources.

The incorporation of biochemicals as biodegradable and biocompatible materials in PMCs has gained a lot of interest. Chitosan-reinforced PMCs show the TS and modulus of 35.40 and 2296.94 MPa, respectively, after the pre-treatment of fibers. Hydroxylapatite-incorporated PMCs can be effectively utilized as implants in different biomedical applications.

Satyanarayana et al. [99] reviewed innovative production technologies for various commercially available biodegradable polymers and composites. The researchers also investigated their feasibility for practical implementation considering better mechanical properties and improved thermal stability by the use of nanotechnology. The composites mainly consist of lignocellulosic fibers. Their study also provides an overview of the recent development that was carried out in the field of biodegradable composites based on market processing methods, morphology, properties, product development and also matrix

reinforcement systems. Critical issues and suggestions for future work along with the enhancement of properties of biodegradable composites were also being focused in their research work. John and Thomas [100] reviewed cellulosic fibers and bio-composites and found that cellulosic-fiber-reinforced polymeric composites are gaining importance in construction industry and automotive industry. The researchers have also shown the classification of the composites such as green composites, hybrid bio-composites and textile bio-composites along with the applications of polymer-reinforced bio-composites. Cellulose-based nanocomposites and electrospinning of nanofibers are also being emphasized in their research work.

Thus, a comprehensive review emphasizing on natural fibers, seed shells, animal fibers, cellulose, biopolymers and biochemicals reported in the current paper will highlight the merits and demerits of PMCs. The review addresses possible applications of PMCs in engineering and medical sciences. Table 1 shows the mechanical properties of the composites with different reinforcements.

3 Conclusions

PMCs have emerged as a revolutionary attempt in the field of composites. The improved properties of polymers have attracted attention of a lot of researchers toward their potential applications in diversified fields. The current review mainly focuses on polymer bio-composites which are biodegradable and have no adverse effect on the environment. Potential weaknesses in a previous work are highlighted while bringing out the potential strengths of previous works. The study also focuses on the different reinforcing materials in PMCs. This study exemplifies that the addition of reinforcing materials enhances the mechanical properties of the polymer to a great extent. The TS and stiffness are observed to be higher in natural fiber PMCs. Seed-shell-reinforced PMCs do not have high TS but show very high compressive strength. Animal-fiber-, protein- and biochemical-reinforced PMCs provide considerable mechanical strength making them a promising material for scaffold and implants in biomedical applications. The maximum TS and modulus were 910 MPa and 23 GPa, respectively, accomplished by a Bo-cell fiber which is a man-made fiber obtained from cellulose. But the major problem encountered during composite development is the poor interaction between the matrix phase and the reinforcing phase. This results in poor interfacial bonding hindering the properties of the developed composite. The researchers are intended to improve the

properties of the composite either through various pretreatment processes or through the addition of CAs and compatibilizers. It results in improved adhesion between the matrix and reinforcements enhancing the mechanical properties of the composite. But in most cases thermal properties do not show significant improvement in comparison to pure resin. Researchers are still exploring the possibility of developing polymer bio-composites from natural resources without compromising any of the properties of the composite. The review will pave the way for developing bio-composites that can possibly replace traditional composites in various potential applications such as automobiles, lightweight structures and insulating materials.

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