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Renewable Biocomposite Properties and their Applications

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Abstract

Recently, with increasing environmental awareness and expanding global waste problems, eco-friendly biofillers have been recognized as a promising alternative to inorganic fillers in the reinforcement of thermoplastic and biodegradable plastics. Therefore, many industries are seeking more eco-friendly materials that will decrease the level of environmental contamination and economic cost. Bacteria cellulose, rice straw, rice husk, natural fiber, lignocellulose, cellulose, and paper sludge are renewable resources owing many beneficial properties; these materials were used to manufacture composite products such as sound absorbing wooden construction materials, interior of bathrooms, wood decks, window frames, decorative trim, automotive panels, and industrial and consumer applications. This chapter elucidates the different renewable biocomposite properties and their applications.

Keywords: renewable materials, composites, properties, applications

1. Introduction

Over several years, fiber-reinforced composites have been attracting great interest because of their many superior properties and applications. The well-known fact is that the reinforcement of fibers in different polymers significantly increases the mechanical properties of the composites. Generally, aircraft and automobile industries prefer to use synthetic fibers such as glass and carbon fibers for reinforcement in polymers. In addition, the increasing performance of composites has been identified by advanced research with two or three polymers/reinforcements or fillers. However, the recycling of these composites is difficult due to difficulty for separation of their components. On the other side, these composites cause

severe environment issues during the landfills or burning. Most of these composites are made from petroleum-based nonrenewable resources [1]. In order to replace the petroleum-based nonrenewable resource-based composites, the eco-friendly biocomposites need to reduce environmental impact. Generally, biocomposites are formed with one or more phases of reinforcement of natural fibers with organic matrix or biopolymers. These reinforcements (cotton, hemp, flax, sisal, jute, and kenaf or recycled wood and paper) and biopolymers (natural biopolymers such as gelatin, corn zein and soy protein; synthetic biopolymers such as poly(lactic acid) (PLA), poly(vinyl alcohol) (PVA); and other microbial fermentation such as microbial polyesters) are renewable and degradable [2, 3]. Meanwhile, in another approach, these biocomposites are formed from the renewable, recyclable, and sustainable agricultural and forestry feedstocks but not food or feed, this can make better change in an environment day-to-day. Systematically, the utilization of bio-based polymers as a reinforced matrix to form biocomposites increases more and more. The spectacular effect on developments of biopolymer-based composites, which lead the rapid growth of biocomposites in the market place, can be seen. In the duration of 2003–2007, globally the average annual growth rate was 38%. During the same period, the annual growth rate was as high as 48% in Europe. On the other hand, from 2007 to 2013, the capacity of utilization of these biocomposites was projected from 0.36 to 2.33 million metric ton by 2013 and 3.45 million metric ton in 2020. Indeed, PLA, PHA, and starch-based plastics were large volumes of production in biocomposites [4]. The U.S. Department of Energy (DOE) had sponsored to the Technology Road Map for Plant/Crop-based Renewable Resources 2020. The main intension of this program is to use plant-derived renewable resources for making 10% of basic chemical building blocks by 2020, and further this concept should be extended to achieve 50% by 2050. The U.S. agricultural, forestry, life sciences, and chemical communities have developed a strategic vision for using crops, trees, and agricultural residues to manufacture industrial products, and have identified major barriers to its implementation [5].

The reinforcement of many agricultural and forestry feedstocks with biopolymers comprises change in mechanical, thermal, and biodegradable properties of the composites. This chapter elucidates the properties of renewable biocomposites and their applications.

2. Properties of biocomposites

The most important characteristic feature of selection materials for various applications is depending on its properties. The properties of materials are often dependent on the isotropic and anisotropic nature of the materials. The properties of materials that relate to different physical phenomena often behave linearly (or approximately so) in a given operating range. Modeling them as linear can significantly simplify the differential constitutive equations that the property describes. On the other hand, the relevant equations are also used to determine the material properties. If we know the original length of a material, then we can determine the gain or loss of its original length by calculating change of the length. Material properties are most reliably measured by standardized test methods. Many such test methods have been documented by their respective user communities and published through ASTM

International [6]. We noted the most important properties of the renewable biocomposites from several researchers' investigations that are listed below.

(1) Mechanical properties, (2) thermal properties, (3) optical properties, (4) degradable properties, and (5) electrical properties.

2.1. Mechanical properties

Most of the plastic materials are used because they have desirable mechanical properties at an economical cost. For this reason, several polymers were used in numerous applications. Indeed, several research studies have focused on such materials to gain knowledge on mechanical behavior of numerous structural factors depending on polymers. Moreover, these mechanical properties of the materials depend on the applied load. For this reason, most of the materials can be predictable their service life for future needs. In addition, mechanical properties were also useful in identification and classification of materials for different applications. The considerable properties of mechanical tests are tensile strength, modulus, impact resistance, compression, hardness, and toughness. These properties also depend on the orientation of the reinforcements and atmospheric conditions.

Generally, the properties of biocomposites depend on a matrix, natural filler, and interfacing between them. For this reason, the stress transfers between the two components. The presence of hydroxyl groups in natural fillers exhibits poor interfacial bonding with the matrix. This result concludes that biocomposites exhibit poor mechanical properties. This effect could be reduced by introducing a suitable compatibilizing agent. The effect of different compatibilizing agents on mechanical properties of natural flour filled [bamboo flour (BF) and wood flour (WF)] with biodegradable polymers [poly(lactic acid) (PLA) and poly(butylene succinate) (PBS)]. The maleic anhydride (MA) grafted biopolymers significantly improved the tensile strength of PBS-BF, PBS-WF, and PLA-BF and PLA-WF composites compared to the untreated biopolymers. This tensile strength can be improved by 25–35 MPa [7].

A novel biodegradable hybrid biocomposite system developed with the reinforcement of kenaf fiber (KF) and corn husk flour and investigated the role of the aspect ratio of natural fibers against their tensile properties. **Figure 1** shows the influence of the aspect ratio reinforcement on mechanical properties before and after passing through the extrusion process. The difference between theoretical and experimental values of the tensile modulus was not significant and the aspect ratio determined after extrusion did not influence the predicted values [8].

The use of petroleum-based polymers in composites creates serious environmental problems; it is necessary to replace it with green composites. Baek et al. [9] developed the green composites using coffee ground (CG) and bamboo flour (BF) as a reinforcement to poly(lactic acid) (PLA) and investigated mechanical, thermal, optical properties. Because of the tensile and flexural properties, BF/PLA and CG/PLA composites decrease with addition of CG and BF fillers, but pure PLA showed a tensile strength of 60.1 MPa and the tensile strength of BF/PLA and CG/PLA composites is decreased from 48 to 27 MPa. The addition of a coupling agent

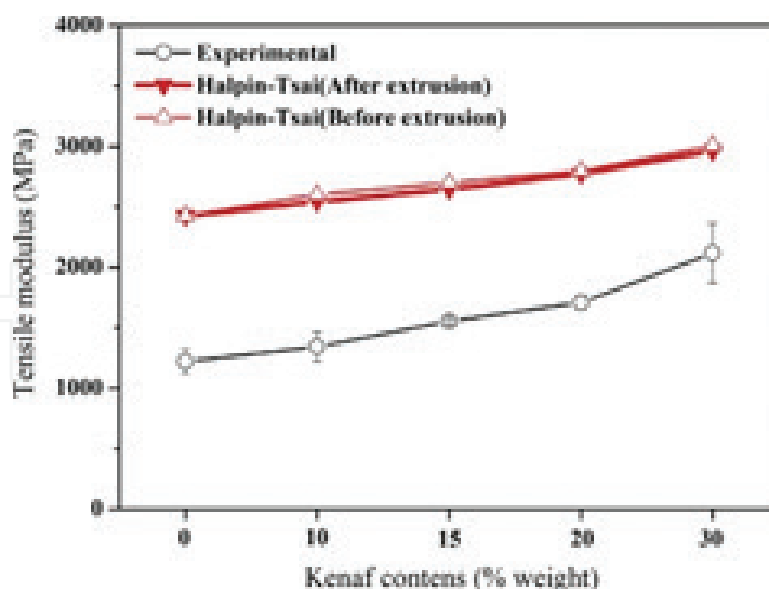


Figure 1. Comparisons of the predicted tensile modulus before and after extrusion.

improved the interfacial adhesion between the filler and PLA, and the tensile strength of the composites increases with increasing 4, 40-methylene diphenyl diisocyanate (MDI), as shown in **Figure 2**.

The similar results obtained in flexural strength of these composites. Without the coupling agent in composites, the flexural strength varies from 98 to 28 MPa, and it is low when compared with pure PLA. With the addition of the coupling agent, the flexural strength might be increased with the increase of MDI, which is shown in **Figure 3** [9].

A similar result was obtained by Kim et al. [10] for cassava and pineapple flour-filled PLA biocomposites. The tensile and flexural strength of the PLA biocomposites decreased with the increasing amount of flour. However, a 3% loading of the compatibilizer in the PLA biocomposite increased the strength up to that observed with the 10% loading flour [10]. To generate the sustainable biocomposites, Sukyai et al. [11] developed the biocomposites with the reinforcement of kenaf fiber (KF) and bacterial cellulose (BC) using the PLA matrix. In particular, BC is nanocellulose, which was anticipated to increase the interfacial area and therefore low volume fractions of additives. That was consequently to attain mechanical property improvement. The elastic modulus of the composites increased concurrently with the increasing KF content. Remarkably, the incorporation of 1 wt% of BC to 60/39 wt% of PLA/KF significantly improved the tensile and flexural strength, which indicates that the BC makes good compatibility between PLA and KF [11]. The tropical crop residues such as particular starch containing bioflours were used for producing biocomposites and the feasibility and industrial potential of using biocomposites were investigated. Polypropylene (PP) and poly(butylene succinate) (PBS) were compounded with bioflours from pineapple skin (P) and from nondestarched (CS) and destarched (C) cassava root by twin-screw extrusion. The impact on mechanical properties observed when the proportion of bioflour was increased to 40% w/w, it reduced the tensile strength by 26–48% and impact strength by 14–40%. However, the different flexural

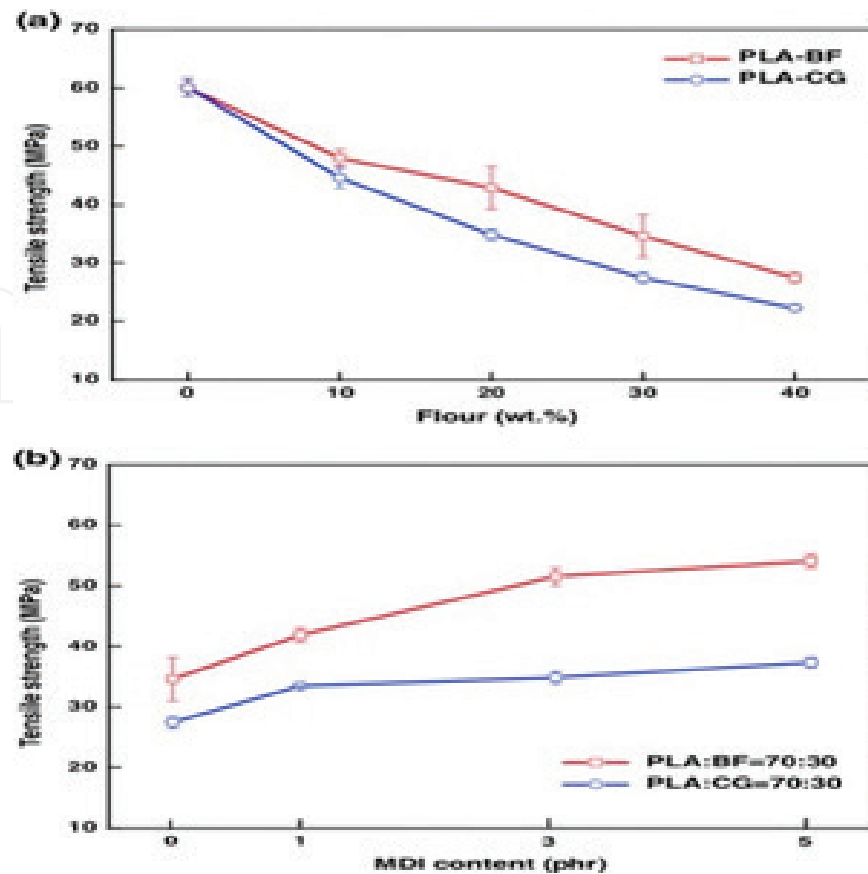


Figure 2. Tensile strength of the green composites with (a) natural fillers (bamboo flour and coffee grounds) and (b) MDI.

strength appeared upon the addition of bioflours; it increased initially but then decreased at higher loads. This effect was also studied by using a compatibilizer of maleic anhydride polypropylene (MAPP), it enhances the flexural strength compared to pure PP, and this resultant material becomes stronger and less flexible [12]. A similar effect was observed while adding 3-glycidoxypolytrimethoxysilane (GPS) as a coupling agent in the PLA/kenaf fiber biocomposites. The flexural strength and flexural modulus of the composites increased with increasing the content of GPS, while compared with pure PLA. This coupling agent significantly increases the interfacial strength between resin and fibers [13]. There are many value-added composite products obtained from the raw materials of biomass and it consist most promising beneficial resources, for example rice straw, rice husk, and paper sludge are the by-products and industrial waste and are beneficial resources as raw biomass. Kim et al. [14] investigated mechanical properties by adding rice straw, rice husk, and paper sludge to wood composites to replace wood particles for manufacturing green pallets using urea-formaldehyde (UF) resin. The obtained mechanical properties of the composites showed the decrement, upon increasing the contents of rice straw and rice husk flours. The presence of wax and silicate creates less interfacial bonding with UF resin. Moreover, the mechanical properties of wood-paper sludge composites are similar to wood particles so it was replaced with paper sludge [14]. Yang et al. [15] studied the effect of compatibilizing agents on rice-husk flour-reinforced polypropylene (PP) composites. The mechanical properties of these composites were studied

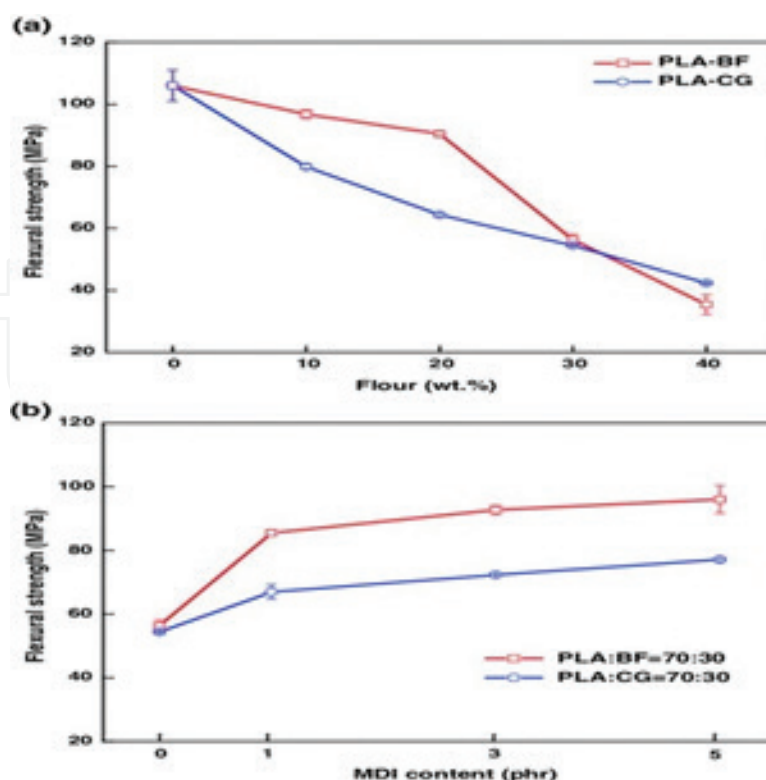


Figure 3. Flexural strength of the green composites with (a) natural fillers (bamboo flour and coffee grounds) and (b) MDI.

at different filler loadings, temperatures, and crosshead speeds. The obtained results indicated that tensile strength of the composites decreased with increasing filler contents in the absence of compatibilizing agent, whereas in the presence of compatibilizing agents, these mechanical properties were significantly increased [15]. Another report showed that the bio-flour-filled [rice husk flour (RHF), wood flour (WF)] maleic anhydride grafted polypropylene (MAPP) composites have good mechanical properties compared with pure polypropylene (PP) composites. The enhancement of mechanical properties was strongly dependent on the amount of MA graft (%) and the MAPP molecular weight, which is shown in **Figure 4** [16].

The most interesting study proved the manufacturing effect on mechanical properties of lignocellulosic material-filled polypropylene biocomposites. The obtained results of tensile strength and modulus of the biocomposites significantly improved with a fabricated twin-screw extruding system compared with a single-screw extruding system [17]. The mechanical properties of the biodegradable polymers and PBS-WF, PBS-BF biocomposites were analyzed with increasing hydrolysis time at 50°C and 90% relative humidity (RH). The resultant properties of these polymers and biocomposites show decrement with the increasing hydrolysis time, due to the easy hydrolytic degradation of the ester linkage of the biodegradable polymers. However, when the antihydrolysis agent trimethylolpropane triacrylate (TMPTA) was treated with PBS, tensile strength was significantly increased with the increasing hydrolysis time as compared to the nontreated PBS. The same results were observed for the PBS-based biocomposites [18]. The addition of paper sludge to thermoplastic polymer composites significantly improved the tensile properties with increasing mixing ratios, and tensile strength

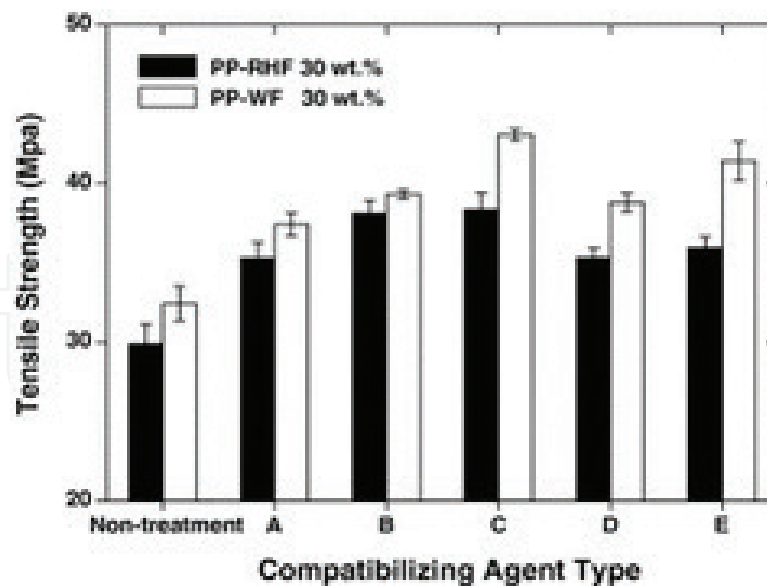


Figure 4. Tensile strength of RHF- and WF-filled PP composites as a function of different MAPP types. A, Polybond 3150; B, Polybond 3200; C, G-3003; D, E-43; E, Bondyram 1004.

vary from 230 to 280 MPa. Moreover, tensile modulus improved with the increasing paper sludge content. On the other hand, flexural properties showed a similar trend as tensile properties [19]. A similar effect was observed in the tensile strength properties of lignocellulosic filler-reinforced polyethylene biocomposites [20].

2.2. Thermal properties

Fiber-reinforced polymer composites are often used as structural components that are exposed to extremely high or low heats. These applications include the following:

- a. Automotive engine components
- b. Aerospace and military products
- c. Electronic and circuit board components
- d. Oil and gas equipment, etc.

In this section, we explore the thermal properties of different natural fiber-reinforced biocomposites.

Lee et al. [21] studied the polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films. In this study, the thermal stability of the composites is described by thermogravimetric analysis (TGA). The spectacular effect indicated that the pure bacterial cellulose has good thermal stability compared with combination of bacterial cellulose and polyaniline composites. The weight loss occurred in two stages for composites. First stage was obtained at 200°C, due to the combination result of bacterial cellulose and the side chain or impurities of polyaniline. The obtained result at this stage indicates the change in macromolecule of cellulose in smaller one. For these reasons, the weight

reduction pertains at low temperatures. On the other hand, due to thermaloxidative degradation of the main polyaniline chain, it establishes the second stage of weight loss at around 300°C [21]. In most of the automotive, military, aerospace applications, thermal expansion and coefficient of thermal expansion (CTE) are determined by thermomechanical analysis (TMA). Kim et al. observed this effect on natural flour-filled biodegradable polymer composites. The TMA method for determining CTE is useful for understanding the dimensional changes of biocomposite materials as well as the thermal stresses caused by increasing temperature. The effect of porous, inorganic filler treated and nontreated PBS-WF biocomposites as a function of inorganic filler type reveals that the slight decrement of thermal expansion and CTE value of PBS-WF hybrid composites was observed with the addition of 3 wt% porous inorganic filler in the biocomposites. This indicates the prevention of thermal expansion at high temperature due to the addition of lower thermal expansion porous inorganic fillers in the biocomposites. A similar effect was also observed in CTE by Kim et al. [22]. Pineapple skin (P) bioflour, nondestarched, and destarched (C) cassava root bioflours were used for the preparation of polypropylene (PP) and poly(butylene succinate) (PBS) biocomposites. TGA analysis reveals that the thermal stability of the composites decreased, as compared with pure PP and PBS materials, due to the lower degradation temperature of the bioflours (261–351°C). Differential scanning calorimetry (DSC) analysis indicated that bioflours improved nucleation and crystallinity [12]. The compatibilizing effect was also considered for improving the interface between the matrix and filler. This can also affect the thermal properties of the final product. Yang et al. [15] observed the thermal analysis of lignocellulosic material-filled PP biocomposites. With the increasing filler content, there was no change in glass transition temperature (T_g) and melting temperature (T_m) of the biocomposites. This indicates that there is no interface between the matrix and natural filler. However, there was significant change found when the compatibilizing agent was introduced between the matrix and natural filler. The storage modulus of the biocomposite increases with the increasing filler (RHF, WF) content and it is higher than neat PP [23]. The similar effect was also observed with addition of the compatibilizing agent, which is shown in **Figure 5**.

For the fabrication of thermosetting polycardanol biocomposite, the surface was treated with jute fibers using GPS and 3-aminopropyltriethoxy silane (APS). The fiber treatment with GPS and APS were improved the interfacial adhesion between jute fibers and polycardanol resin, compared with untreated jute fiber. This result indicates that the thermal stability and thermomechanical stability also improved [24]. The influence of a zeolite type on thermal properties of natural flour-filled PP composites revealed that the addition of the zeolite content to the PP-RHF and PP-WF composites had peculiar behavior on thermal stability. With the increasing content of natural and synthetic zeolite contents, the thermal stability and degradation temperature also increase. In the presence of 3 and 5% of natural and synthetic zeolite at PP-RHF and PP-WF composites, the thermal stability for 5% mass loss was in the range of 303–329°C and 322–331°C, respectively. However, the thermal stability and degradation temperature was not significantly changed with the increasing natural zeolite content. Interestingly, this property significantly improved in the presence of quartz and the formation of metal oxides in the pozzolan content on the PP and natural flour surface. These results suggest that the addition of inorganic porous materials to reinforcing fillers enhanced the thermal

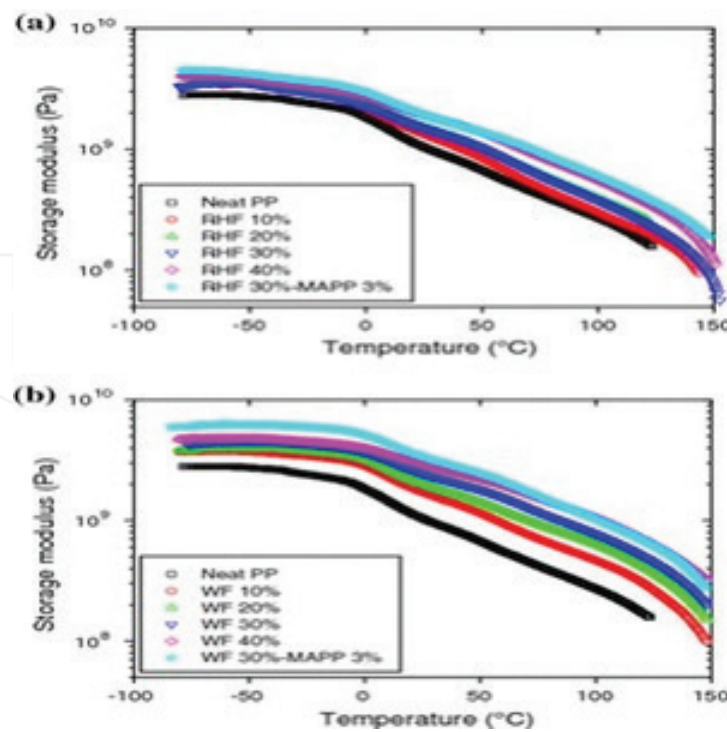


Figure 5. Storage modulus of biocomposites from -80 to 100°C as a function of temperature. (a) RHF filled biocomposite; (b) WF filled biocomposite.

stability of the hybrid composites [25]. In the same manner, the thermal stability and thermal expansion study was performed for bioflour-filled PP biocomposites with different pozzolan contents. With the increasing pozzolan content, at 5% mass loss the thermal stability of the biocomposite increased. On the other hand, the CTE and thermal expansion of the biocomposites decreased with the increasing pozzolan content. There is no significant change in glass transition temperature (T_g), melting temperature (T_m), and percentage of crystallinity (X_c) of the biocomposites. However, the enhancement of interfacial adhesion was observed in maleic anhydride-grafted PP (MAPP)-treated biocomposites, which showed higher thermal stability, thermal expansion, and X_c compared with nontreated biocomposites even at 1% pozzolan content [26]. Another study revealed the effect of the addition of two different compatibilizing agents on thermal properties, maleic anhydride (MA)-grafted polypropylene (MAPP) and MA-grafted polyethylene (MAPE) to bioflour-filled polypropylene (PP) and low-density polyethylene (LDPE) composites. With the increasing MAPP and MAPE content, the thermal stability, storage modulus (E'), $\tan \delta_{\max}$ peak temperature (glass transition temperature: T_g), crystallinity (X_c), and loss modulus (E''_{\max}) peak temperature (β relaxation) were slightly increased except melting temperature (T_m). The improvement in these properties encountered due to good interfacial adhesion between the bioflour and PP matrix in the presence of compatibilizing agent treatment [27]. It is well-known fact that the composite systems must have good thermal stability and thermal expansion properties, which affect the quality of the final products. For example, during the summer, dashboard is affected by the high temperature inside vehicle. On the other hand, the thermal stability of these composite systems is very important because these materials must withstand against heat during the fire. To study this

effect, Yang et al. [15] studied the effect of lignocellulosic filler on thermoplastic polyester polymer biocomposites. In TGA study, the thermal stability slightly decreased and the ash content increased with increasing the filler loading. This result revealed that there is no interfacial bonding between the filler and matrix. To improve the interface adhesion, a suitable compatibilizer was used for improving the thermal properties. In TMA analysis, the thermal analysis, the thermal expansion of the composites was found to decrease with increasing the filler and incorporating compatibilizing agent. This result elucidates that the thermal expansion of the composite materials was prevented by using the lignocellulosic filler under different atmospheric conditions. These results are shown in **Figures 6 and 7** [28].

Another study on thermal properties of rice husk flour (RHF)-filled polypropylene (PP) and high-density polyethylene (HDPE) composites revealed that the thermal stability of PP and HDPE was higher than RHF. Moreover, with the increasing RHF content, the thermal stability decreases and the ash content increases. On the other hand, the activation energy of the RHF-filled PP composites increased slowly in the initial stage and thereafter remained almost constant, whereas that of the RHF-filled HDPE composites decreased between 30 and 40 mass% of RHF contents. This is due to the interfacial adhesion and dispersion of RHF in the PP and HDPE matrix [29].

2.3. Biodegradation properties

In this modern society, petroleum-based synthetic polymers are widely used for many applications, such as polyolefin in packaging, bottle, and molding products. Globally, the annual disposal of petrochemical plastics reached nearly 150 million tons, which creates serious environment problems, especially with the continuously increasing production and consumption

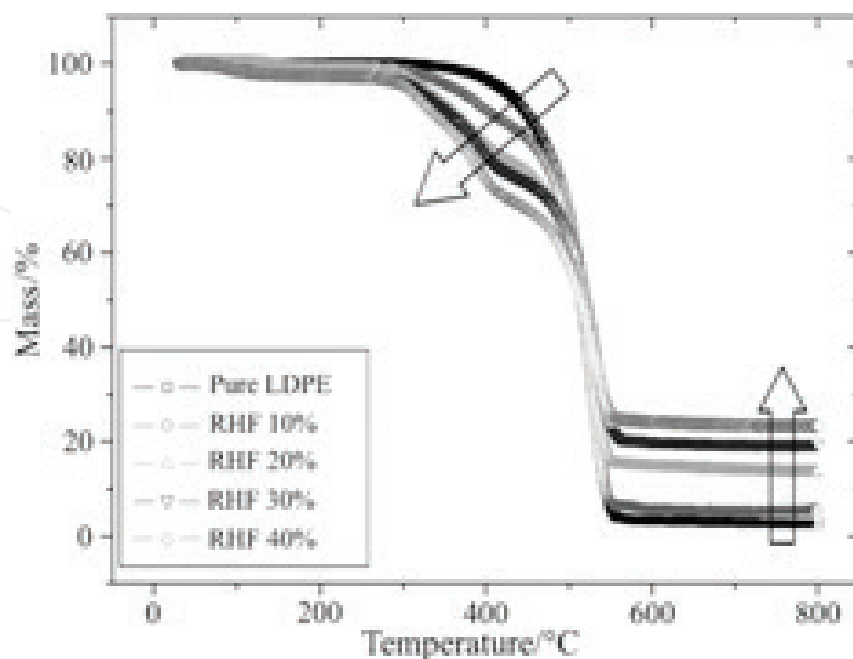


Figure 6. TG curves of RHF-filled LDPE composites at a heating rate of $40^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere.

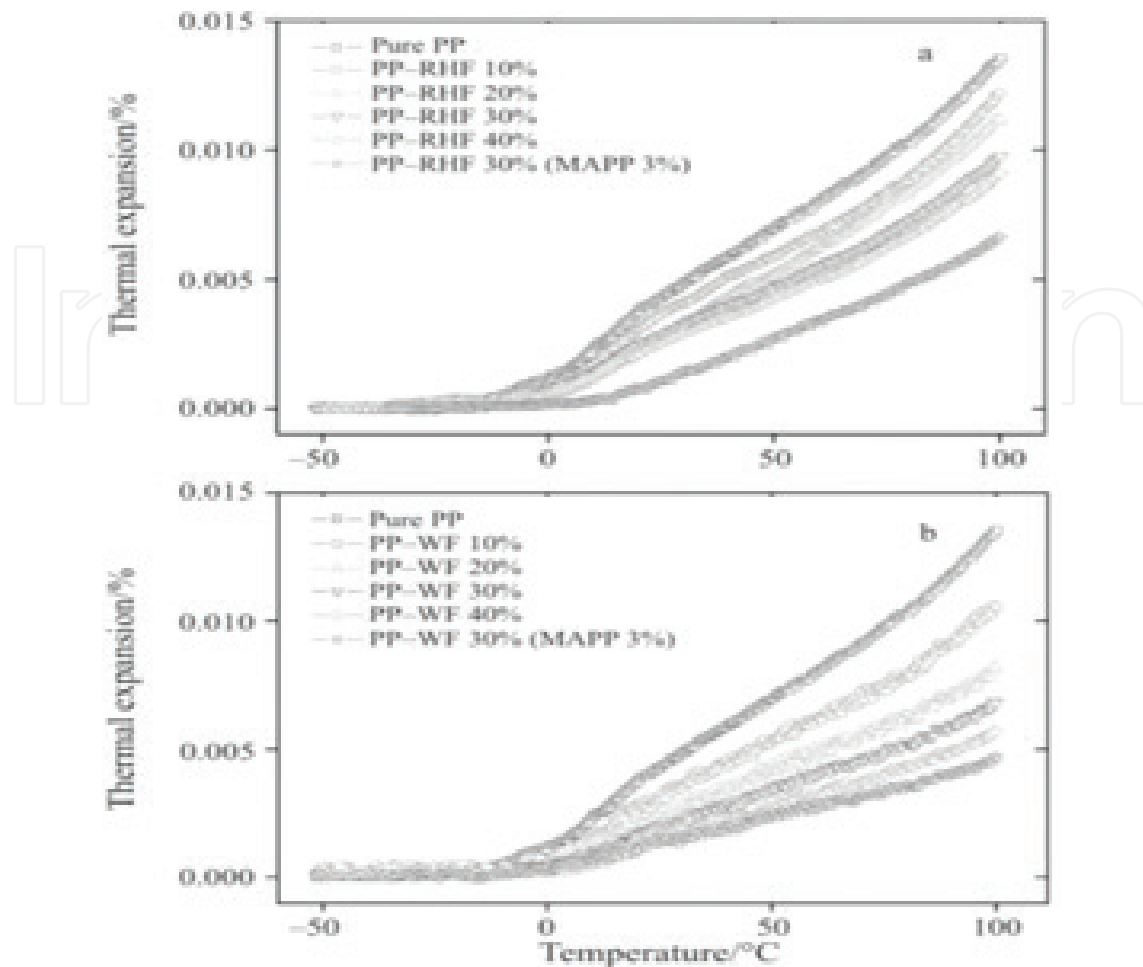


Figure 7. Thermal expansion of the RHF-PP and WF-PP composites: (a) RHF-PP composites, (b) WF-PP composites.

of these materials. Moreover, these plastic wastes capable of resistance of microbial attack, this caused undesired pollutant in soil, rivers and marine. Nowadays eco-friendly biodegradable polymers receive great attention in order to replace the consumption of petroleum-based plastic materials. These biodegradable polymer materials have potential to complete degradation into natural ecosystems such as active sludge, natural soil, lake, and marine. On the other hand, these eco-friendly polymers are capable chemical transformation by the action of biological enzymes or microorganisms. Several researchers are reported that the biodegradability of the biocomposites was most important factor for many composites.

Kim et al. [30] investigated the biodegradability of PBS and bioflour, which is a poly(butylene succinate) (PBS) biocomposite filled with rice-husk flour (RHF) reinforcing in natural and aerobic compost soil. This result indicated the percentage of weight loss of HDPE, PBS, and biocomposites, which is shown in **Figure 8**. The percentage weight loss of biocomposites decreased rapidly with increasing the RHF content. This indicates that the cellulosic materials were easily attacked by microorganisms and enhanced by the degradation capability of the composites compared with PBS and HDPE matrix. On the other hand, the significant comparison identified the percentage weight loss of the biocomposites in a natural and compost

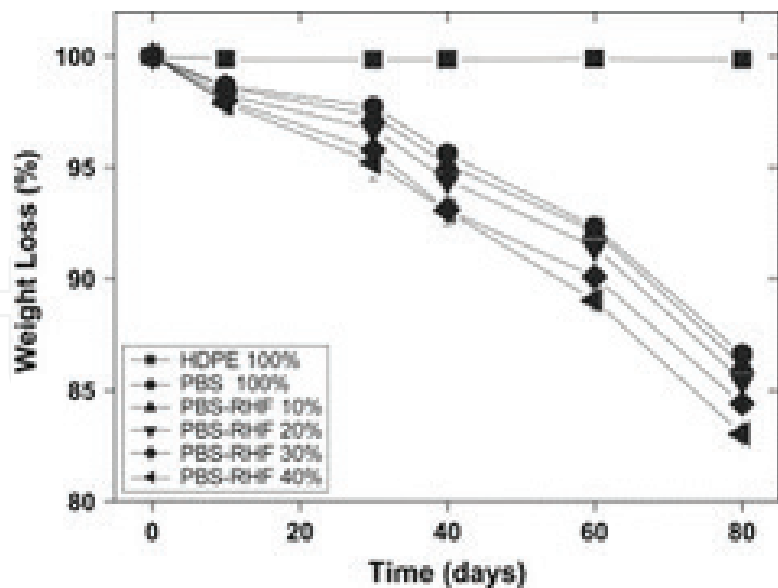


Figure 8. Percentage weight loss of HDPE, PBS, and biocomposites for 80 days.

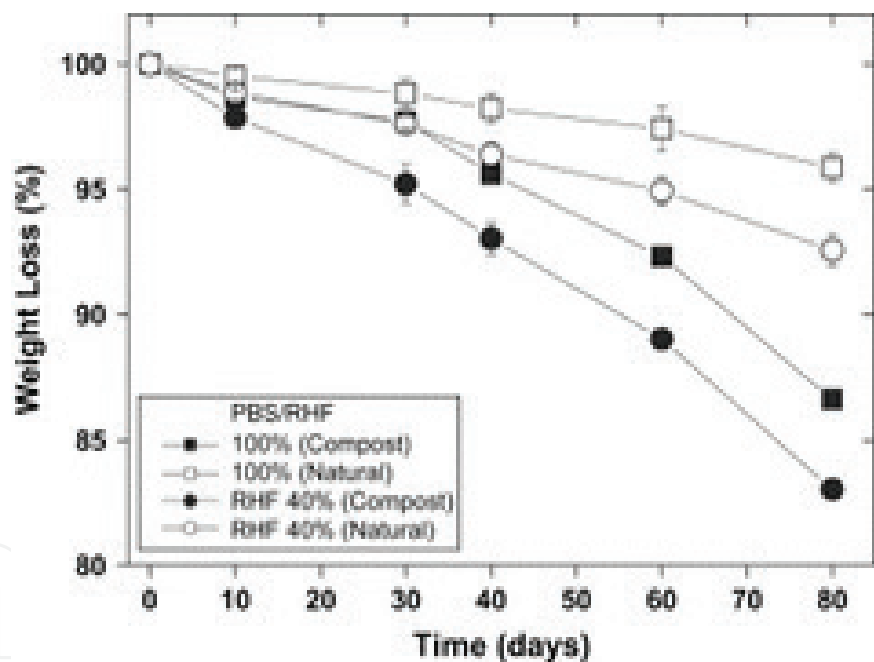


Figure 9. Comparison of the percentage weight loss of PBS and biocomposites at 40 wt% filler loading in natural and compost soil.

soil environment with 40 wt% filler loading. Herein, the faster degradation rate was identified in a compost soil burial test compared with a natural soil burial test over 80 days. Due to the composting environment in the chamber, the enhanced biodegradation rate of biocomposites is shown in **Figure 9** [30].

A similar study investigated the biodegradability of agro-filled PBS biocomposites and their weight loss percentage. Biodegradation generally caused by microorganisms involves

hydrolytic depolymerization of cellulose materials to lower molecular weight compounds, yielding monomeric glucose units. In addition, major deterioration of cellulose and wood-based lignocellulosic materials is caused by microorganisms. **Figure 10** shows the effect of filler particle size on weight loss of the agro-flour-filled PBS biocomposites at 40 wt% filler loading. The significant effect of size variation of filler particle size on weight loss can be seen. Generally, the smaller particle size possesses a higher surface area that makes better contact with the PBS matrix, this indeed the weight loss of the larger particle size (80–100 mesh) filled-PBS biocomposites was slightly greater than that of the smaller particle size (200 mesh) filled PBS biocomposites.

Iovino et al. [31] investigated the biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions. The composite formed by reinforced thermoplastic starch (TPS) and short natural fiber (coir) with poly(lactic acid) (PLA), with and without the incorporation of maleic anhydride (MA) as a coupling agent. The biodegradation test was carried on materials of TPS and matrix (containing 75% of PLA and 25% of TPS). The result of the incubation period reveals that the TPS matrix showed a higher level of biodegradation (higher amounts of evolved CO₂) than PLA, this might be arise due to attack of microorganisms on TPS. The fibers seemed to play a secondary role in the process as confirmed by the slight differences in carbon dioxide produced. The compatibilized composite revealed a lower percentage of evolved CO₂ than the uncompatibilized one [31]. Similarly, the degradation of sago-starch-filled linear low-density polyethylene (LLDPE) composites under a soil burial test was observed the presence of holes on samples due to microbial activity. Moreover, the loss in properties (tensile strength, elongation at break and weight loss) of the composites was identified. After 12 months of soil burial, the tensile strength and elongation at break of the composites decreased. Weight loss of the composites changed from 0.6% during the first month to 2% in the 12 month [32]. Pradhan et al. [33] studied the compostability and

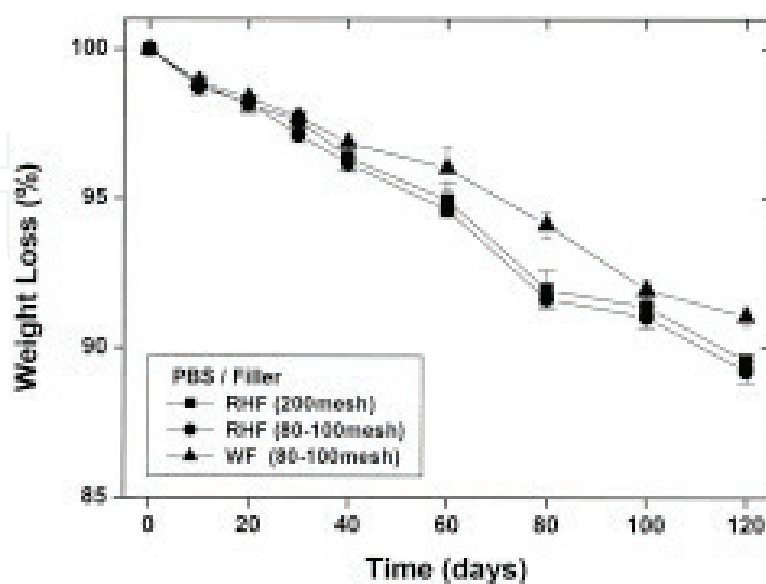


Figure 10. Comparison of the percentage weight loss of agro-flour-filled PBS biocomposites in natural soil at 40 wt% filler loading.

biodegradability of PLA-wheat straw and PLA-soy straw-based green composites. The result of this study elucidates that under aerobic composting the soy and wheat straw degraded rapidly over 70% within 45 days. The similar result obtained in the process of composites degradation irrespective of the biomass used, this rate of degradation was higher than that of pure PLA. Indeed, the faster rate degradation in composites may be due to the presence of degradable natural biomass in composites and due to reduced average molecular weight of PLA [33]. Lu et al. observed the biodegradation behavior of PLA/distiller's dried grains with soluble (DDGS) composites. These materials consist of bio-based and strong potential for industrial applications. The composites were made by adding 20% DDGS to the 80% of PLA and biodegradation experiments were conducted in soil under landscape conditions. The result of this experiment shows that during 24 weeks of degradation time the weight loss of the composites was 10.5%, while the weight loss of pure PLA was only 0.1% during the same time interval. With increasing the degradation time, the surface cracks and voids caused by erosion and loss of polymer chain length were clearly observed as shown in **Figure 11** [34].

The untreated and treated with acetic anhydride-treated (AA-) abaca fibers were reinforced with aliphatic polyesters (poly (ϵ -caprolactone) (PCL), poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), PBS, and PLA). The biodegradability of obtained composites was studied by the soil-burial test. The result of the test reveals that the presence of abaca fiber or AA-abaca did not show any effect of weight loss on PCL composites, because PCL itself has a relatively high biodegradability. However, the addition of abaca fibers was shown to accelerate the weight loss of PBS and PHBV composites. Moreover, no weight loss was observed in pure PLA and PLA/AA-abaca composites, but PLA/untreated abaca composites showed 10% weight loss after 60 days due to degradation of fiber by microbial activity [35]. Yussuf et al. [36] investigated the biodegradability difference between PLA/kenaf fibers (KF) and PLA/rice husk flour (RHF) composites by natural soil burial test. The result of this test elucidates that the biodegradability of these composites slightly increased and reached 1.2 and 0.8% for PLA-KF and PLA-RHF, respectively, for a period of 90 days. Moreover, this percentage change in biodegradability of composites is higher as compared to pure PLA, because microorganisms are easily attacked in the presence of natural fibers [36]. Another study emphasized the effect

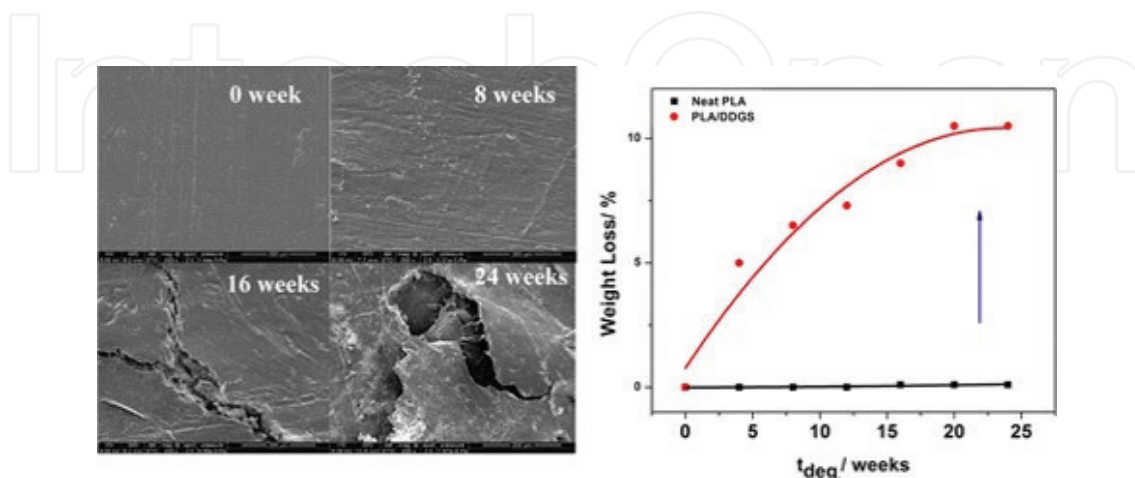


Figure 11. SEM micrographs of PLA/DDGS 80/20 composites after 0, 8, 16, and 24 weeks. Biodegradation time dependence of weight loss of pure PLA and PLA/DDGS (80/20) composites in soil medium [34].

of starch on biodegradability of PLA and poly (hydroxyester-ether) (PHEE) composite bars in soil for 1 year. Due to the fast attack of microorganisms on starch, the rates of weight loss increased in the order pure PLA (~0%/year) < starch/PLA (0–15%/year) < starch/PHEE/ PLA (4–50%/year) and increased with increasing starch and PHEE contents [37]. Alimuzzaman et al. [38] studied the biodegradability of nonwoven flax fiber-reinforced PLA biocomposites under soil burial test during 120 days. The obtained result of the test emphasized that the percentage of weight loss of the PLA, flax fibers, and biocomposites increases with increasing the soil burial time for all samples. The weight loss of PLA and flax fibers after 120 days is found to be 3.08 and 91.41%, respectively. This indicates that the flax fibers show more biodegradability than PLA. The similar result obtained in composites due to presence of flax fibers. Moreover, the weight loss also increases with increasing the content of flax fibers to the pure PLA. During the soil burial test, the presence of various microorganisms and water in the soil can attack flax composites easily. This induces the fiber degradation and resulted degradation of composites [38].

3. Applications of renewable biocomposites

Biocomposites materials, which were formed by a matrix (resin) with the reinforcement of natural fibers such as wood fibers (soft wood, hard wood, newspaper, and magazine fibers) and nonwood fibers (kenaf, flax, jute, hemp, coir, cotton, sisal, and pineapple). These composite materials exhibit ultimate mechanical, thermal, and biodegradable properties. Because of the presence of these superior properties, the composite materials have significant applications in various fields such as automobile, military, aerospace, naval, construction, and packaging.

3.1. Automobile applications

The usage of the biocomposite makes the car lighter, renders greater resistance to heat, external impact, and improves fuel capacity. This leads further to manufacture mid-end and low-end cars as well. The pioneering research on composites and large mass production techniques forced to decline the prices and increase demand for various applications including the automotive sector [39].

Akampunguza et al. [2] reviewed the application of biocomposites in the automotive industry. In this review, they identified future significance of biocomposites in the automotive industry through bioconcept cars. Though these seldom make it to the market, they are useful to give an idea to the industry on the possibilities of particular materials and designs. In 2001, Toyota Motor Corporation brought eco-friendly model an ES3 concept car made with polyester reinforced with hemp fibers composite parts such as carpets, lightweight seats, body panels, and other interior parts exhibited to give awareness of this cleaner manufacturing process. With this inspiration and response in 2003, they bring another model Toyota Raum, which had its interior parts made by using hemp fibers and its springboard was made from potato-derived PLA reinforced with sugarcane bagasse. In 2008, at British Motor Show in London, U.K.-based Lotus car displayed lotus Eco Elise green technology with aimed at making the use of eco-friendly materials and a cleaner manufacturing process in accordance to achieve

weight and carbon miles reduction with the features of components made from bioplastic and biofibers such as sweet potatoes and sugarcane. Renault has been developing a series of bioconcept cars for the racetrack with the first generation introduced in 2006. Volkswagen Scirocco a bioconcept car was configured as a racing car. Several parts of the car body such as the rear hatch, the driver's door, and the front lid have been produced by eco-friendly materials by compression molding. In March 2014, at 84th Geneva International Motor Show, UPM Company displayed biofore concept car with the collaborated Helsinki University of Applied Sciences. The improved manufacturing methods and brilliant technology drive the car's weight reduction by more than 15%. The researchers believed that the biofore car would be the role model for the advance development in manufacturing and technology of actual car making [2]. Four Motors GmbH of Reutlingen, Germany, was presented with the composites in the third generation of bioconcept cars in 2015, which has an extremely efficient TDI engine and travels with a novel, low-pollutant biodiesel based on rapeseed oil. The lightweight body is made from a reinforced natural fiber thermoset, and other components in the interior and the engine compartments are made from bio-based plastics [40].

3.2. Marine applications

Several researchers discovered that the biocomposites have potential marine applications due to their good mechanical properties and biodegradability. Due to these properties, the biocomposites become an alternative to the synthetic fiber-reinforced composites. Le et al. [41] conducted the experiment on seawater aging of flax/PLA biocomposites. The obtained result of this experiment describes that under seawater aging mechanism the absorption of water determined the degradation of hydrolysis of the matrix, structural change, degradation of the fiber/matrix interface, different swelling at composite interfaces and the degradation of fibers reduced the mechanical properties of the composites. However, the matrix and fiber cracks also appear at longer periods. This accomplishes that a special care is needed to integrate marine structures due to biodegradable nature of biocomposites. Indeed, with the eco-friendly impact of usage recyclable materials, now the extensive research is continuing in this area for optimizing lifetime, degradation control, and inherent losses of properties [41]. In the similar study, for the innovation in sailing yacht design must include the current environmental concerns such as depletion and waste management. This leads to incorporate natural fibers into the matrix to form eco-friendly composite materials for possible usage in marine applications. Moreover, they offer high specific stiffness and low environment footprint. The aging mechanism of flax/PLA biocomposites was observed under natural seawater for the period of 2 years. This study elucidates that biocomposites suffer from relatively high moisture absorption, which is controlled by the vegetal fibers [42]. There is necessity to control aging of biocomposites in a seawater environment of both natural fiber and matrix. The extra coating layer of the similar biopolymer on biocomposite may enhance the reduction of weight gain by the interface of the fiber and matrix. The mechanical and thermal properties of the biocomposites after immersion show that the protective layers reduce hydrolysis of the matrix, retain the composite properties, and enhance their durability [43]. DuPont™ specially made marine composite with Kevlar, which is useful to provide an ideal balance of strength, stiffness, and lightweight properties for many marine applications. This enhances the higher

speeds in patrol and service boats that can be achieved by increasing engine power. These composites made with Kevlar be lighter yet tougher, damage tolerant and perform better under hydrodynamic fatigue loading [44]. Davies [45] studied the environmental degradation of composites for marine structures and reported that the use of composites in highly loaded marine components, such as tidal turbine blades or composite propellers, is increasing and requires a detailed understanding of coupling between stress and seawater. A very few experimental data available rather than the theoretical framework, and the time being process for conducting couple of experiments and require specific test equipment. This is an area where further work is urgently required [45].

4. Conclusions

We conclude that renewable biocomposites play a vital role in manufacturing many of the interior and exterior part of automobile, marine, sound absorbing wooden construction materials, and consumer applications. Indeed, several researchers reported that the reinforcement of natural fibers with biopolymers shows good mechanical, thermal, and biodegradable properties. Moreover, the enhancement of these properties was found with the incorporation of a compatibilizing agent. Nevertheless, the renewable biocomposites made from bacteria cellulose, rice straw, rice husk, natural fiber, lignocellulose, cellulose, and paper sludge renewable resources possess many beneficial properties compared to other inorganic fillers. The biocomposites are best alternatives and eco-friendly compared with petroleum-based composites.

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References

- [1] Ramamoorthy SK, Skrifvars M, Persson A. A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers. *Polymer Reviews*. 2015 Jan 2;55(1):107–62. DOI: 10.1080/15583724.2014.971124
- [2] Akampumuza O, Wambua P, Ahmed A, Li W, Qin X. Review of the applications of biocomposites in the automotive industry. *Polymer Composites*. 2016 Feb 1. DOI 10.1002/pc.23847
- [3] Misra M, Nagarajan V, Reddy J, Mohanty AK. Bioplastics and green composites from renewable resources: where we are and future directions. 18th International

Conference on Composite Materials, The Korean Society of Composite Materials, Korea. 21–26 Aug 2011.

- [4] Faruk O, Bledzki AK, Fink HP, Sain M. Biocomposites reinforced with natural fibers: 2000–2010. *Progress in Polymer Science*. 2012 Nov 30;37(11):1552–96.
- [5] Mohanty AK, Misra M, Drzal LT. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *Journal of Polymers and the Environment*. 2002 Apr 1;10(1–2):19–26.
- [6] https://en.wikipedia.org/wiki/List_of_materials_properties
- [7] Kim HS, Lee BH, Lee S, Kim HJ, Dorgan JR. Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites. *Journal of Thermal Analysis and Calorimetry*. 2010 Nov 11;104(1):331–8.
- [8] Kwon HJ, Sunthornvarabhas J, Park JW, Lee JH, Kim HJ, Piyachomkwan K, Sriroth K, Cho D. Tensile properties of kenaf fiber and corn husk flour reinforced poly(lactic acid) hybrid bio-composites: role of aspect ratio of natural fibers. *Composites Part B: Engineering*. 2014 Jan 31;56:232–7.
- [9] Baek BS, Park JW, Lee BH, Kim HJ. Development and application of green composites: using coffee ground and bamboo flour. *Journal of Polymers and the Environment*. 2013 Sep 1;21(3):702–9.
- [10] Kim KW, Lee BH, Kim HJ, Sriroth K, Dorgan JR. Thermal and mechanical properties of cassava and pineapple flours-filled PLA bio-composites. *Journal of thermal analysis and calorimetry*. 2011 Feb 13;108(3):1131–9.
- [11] P. Sukyai, K. R. Sriroth, B. H. Lee, J. K. Hyun, “The Effect of Bacterial Cellulose on the Mechanical and Thermal Expansion Properties of Kenaf/Poly(lactic Acid) Composites”, *Applied Mechanics and Materials*, Vols. 117–119, pp. 1343–1351, 2012.
- [12] Tran T, Lee BH, Yang HS, Chotineeranat S, Sriroth K, Kim HJ. Use of starch granules melting to control the properties of bio-flour filled polypropylene and poly(butylene succinate) composites: mechanical properties. *Starch-Stärke*. 2011 Oct 1;63(10):637–48.
- [13] Lee BH, Kim HS, Lee S, Kim HJ, Dorgan JR. Bio-composites of kenaf fibers in polylactide: role of improved interfacial adhesion in the carding process. *Composites Science and Technology*. 2009 Dec 31;69(15):2573–9.
- [14] Kim S, Kim HJ, Park JC. Application of recycled paper sludge and biomass materials in manufacture of green composite pallet. *Resources, Conservation and Recycling*. 2009 Oct 31;53(12):674–9.
- [15] Yang HS, Kim HJ, Park HJ, Lee BJ, Hwang TS. Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites. *Composite Structures*. 2007 Jan 31;77(1):45–55.
- [16] Kim HS, Lee BH, Choi SW, Kim S, Kim HJ. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled

- polypropylene composites. *Composites Part A: Applied Science and Manufacturing*. 2007 Jun 30;38(6):1473–82.
- [17] Yang HS, Wolcott MP, Kim HS, Kim S, Kim HJ. Properties of lignocellulosic material filled polypropylene bio-composites made with different manufacturing processes. *Polymer Testing*. 2006 Aug 31;25(5):668–76.
- [18] Yang HS, Wolcott MP, Kim HS, Kim S, Kim HJ. Effect of different compatibilizing agents on the mechanical properties of lignocellulosic material filled polyethylene bio-composites. *Composite Structures*. 2007 Jul 31;79(3):369–75.
- [19] Son J, Yang HS, Kim HJ. Physico-mechanical properties of paper sludge-thermoplastic polymer composites. *Journal of Thermoplastic Composite Materials*. 2004 Nov 1;17(6):509–22.
- [20] Kim HS, Kim HJ. Enhanced hydrolysis resistance of biodegradable polymers and bio-composites. *Polymer Degradation and Stability*. 2008 Aug 31;93(8):1544–53.
- [21] Lee BH, Kim HJ, Yang HS. Polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films. *Current Applied Physics*. 2012 Jan 31;12(1):75–80.
- [22] Kim HS, Lee BH, Kim HJ, Yang HS. Mechanical–thermal properties and VOC emissions of natural-flour-filled biodegradable polymer hybrid bio-composites. *Journal of Polymers and the Environment*. 2011 Sep 1;19(3):628–36.
- [23] Yang HS, Gardner DJ, Kim HJ. Viscoelastic and thermal analysis of lignocellulosic material filled polypropylene bio-composites. *Journal of thermal analysis and calorimetry*. 2009 Nov 1;98(2):553–8.
- [24] Zhou Q, Cho D, Song BK, Kim HJ. Novel jute/polycardanol biocomposites: effect of fiber surface treatment on their properties. *Composite Interfaces*. 2009 Jan 1;16(7–9):781–95.
- [25] Kim HS, Kim HJ. Influence of the zeolite type on the mechanical–thermal properties and volatile organic compound emissions of natural-flour-filled polypropylene hybrid composites. *Journal of Applied Polymer Science*. 2008 Dec 5;110(5):3247–55.
- [26] Kim HS, Choi SW, Lee BH, Kim S, Kim HJ, Cho CW, Cho D. Thermal properties of bio flour-filled polypropylene bio-composites with different pozzolan contents. *Journal of Thermal Analysis and Calorimetry*. 2007 Sep 1;89(3):821–7.
- [27] Kim HS, Kim S, Kim HJ, Yang HS. Thermal properties of bio-flour-filled polyolefin composites with different compatibilizing agent type and content. *Thermochimica Acta*. 2006 Dec 1;451(1):181–8.
- [28] Yang HS, Wolcott MP, Kim HS, Kim HJ. Thermal properties of lignocellulosic filler-thermoplastic polymer bio-composites. *Journal of Thermal Analysis and Calorimetry*. 2005 Sep 1;82(1):157–60.
- [29] Kim HS, Yang HS, Kim HJ, Park HJ. Thermogravimetric analysis of rice husk flour filled thermoplastic polymer composites. *Journal of Thermal Analysis and Calorimetry*. 2004 May 1;76(2):395–404.

- [30] Kim HS, Kim HJ, Lee JW, Choi IG. Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil. *Polymer Degradation and Stability*. 2006 May 31;91(5):1117–27.
- [31] Iovino R, Zullo R, Rao MA, Cassar L, Gianfreda L. Biodegradation of poly (lactic acid)/starch/coir biocomposites under controlled composting conditions. *Polymer Degradation and Stability*. 2008 Jan 31;93(1):147–57.
- [32] Danjaji ID, Nawang R, Ishiaku US, Ismail H, Ishak ZM. Degradation studies and moisture uptake of sago-starch-filled linear low-density polyethylene composites. *Polymer Testing*. 2002 Dec 31;21(1):75–81.
- [33] Pradhan R, Misra M, Erickson L, Mohanty A. Compostability and biodegradation study of PLA–wheat straw and PLA–soy straw based green composites in simulated composting bioreactor. *Bioresource Technology*. 2010 Nov 30;101(21):8489–91.
- [34] Lu H, Madbouly SA, Schrader JA, Srinivasan G, McCabe KG, Grewell D, Kessler MR, Graves WR. Biodegradation behavior of poly(lactic acid)(PLA)/distiller's dried grains with solubles (DDGS) composites. *ACS Sustainable Chemistry & Engineering*. 2014 Oct 23;2(12):2699–706.
- [35] Teramoto N, Urata K, Ozawa K, Shibata M. Biodegradation of aliphatic polyester composites reinforced by abaca fiber. *Polymer Degradation and Stability*. 2004 Dec 31;86(3):401–9.
- [36] Yussuf AA, Massoumi I, Hassan A. Comparison of polylactic acid/kenaf and polylactic acid/rice husk composites: the influence of the natural fibers on the mechanical, thermal and biodegradability properties. *Journal of Polymers and the Environment*. 2010 Sep 1;18(3):422–9.
- [37] Shogren RL, Doane WM, Garlotta D, Lawton JW, Willett JL. Biodegradation of starch/poly(lactic acid)/poly (hydroxyester-ether) composite bars in soil. *Polymer Degradation and Stability*. 2003 Mar 31;79(3):405–11.
- [38] Alimuzzaman S, Gong RH, Akonda M. Biodegradability of nonwoven flax fiber reinforced polylactic acid biocomposites. *Polymer Composites*. 2014 Nov 1;35(11):2094–102.
- [39] <http://www.marketsandmarkets.com/Market-Reports/automotive-composite-market-10869121.html>
- [40] http://www.fourmotors.com/2_bioconcept-cars/0_scirocco/
- [41] Le Duigou A, Davies P, Baley C. Seawater ageing of flax/poly(lactic acid) biocomposites. *Polymer Degradation and Stability*. 2009 Jul 31;94(7):1151–62.
- [42] Le Duigou A, Bourmaud A, Davies P, Baley C. Long term immersion in natural seawater of Flax/PLA biocomposite. *Ocean Engineering*. 2014 Nov 1;90:140–8.

- [43] Le Duigou A, Deux JM, Davies P, Baley C. Protection of flax/PLLA biocomposites from seawater ageing by external layers of PLLA. *International Journal of Polymer Science*. 2011 Sep 21;2011:140-148.
- [44] <http://www.dupont.com/products-and-services/fabrics-fibers-nonwovens/fibers/uses-and-applications/composites.html>
- [45] Davies P. Environmental degradation of composites for marine structures: new materials and new applications. *Philosophical Transactions of the Royal Society A*. 2016 Jul 13;374(2071):20150272.

