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# Polyethylene/Polyhydroxyalkanoates-based Biocomposites and Bionanocomposites

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## Abstract

The development of advanced polymer composite materials having superior mechanical properties has opened up new horizons in the field of science and engineering. Polyethylene (PE) is considered one of the most widely used thermoplastics in the world due to its excellent properties which have excellent chemical inertness, low coefficient of friction, toughness, near-zero moisture absorption, ease of processing and electrical properties. Polyhydroxyalkanoates (PHAs) are garnering increasing attention in the biodegradable polymer market because of their promising properties such as high biodegradability in different environments. This chapter covers polyethylene/polyhydroxyalkanoates-based biocomposites and bionanocomposites. It summarizes many of the recent research accomplishments in the area of PE/PHAs-based biocomposites and bionanocomposites such as state-of-the-art regarding different methods of their preparation. Also discussed are different characterization techniques and use of PE/PHAs-based biocomposites and bionanocomposites in biomedical, packaging, structural, military, coating, fire retardant, aerospace and optical applications, along with recycling and lifetime studies.

**Keywords:** Polyethylene, polyhydroxyalkanoates, biocomposites, bionanocomposites, melt blending, milling, Brabender mixing, characterization

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## 6.1 Introduction

The recent use of renewable resources for the production of polymer-based materials has attracted growing attention, both in academia and industry, as a result of the increasing demand of environmentally friendly materials and their important economic point of view [1]. These environmentally friendly polymers can undergo biological degradation in soil, compost, sewage, and marine environments, which circumvents waste accumulation. Biodegradation is an essential part of the process of environmental breakdown of polymer substrates into organic waste [2]. The versatility of plastic materials in terms of mechanical properties and durability has been manipulated by mankind to enhance quality of life without realizing they have become increasingly ubiquitous [3]. The most extensively studied thermoplastic biopolymers are the polyhydroxyalkanoates (PHA) and polyethylene (PE). A variety of resins (e.g., starch, proteins, etc.) and fibers (e.g., flax, ramie, kenaf, jute, etc.) has been used to fabricate biocomposites for many applications. In many cases, only one component of the composites, either the fibers or the resin, has been biodegradable [4].

The growing awareness of environmental and waste management issues, including fossil resources and rising oil prices, are some of the major reasons why bioproducts are increasingly being promoted for sustainable development. This chapter presents a broad review on different preparations and characterizations of PE/PHAs-based biocomposites and bionanocomposites. Recent advances in the research, development and various applications of polyethylene/polyhydroxyalkanoates-based biocomposites and bionanocomposites are discussed. Recycling and lifetime studies on PE/PHAs-based biocomposites and bionanocomposites are also discussed.

## 6.2 Polyethylene/Polyhydroxyalkanoates-Based Biocomposites and Bionanocomposites

Biopolymers or organic plastics are a form of plastics derived from renewable biomass sources, such as vegetable oil, starch, proteins, etc., unlike fossil fuel plastics which are derived from petroleum [5]. They provide the advantages of conservation of fossil resources and reduction in CO<sub>2</sub> emissions; these advantages make them an important innovation for sustainable development. Recently, biobased PE or polyethylene terephthalate (PET) has been a widely available biopolymer. An important

member of the family of polyolefin resins, PE or PET is a light, versatile synthetic resin made from the polymerization of ethylene. On the other hand, PHAs are biogenic polyesters that can be naturally accumulated in microbial cultures. Among this latter category, obtained via so-called biorefineries, *algae* serve as an excellent pathway for plastic production owing to their numerous advantages such as high yield and the ability to grow in a range of environments [5]. PHA further represents a family of biodegradable polymers produced from renewable resources and they are ideal candidates to replace petroleum-based plastics, with multiple applications in surgical sutures, tissue engineering scaffolds [6–8], meshes and implants [9, 10] and controlled drug [11]. PHAs are a group of linear biobased polyesters produced in nature by the fermentation of sugars or lipids by bacteria that utilize the polymer for carbon and energy storage in their cells [12].

Composites can be defined as those materials that contain two or more distinct constituent phases, on a scale larger than the atomic. The term “biocomposites” refers to those composites that can be employed in bio-engineering. They can be considered as composites that present natural reinforcements (like vegetable fibers) in their composition. They can be classified as (i) partial biodegradable with non-biodegradable polymer matrices such as thermoplastic polymers (e.g., polypropylene (PP), polyethylene (PE)) and thermoset polymers (e.g., epoxy, polyester); or (ii) fully biodegradable with biodegradable polymer matrices such as renewable biopolymer matrices (e.g., soy plastic, starch plastic, cellulosic plastic) and petro-based biodegradable polymer matrices (e.g., aliphatic co-polyester, polyester amides) [13]. Biocomposites are divided into non-wood fibers (wheat, kenaf, jute, sisal, flax and hemp) and wood fibers (hardwood and softwood), all of which have cellulose and lignin. The natural fibers which are the non-wood fibers are more attractive for the industry due to the physical and mechanical properties which they present. Also, these fibers are relatively long fibers, and present high cellulose content, which delivers a high tensile strength and degree of cellulose crystallinity. Biocomposites usually mimic the structures of the living materials involved in the process, together with the strengthening properties of the matrix that was used, but still providing biocompatibility, e.g., in creating scaffolds in bone tissue engineering. The degree of biodegradability in biobased polymers depends on their structure and their environmental service.

Bionanocomposites offer an opportunity for the use of new high performance, light weight green nanocomposite materials in order to replace conventional non-biodegradable petroleum-based plastic materials. There is growing interest in developing biobased polymers and innovative process

technologies for different applications. Polymer nanocomposites are materials with many more improved properties than the constituent polymers. The nanoscale dispersion of the filler in the polymer matrix leads to the generation of a tremendous amount of interfacial contacts between the organic and inorganic components.

Polymer-clay nanocomposites have recently received significant attention as an alternative to conventional filled polymers. Polymer-clay nanocomposites are a class of hybrid materials composed of organic polymer materials and nanoscale clay fillers. The polymer-clay nanocomposites exhibit large-scale improvements in mechanical and physical properties compared with pure polymer or conventional composites due to their nanometer size dispersion [4]. These include increased modulus and strength, decreased gas permeability, increased solvent and heat resistance and decreased flammability [14]. Research has indicated that organo-clays show much promise for starch-based polymer nanocomposites in terms of improvement in their mechanical properties and stability over those of the unfilled formulations [15].

## 6.2.1 Preparation

### 6.2.1.1 *Milling Processes*

Mechanical milling is considered a process whereby solid powders are generated, reduced in size and mixed together to produce alloys at the molecular level. Mechanical alloying is a solid-state powder processing technique involving repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill [16]. Mechanical milling and mechanical alloying are techniques originally developed in the late 1960s for solid-state processing of metals. Mechanical alloying is widely used in the metals industry for producing composite metal powders with fine microstructures [17, 18]. The application of these techniques was extended to blending polymers and producing coatings; the terminology was borrowed from the metals industry with a different meaning. In the case of polymers and ceramics, the new meaning simply implies an improved dispersion of phases or the creation of a uniform coating without the formation of a new phase.

Ball mills consisting of a vial, balls and a motor, are used in the mechanical alloying process. There are different ball mill configurations, but the most important parts common to all configurations are the vial and balls. During mechanical alloying, powders are placed in the vial with two or more metallic or ceramic balls. The mill's motor vigorously shakes the

vial, resulting in high energy impacts between the balls and the material. These impacts trap material between the balls, or a ball and the vial wall, with each agitation. As milling occurs, the particles are repeatedly fractured, deformed, and fused together. This process of repeated fracturing and cold-welding causes a refinement in microstructure with milling time. The result is a two-phase lamellar microstructure with an interlamellar distance dependent on total milling energy [17, 19–21]. There are two types of ball milling process: cryogenic ball milling and carbon dioxide-assisted ball milling.

#### 6.2.1.1.1 Cryogenic Ball Milling

Cryogenic ball milling is a mechanical alloying process in which the high energy impact conditions in a ball mill pulverize the mixed plastics into a powder. A SPEX 8000 Mixer/Mill manufactured by SPEX CertiPrep and SamplePrep incorporated for the mechanical alloying was used by Smith *et al.* [22, 23]. The equipment is a high energy shaker mill capable of mixing up to 10 mL of material per batch. Milling was performed to incorporate two rubbery polymers, polyisoprene (PI) and polyethylene-alt-propylene (PEP), into a commodity thermoplastic, polymethyl methacrylate (PMMA), which are known to be immiscible. They found that blend was formed with acceptable mechanical properties [22]. It took nearly 10 h to pulverize the mixed polymer to a size of 2 mm. The process was carried out at cryogenic temperatures by means of liquid nitrogen [22, 23]. Impact tests on PI/MI/PMMA 22/6/72 blends were reported to show an improvement in the impact strength.

#### 6.2.1.1.2 Carbon Dioxide-Assisted Ball Milling

A mechanical alloying was performed in order to reprocess mixed polymer waste of unspecified composition by means of a high-energy ball milling process in a liquid carbon dioxide medium [24]. The process was found effective to pulverize polymer particles or shredded polymer films in a very short milling time, promoting a substantial size reduction and mechanochemical modification on the material, resulting in good mechanical properties of the blend. The process claimed to compatibilize polymeric mixtures, regardless of the chemical composition. The process was reported effective to co-pulverize polymer particles in a very short milling time (10 min compared to 10 h in the previous case), while compatibilizing the immiscible polymers involved in the mixed polymer waste [25]. The punch strength was reported to improve with the milling process.

Polyethylene/carbon nanotube nanocomposite has been produced using mechanical milling method [26]. A high energy ball mill with 70 mm

diameter and steel balls with different diameters were employed. The medium-density polyethylene (MDPE) and multi-walled carbon nanotube (MWCNT) at constant weight ratio of ball/powders (i.e., 10) were added to the ball mill and milled 10 h. In order to clarify the role of both MWCNT content and milling time on the morphology of MDPE some ball-milled nanocomposite samples were investigated using scanning electron microscopy (LEO 1450 VP). To evaluate the role of milling time on the microstructure of produced nanocomposites, a very thin film of MDPE/MWCNTs was prepared and studied by transmission electron microscopy (LEO 912 AB). Results on the microscopic structure of the MDPE/CNTs nanocomposite materials produced by mechanical milling method showed that the milling process can be a simple method for producing MDPE/MWCNTs nanocomposite and addition of carbon nanotube to MDPE resulted in a change in its morphology at constant milling parameters [26]. Using the milling process, Dika nutshell powder (DNS) filled-recycled PP/PET biocomposite was prepared by reactive compatibilization using maleic anhydride-grafted-polypropylene (MAPP) and epoxy resin (EPR) as dual compatibilizers. The mechanical and rheological properties, together with sorption behavior of the compatibilized biocomposites, were studied at filler loadings of 0, 2, 4, 6, 8, and 10 phr (parts per hundred parts of resin). The PP/PET composition was fixed at 30/70 wt%. The results showed that when MAPP alone was used as compatibilizer, property improvements were not substantial due to the low reactivity between MAPP and PET, which produces an insignificant amount of copolymers as coupling agent at the interfaces. Effective compatibilization was achieved by adding EPR, as suggested by impressive improvement in the properties investigated. Outstanding property improvements, especially oil resistance, tensile and impact strengths (higher values), and elongation at break (lower value) were obtained with increases in EPR and filler loadings [27].

The environmental performance of PHA, from agricultural production through the PHA fermentation and recovery process—"cradle to gate"—was estimated by Kim and Dale [28]. Two types of PHA production systems were investigated: corn grain-based PHA and corn stover-based PHA. The environmental burdens associated with the corn wet milling process, in which dextrose, corn oil, corn gluten meal and corn gluten feed are produced, are allocated to dextrose and its co-products by the system expansion approach. Greenhouse gases include carbon taken up by soil, nitrous oxide ( $N_2O$ ) released from soil during corn cultivation, carbon contents in biobased products, as well as carbon dioxide, methane and nitrous oxide released from industrial processing. The soil carbon and nitrogen dynamics in corn cultivation were predicted

by an agro-ecosystem model, the DAYCENT model. The environmental performance of the PHA production system was compared to that of a conventional polymer fulfilling an equivalent function. The environmental performance was addressed as non-renewable energy and selected potential environmental impacts, including global warming, photochemical smog, acidification, and eutrophication. The primary contributing process to most environmental impacts except for photochemical smog and eutrophication was the PHA fermentation and recovery process [28]. A biocomposite with ramie natural fibers was environmentally degraded using the milling process [29]. A biocomposite of the ramie fiber/cellulose nanofiber reinforced corn starch resin (R/C/S, 31/5/64 wt%) was used. Cellulose nanofibers used for the composite preparation were 1  $\mu\text{m}$  long and 20–30 nm in diameter and contained 100% cellulose. At first, an aqueous solution of cellulose nanofibers was thoroughly mixed for 5 h with liquid corn starch via ball mill mixing using ceramic balls. The biocomposite was developed by reinforcing with two layers of ramie fiber in corn starch resin. The cellulose nanofiber reinforced corn starch resin was inside the biocomposite. Hand lay-up method followed by compression molding was used for the composite preparation [29].

Production of PHAs in activated sludge treating wastewater represents an economical and environmental promising alternative to pure culture fermentations. A process for production of PHA from a paper mill wastewater was examined at laboratory scale by Bengtsson *et al.* [30]. The three-stage process examined consisted of acidogenic fermentation to convert wastewater organic matter to volatile fatty acids (VFAs), an activated sludge system operating under feast/famine conditions for enrichment of PHA producing organisms and accumulation of PHA in batch experiments. After fermentation of the wastewater, 74% of the soluble carbon oxygen demand (COD) was present as VFA (acetate, propionate, butyrate and valerate) and the resulting PHA after batch accumulation consisted of 31–47 mol% hydroxybutyrate and 53–69 mol% hydroxyvalerate. The maximum PHA content achieved was 48% of the sludge dry weight and the three-stage process exhibited a potential to produce 0.11 kg of PHA per kg of influent COD treated. A process for production of PHA by activated sludge for treating paper mill wastewater was further investigated by Bengtsson *et al.* [30]. The applied strategy was to select glycogen accumulating organisms (GAOs) by alternating anaerobic/aerobic conditions. Acidogenic fermentation was used as pretreatment to convert various organic compounds to volatile fatty acids, which are preferable substrates for PHA production. Enrichment resulted in a culture dominated by GAOs related to *Defluviicoccus vanus* (56%) and *Candidatus Competibacter*

*phosphatis* (22%). Optimization of PHA accumulation by the enriched GAO culture was performed through batch experiments. Accumulation of PHA under anaerobic conditions was limited by the intracellular glycogen stored. Under aerobic conditions significant glycogen production (to 25% of sludge dry weight) was observed alongside PHA accumulation (to 22% of sludge dry weight). By applying a subsequent anaerobic period after an initial aerobic, the produced glycogen could be utilized for further PHA accumulation and by this strategy PHA content was increased to 42% of sludge dry weight. The PHA yield over the entire process was 0.10 kg per kg of influent COD treated, which is similar to what has been achieved with a process applying the feast/famine enrichment strategy with the same wastewater.

#### 6.2.1.2 *Intermix and Brabender Mixing*

Intermix is a polymer mixer that uses intermeshing rotors. Brabender measuring mixers are interchangeable measuring heads which are used for determining thermoplastics, thermosets, elastomers, ceramic molding compounds pigments, fillers and more plastic and plastifying materials under praxis-oriented conditions. They are cost effective and reliable, with little expenditure of material and time. The measuring mixers consist of a mixer backstand with gear unit and a mixer bowl. They are connected to the drive unit through a shear pin coupling protecting both mixer and the drive unit from damage due to overload. The blades are made of special steel which are counter-rotation towards each other at different speeds in order to provide excellent compounding and mixing characteristics.

Different PE/PHAs blends have been developed in order to improve their performance. The blending of these polymers offers more scope to expand their range of applications. Tsui and Frank [31] investigated a small molecule nucleating agent, orotic acid (OA), in order to enhance crystallinity and crystallization kinetics in poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) for the purpose of addressing embrittlement and reducing solidification time after thermal processing. They prepared a blend of P(3HB)/PCL by melting the mixture in an internal mixer with compositions of PCL varying from 0 to 30 wt% to study the miscibility, morphology and physical-chemical properties of these systems. The effectiveness of monohydrated (OA-m) and anhydrous (OA-a) forms of OA as nucleating agents for isothermal and non-isothermal crystallization of PHBV films were also investigated and compared. Based on differential scanning calorimetry, both forms of OA were able to increase crystallization temperature of PHBV and also formed more uniform crystal structures. In addition,



the faster crystallization of (OA-a) led to fibrillar film morphology of the PHBV/OA blends. Barone and Schmidt [32] prepared PE-based composites by using keratin fibers obtained from chicken feathers. These fibers of similar diameter but varying aspect ratio were mixed into low-density polyethylene (LDPE) using a Brabender mixing head. From uniaxial tensile testing, an elastic modulus and yield stress increase of the composite over the virgin polymer was observed over a wide range of fiber loading. Not only is it imperative to use a fiber of higher modulus, but it is important to have good fiber/polymer interaction to obtain reinforcement from fibers. The keratin feather fibers can be directly incorporated into the polymer using standard thermomechanical mixing techniques. The density of the composite upon introduction of keratin feather fiber did not increase, but reduced by 2%.

Choi *et al.* [33] investigated the microstructure and thermal and mechanical properties of PHB/HV–organoclay nanocomposites prepared by melt intercalation using Cloisite 30B, a monotallow bis-hydroxyethyl ammonium-modified montmorillonite clay. Their study described the production of an intercalated PHBHV-clay nanocomposite using melt blending process in a Brabender mixer at 165 °C, 50 rpm agitation rate for 15 min. Similar melt extrusion was used by Maiti *et al.* [34] in order to produce a well-dispersed PHB/layered silicate nanocomposite. They prepared PHB/layered silicate nanocomposites via melt extrusion. The extent of intercalation depends on the amount of silicate and the nature of organic modifier present in the layered silicate. The biodegradability of pure PHB and its nanocomposites was studied at two different temperatures under controlled conditions in compost media. The rate of biodegradation of PHB was enhanced dramatically in the nanohybrids. The change in biodegradation was rationalized in terms of the crystallization behavior of the nanohybrids as compared to that of the neat polymer.

### 6.2.1.3 Melt Blending

Melt blending polymers is a much more economical and convenient methodology at the industrial scale rather than synthesizing new polymers to achieve the properties unattainable with existing polymers. However, most polymer pairs are immiscible and this can lead to phase-separated materials. Synthesizing new polymers often has three inherent problems if the morphology and the interfaces of the blend are not well-controlled: (1) poor dispersion of one polymer phase in the other one; (2) weak interfacial adhesion between the two phases; and (3) instability of immiscible polymer blends [35]. Melt blending is one of the common methods used

for the preparation of PE/PHAs-based biocomposites and bionanocomposites [36–40]. The composites prepared by melt blending are essentially free of contamination that results from residual monomer or solvent. Furthermore, solvent casting or melt mixing method of composite fabrication enabled the formation of intercalated morphology, where melt blending results in submicron aggregates [41].

Sanchez-Garcia *et al.* [42] presented novel PET nanocomposites with enhanced barrier properties to oxygen, water, and limonene based on a new specifically developed food-contact-complying highly swollen montmorillonite grade. They compared the thermal and barrier properties of organically modified kaolinite and organically modified montmorillonite (OMMT) in PHB-based nanocomposites prepared by melt blending with polycaprolactones (PCL) added as a plasticizer. The result was a nonmiscible but compatible interphase blend. It was found that the nanocomposites exhibited increased gas, aroma and water vapor barrier performance. Furthermore, the examination of the scanning electron micrographs taken in criofractured cross-section specimens of the samples revealed that a homogeneous distribution of the clays in the PET matrix and good interfacial adhesion must have been achieved for 5 wt% clay contents, since no filler agglomerates and/or phase discontinuity can be discerned in the reinforced sample by this technique. The oxygen permeability coefficient was derived from oxygen transmission rate (OTR) measurements. They observed in the OTR curves at 0% relative humidity (RH) of the PET +5% nanoter sample and of the neat PET that the equilibrium transmission rate was higher in the unfilled blend than in the nanocomposite, indicating that a lower permeability was clearly reached in the nanocomposite systems, and that the diffusion was clearly faster in the unfilled blend [42].

Gui *et al.* [43] successfully toughened poly(lactide) (PLA) by melt blending with poly(ethylene glycol-co-citric acid) (PEGCA). During thermal processing, the addition of PEGCA delayed the melting of PLA and lowered the viscosities of the blends. The PLA/PEGCA blends exhibited a phase-separated morphology. The spherical or elliptical PEGCA phase was dispersed in the continuous PLA phase. The sizes of the dispersed phase increased with increased PEGCA content. The glass transition temperature of PLA decreased with the addition of PEGCA. The crystallization behaviors of PLA and PEGCA in their blends were influenced by each other. Ductility and toughness of PLA were significantly improved by the presence of PEGCA. The hydrophilicity of PLA was also greatly improved by PEGCA. Biosourced and biodegradable poly(ethylene oxide-b-amide-12) (PEBA) was used as a toughening agent for PLA via melt compounding [44]. PLA/PEBA blends are an immiscible system with a two-phase

morphology. By increasing the content of PEBA, the binary blends displayed a marked improvement in toughness. The possibility of using kenaf cellulose (KC) was investigated in the production of LDPE/KC/polyethylene glycol (PEG) biocomposites by Tajeddin *et al.* [45]. They carried out melt blending of LDPE and KC in order to evaluate effects of varying the concentrations of KC and PEG on the synthesis process. Their results showed that the mechanical properties of the biocomposites decreased slightly as the KC content was increased from 0 to 50 wt% in the biocomposite formulation; again, there was a good homogeneity between samples with added PEG. The addition of KC improved the thermal resistance of these biocomposites; PEG also had a positive role in the thermal behavior of the composites.

#### 6.2.1.4 Extrusion

Extruders are a fundamental part of any extrusion (e.g., for producing pipes, profiles, blown and flat films, mono- and multifilaments, coated wire) and compounding line (e.g., for the incorporation of additives in general, polymer modification and polymer blending), and are also used in blow molding and injection molding machines, although in modified form [46]. Polymer is one of the commonly extruded materials, and its advantages include: the ability to handle high-viscosity polymers in the absence of solvents, large operational flexibility as a result of the broad range of processing conditions (0–500 atm and 70–500 °C), the feasibility of multiple-injection, and control of both residence time (distribution) and the degree of mixing [47]. Extrusion is the most widely used technology for green biocomposite; biopolymers reinforced with biofibers can generally be called green composites. The majority of biocomposites which are natural filler and thermoplastic mixture are manufactured through the extrusion process [48]. Biocomposite can be produced by means of extrusion molding, injection molding or compression molding technologies [49]. Extrusion of PE/PHAs-based biocomposite and bionanocomposite materials are generally linked with another processing step such as thermoforming, injection molding, fiber drawing, film blowing, bottle blowing or extrusion coating.

Flax fiber was mixed with high-density polyethylene (HDPE) with fiber content from 10 to 30% by mass and processed by extrusion and injection molding to biocomposites [50]. The mechanical properties, surface properties, and thermal properties of biocomposites were measured and analyzed to compare the effect of different flax fiber concentrations on the biocomposites. Results showed that increasing fiber content increased

the tensile and flexural strengths and modulus, increased water absorption, and decreased melt flow index, molding shrinkage and melting point of biocomposites. PHAs can be processed mainly via injection molding, extrusion and extrusion bubbles into films and hollow bodies [51]. Singh and Mohanty [52] prepared renewable resource-based green composites from wood fiber and a bacterial polyester, i.e., PHBV, via extrusion-injection molding process. The fabricated PHBV-based biocomposites contained 10–40 wt% of the maple wood fiber. The effects of increasing wood fiber weight contents on the mechanical, thermomechanical and morphological properties of the PHBV-based biocomposites were evaluated. The tensile and flexural modulus of PHBV-based biocomposites reinforced with 40 wt% of wood fiber was improved by ~167% when compared with neat PHBV [52]. The storage modulus values of the PHBV-based biocomposites also exhibited the increasing trend with the enrichment of wood fiber in PHBV matrix. The effectiveness of fibers on the storage modulus of the composite was evaluated by a coefficient factor,  $C$ . Singh *et al.* [53] prepared renewable resource-based green biocomposites using a bacterial polyester, i.e., PHBV, and natural bamboo fiber. Fabrication of the biocomposites was carried out by injection molding following extrusion compounding of PHBV and bamboo fiber with 30 or 40 wt% fiber. Little variation in the thermomechanical and impact properties was observed when the fiber content was varied. The tensile modulus of biocomposites at 40 wt% fiber improved by 175% as compared to that of neat PHBV and the storage modulus was affected slightly by the variation of fiber content from 30 to 40 wt% in biocomposites. However, notch impact strength of PHBV decreased with the fiber addition and the reduction was greater in the case of bamboo fiber biocomposites [54].

#### 6.2.1.5 Injection Molding

The term “injection molding” can be considered as an oversimplified description of a quite complicated process that is controllable within specified limits. Injection molding is a manufacturing process commonly used for the fabrication of plastic parts. It can be performed with different materials such as metals, elastomers, glasses, confections and, most commonly, thermosetting and thermoplastic polymers. Different kinds of products are manufactured using injection molding and they vary greatly in their size, complexity, and application. The process requires the use of an injection molding machine, raw plastic material, and a mold. The plastic is melted in the injection molding machine and then injected into the mold, where it cools and solidifies into the final part. Although most biocomposites

(natural filler and thermoplastic mixture) are produced by extrusion molding process, injection molding products now have marketing potential [48]. Some research has been done by extrusion forming and batch process microcellular forming in order to investigate the forming of biocomposites [55–61], but studies on the forming of injection-molded parts are few [62].

Injection molding is one of the most commercially important fabrication processes for molding a broad spectrum of thermoplastics [60]. Therefore, it is very important to investigate the formability of biocomposites through injection molding process, and to further characterize the properties of the formed material. Javadi *et al.* [63] prepared solid and microcellular components made of PHBV/poly(butylene adipate-*co*-terephthalate) (PBAT) blend (weight ratio of PHBV:PBAT = 30:70), recycled wood fiber (RWF), and nanoclay (NC) via a conventional and microcellular-injection molding process, respectively. The morphological, thermal, and mechanical properties were investigated. They found that the addition of 10% RWF (both untreated and silane-treated) generally increased the specific Young's modulus and tensile strength, but decreased the specific toughness and strain-at-break in both solid and microcellular components. In addition, higher specific toughness and strain-at-break was observed in the PHBV/PBAT/untreated-RWF composite compared with the PHBV/PBAT/silane-treated RWF composite, particularly in the microcellular components. The nanoclays exhibited an intercalated structure in the composites based on XRD analysis and did not induce significant changes in the cell morphology and mechanical properties of the PHBV/PBAT/silane-treated RWF composite. However, they did improve its thermal stability. The processability and the performance of a biodegradable polymer, Mater-Bi, and its blends with either a sample of PHAs or with bacterial biomass containing PHAs prepared by compression and injection molding were recently compared [64]. The addition of PHA or directly the biomass containing it, improved the processability of the matrix. The mechanical behavior of the systems was compared considering two different preparation methods. The injection-molded samples showed poorer mechanical performances than those of the compression-molded systems. The same behavior was observed in the injection-molded specimens and the compression-molded specimens but the absolute values of the injection-molded specimens were lower. This is likely due to a more intense degradation undergone by the matrix due to both the higher processing temperature and the higher mechanical stresses during the forming operation. The impact strength significantly improves when PHA is added, while it is reduced when bacterial biomass is used instead. In the latter case this is likely due to the easier propagation of microcracks during the impact tests.

This simply shows that the production of injection-molded parts is a complex process. Without the right combination of material, part, mold design and processing parameters, a multitude of manufacturing defects can occur, thus incurring high costs. The injection molding process itself is a complex mix of time, temperature and pressure variables with a multitude of manufacturing defects that can occur without the right combination of processing parameters and design components. Up till now, most production engineers and scientists have been using trial-and-error method to determine initial settings for a number of parameters, including melt temperature, injection pressure, injection velocity, injection time, packing pressure, packing time, cooling temperature, and cooling time, which depends on the engineer's experience and intuition to determine initial process parameter settings. However, the trial-and-error process is costly and time consuming [65]. Therefore, optimizing the process parameters for injection molding technology is very important. Optimization is the procedure that will make the molding system or design as functional as possible, especially when mathematical techniques are involved. Optimization of the molding parameters will help to improve the molding parameters and will have an effect on the warpage in injection molding. Warpage is one of the common effects on the molded parts after being taken out of the injection molding process. Optimization will help to predict the sensitivity of the warpage before the manufacturing process.

Hussin *et al.* [66] optimized the injection molding process parameters, such as injection speed, injection pressure, holding pressure, melting temperature, holding time, cooling time and runner size, using the Taguchi method. To improve the quality characteristic (shrinkage) of an injection-molded product, analysis of variance (ANOVA) was implemented in order to analyze and optimize the processing parameters such as mold temperature, melt temperature, packing time, packing pressure, and cooling time, cooling temperature, ambient temperature and runner size. An integrated, simulation-based optimization procedure that can be used to determine the optimal process conditions for injection molding without user intervention was presented by Zhou and Turng [67]. The idea was to use a non-linear statistical regression technique and design of computer experiments to establish an adaptive surrogate model with short turnaround time and adequate accuracy for substituting time-consuming computer simulations during system-level optimization. A special surrogate model based on the Gaussian process (GP) approach, which has not been employed previously for injection molding optimization, was introduced in their study. GP is capable of giving both a prediction and an estimate of the confidence (variance) for the prediction simultaneously, thus providing direction as to

where additional training samples could be added to improve the surrogate model. While the surrogate model is being established, a hybrid genetic algorithm was employed to evaluate the model in order to search for the global optimal solutions in a concurrent fashion. The examples presented in their study show that the proposed adaptive optimization procedure helps engineers determine the optimal process conditions more efficiently and effectively.

#### 6.2.1.6 In-Situ Polymerization

*In-situ* technique involves a chemical reaction that results in the formation of a very fine thermodynamically stable reinforcing phase within a matrix. *In-situ* polymerization process occurs when nanoparticles are dispersed in a liquid monomer or relatively low molecular weight precursor as well as in their solution; here the polymerization formed *in situ* results in nanocomposite. The process also occurs when a homogeneous mixture is formed, initiator is added and it is exposed to appropriate source of light or heat. *In-situ* polymerization simply means “in the polymerization mixture.” *In-situ* polymerization is based on direct composite preparation, via polymerization, using the catalytic system in the presence of the filler, in the present case in the presence of nanoparticles [68, 69]. In this type of polymerization, the dispersion of the inorganic particles in the polymer matrix is enhanced and the compatibility between the inorganic particles and the polymer is improved. Therefore, *in-situ* polymerization is perhaps considered the most promising technique to produce polymer nanocomposites [70] and many studies have been carried out on the production of PE nanocomposite via *in-situ* polymerization [71–76].

Some researchers have used methylaluminoxane (MAO) to form a supported cocatalyst during *in-situ* polymerization process. Leone *et al.* [73] obtained highly filled PE-based nanocomposites by *in-situ* polymerization technique. An organically modified montmorillonite, Cloisite 15A (C15A), was treated with MAO to form a supported cocatalyst (C15A/MAO) before being contacted with a zirconocene catalyst. The reaction of MAO with the clay replaces most of the organic surfactant within the clay galleries and destroys the typical crystallographic order of the nanoclay. The catalytic activity in the presence of C15A/MAO was higher than in ethylene polymerization without any inorganic filler and increases with MAO supportation time. This indicated that part of the polymer chains grew within the clay galleries, separated them, and made it possible to tune the final morphology of the composites. Zapata *et al.* [70] produced polyethylene nanocomposites containing silver

nanoparticles with antimicrobial properties via *in-situ* polymerization. The silver nanoparticles were added together with the catalytic system (metallocene catalyst and MAO, as cocatalyst) directly to the reactor. The polymerization activity did not present significant changes with the incorporation of the silver nanoparticles in comparison to the homopolymerization without filler. The effect of various silver nanoparticle contents on silver ion release and antimicrobial efficacy against *Escherichia coli* were studied. Nanocomposites containing higher nanosilver concentrations (5 wt%) showed the highest silver ion release, and after 24 h reached 99.99% of efficacy against the bacteria compared with the neat PE. From their results, they observed that the nanospheres were well dispersed throughout the PE matrix.

Oh *et al.* [79] recently prepared tungsten oxide ( $\text{WO}_3$ ) and HDPE composites prepared by the *in-situ* metallocene polymerization method which consisted of attaching a metallocene catalyst complex onto the surface of the nuclei ( $\text{WO}_3$ ), followed by surface-initiated polymerization. A kinetic equation was employed to analyze the nonisothermal crystallization characteristics of the composites. The Avrami exponent,  $n$ , determined from the nonisothermal crystallization kinetics analysis indicated random 3-dimensional morphology development for the  $\text{WO}_3$ /HDPE composites. The nonisothermal crystallization analysis of a HDPE and its  $\text{WO}_3$  nanocomposites provides the important information that the interaction between the polymer molecules and the heterogeneous nuclei surface decides the crystalline structures of these materials. Only few studies have been carried out on the production of PHAs nanocomposite via *in-situ* polymerization [80, 81]. The degree of dispersion of nanoparticles and nanoclay platelets into the polymer matrix determines the structure of nanocomposites. The reinforcing particles should be well dispersed in the host polymer matrix at a high level of loading, and be well bonded to the matrix phase to achieve maximum reinforcement [82, 83].

### 6.2.2 Characterizations

With the development of materials science and the industrial and practical needs of PE/PHAs-based biocomposites and bionanocomposites, rapid characterization techniques are of substantial importance. Many characterization techniques are used to investigate nanoscale structures at the morphological and/or molecular levels. This section provides key methods of characterization of the structural properties of PE/PHAs-based biocomposites and bionanocomposites, including tensile characterization, thermal characterization, morphological characterization, X-ray diffraction,



spectroscopic characterization, rheological characterization, among others. Many characterization techniques should ideally be linked to the desirable properties of PE/PHAs-based biocomposites and bionanocomposites such as strength, thermal stability, mechanical properties and structural properties.

### 6.2.2.1 *Tensile Characterizations*

Tensile characterization is a fundamental materials science test whereby a sample is subjected to a controlled tension until failure. The results from the test are commonly used to select a material quality control, an application and to predict how a material will react under different types of forces. Tension properties that can be used to predict the behavior of materials include the following: strength, ductility, elastic or plastic deformation, Young's modulus, Poisson's ratio, yield strength and strain-hardening characteristics. All these characteristics have resulted in improvements in the material's applications [84]. Many researchers have characterized PE/PHAs-based biocomposites and bionanocomposites using tensile characterizations [74, 77, 85–89].

Díez-Pascual and Díez-Vicente [89] recently investigated the dynamic mechanical study of PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles. A common reason for adding inorganic nanofillers to biopolymers is to increase the mechanical properties of the resultant composites. The room temperature static mechanical properties were evaluated by tensile tests, Young's modulus ( $E$ ), tensile strength ( $\sigma$ ), elongation at break ( $\epsilon_b$ ) and toughness ( $T$ ) derived from the stress-strain curves of the different composites. They observed that the neat PHB gave a Young's modulus of  $\sim 1.2$  Gpa. The addition of ZnO nanoparticles led to a gradual rise in  $E$ , showing a maximum augment of 43% at 10.0 wt%. The mechanical properties of polymer composites are affected by many factors, the most important of which are the state of dispersion of filler, the degree of crystallinity of the matrix and the filler-matrix interactions. Therefore, the strong  $E$  enhancement attained in these nanocomposites was attributed to the combination of fairly good nanoparticle dispersion, a strong interfacial adhesion between the phases through interactions via H-bonding and the increase in the crystallinity of PHB [89].

### 6.2.2.2 *Thermal Characterizations*

Thermal characterization is a branch of materials science where the properties of materials are studied as they change in temperature. It is a range of

advanced techniques for characterizing the thermal behavior of materials. It is an indispensable technique used for finding solutions to materials-related problems in both quality control and research. A workhorse for the characterization of polymeric materials is thermal analysis, especially differential scanning calorimetry. Changes in the structural and compositional parameters of the polymer material usually affect its melting transitions or glass transitions and these can be in turn linked to many performance parameters. It is an important technique for measuring crystallinity of semicrystalline polymer. There are different thermal analysis techniques; among them are thermogravimetric analysis, differential thermal analysis, thermochemical analysis, dynamic mechanical thermal analysis and dielectric thermal analysis etc. A lot has been done on thermal characterization of PE/PHAs-based biocomposites and bionanocomposites.

Trujillo *et al.* [90] investigated the thermal analysis of HDPE on carbon nanotube prepared by *in-situ* polymerization. Differential scanning calorimetry (DSC) results of their investigation showed that under both isothermal and dynamic crystallization conditions, the crystals produced within the nanocomposite HDPE matrix were more stable than those produced in neat HDPE or in physical blends prepared by melt mixing of HDPE and untreated CNT. The remarkable stability of the crystals was reflected in melting points up to 5 °C higher than neat HDPE and concomitant thicker lamellae. The thermal analysis of ultrahigh molecular weight polyethylene (UHMWPE) nanocomposites with various organoclay contents prepared by using the solution intercalation method was investigated by Shin *et al.* [91]. The melting transition temperatures ( $T_{ms}$ ) and ultimate strengths of the hybrids increase with increasing clay content; the maximum values of these properties were obtained for the hybrid containing 2 wt% of the organoclay. However, the thermal degradation stability and initial modulus are at their maximum values when the amount of organoclay in the hybrid is 1 wt%. Jin-hua *et al.* [92] studied the thermal analysis of linear low-density polyethylene (LLDPE) matrix incorporated by multi-walled carbon nanotubes (MWNTs) using screw extrusion and injection technique. They observed in their DSC result that  $T_m$  and  $T_c$  increased very slightly in the LLDPE/MWNTs nanocomposite compared with those in neat LLDPE, and increased with an increase of MWNTs concentration, which indicated that the MWNTs presence does not prevent LLDPE crystallization and melting, and acts as a nucleation reagent for the LLDPE crystallization; meanwhile, the crystallization enthalpy ( $\Delta H_c$ ) and melting enthalpy ( $\Delta H_m$ ), which are determined from the area under the exotherm and endotherm, are increased in the nanocomposites as compared with that of neat LLDPE. The incorporation of MWNTs enhances the

crystallization of LLDPE in the nanocomposites compared with that of neat LLDPE, which should be attributed to the strong heterogeneous nucleation of MWNTs. They further observed from their thermogravimetric analysis (TGA) result, that the decomposition temperature (onset of inflection) for neat LLDPE was lower than that of its nanocomposites, indicating that the thermal stability of nanocomposites had been improved because of addition of MWNTs. Besides that, the residual weight of LLDPE/MWNTs nanocomposites increases steadily with the increase of MWNTs loading. The weight loss at 432 °C for neat LLDPE was about 85%, whereas LLDPE/MWNTs nanocomposites are only around 58–72%. This also indicated that the thermal stability of LLDPE was significantly improved on incorporation of MWNTs [92].

Rajeshwari [93] recently carried out thermogravimetric analysis on inorganic nanoparticle filled HDPE nanocomposites at multiple heating rates (viz., 5, 15, 25 and 35 °C/min) under oxygen gas atmosphere to find the thermal stability, thermal resistance and thermal decomposition kinetic behavior of various concentrations (0–9.5 wt%) of AlN/HDPE composites. The TG-DTG thermograms of all compositions of inorganic nanoparticles (AlN) reinforced HDPE nanocomposites were at a heating rate of 150 °C/min. The initial decomposition temperature (IDT), which is sometimes used to know the thermal stability of materials, was considered when weight loss reaches 5%. At temperature at 15% weight loss ( $T_{15}$ ) and temperature at 25% weight loss ( $T_{25}$ ), it was observed that the incorporation of inorganic AlN nanoparticles into HDPE polymer matrix resulted in an increase of thermal resistance (IDT). This might be due to the good adhesion between AlN nanoparticles and HDPE polymer matrix obstructing the heat propagation and thereby decreasing the decomposition rate. The  $T_{max}$  (DTG peak temperature) shows that the thermal stability of the material has been revealed to improve with the increase in inorganic AlN nanoparticles content. High heat energy was essential for filled nanocomposites to attain the same proportion of weight loss as that required for neat HDPE polymer.  $T_{15}$  and  $T_{25}$  results have shown trends analogous to that of IDT and  $T_{max}$ .  $T_{15}$  and  $T_{25}$  decomposition of AlN/HDPE nanocomposites was found higher than that of neat HDPE. This can be attributed to the presence of inorganic nanoparticles, which have relatively higher thermal stability than pure HDPE. Carbonaceous char (CC) of AlN/HDPE nanocomposites at 550 °C was found to be ~ 0.471–26.739, and increases with increasing inorganic nanoparticles (AlN) loading. Syed *et al.* [94] reported that the increasing char yield is directly correlated to the strength of flame retardation. The average value of the oxidation index (OI) for the present composites lies between 0.033

and 1.861; this indicated that AlN/HDPE composites are thermally more stable than that of pristine HDPE.

One of the main drawbacks of PHB is its low thermal stability [89]. It is therefore very important to analyze the influence of nanoparticles on the thermal degradation of this biopolymer. In the investigation of Díez-Pascual and Díez-Vicente [89], the thermal properties of PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles were studied. The bare nanoparticles exhibited a very small weight loss ( $\sim 0.8$  wt%) below 300 °C, probably due to the removal of physically and chemically adsorbed water on their surface. Regarding the polymeric samples, neat PHB displayed a single degradation stage that started at  $\sim 290$  °C and showed the maximum rate at around 330 °C. The degradation occurred via random chain scission mechanism, producing shorter chain fragments with carboxylic terminal groups and with crotonic acid as one of the characteristic byproducts. Analogously, a one-step degradation process was observed for the nanocomposites, albeit shifted to higher temperatures, pointing out the thermal stabilization effect caused by the nanoparticles. Thus,  $T_i$  increases by 8, 21 and 24 °C upon addition of 2.0, 5.0, and 10.0 wt% ZnO, respectively. A similar trend was found for  $T_{10}$  and  $T_{max}$ , with increments by up to 34 and 42 °C, respectively, at the highest loading tested. Their results demonstrate that the incorporation of ZnO improved the heat resistance of PHB matrix, ascribed to the barrier effect of the nanoparticles that effectively hinder the transport of decomposition products from the bulk of the matrix to the gas phase. Besides, the high thermal conductivity of ZnO should facilitate heat dissipation within the composite, thus resulting in enhanced thermal stability [95]. Further, a gradual rise in the char residue (CR) was observed with increasing ZnO content, indicating that the thermal decomposition of the matrix was retarded in the nanocomposites. The nanoparticles acted as an insulator and mass transport barriers that obstructed the escape of volatile products generated during the degradation process.

Polyhydroxyalkanoates-based nanobiocomposites were prepared by melt intercalation [96] and the two main PHAs, poly(hydroxybutyrate) and poly(hydroxybutyrate-co-hydroxyvalerate), were studied by Bordes *et al.* [96]. Differential scanning calorimetry (DSC) measurements were carried out in order to study the influence of clays on the nonisothermal crystallization kinetics and the resulting crystallinity of both PHB and PHBV4. The characteristic temperatures were determined from DSC. It was observed that, in the case of the PHA/clay systems, the crystallization during cooling started earlier while the cold crystallization was considerably reduced, which suggested that the clay enhances the crystallization. Moreover, this

phenomenon was much more pronounced with the increasing polymer/clay affinity or filler content. This crystallization behavior can be attributed to the nucleating effect of clay, which is much more pronounced in the case of C30B. This was linked to the higher degree of C30B dispersion, compared to the non-modified montmorillonite (CNa) [96].

### 6.2.2.3 Morphological Characterizations

Morphological characterizations of polymeric materials are done by electron microscopy. Electron microscopy employs a source which is a set of lenses and an adjustment system to enlarge the image taken from a specimen. Electron microscopy uses electrostatic lenses to focus the electron beam and can achieve magnifications. Two main types of electron microscopy, known as transmission electron microscopy (TEM) and scanning electron microscopy (SEM), are used to characterize polymeric materials. Scanning electron microscopy measures low energy secondary electrons emitted from the specimen surface due to excitations in the specimen itself produced by the primary electron beam, while TEM uses transmission geometry and requires (microtomed) thin samples. Scanning electron microscopy can achieve magnifications an order of magnitude higher than TEM. Morphological characterizations of PE/PHAs-based biocomposites and bionanocomposites using TEM and SEM will be discussed in the following subsections.

#### 6.2.2.3.1 TEM Application for the Morphological Characterizations of Polyethylene/Polyhydroxyalkanoates-Based Biocomposites and Bionanocomposites

Trujillo *et al.* [90] also investigated the morphology of HDPE on carbon nanotube prepared by *in-situ* polymerization. The TEM results of their investigation also showed that under both isothermal and dynamic crystallization conditions, the crystals produced within the nanocomposite HDPE matrix were more stable than those produced in neat HDPE or in physical blends prepared by melt mixing of HDPE and untreated CNT. Their result shows that changes induced on HDPE by CNT are due to the way the nanocomposites were prepared; since the macromolecular chains grow from the surface of the nanotube where the metallocene catalyst has been deposited, this produces a remarkable nucleating effect and bottle brush morphology around the CNT. The morphological analysis of ultrahigh molecular weight polyethylene (UHMWPE) nanocomposites with various organoclay contents prepared by using the solution intercalation method was further investigated by Shin *et al.* [91]. Up to a clay loading of 4 wt%,

the clay particles were found to be highly dispersed in the UHMWPE matrix without any agglomeration of particles. However, for clay content above 6 wt% some agglomerated structures form in the polymer matrix.

The morphology of a novel biodegradable nanocomposite was fabricated based on PHBHHx and silane-modified kaolinite/silica core-shell nanoparticles (SMKS), via solution-casting method using chloroform as solvent was studied by Zhang *et al.* [97]. From their result, TEM images of the SMKs nanoparticles clearly show the distribution of silica on the surface of kaolinite particles. Specifically, a thin layer of silica about 10 nm and some silica spheres around 10 nm in diameter were introduced onto the surface of kaolinite compared to ORK. Transmission electron microscopy indicated that SMKs was finely distributed in the PHBHHx matrix compared with the other two kinds of fillers. Transmission electron microscopy image of ORK particles in the polymer showed large aggregated clusters that were several microns in diameter. Silane-modified kaolinite/silica core-shell nanoparticles particles were dispersed better in the polymer matrix but still aggregated into submicron-sized clusters. Silane-modified kaolinite/silica core-shell nanoparticles particles achieved the best dispersion compared to the other two kinds of fillers, as demonstrated by the TEM image of the presence of stacked hexagonal silicate layers, which were well dispersed in the PHBHHx matrix. Transmission electron microscopy images confirmed that SMKs nanoparticles were well dispersed in the PHBHHx matrix. Other investigations that have used TEM to characterize PE/PHAs based biocomposites and bionanocomposites are [69, 70, 74, 77, 87].

#### 6.2.2.3.2 Application of SEM for the Morphological Characterizations of PE/PHAs -Based Biocomposites and Bionanocomposites

Jin-hua *et al.* [92] further revealed the dispersion of MWNTs in the LLDPE matrix. Scanning electron microscopy observations performed for cryo-fractured surfaces of LLDPE/MWNTs nanocomposites showed that a fibrous fractured surface was observed due to the elongation at break of LLDPE/MWNTs nanocomposites. The random dispersed bright dots because of MWNTs high conductivity are the ends of the broken carbon nanotubes. In addition, it was found that some MWNTs are broken apart, and, as a result of poor interfacial adhesion, some MWNTs are pulled out of the matrix before the breakage, forming caves on the fractured surface; moreover, other MWNTs are observed with their one end still strongly embedded in the LLDPE matrix as an inset. Such interesting and typical breakage phenomenon of the MWNTs indicated that a strong interfacial adhesion exists between MWNTs and LLDPE matrix and that the load transfer takes place efficiently from the matrix to the nanotubes. The strong

interfacial adhesion is usually responsible for the significant enhancement of the mechanical properties. The fractographic observations of a novel biodegradable nanocomposite fabricated based on PHBHHx and silane-modified kaolinite/silica core-shell nanoparticles (SMKS) via solution-casting method using chloroform as solvent was further studied by Zhang *et al.* [97] using SEM. According to Wang *et al.* [98], the roughness of the fracture surface is associated with fracture properties and critical strain energy release rates. A smooth featureless fracture surface was attributed to brittle failures, and rougher fracture surfaces are attributed to tougher composites. In the case of neat PHBHHx, semicrystalline polyester, the fracture surface was even, which was consistent with no plastic deformation before rupture. For the PHBHHx/SMK, the fracture surface was somewhat rough but did not become stress whitened. In the case of PHBHHx/SMKS, an unevenness and roughness was observed in the fracture surface which illustrated the plastic deformation before rupture. It indicated that there was a strong bonding and good interfacial adhesion between SMKS and PHBHHx matrix. Other investigations that have used SEM to characterize PE/PHAs-based biocomposites and bionanocomposites are in refs. [42, 43, 69, 71, 72, 79, 81, 86, 87].

#### 6.2.2.4 X-Ray Diffraction

The phenomenon of X-ray diffraction is based on the atomic planes of crystal which cause incident beam of X-rays to interfere with one another as they leave the crystal. X-ray diffraction analysis (XRD) is one of the common techniques widely used to characterize the microstructure of nanocomposite as well as pure clay or pure organoclay. It measures the average spacing atoms between layers or rows of atoms and determines the orientation of a single crystal or grain. It is also used to find the crystal structure of unknown materials. It further measures the size, shape and internal stress of small crystalline regions. X-ray diffraction analysis has been used by researchers to characterize PE/PHAs-based biocomposites and bionanocomposites [71, 74, 77, 78, 81, 84, 88, 99].

The effects of organoclay type compatibilizer, and the addition order of components during melt-blending process on the morphology and thermal, mechanical, and flow properties of ternary nanocomposites based on LDPE were investigated by Coskunes and Yilmazer [100]. Interlayer spacing of the silicate layers was determined using the peak positions according to Bragg's law:  $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ . In their investigation, the XRD data of the neat organoclays, LDPE/organoclay binary nanocomposites, and LDPE/E-MA-GMA/organoclay ternary nanocomposites showed that the intensity

values are shifted for clarity. The basal spacing of neat organoclays was determined as 31.9 Å, 20.1 Å, and 17.9 Å for Cloisites 15A, 25A, and 30B, respectively; and these values are in accordance with the values of basal spacings reported in the manufacturer's data sheet. From their investigation, Cloisite 15A organoclay was shown to have two peaks. The peak at 12.8 Å corresponds to unintercalated clay. Among the binary nanocomposites of LDPE/organoclays, intercalated structure was obtained in the material containing 2 wt% Cloisite 25A. The binary composite had a peak at 3.09 in the XRD pattern, indicating a basal spacing of 28.5 Å. In the XRD pattern, there was also another broader peak with basal spacing of 16.4 Å, which could be due to the unintercalated layers. The peaks at d-spacing values smaller than the neat organoclay's basal spacing belong to the unintercalated organoclay [100]. Thiré *et al.* studied PHBV as an option for the production of disposable goods [101]. XRD patterns of PHBV films and PHBV/MAT nanocomposites exhibit well-defined peaks ( $2\theta$ ) at 13.6°, 17.1°, 21.7°, 22.7°, 25.6° and 30.7°, which correspond to the (020), (110), (101), (111), (121) and (002) reflections of the orthorhombic crystalline lattice, respectively. They further observed that the peak positions remain practically unchanged in PHBV/MAT diffractograms. This fact suggested that the PHBV crystalline lattice does not change appreciably in the presence of attapulgite. The characteristic peak of attapulgite which appears at  $2\theta = 8.42^\circ$  was observed in PHBV/MAT nanocomposites diffraction patterns. This peak was attributed to the primary diffraction of the (110) crystal face.

#### 6.2.2.5 Spectroscopic Characterizations

Spectroscopic characterization is used to analyze the interaction between matter and electromagnetic radiation. Spectroscopic data is always represented by spectrum, a plot of response of interest against wavelength or frequency. There are different types of spectroscopic techniques used in the characterization of composite materials; ultraviolet-visible spectroscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, mass spectroscopy, etc.

Rodrigues *et al.* used solid-state nuclear magnetic resonance (NMR) spectroscopy to characterize HDPE/organoclay nanocomposites because it is an important tool for the study of both molecular structure and dynamic behavior. Solid-state techniques aid in the observation of changes in structural and dynamic behavior, focusing on the polymer chains in the nanocomposite material [99]. The main purpose of their study was to apply both conventional techniques and NMR to obtain as much information



as possible on nanocomposites, especially those that are PE based. Low-field NMR was used to understand changes in the molecular mobility of the polymer matrix after organoclay is incorporated. According to their investigation, the relaxation data showed different molecular domains for PE and especially for the nanocomposite. The measurement of relaxation time, using low-field NMR, proved useful to evaluate changes in the molecular mobility of nanocomposites and can infer whether a sample is exfoliated and/or intercalated, since lamellar filler is used [99]. Zapata *et al.* [69] observed the presence of the oleic acid on silver nanoparticles using infrared spectroscopy. Their result shows the typical signal for the symmetric and asymmetric stretching of the  $\text{CH}_2$  groups of oleic acid was indicated by bands at  $2850$  and  $2920\text{ cm}^{-1}$ , respectively. The  $\text{CH}_2$  scissoring and rocking bands appear around  $1464$  and  $722\text{ cm}^{-1}$ , respectively. Another band characteristic of oleic acid is that at  $1709\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  stretching. For the unsaturated carboxylates,  $\text{COO}^-$  stretching bands appear at  $1560\text{ cm}^{-1}$ . Therefore, this spectrum confirmed the presence of the oleic acid in the silver nanoparticles. Araujo *et al.* [81] characterized PHB and polyaniline hydrochloride (PANI-HCl), nanocomposites II (before and after irradiation at  $25\text{ kGy}$ ) and nanocomposite IV with FTIR. Their result shows that PHB spectrum exhibited  $\text{C}=\text{O}$  stretching at  $1724\text{ cm}^{-1}$  and  $\text{C}-\text{O}$  stretching at  $1283\text{ cm}^{-1}$ . These results are in good agreement with previous reports on FTIR data of PHB. Polyaniline hydrochloride spectrum exhibited band at  $\sim 1573\text{ cm}^{-1}$ , attributed to  $\text{C}=\text{N}$  stretching of the quinoid diimine unit ( $\text{N}=\text{Q}=\text{N}$ ).  $\text{C}-\text{C}$  aromatic ring stretching of the benzenoid diamine unit ( $\text{N}-\text{B}-\text{N}$ ) appears at  $1481\text{ cm}^{-1}$ . The very close intensities presented by these two bands identify the emeraldine oxidation state of PANI. The behavior of polymer single-walled carbon nanotube composites under the harsh conditions of the space environment is modeled based on the effects of accelerated proton beams.

Daniel and Chipara [102] investigated the radiation-induced modifications in graphite nanoparticles and single-walled carbon nanotubes dispersed within HDPE by electron spin resonance (ESR) spectroscopy. Their experimental data revealed that both nanocomposites are sensitive to the incoming radiation; however, single-walled carbon nanotubes are less sensitive to proton irradiation (in air) than graphite. The ESR spectra of single-walled carbon nanotubes dispersed within HDPE consist of two overlapping signals, both of them characterized by almost Lorentzian line shapes. The wide signal, located at  $g$ -factor values larger than 2.00, was assigned to magnetic impurities originating from catalyst residues. The shift of the resonance line position of the wide line from the theoretical value  $g = 2.0023$  (including relativistic correction) reflected the

competition between the local molecular field acting on electronic spins and the external applied magnetic field. The other line was ascribed to conducting electrons delocalized over the conducting domains of SWNTs. This narrow and weak line was assigned to carbon nanotubes. The position of this line was slightly shifted from the theoretical position by spin-orbit interactions; nevertheless, the local magnetic field acting on the uncoupled electronic spin has strong temperature dependence, derived from the temperature dependence of the magnetization. This provided a simple path for the deconvolution of ESR lines. No ESR line due to free radicals generated by the irradiation of the polymeric matrix was noticed. This behavior was expected, as the glass transition temperature of HDPE is below  $-60\text{ }^{\circ}\text{C}$ , and consequently the macromolecular chains motions occurring in the amorphous domains are excited at room temperature. This allows for the diffusion and recombination of free radicals. Hence, the changes in the ESR spectra reflect the modifications of carbon nanostructures and of magnetic residues. In the case of high-density PE filled with graphite, the resonance line at room temperature was highly asymmetric, reflecting that the electrons are located in conducting domains, where the microwave field was damped via the skin effect. The room temperature spectrum of PE-graphite nanocomposites showed the usual perpendicular components that were expected for a two-dimensional conducting system. The effect of proton irradiation on PE filled with graphite was unexpectedly strong. Important symmetry changes are triggered by the irradiation; the sample irradiated with  $3 \times 10^{10}$  protons/cm<sup>2</sup> showed a low local symmetry, suggesting the disruption of the two-dimensional conducting islands. Such changes can be assigned to irreversible local heating effects. The spectral changes for pristine graphite dispersed within HDPE can be explained by the fracture of graphite layers under the effect of ionizing radiation [102].

#### 6.2.2.6 *Rheological Characterization*

Rheology is known to be the investigation of flow and deformation of matter under the influence of an external periodic stress or flow field. Response is either non-Newtonian (for macromolecular or self-assembled fluids) or Newtonian (for small molecular fluids). One of the aims of rheology is to establish relationships between deformation or flow and applied stress. The rheometers are operated either in a constant shear mode or constant stress. An important tool used in characterizing materials in order to determine their performance is shear rheology. Dynamic shear rheology and steady shear rheology are the two techniques that are normally used to determine the shear rheological behavior of a material. These techniques are used to

determine the flow behavior and structure evolution of a material under the influence of a steady-state deformation.

Capillary and parallel plate rheometers have been used by researchers in order to verify the processibility of nanocomposite samples and to establish the nanodispersion structure [103–108]. Botta *et al.* [109] comprehensively studied the rheological behavior under shear and isothermal and nonisothermal elongational flow of LDPE and ethylene-vinyl acetate copolymer (EVA)-based nanocomposites. The characterization was done in order to evaluate their “filmability,” that is, the ability of these material to be processed for film-forming applications. The influence of two different kinds of organoclay—namely Cloisite 15A and Cloisite 30B—and their concentration was evaluated. The presence of filler clearly affects the rheological behavior in oscillatory state of polyolefin-based nanocomposites but the increase of complex viscosity and the shear thinning are not dramatic. A larger strain-hardening effect in isothermal elongational flow was shown by the nanocomposites compared to that of the pure matrix, particularly for EVA-based nanocomposites. Ten [110] used a strain-controlled rheometer to measure dynamic rheological properties of PHBV/CNW composites. The measurements were performed  $\pm$  P-hat Al ring Sample ( $2.5 \times 2.5 \text{ cm}^2$ ) 62 at  $175 \text{ }^\circ\text{C}$  using parallel plate geometry (25 mm diameter). The gap between the two plates was 0.5 mm. Samples were equilibrated at  $175 \text{ }^\circ\text{C}$  for 5 min before tests. A strain sweep test was first performed to determine the linear viscoelastic region of the composites and a shear strain of 0.6% was chosen for all subsequent frequency sweep tests. The frequency was varied from 1 to 500 rad/s. Neat PHBV showed typical polymer melt behavior in the terminal region:  $G'$  and  $G''$  increased with shear frequency  $\omega$  and  $G''$  was larger than  $G'$ . The larger  $G''$  indicated the fact that the PHBV melt was highly viscous rather than elastic at the test temperature. The addition of CNWs increased  $G'$  and  $G''$  of the composites, especially within the terminal region.  $G'$  and  $G''$  also appeared to be more independent of shear frequency with increasing CNW content, a sign of transition from “liquid-like” rheological behavior to a “solid-like” one.

Girish and Waigaonkar [111] recently investigated the effects of nanocomposites of fumed silica (FS) with rotationally moldable LLDPE. Thermal transitions in the LLDPE-FS nanocomposites were investigated and correlated with their melt flow characteristics. The effect on melt processing during rotational molding and compounding were analyzed by melt flow index (MFI) and torque rheometry studies. Being a stress-free process, in rotational molding, proper MFI (and hence viscosity of the melt) is very important. If the viscosity is very low, the polymer melt will not adhere to the mold, causing annulled casting. A high melt viscosity causes

inadequate mold flow, increasing the processing time and the amount of entrapped gases, resulting in a defective part [111]. From their investigation, there was a consistent trend of increase in MFI with temperature for all the compositions. The viscosity of the melt increased with FS but was reduced with temperature. From the variation of shear rate with temperature, they observed that because of the reduction in viscosity, the shear rate increases for a constant load. Since LLDPE with increasing FS has shown lowest shear rate, increased resistance to melt shear was visible. This led them to examine the torque requirements during polymer compounding. They found that the melt torque increases with FS. At 4% FS composition, initial torque recorded 45–50 N-m at 150 °C and 30–35 N-m at 210 °C. In torque rheometry, the initial torque increase suggests the resistance offered to screw rotation because of loading of polymer blend inside the chamber. For this composition, a maximum of 10% increase in melt torque was observed when compared with natural LLDPE. After melting, the torque generally remained constant, indicating the thermal stability of the material. The increased torque needs to be accounted for in polymer compounding. The degradation takes place at lower temperatures when FS content is high. It was found that the polymer blends with 4% and above FS, tend to degrade at 210 °C under shear and prolonged exposure to heat. Since FS has lower heat capacity (740 J/kg K) than LLDPE (2080 J/kg K), it tends to attain increased temperatures in the polymer matrix for the same heat input [111].

#### 6.2.2.7 *Viscoelastic Characterizations*

The property of materials that exhibit both viscous and elastic characteristics when going through deformation is known as viscosity. Viscous materials have the ability to resist shear flow and strain linearly with time when a stress is applied. The viscosity of materials can be categorized as having a linear, nonlinear or plastic response depending on the change of strain rate versus stress inside the material. Newtonian material exhibits a linear response and when material exhibits a nonlinear response to the strain rate, it is categorized as non-Newtonian fluid. A thixotropic material occurs when viscosity decreases as the shear/strain rate remains constant. When stress does not depend on strain rate, the material exhibits plastic deformation. Polymers that are made of long molecular chains have unique viscoelastic properties that combine the characteristics of elastic solid and Newtonian fluid. The classical theory of elasticity describes the mechanical properties of elastic solid where stress is proportional to strain in small deformations. Such response to stress does not depend on strain rate. The viscoelastic property of a polymer is studied by dynamic mechanical

analysis where a sinusoidal force (stress  $\sigma$ ) is applied to a material and the resulting displacement (strain) is measured. For a perfectly elastic solid, the resulting strain and the stress will be perfectly in phase [112].

A lot of research has been conducted on viscoelastic characterizations of PE/PHAs-based biocomposites and bionanocomposites [12, 103, 109, 113–119]. Many of them have studied their dynamic mechanical analysis. Dynamic mechanical analysis (DMA), also known as dynamic mechanical spectroscopy, is a technique used to study and characterize materials. It is most useful for studying the viscoelastic behavior of polymers. Whenever nanoparticles are reinforced in base resin, their dispersion in the polymer matrix is critical. Girish and Waigaonkar [111] performed further DMA in order to find the viscoelastic properties, viz. storage modulus ( $E'$ ), loss modulus ( $E''$ ) and tan delta. The strain sweep test was performed at a frequency of 1 Hz. The temperature was ramped from 150 °C to 100 °C at the rate of 3 °C/min at frequency of 1 Hz and amplitude of 20  $\mu\text{m}$ . The frequency sweep test at room temperature (isothermal at 30 °C) ranged from 0.01 to 200 Hz at a set amplitude of 20  $\mu\text{m}$ . The frequency points were equally distributed in log scale with 15 points per decade. All measurements were performed under nitrogen atmosphere. Their result showed that for a temperature range from 150 °C to 100 °C, there was an increase in storage modulus up to 4% concentration. The storage modulus increased from 1143 to 1408 MPa at 30 °C when the FS was increased from 1% to 4%. Thus a considerable improvement in reversible deformation of the material was seen with incorporation of FS. The reduction of storage modulus at higher concentrations (FS% > 5) may be attributed to unavoidable agglomeration leading to the formation of weak grain boundaries. The increase in loss modulus from 96 to 107 MPa (up to 4% of FS) can be attributed to improved stiffness of the nanocomposites, as the tan delta values remain nearly constant. For the LLDPE-FS composites tested,  $\alpha$   $T_g$ , representing the onset of melting of low molecular weight polymer chains, shifted from 43.5 °C (LLDPE natural) to 49 °C (LLDPE-1%FS) and to 54 °C (LLDPE-8%FS). This implies a slight increase in operating thermal range for the nanocomposites. Below  $\alpha$   $T_g$ , the reinforcement effects of FS were seen in LLDPE. The first peak in loss modulus ( $E''$ ), as well as the tan delta curves around 120 °C, denote  $\gamma$   $T_g$  representing the small-scale movements in polymer chains usually associated with inter- and intramolecular motions. These transitions are related to either localized movement in the main chain or very large side-chain movements. For the LLDPE-FS composites tested, no significant change was observed in  $\gamma$   $T_g$  [111]. A suitable blend of FS in LLDPE was recommended for rotational molding based on rheological studies and dynamic mechanical analysis.

Grigoriadi *et al.* [120] investigated the effect of filler content and aspect ratio on the thermomechanical behavior of unmodified low-density LDPE-based layered silicate clay nanocomposites. LDPE-based nanocomposites, without any polymer modification and with two kinds of clays, one with low aspect ratio (i.e., synthetic laponite; Lp) and another with high aspect ratio (i.e., montmorillonite), were characterized using dynamic mechanical analysis. The LDPE reinforced with organo-montmorillonite (OMt) had better performance in the whole temperature range than that with organo-laponite (OLp). From their DMA result, one peak was observed at approximately 20 °C, associated with the  $\beta$ -relaxation of LDPE. Due to the fact that the DMA measurements started at approximately 120 °C, it was not possible to draw any conclusion regarding the effect of OMt/OLp addition on the  $\gamma$ -relaxation. The  $\gamma$ -relaxation is generally accepted as the  $T_g$  of PE. Regarding the  $\beta$ -relaxation, the addition of OMt seems to result in a very small shift of the peak to higher values in the case of 10 wt% content, while OLp did not significantly affect the peak. In PE the  $\beta$ -relaxation was believed to offer information about the chain architecture of PE. They suggested that this relaxation was due to motion in the amorphous phase near branch points. They then proposed that the existence of higher aspect ratio clay platelets in the case of LDPE/OMt nanocomposites resulted in a higher degree of branching of the amorphous phase and therefore in a small increase in the activation temperature of such movements. It was concluded that the relatively high aspect ratio OMt can induce superior dynamic mechanical properties to the LDPE polymer compared to lower aspect ratio OLp. This was linked to the higher active surface area and preferential orientation of longer platelets resulting in higher mechanical enhancement [120].

Dynamic mechanical analysis of PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles was studied by Díez-Pascual and Díez-Vicente [89]. The addition of inorganic nanofillers to biopolymers was to increase the mechanical properties of the resultant composites. The temperature dependence of the storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ ) for neat PHB and the composites with different ZnO contents was evaluated by DMA. They found out from their investigation that at temperatures below the  $T_g$ ,  $E'$  rises progressively upon increasing ZnO concentration; thus, at 25 °C, a maximum value of ~1.2 GPa (about 51% increase compared to that of neat PHB) was attained. This demonstrated the strong reinforcing effect of these nanoparticles. The storage modulus revealed the capability of a material to store mechanical energy without dissipation; the higher the storage modulus, the stiffer the material was. This improvement was related to the increase in the crystallinity of the

matrix, since the crystalline regions are known to enhance the modulus of semicrystalline polymers, combined with a strong filler-matrix interfacial adhesion due to H-bonding interactions between the  $-OH$  groups of ZnO and the carbonyl of the ester groups of PHB. At temperatures above  $T_g$ , the differences between  $E'$  of each composite and the matrix are in general less significant, indicating that the stiffening effect was more pronounced below the matrix softening point.

#### 6.2.2.8 *Electrical Characterizations*

The electrical properties of composite materials based on carbon additives and polymer matrices, either particles or fibers, have been intensively studied for over two decades [121–124]. Depending on the additive concentration, the electrical conductivity of a composite material varies from that of the polymer matrix to that of the carbon additive, due to the formation of a percolative network of the conducting additive at a certain critical concentration [125, 126]. There exist a critical volume fraction of filler particles in the conductive filler/polymer composites, in which the minor fillers form a continuous cluster network throughout entire composites [127]. This is followed by a sharp change in the electrical properties (such as dielectric constant); which means, the composites goes through an insulator-conductor transition at percolation concentration. Accordingly, agglomeration of conductive fillers is favorable for the formation of infinite interconnected clusters to some extent, thereby enhancing the electrical performances of the composites. Typical percolation systems are conductor-loaded dielectric materials; besides, the permittivity of a composite revealing the percolation behavior is inversely proportional to the difference between the critical filling volume fraction (the threshold value of percolation,  $p_c$ ) and the real filling volume fraction of fillers. Therefore, if high values of permittivity are needed for composite materials, the filling volume fraction of fillers should be similar to the critical value but not higher than it; again, if an appropriate value of the filling volume fraction is chosen, a very high permittivity value of the composite material can be realized. However, the dielectric properties of the composites having the percolation characteristic are known to be quite sensitive to the constitution of the material; a little change in the constitution can produce significant changes in the performances of composites, e.g., insulator-conductor transition [128].

There is a great interest in conductive polymers as a material that has magnetic and electrical properties. During the last decade, the study on inherently conductive polymers, such as PANI, polypyrrole (PPy) and polythiophene (PTh), have been increased intensively due to their special

properties [129–131]. Again, in the last decade, nanodielectrics have emerged as an important dielectric material system to provide advanced dielectric properties for power equipment applications [132–134]; cross-linked PE/silica nanocomposites regarded as a promising candidate for power cables in the future are among the studies. Roy *et al.* [135] studied the role of the interface of polymer nanocomposite dielectric. From their study, the incorporation of silica nanoparticles into PE increased the breakdown strength and voltage endurance significantly compared to the incorporation of micron-scale fillers. In addition, dielectric spectroscopy showed a decrease in dielectric permittivity for the nanocomposite over the base polymer. The reduction in the dielectric permittivity when the nanoparticles are incorporated into base resin may be a significant interfacial polarization associated with the material loaded with micron-size filler, which was mitigated when the particulate size approaches the order of nanometric range. It may also be as a result of an increase in glass transition temperature of nanocomposites over base resin, which suggested that there was a reduction in polymer chain mobility in the interaction zone. This reduction in chain mobility (in addition to the physical and chemical bonding of the polymer chain with silica particles, as in the case of surface treated fillers) might contribute to the reduction in polymer chain relaxation [135]. An investigation suggested that particulates of nanometric dimensions contribute to the process of tether chain entanglement, which might have significant impact on this interaction zone. Since with nanoparticles, surface area increases, tethered zones will also become more significant and restrict the polymeric chain movement; thus lowering the permittivity [136]. A dramatic improvement in electrical properties of nanofilled material over base resin was demonstrated in the voltage endurance tests. An improvement of two half-orders of magnitude in lifetime for untreated nanofilled material over base resin clearly provided an opportunity for the design of new materials [135]. Smith *et al.* [137] used a crosslinked PE/SiO<sub>2</sub> system to study some underlying mechanisms in nanodielectrics. The material formulation they used allowed alteration of both the interfacial area (through particle size adjustment) and the chemical nature of the interface. From their result, there was an increase in the low frequency permittivity, presumably due to moisture (and perhaps derivatives of the crosslinking peroxide such as cumene and cumyl alcohol), which can introduce polarization at the polymer/microparticle interface, raising the bulk  $\epsilon'$  in this frequency region. The interfacial polarization was as a result of the separation of space charges at the interface, modifying the local electric field condition.



Conducting polymers are a special class of organic polymers that have alternate single-double bond conjugation and can conduct electricity. The electrical properties of carbon nanofiber or carbon nanotubes (CNT) have begun to be intensively investigated mainly due to the particular properties of nanocomposites as compared with those of traditional composites. Both the direct current (dc) and the alternating current (ac) electrical conductivity of polymer nanocomposites based on multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) have been recently investigated [138–141]. Linares *et al.* [125] studied the electrical properties of a series of nanocomposites based on HDPE as a matrix and either carbon nanofiber (CNF) or MWCNT as a nanoadditive. The measurements of the electrical conductivity over a broad-band of frequencies ( $10^{-2} > f/\text{Hz} > 10^9$ ) allowed the improvement of the description of the electrical properties of polymer nanocomposites based on either carbon nanofibers or carbon nanotubes. Despite the lack of a continuous conducting network between particles at low concentrations, the nanocomposites exhibited a significant dc electrical conductivity due to tunnel conduction. At low nanoadditive concentrations, the frequency dependence of the electrical conductivity was mainly caused by the influence of large polymeric gaps between conducting clusters. As nanoadditive concentration increases, the size of the finite size cluster tends to increase and the frequency dependence of the conductivity reflected the features of anomalous diffusion in fractal structures, as expected according to percolation theory. A master curve for the electrical conductivity as a function of frequency can be constructed, although, for the investigated nanocomposites, this behavior should be contemplated as a working rather than universal law [125].

### 6.2.3 Applications of PE/PHAs-Based Biocomposites and Bionanocomposites

Recently, biobased plastics have received great attention because of limited fossil-based resources and environmental pollution caused by petroleum-based plastics [142–145]. Biobased plastics are materials produced from renewable agricultural and forestry feedstocks. With advantages of sustainability, environmental friendliness, and decomposability, the biobased plastics market is currently growing at an annual rate of 30% [146]. The first generation of biobased polymers was focused on deriving polymers from agricultural feedstocks such as corn, potatoes, and other carbohydrate feedstocks [147]. In recent years, the focus has never the less shifted to significant breakthroughs in biotechnology. These biobased polymers

have also shown enormous growth in recent years in terms of technological developments and their commercial applications. Polyethylene/polyhydroxyalkanoates-based biocomposites and bionanocomposites have a wide range of potential applications because of their distinct features such as biodegradability, biocompatibility and negligible cytotoxicity to the cells. Hence, the potential application of PHA used as replacement for petrochemical-based polymers is finding popularity in a variety of fields such as packaging, coating materials, structural, military, medical and biomedical.

#### 6.2.3.1 *PE/PHAs-Based Biocomposites and Bionanocomposites in Biomedical Applications*

Nanomaterials offer very interesting biological and physiochemical properties for biomedical applications due to their large surface area and the ability to interact and interface with the cells and tissues. Nanocomposites have become of huge interest to biomedical technologies such as tissue engineering, controlled drug delivery, dental applications, and bone replacement/repair. Biodegradable polymers are finding significant applications in the medical field. Polyhydroxyalkanoates, especially P(3HB), P(3HB-3HV), P(4HB), P(3HO) and P(3HB-3HHx), are frequently used in tissue engineering [148]. The suitability of PHA for inclusion in drug delivery or other biomedical applications will depend not only on the biodegradation properties but also on their biocompatibility. For use in medical applications, materials must be biocompatible, which means that they should not cause severe immune reactions when introduced to soft tissues or blood of a host organism during degradation in the body [149]. Polyhydroxyalkanoates are widely used as bone plates; Doyle *et al.* [150] demonstrated that materials based on PHB produce a consistent favorable bone tissue adaptation response with no evidence of an undesirable chronic inflammatory response after implantation periods up to 12 months. Bone was rapidly formed close to the material and subsequently became highly organized, with up to 80% of the implant surface lying in direct apposition to new bone. The materials showed no conclusive evidence of extensive structural breakdown *in vivo* during the implantation period of the study. The PHAs are widely used in the synthesis of osteosynthetic materials such as bone plates, surgical sutures and other materials for medical use [151]. PHAs have been used as osteosynthetic materials in the stimulation of bone growth owing to their piezoelectric properties in bone plates, surgical sutures and blood vessel replacements [152]. For use in sutures, a polymeric material must exhibit exceptional tensile strength in order to be effective in wound closures [6]. Polyhydroxybutyrate and

poly(hydroxybutyrate-co-hydroxyvalerate) sutures were shown to be able to facilitate healing of muscle-fascial wounds [153, 154]. P(HB-co-HV) films facilitated wound healing following oral surgery in dogs [155]. The most common type of PHA used for fabrication of surgical material is poly(4-hydroxybutyrate) (P4HB). As suture material, oriented P4HB fibers (545 MPa) are stronger than polypropylene sutures (410–460 MPa). Again, the Young's modulus of P4HB sutures is significantly lower than other monofilament sutures produced from other substances that are on the market [156]. They are useful in the slow release of drugs [157–159] and hormones [160]. For instance, PHB readily hydrolyzed to R-3-hydroxybutyric acid and used in the syntheses of Merck's antiglaucoma drug Truspot in tandem with r-1,3-butanediol. It is also used in the synthesis of beta lactams [152]. However, the use of PHB in such applications is restricted by its poor rate of biodegradation and high resistance to hydrolysis in sterile tissues. PHB has been successfully used as a graft matrix for neuronal generation after spinal cord injury in rats [161]. Another investigation has shown that PHA matrices allow proliferation of neural stem cells. Poly(hydroxybutyrate-co-hydroxyvalerate) allows for the most penetration of stem cells into the polymer matrix, presumably as a result of the porosity of P(3HB-co-3HHx) [162]. Scaffolds produced from unblended P(HB-co-HHx) were also shown to be effective in cartilage repair [163]. The PHB films were also found to provide scaffolding to patch a large bowel defect in rats and were shown to degrade more readily *in vivo* [164]. Matrices fabricated from P(HB-co-HV) implanted into cartilage defects in rabbits exhibited better healing response than scaffolds fabricated from collagen impregnated with calcium phosphate [165].

The main goal of chemotherapy is sustained, controlled, and targeted delivery of anticancer drugs for an extended period of time. This goal can be achieved using polymeric nanoparticles. Polymeric nanoparticles have long been used as carriers for systemic and targeted drug delivery. Nanoparticles loaded with anticancer agents can successfully increase the drug concentration in cancer tissues and act at cellular levels, enhancing antitumor efficacy. The nanoparticles can be endocytosed/phagocytosed by cells, resulting in internalization of the encapsulated drug by the cell [166]. Rajan *et al.* [167] investigated the properties of biopolymer composite nanoparticles based on the encapsulation of the anticancer drug 5-fluorouracil (5-FU) with the HYL enzyme and chitosan/polyethylene glycol/gelatin (CS/PEG/G). Their study examined the performance of novel hyaluronidase enzyme core-5-fluorouracil-loaded chitosan-polyethylene glycol-gelatin polymer nanocomposites, which were prepared using an ionic gelation technique, as targeted and controlled drug delivery vehicles.

The encapsulation efficiency and loading capacities of the nanoparticles demonstrated that these nanocomposites displayed sufficient binding ability, which depends on the pH and initial concentration of the drug. Rajan and Raj [168] developed a novel drug vehicle for the controlled release of an antituberculosis drug, rifampicin (RIF), by using chitosan (CS)-polylactic acid (PLA)-polyethylene glycol (PEG)-gelatin (G) nanoparticles. The use of CS in combination with PEG and G shows potential as new compression coats for controlled drug delivery. These coatings were able to suppress the release of RIF until it reached the targeted place. The drug release was based on time and pH controlled system due to the water insolubility of RIF and the matrix formation of CS-PLA/PEG/G, the solubility of which depends on the pH of the media. Drug permeation and *in-vitro* testing are suggested for further study in the development of *in-vivo* drug delivery system. Consequently, these systems showed great promise with regard to the circumvention of the present limitations in the management of tuberculosis diseases. These results indicated that RIF-coated CS-PLA/PEG/G nanoparticles could be a potential carrier for controlled drug delivery.

Polyethylene terephthalate has been used in medical devices for more than five decades. The current medical applications of PET are surgical mesh, implantable sutures, vascular grafts, and sewing cuffs for heart valves and components for percutaneous access devices. The notable biological characteristics of PET include the promotion of tissue ingrowth, biostability, a well-characterized fibrotic response and a long history of human implantation [169]. High-density polyethylene is one of the most often used polymers in biomedical applications. The limitations of HDPE are its viscoelastic behavior, low modulus and poor bioactivity. To improve HDPE properties, hyaluronan (HA) nanoparticles can be added to form polymer composite that can be used as alternatives to metals for bone substitutes and orthopedic implant applications [116]. Low and medium molecular weight forms of HA stimulate angiogenesis, proliferation, differentiation, and migration. High molecular weight forms of HA suppress angiogenesis, inhibit cell proliferation, and decrease the migratory ability of cells [170–175]. Based on the experimental results, it was found that prepared HDPE nanocomposite properties improved due to the addition of HA nanoparticles and irradiation. So, the prepared HDPE/HA nanocomposite appears to have fairly good comprehensive properties that make it a good candidate as bone substitute [116].

Another polymeric material used in medicine since the 1960s is ultra-high molecular weight polyethylene (UHMWPE). Ultrahigh molecular weight polyethylene is highly resistant to corrosive chemicals and

has very low moisture absorption and very low coefficient of friction; it has the characteristic of self-lubrication and high resistance to abrasion. UHMWPE emerged as a bearing material in many joint replacement devices. It was recently found that generation of particulate debris from the articulating surface of this polymer is connected with osteolysis and loosening of implants. Investigation has been carried out in order to look into these problems and highly crosslinked UHMWPE materials are clinically introduced. Additional important medical advancement for application of UHMWPE in the last ten years has been the increase in use of fibers for sutures, where maximum strength and minimum weight are required [176]. Due to characteristics such as low friction factor, high wearability and chemical resistance to corrosive media, and also its relatively high strength, UHMWPE has been used for the manufacturing of implants (artificial joints, face surgery, etc.). The reason for its wide use as a material for implants is related to its similarity to the chemical nature and physical-mechanical properties of biotissues [177–179]. Ultrahigh molecular weight polyethylene-based nanocomposites with biocompatible fillers are currently not well-studied subjects in modern medical materials science [180–182]. The high-energy treatment of UHMWPE-based composites can be used in combination with filling by HA nanoparticles as a method of sterilization of products for medical applications (orthopedic implants) [183].

#### 6.2.3.2 *PE/PHAs-Based Biocomposites and Bionanocomposites in Packaging Applications*

The use of conventional plastics comes with a multitude of drawbacks: the large amount of energy that is required to produce the plastic, the waste that is a result of plastic production, and the use of materials that do not biodegrade readily. In order to shift the production of plastics towards a more sustainable path, research is being conducted to determine the types of renewable bioplastic resources that could be converted into plastic form [184]. Bioplastics are plastics that are derived from renewable biomass sources, such as corn starch, pea starch, vegetable fat and oil. A common theme for various bioplastics that will replace conventional plastics is their tendency to be biodegraded, compared to petroleum-based plastics that are resistant to chemical and biological attacks [184]. Packaging is the biggest polymer processing industry with the food sector being its principal customer. In the wake of future laws in relation to reducing the weight and volume of these products, cheap and biodegradable polymeric products are receiving growing attention in this market [185]. The term sustainable

packaging has been introduced to address the contribution of packaging into sustainable development. One of the thrusts introduced by sustainable packaging is to integrate economic, social and environmental factors in order to provide a packaging system which is more efficient and at the same time able to minimize resource consumption, waste and emissions throughout its life cycle [186]. Recently, there has been great interest in the production of plastics with various applications in packaging such as for foods, pharmaceuticals, chemicals, detergents, cosmetics, compost bags, grocery bags, shipping bags, cutlery, plates and toys. Of all the materials, plastics are the most frequently used for packaging [186].

There have been many investigations on the use of biodegradable polymers, such as PLA, PHAs, and polycaprolactone (PCL), for polymer blending, [187, 188]. Due to its mechanical characteristics, PHA has an advantage over other biodegradable polymers. There are several types of PHAs, namely PHB, PHBV, PHB-co-HHx and polyhydroxyoctanoate (PHO). Compared to the homopolymer PHB, PHA copolymer such as PHBV has better thermal and mechanical properties and, hence, wider processing window [186]. The presence of hydroxyvalerate (HV) units was found to increase the toughness, exhibit the isomorphic phenomenon and decrease the melting point of PHB [189]. Some grades of additivated PHB are similar in their material properties to PP, and offer good resistance to moisture and aroma barrier properties [5]. PHB is a high crystallinity thermoplastic with a very low water vapor permeability which is close to that of LDPE. The main disadvantage for the commercial use of the PHB homopolymer is represented by an unfavorable aging process. Generally, PHAs have better oxygen barrier property than PP, PLA, PE, PET and PCL. Another advantage of PHAs is that they are not soluble in water [190, 191]. Due to their good oxygen and water barrier properties, PHAs are very suitable to be applied as food packaging plastics [191]. The potential of PHAs for truly biodegradable packaging was recognized in the 1980s with the commercial release of Biopols, thermoplastic resins of P(3HB) with various copolymer loadings of (3HV), by Imperial Chemical Industries (ICI, now Zeneca). The biodegradability of PHAs stems from the fact that they will break down "fully" to water and carbon dioxide [192].

These days, most materials used for food packaging are practically undegradable, causing a serious global environmental problem. New bio-based materials have been used to develop edible and biodegradable films as a big effort to extend shelf life and improve quality of food while reducing packaging waste [193]. However, the application of edible and biodegradable polymers has been restricted because of problems related to the

performance of such polymers (such as brittleness, poor gas and moisture barrier), processing (such as low heat distortion temperature), and cost. For example, starch has received considerable attention as a biodegradable thermoplastic polymer. However, it has a poor performance by itself because of its water sensitivity and limited mechanical properties [194] with high brittleness, which is related to the anarchical growth of amylose crystals with time [195]. The application of nanotechnology to these polymers could open new possibilities for improving not only the properties but also the cost/price efficiency [196]. A uniform dispersion of nanoparticles has led to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior and the consequent mechanical and thermal properties of the material. Fillers with a high ratio of the largest to the smallest dimension (i.e., aspect ratio) are particularly interesting because of their high specific surface area, providing better reinforcing effects [197–199]. Besides reinforcing nanoparticles, whose main role is to improve mechanical and barrier properties of the packaging materials, there are several types of nanostructures responsible for other functions, sometimes providing active or “smart” properties to the packaging system such as antimicrobial activity, enzyme immobilization, biosensing, etc. [200].

Although several nanoparticles have been recognized as possible additives to enhance polymer performance, the packaging industry has focused its attention mainly on layered inorganic solids like clays and silicates, due to their availability, low cost, significant enhancements and relatively simple processability [200]. According to De Azeredo, the concept of polymer-clay nanocomposites (PCN) was developed in the late 1980s and first commercialized by Toyota [200]; but only since the late 1990s has research been published on development of PCN for food packaging [201]. Some research groups started the preparation and characterization of various kinds of biodegradable polymer nanocomposites showing properties suitable for a wide range of applications [202]. So far, the most studied biodegradable nanocomposites suitable for packaging applications are starch and its derivatives, polylactic acid (PLA), poly(butylene succinate) (PBS), PHB, and aliphatic polyester as PCL [203]. Díez-Pascual and Díez-Vicente [89] recently prepared PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles via solution casting technique for food packaging. The nanoparticles were dispersed within the biopolymer without the need for surfactants or coupling agents. The migration levels of PHB/ZnO composites in both nonpolar and polar simulants decreased with increasing nanoparticle content, and were well below the current legislative limits for food packaging materials. These biodegradable

nanocomposites showed great potential as an alternative to synthetic plastic packaging materials especially for use in food and beverage containers and disposable applications.

### 6.2.3.3 *PE/PHAs-Based Biocomposites and Bionanocomposites in Structural Applications*

In the past four decades, polymer composites have become attractive construction materials for new structures. The use of polymer composites have gained importance in the strengthening/rehabilitation of existing bridges and buildings due to their significantly different physical or chemical properties which remain separate and distinct within the finished structure. About 30% of all polymers produced each year are used in the civil engineering and building industries. In addition to construction, polymer composites are also used in transportation (molded parts, fuel and gas tanks), aerospace (satellites and aircraft structures). Such properties associated with polymer composites, in addition to their performance and applications, are continually being researched [204]. The technological methods, analysis and design of polymer composites in construction are also still being researched. When designed in a proper way, the new combined material exhibits good properties, which can be better than the individual material. Lighter materials lead to easy handling during assembly, reducing installation and transportation costs. Polymer composites also offer greater design freedom, enabling the creation of complex shapes. Reinforcements are usually stronger than the polymer matrix that improves the mechanical properties of the polymer composite [205]. Thermoplastic matrix polymer composites have gained importance in the commercial success of the semi-structural and structural applications.

Polyethylene is one of the most widely used thermoplastics in the world because of its good properties that can be used in structures such as toughness, near-zero moisture absorption, excellent chemical inertness, low coefficient of friction, ease of processing and low electrical conductivity [206]. New composites that include PE as the matrix is now used in construction due to better mechanical and physical properties compared to the polymer alone. The ever-increasing demand for improved properties of polymer matrices, especially for lightweight structures, and multifunctional characteristics have strongly shifted the focus of researchers to nanomaterials as reinforcements [207]. The properties of PE composites are based on the molecular weight of PE, experimental conditions, the types of reinforcement and quantity. It is thus important to know the structure and properties of PE composites in order to control and modify the needed properties



for different structural applications. Fiber reinforced plastic (FRP) composites are used in a wide range of applications in construction because of the benefits they provide over traditional building materials. Primary benefits include reduced weight, requiring less supporting structure, and excellent resistance to corrosion and rot, which can significantly reduce the durability of structures built with wood and steel [208]. The flexural behavior of concrete specimens reinforced with chopped PE fiber for concrete reinforcement was developed in Japan [209]. The chopped filaments were incorporated into concrete by mixing. It was observed that the fiber reinforcement significantly improves the toughness by sustaining useful load beyond the first crack load. Post-crack behavior was greatly affected by loading velocity, because it was governed by the viscoelastic characteristics of PE fiber [209]. Soroushian *et al.* [210] reported optimization of the combined use of two different fiber types in cementitious matrixes. The two fiber types were a high-modulus polyethylene fiber and a fibrillated PE pulp. Through a factorial experimental design, the effects of different volume fractions of the two fibers, and their interaction, on the impact resistance, flexural strength and toughness, compressive strength, bulk specific gravity, volume of permeable pores, and water absorption capacity of cementitious materials manufactured with a high-performance mixer were investigated. In the case of impact resistance, they observed that the positive effect of each fiber was pronounced in the presence of the other fiber type. For flexural strength and toughness, the combined use of polyethylene fiber and pulp produced desirable results. The negative effects of fibers on compressive strength were less pronounced when the two fiber types were used in combination. The interactions between PE fiber and pulp in deciding the specific gravity, volume of permeable pores, and water absorption capacity of cementitious materials were either negligible or only moderately significant.

Polymer nanocomposites, especially those with CNTs, are very attractive for conductive composites with good structural characteristics. CNTs/CNFs are potential candidates for use as nanoreinforcements in cement-based materials. CNTs/CNFs exhibit extraordinary strength with moduli of elasticity on the order of TPa and tensile strength in the range of GPa, and they have unique electronic and chemical properties [211–213]. Therefore, CNTs/CNFs appear to be among the most promising nanomaterials for enhancing the mechanical properties of cement-based materials and their resistance to crack propagation, while providing such novel properties as electromagnetic field shielding and self-sensing [214, 215]. CNTs/CNFs have been extensively studied in polymeric composites [216–218]. Nam *et al.* [219] have proposed the stochastic predictions of the interfacial

characteristic of carbon nanotube polyethylene composites. The effect of the single-walled carbon nanotube (SWCNT) radius, the temperature and the pulling velocity on interfacial shear stress (ISS) were studied by using molecular dynamics (MD) simulations. Based on their MD results, the mechanical output (ISS) was best characterized by the statistical Weibull distribution. So far, the few studies on polymer nanocomposites suitable for structural applications are on PE carbon nanotube composite.

#### 6.2.3.4 *PE/PHAs-Based Biocomposites and Bionanocomposites in Military Applications*

Nanotechnologies promise revolutionary technological changes for a wide range of military applications and platforms. Technologies to be incorporated within the platforms which are directly relevant to the defence arena include: aerodynamics, mobility, stealth, sensing, power generation and management, smart structures and materials, resilience and robustness, etc. [220]. Polymer/clay nanocomposites (PCNs) offer opportunities in many areas for military applications. These nanocomposites offer the possibility to address military restrictions in advanced system concepts. Thermal stability and enhanced fire retardancy through char formation have motivated investigation of PCNs as a component to anti-flammability additives for aircraft interiors [221]. Gilman found out that the polymer layer-silicate (clay) nanocomposite have the unique combination of reduced flammability and improved physical property. It is important to note that, in PE systems, the exfoliation of the silicate layers does not lead necessarily to better barrier properties. A good interface between the clay and the polymer matrix is required to reach a high performance level. The control and improvement of interfacial resistance is a key point for the development of new promising materials with enhanced barrier and mechanical properties [222]. Superior barrier properties against gas and vapor transmission have resulted in military applications for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems. Also, depending on the type of polymeric host, PCNs display interesting ionic conductivity for solid-state electrolytes in batteries [223].

Some researchers have reported a few promising applications of nanocomposites in body armor. Shear thickening fluids [224–227] consist of a fluid containing a dispersion of particles and this fluid stiffens and resists deformation if sheared rapidly by an external force. Reports from the US Army Research Laboratory indicate promising results when combining inorganic nanoparticles (of silica) in PE glycol [228]. When this shear thickening fluid is impregnated into conventional Kevlar, the ability of


the material to absorb energy is greatly improved. For example, the ballistic performance (in terms of absorbed energy) was more than doubled so that four layers of Kevlar impregnated with the shear thickening fluid absorbed as much energy as would have been absorbed by 10 layers without the shear thickening fluid. This will lead to more flexible armor with reduced weight. Such materials find applications for body/personal armor where flexibility of movement is required besides protection against blunt weapons (stones, sticks and bars) for arms and legs [228]. Nanometer-sized clay particles (often montmorillonite) finely dispersed in selected polymer matrices are used as the reinforcement phase and provide enhancements in stiffness, toughness, tensile strength, thermal stability, gas-barrier properties, and importantly, flame-retardant character [229]. The thermal properties of polymer nanocomposites are improved so that melting and dripping are delayed and the rate of burning is reduced by more than half. A further advantage is that the addition of the clay nanoparticles improves the mechanical properties of the fabric significantly, which can be utilized to reduce the thickness and weight. Dispersion of silicate layers in a polymer is difficult. For dispersion, compatibilizing agent, a molecule constituted of one hydrophilic and one organophilic function, is commonly used [230].

Military officers on land, sea, and in the air are faced with many complex hazards which are deliberately aimed at maiming or killing them. Hence, it is inevitable for them to wear protective clothing like body armor, chemical and biological protective clothing, etc. At present, textile fibers such as kevlar, nomex and nylon find immense applications in protective wear for military personnel. High strength, antiballistic, flame-retardant characteristics are some of the vital properties that make these fibers uniquely suitable for defense and other high technological applications [229]. Several nanoparticles like carbon nanofibers, SWCNT, MWCNT, nano-TiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, and aluminosilicate nanoclay were dispersed in a polymer matrix, instead of using conventional fillers, to produce novel composites with enhanced mechanical, electrical, and thermal properties [229]. For example, as little as 1–5 per cent weight of nm-sized clay particles in crosslinked resins can provide big improvements in mechanical and thermal properties; reduced permeability to gases, moisture, and hydrocarbons; and increased flame resistance to textile polymers [231]. The protection of the military from exposure to hazardous chemicals, such as chemical warfare agents, is a very important mission that needs to be accomplished on today's battlefield and that of the future. This protection is currently accomplished using an activated carbon system, using semipermeable material systems, and using impermeable barrier materials. The activated carbon system is used

in protective overgarments and affords protection by adsorbing hazardous chemicals. The impermeable barrier materials consist of rubber, coated and multilayered laminate fabrics found in gloves, boots, and for special purposes (e.g., depot storage/demolition/explosive ordnance disposal ensembles), which afford protection by acting as physical barriers to chemicals [229]. However, these materials inherently possess either cost or logistic barriers, which make their fielding undesirable unless a catastrophic effect is eminent. A lightweight, low-cost, low-packing-volume, chemical and biological protective barrier material would make collective protection feasible for conventional chemical and biological protective clothing and shelter systems, therefore enhancing the safety of soldiers during unpredictable chemical and biological attacks. Nanocomposites based on clay, MgO [232] and TiO<sub>2</sub> [233] have been developed which give excellent protection as well as operational advantage to the soldiers. This increase in barrier properties was accomplished without significantly changing the physical properties of the polymers.

Polymer matrices containing CNTs is a very active area of research and development for creating multifunctional materials. Polymers which are normally electrically insulating but have other advantages of being flexible, having low density, and are easily formed, can be combined with CNTs, which have excellent electrical conductivity, extreme mechanical strength, and high thermal conductivity. By combining these two materials, a nanocomposite with extremely useful properties can be obtained [229]. The most useful application areas are electromagnetic shielding, microwave absorption, ballistic protection, and chemical sensor clothing [234]. A wide range of polymer materials, such as poly(vinyl alcohol), poly(methyl methacrylate), PP, PE, PET, etc., have been used with CNTs to form films, fibers, and bulk composites through different spinning technologies like melt spinning, solution spinning, and electrospinning [235]. Chen [236] developed a new, general-purpose micro-stereo lithographic method (Flash-6iSL) for rapid prototyping of microstructures made of CNT-reinforced nanocomposites. He stated that rapid prototyping of nanocomposite part will have a significant impact in the U.S. Navy. He further developed novel micro/meso-devices using CNT nanocomposites. In order to control the spatial resolution for nanomanufacturing, he investigated laser nanosphere lithography for glass and semiconductors. He demonstrated that by adding a small amount of carbon nanofibers to the PE matrix, he can easily ablate the PE nanocomposite. The nanofibers serve as “nano-receivers” of the laser energy and then convert the photon energy into heat (“nano-heaters”). Numerical heat conduction simulation showed that the PE matrix was partially melted or evaporated due to pyrolytic

decomposition. Biofouling is considered as one of the main concerns for naval structures. These structures are affected by fouling of various kinds like deposition or particulate, scaling or crystallization, microbiological, debris or macrofouling, corrosion and corrosion products [237]. For naval structures, biofouling causes increased hydrodynamic drag, resulting in increased fuel consumption and decreased speed and range. Carbon nanotube-based epoxy nanocomposite coating was synthesized on the naval material to increase its antibacterial efficiency [237].

The military also uses PHA for food packaging. These materials are low cost and effective for application in many departments of defense. Biodegradability can also be useful in military applications for which traditional disposal options are lacking. Specific but minor functions for biodegradable polymers include limiting moisture, aroma, and lipid migration between food components [238]. Since 2002, the U.S. Army Natick Soldier Systems Center has been conducting extensive research into the use of no-foil polymer nanocomposite structures for military food rations (meals ready-to-eat, or MREs). The goal of the research is to reduce the amount of solid waste associated with the current packaging as well as reducing costs through material savings. Each year, 14,177 tons of MRE packaging waste is generated because the foil layer, which is susceptible to pinholing, does not allow the pouch to be recycled. One Army ration creates 471.7 kg of waste, while a Navy ration creates 1723.6 kg of solid waste [239]. According to the U.S. Army [240], the current MRE packages, which are three- to four-layer retortable pouches with a foil layer, do not meet the rigorous standards  the military MRE packaging needs to withstand the following conditions: air-droppable, a minimum three year shelf life at 26.6 °C and six months at 37.7 °C. The use of nanocomposite polymers, which offer higher barrier properties, will extend shelf life and greater product protection for military rations.

#### 6.2.3.5 *PE/PHAs-Based Biocomposites and Bionanocomposites in Coating Applications*

The science of polymer synthesis gives room for excellent control over the properties of a bulk polymer sample. Notwithstanding, surface interactions of polymer substrates are an important area of study in nanotechnology and in all forms of coating applications. In these cases, the surface characteristics of the polymer and material, and the resulting force between them, largely determine the utility and reliability of these polymers for coating applications. Biobased polymers applied as dispersion coatings on paper and paperboard for packaging applications and bioplastics with the same

intended use provide sufficient barrier properties with respect to fats, but are usually only moderate water vapor barriers [241]. Other weaknesses may include inferior mechanical properties, insufficient heat tolerance, and high moisture sensitivity relative to petroleum-derived plastics. Rather than the more common petrochemical coatings, biopolymers are available as coatings for paper. One of the areas of applied grafting techniques is polymeric coatings. In the formulation of waterborne paint, latex particles are usually surface modified in order to control particle dispersion and coating characteristics such as viscosity, film formation, coating rheology and environmental stability (UV exposure and temperature variations). The dispersing aids adsorb (as in a grafting onto scheme) onto latex particles, giving them functionality. The association of other additives, such as thickeners, with adsorbed polymer material gives rise to complex rheological behavior and excellent control over a coating's flow properties [242]. A number of starch and proteins have received particular attention for the production of edible and biodegradable films and coatings for packaging [243–246]. Films and coating may be used to protect export fruits and nuts from physical damage, to reduce shriveling of the fruits and to reduce rancidity of nuts [241]. Coatings are not limited to the food industry; gums are also used in coatings for fiberglass, fluorescent lamps, glass, metals, optical products, paper products, latex and textiles [247].

Progress made in the area of nanocomposites has made it possible to intensify  $\text{TiO}_2$  effectiveness by modifying its surface with noble metal deposition. The purpose of doping  $\text{TiO}_2$  nanoparticles with metals is to create a heterojunction [248]. The applications for doped  $\text{TiO}_2$  nanocomposites range from antimicrobial coatings on textiles, the inactivation of endospores, solid-surface antimicrobial coatings, and aqueous system-based biocides [249–251]. The surface modification of PET polymer was made by oxygen and nitrogen plasma at different treatment times [252]. Polyethylene terephthalate polymer surface was modified in order to achieve improved attachment of fucoidan, which is a bioactive coating with antithrombogenic properties. The attachment of fucoidan was improved by oxygen plasma treatment, specifically due to the surface roughening. The adhesion work, the surface energy and the surface polarity of PA6 (polyamide-6) fibers were found to improve by dielectric barrier discharge (DBD) treatment in helium at atmospheric pressure. The self-cleaning and UV protective properties of PET fibers were improved after a modification of PET fibers with oxygen plasma and loading of  $\text{TiO}_2$  prepared by an aqueous sol-gel process [253]. Cotton has also shown self-cleaning properties after RF plasma and  $\text{TiO}_2$  treatment [254].  $\text{TiO}_2$  on textile substrates was also used for a biomedical application to improve

antimicrobial effectiveness of the fabric [255]. The use of radio-frequency oxygen plasma at a higher power input increased the roughness of fibers and likewise the adhesion of  $\text{TiO}_2$  onto treated fabric. Treatment of PA and PET with corona plasma increased the adhesion of colloidal silver, which affected the antifungal protection of the fabrics [256]. The quantity of silver on plasma treated fabric was three times higher than on untreated fabric.

Carbon nanofiber and carbon black nanoparticles are also among the most commonly used nanosize filling materials in the textile industry [257]. Carbon nanofibers can effectively increase the tensile strength of composite fibers due to their high aspect ratio, while carbon black nanoparticles can improve their abrasion resistance and toughness. Several fiber-forming polymers used as matrices have been investigated, including polyester, nylon and PE with the weight of the filler from 5 to 20% [258]. Carbon black nanoparticles improve the resulting composite fiber's abrasion resistance and toughness. Composite fibers which incorporate GNFs have improved tensile strength. Polyester, nylon and PE have been used as the matrices for both of these nanofillers [259]. Carbon nanotubes can also serve as a multifunctional coating material. For example, paint/MWNT mixtures can reduce biofouling of ship hulls by discouraging attachment of algae and barnacles. They are a possible alternative to environmentally hazardous biocide-containing paints. Mixing CNTs into anticorrosion coatings for metals can enhance coating stiffness and strength and provide a path for cathodic protection [260].

Polyhydroxyalkanoates are also gaining attention among biodegradable polymers due to their promising properties, such as high biodegradability in different environments, not just in composting plants, and their versatility. Indeed, PHAs can be formulated and processed for use in many applications, which include paper coatings [5]. Coating in this regard comprises the application of a thin biobased or non-biobased layer to the bioplastics. Such coatings can lower the oxygen and vapor permeability, increase tensile strength and result in higher elastic properties. Methods of making PHA coating compositions having molecular weights greater than about 125,000 were provided in a patent by Asrar *et al.* [261]. The effect of coating molecular weight on sealing properties was examined. Hot tack measurements were obtained on PHA-coated board. The seal bar temperature was 138 °C. The seal strength presented as a function of cooling time for a sample that had shown good heat sealing properties and for a sample that had shown poor heat sealing properties. The PHA coating compositions derived therefrom have improved properties suitable for applications in which excellent heat sealability and moisture resistance is desired. PHAs can be used for paper coating and recent application developments based on

medium-chain-length PHAs include biodegradable cheese coatings [262]. A perspective area of PHB application is the development of implanted medical devices. Surgical meshes with PHB coating for hernioplastic surgery is one of the potential medical devices based on PHB. Bonartsev *et al.* [263] have obtained toxicological certificates from the Institute of Medical Technique (Ministry of Health, Russia) for application of surgical meshes with PHB coating (no. 371-06 and no. 371-06, 02.10.2006) [263].

#### 6.2.3.6 PE/PHAs-Based Biocomposites and Bionanocomposites in Fire-Retardant Applications

Bionanocomposites form a special class of materials possessing a range of unique characteristics with respect to gas and water vapor permeability, thermal stability and fire resistance [264]. Understanding the performance of biocomposites is crucial in fire-retardant applications. Tensile, flexural, and impact properties are the basic mechanical performances of biocomposites that have been extensively investigated in the last two decades. Besides the mechanical properties, other properties of biocomposites, such as acoustic insulation and fire retardancy, are also being explored, leading to wide potential applications [265]. Fire retardance is an important measure of performance for fiber composites, including biocomposites. In aircraft, train, and building interiors, fire-retardant composite structures are highly desirable [266]. Liu and Berglund [267] investigated fire-retardant and ductile clay nanopaper biocomposites based on montmorillonite in the matrix of cellulose nanofibers and carboxymethyl cellulose. Three-component nanocomposite films were prepared based on sodium montmorillonite clay (MTM), a water-soluble cellulose derivative (CMC) of fairly high molar mass, in combination with nanofibrillated cellulose (NFC) from wood pulp. The nanocomposite was cast from an aqueous colloidal dispersion. First, the effects of CMC content on CMC/MTM compositions with high volume fraction of MTM (36–83 vol%) were studied. In addition, fire retardance and oxygen permeability characteristics were measured. The effect of NFC nanofiber addition to the matrix phase was then evaluated. The following were observed from their results: For pure CMC, there is only one degradation stage and the decomposition rate is very fast. For CMC/MTM nanocomposites, the decomposition rate was dramatically reduced with decreasing CMC content. The main reason is that the MTM nanoplatelets formed continuous protective solid layers, that oxygen diffusion was hindered and oxidation kinetics became slower. According to them, one may speculate that silicate layer fusion and/or char formation of the CMC are contributing mechanisms. These observations



are very interesting since the fire retardance characteristics of this system are likely to be favorable [267]. Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions was studied by Liu *et al.* [266]. Fire retardance and oxygen permeability characteristics were measured in their investigation. They measured the self-extinguishing characteristics of clay nanopaper using a 45 flammability test. They found that pure NFC has high flammability and burns quickly and completely; however, clay nanopaper was immediately self-extinguishing upon removal of the flame.

Fire performance of wood-plastic composites (WPCs) is quite important if they are designed for furniture and residential building applications [268]. To better understand the behavior of fire retardants on the fire performance of wood flour/PE composites, five fire-retardant systems (decabromodiphenyl oxide, magnesium hydroxide, zinc borate, melamine phosphate, and ammonium polyphosphate) were investigated [269]. All five reagents improved the fire performance of WPCs. Interestingly, adding wood flour alone can dramatically ameliorate the fire performance too. Toughening agents were explored to improve the reduced impact strength caused by adding wood fibers into polymer matrices. PHA was found to increase the impact strength of wood/PLA composites but compromised tensile strength and thermal stability [270]. Styrene-butadiene-styrene (SBS) block copolymer can also improve the impact resistance and elongation at break at the expense of tensile strength [271]. Garcia *et al.* [272] reported on WPCs with improved fire retardancy and durability performance through the addition of a combination of fire retardants and light stabilizers. Stark *et al.* [273] evaluated various fire retardants in PE matrix WPCs. It was determined that magnesium hydroxide and ammonium polyphosphate improved the fire performance of the WPCs.

#### 6.2.3.7 *PE/PHAs-Based Biocomposites and Bionanocomposites in Aerospace Applications*

Aerospace applications now require the best performance and traditional materials cannot meet the highly specialized requirement; therefore, advanced composite materials with much better and controllable functional properties have become widely used in aerospace structures [274]. Composite materials are becoming significantly important in different types of construction of aerospace structures. Aircraft parts made from composite materials, such as fairings, spoilers, and flight controls, were developed during the 1960s for their weight savings over aluminum parts [275]. New generation large aircraft are designed with all composite

fuselage and wing structures and the repair of these advanced composite materials requires an in-depth knowledge of composite structures, materials, and tooling. The primary advantages of composite materials are their high strength, relatively low weight, and corrosion resistance [275]. Commercial aircraft, military aircraft, space aircraft, and helicopters, all make substantial use of composites, both for interior and exterior structures [276]. Polymer composite structures such as wing-covers, aircraft leading edges, and composite fuselages have become standard use in advanced aircraft, which not only reduce structural weight, but also provide better stiffness, toughness, fatigue strength, energy absorption, and thermal stability than traditional materials [277, 278]. Currently, composite materials represent 50% of the weight for Boeing 787 Dreamliners and 52% for Airbus 350 XWB airplanes [279]. The possibility to use thermoset nanocomposites for producing structural parts depends on the ability to control the interworking of the composition (resin, curing agent, nanoparticles) and its effect on the polymerization process (density, cross-linking efficiency, cure kinetics) [280]. These issues are also dependent upon method of dispersion and cure temperature. The effect of nanofillers in polymeric composites on the kinematic viscosity of the polymer matrix has been studied for different filler-resin composites. In many cases, the amount, the dispersion and the surface state of the nanoparticles have great influence on the rheological behavior and, by default, on the mechanical properties of the nanocomposites [281]. Montmorillonite belongs to the layered silicates nanoclay class, representing nanoparticles with anisotropic, plate-like, high-aspect-ratio morphology, which leads to an improved permeation barrier. Using montmorillonite, the matrix is expected to have increased dimensional stability at low reinforcement loading [280]; a characteristic that makes it useful in the aerospace and automotive industries.

Polymer composites have been fabricated mainly by using high strength synthetic fibers such as carbon, glass and aramid and low strength polymeric matrix; such composites have dominated the aerospace industry [282]. The use of polymer/CNT nanocomposites in structures has several predictable impacts on aerospace and defense, the most obvious of which is significant airframe weight reduction stemming from polymer/CNT nanocomposites low density and complemented by its high strength and modulus. Experiments on fully integrated nanotube composites using CNT have demonstrated major enhancement of mechanical properties [283]. As a result of the higher tensile strength that CNT exhibits, together with advanced energy dissipation mechanisms of CNT reinforced structures, more damping can be achieved with a smaller and lighter amount

of structural members of the design for aerospace. The number of CNT walls and their size affect stress concentration in the composites and thus short and round particles are the strongest ones (i.e., diamond); but longer fibers are flexible and may work for damping, while CNT may act as a nanoscale spring and a crack-trapping material in the composite. These damping phenomena could be multiplied when CNT are dispersed [283]. Organic polymer with uniformly dispersed CNTs could enable polymer materials to withstand the harsh space environment and may be used for the purpose of critical weight reduction on current and future space systems [284]. The primary structural aluminum materials were entirely replaced by CNT/high-density polyethylene nanocomposites. The results achieved an average of 17.30% weight reduction in the low initial mass category. The average fuel savings for all CNT-reinforced air frames was about 10% [284]. It can be summarized that this type of analysis gives an insight into the ultimate advantages of CNT/polymer nanocomposites for aerospace application.

Polyhydroxyalkanoates are microbial-produced biopolymers that have gained much attention due to their biocompatibility, biodegradability, and diverse structural composition, imparting them with physicochemical properties close to those of PVC and PET. These combinations of excellent physicochemical properties have led to the increasing commercial exploitation of PHA in different niche applications, including aerospace and the military [285]. Tandon and Ran [286] also enhanced the thermomechanical properties of conventional aerospace carbon fiber-reinforced (IM7) composites using carbon nanofiber. They manufactured IM7/CNF matrix unidirectional laminate aerospace structures using the filament-winding technique.

#### 6.2.3.8 *PE/PHAs-Based Biocomposites and Bionanocomposites in Optical Applications*

Optical characteristics of polymer nanocomposites can change upon the decrease of particle sizes to very small dimensions, which are, in general, of major interest in the area of nanocomposite materials. Polyethylene is used extensively for high-voltage cable insulation. It is also employed in communication systems, many of which are miniaturized for use in space and defense programs. Thus, an understanding of the interactions of photons and of charged particles with thin films of polyethylene is very important [287]. Bownass *et al.* [288] successfully demonstrated that polyethylene oxide (PEO) can be used to detect humidity in passive optical networks at around the single value of 80% relative humidity (RH) for optical

telecommunication wavelengths between 1.1 and 1.55 mm. The sensing mechanism is based on the humidity-induced change in the refractive index of the polyethylene oxide overlay on a polished surface of a half-block single-mode fiber device. Polyethylene oxide, or poly(ethylene glycol) (PEG), is known to be highly hydrophilic in its response to water vapor. This makes PEG a favorite material for humidity sensing applications. For the purpose of building a plastic optical fiber humidity sensor, Acikgoz *et al.* [289] determined the index of refraction and swelling behavior of a PEG thin film by using an optical waveguide spectroscopic method. They observed that the phase change in the thicker PEG coatings slightly shifted to lower humidity. This might be due to the rather easy penetration of water molecules into the thicker polymer networks, which causes quicker gel formation. This is why a thicker film shows rapid swelling response at lower RH values around 75%. In addition, after gel formation in a thicker film, there is a steeper increase in the output intensity of the fiber sensor [289]. Polyethylene conduit provides mechanical protection to fragile cable materials like fiber optic and coaxial cables; it increases the cable's strength and durability [290]

Significant scientific and technological interest has been focused on polymer inorganic nanocomposites (PINCs) over the last two decades. The use of inorganic nanoparticles in the polymer matrix can provide high-performance novel materials that find applications (such as optical application) in many industrial fields [291]. Nanoparticles have already been incorporated into glass to make colored glasses that are known as gold ruby glasses. Scientists such as Neri [292] described the preparation of gold ruby glasses in the seventeenth century. In the nineteenth and early twentieth centuries, scientists such as Faraday [293] realized that the color of small Au particles depended on the size and distance between the particles. The size of Au nanoparticles was also experimentally determined for the first time by Siedentopf and Zsigmondy in 1903 by a light scattering method [294]. After Au was first used as an inorganic nanofiller in PINC for optical applications, other metals such as Ag, Cu, and Pt were also used with natural polymers for similar optical applications [294]. Yano *et al.* [295] have shown nanocellulose's extraordinary potential as a reinforcement material in optically transparent plastics, for instance, as a substrate for bendable displays. According to the authors, the composite remained optically transparent even at high fiber contents.

PHAs are optically active biopolyoxoesters composed of (*R*)-3-hydroxy fatty acids which represent a complex class of storage polyesters [296]. Due to their piezoelectric nature, it is also possible to use PHAs to make the

following articles: pressure sensors for keyboards, stretch and acceleration measuring instruments, material testing, shock wave sensors, lighters, gas lighters; acoustics – microphones, ultrasonic detectors, sound pressure measuring instruments; oscillators – headphones, loudspeakers, for ultrasonic therapy and atomization of liquids [297]. Polybutylene terephthalate is used for housings in electrical engineering, but also in automotive construction as plug connectors and in household items such as showerheads or irons. It is also used in the keycaps of some mechanical keyboards because of its resistance to wear.

#### 6.2.3.9 *Recycling and Lifetime Studies on PE/PHAs-Based Biocomposites and Bionanocomposites*

Plastics are a combination of high molecular weight compounds, called polymers, which include PS, PP, PE and PVC. Plastics play a major role in our daily lives. Throughout the world the demand for plastics, particularly bags, plastic packaging, thin films, etc., continues to quickly grow. As a consequence, the problem of plastic waste is growing as well. Plastics are the fastest growing materials of the waste stream and because most of the plastics are basically non-biodegradable, littered plastics have become a crucial environmental problem [298]. Usually plastics do not have the capability to degrade and thus recycling has to be done in some cases to decrease this disposal problem, but this cannot be a good remedy. Although many new technologies are developed to make plastic degradable, like photodegradable plastics [299], researchers are looking for better alternatives so as to resolve this problem and make the material degradable or have a controlled lifetime [300].

Plastic recycling is one of the common ways used for reducing plastic wastes. This has to be carried out in a sustainable manner. However, it is a suitable method due to the potential environmental and economic benefits it can provide. There is a wide variety of recycled plastic applications and the market is growing. Mechanical recycling, i.e., direct reprocessing of thermoplastics, is the most effective, reliable and economical method for recycling of plastics waste. However, mechanically recycled plastics normally have less desirable properties when compared with the same materials manufactured from virgin compounds [301]. The quality of plastics projected for recycling is greatly dependent on their history and origin [302]. Furthermore, melt processing, which is used in plastics recycling, may cause oxidative and thermomechanical degradation of the polymers [303]. The result of the degradation processes is a modification of the molecular structure of the polymer and a subsequent deterioration

of various properties. Therefore, suitable recycling must take into consideration the oxidative damage introduced to a polymer during its lifetime. It is necessary to deal with processing and long-term stability of recyclates through appropriate deactivation of structures with prodegrading properties, especially peroxides and hydroperoxides. This is achieved by restabilization of recyclates. Restabilization has to take into account previous damage, subsequent application and residual stabilizer content. A balanced combination of suitable stabilizers and co-stabilizers contributes to processing stability and to service lifetime of a recyclate during its intended applications. The type and amount of required stabilizers depend on the reprocessing conditions as well as on the intended use of the recycled materials, which means that the consumed stabilizers often must be replaced.

Therefore, the development and use of biodegradable polymers is gaining more serious attention. Among the various biodegradable polymers, a class that is drawing considerable attention is the PHAs and PLA [304]. PHAs are attractive because of their biodegradability and physical properties that closely resemble some conventional plastics such as LDPE and PP [305]. In addition, because of the varied types of monomers (about 150 different structures), it is possible to make PHA copolymers having a wide range of properties. PHAs are a family of linear polyesters of 3-, 4-, 5- and 6-hydroxyacids, synthesized by a wide variety of bacteria through the fermentation of sugars, lipids, alkanes, alkenes and alkanolic acids. They are found as discrete cytoplasmic inclusions in bacterial cells. Once extracted from the cells, PHAs exhibit thermoplastic and elastomeric properties. PHAs are recyclable, are natural materials and can be easily degraded to carbon dioxide and water. Hence they are excellent replacements for petroleum-derived plastics in terms of processability, physical characteristics and biodegradability. In addition, these polymers are biocompatible and hence have several medical applications [306]. Perhaps one of the greatest advantages that PHAs possess over other biodegradable polymers is their ability to degrade under both aerobic and anaerobic conditions. They can also be degraded by thermal means or by enzymatic hydrolysis. In a biological system, PHAs can be degraded using microbial depolymerises as well as by nonenzymatic and enzymatic hydrolysis in animal tissues [307]. The biodegradability of a polymer is governed primarily by its physical and chemical properties. It has been found that low molecular weight PHAs are more susceptible to biodegradation. The melting temperature is another important factor to be considered when studying

biodegradation. As the melting point increases, the biodegradability decreases. With increasing melting temperature, the enzymatic degradability decreases. Tokiwa and Suzuki found that lipases cannot hydrolyze the optically active P(3HB). This could be due to the high melting temperature (178 °C) of the latter [308].

In general, there are four mechanisms by which plastics degrade in the environment: photodegradation, hydrolytic degradation, thermooxidative degradation and biodegradation by microorganisms [309]. Generally, natural degradation of plastic begins with photodegradation, which leads to thermooxidative degradation. Ultraviolet light from the sun provides the activation energy required to initiate the incorporation of oxygen atoms into the polymer [309, 310]. This causes the plastic to become brittle and to break into smaller and smaller pieces, until the polymer chains reach sufficiently low molecular weight to be metabolized by microorganisms [309]. These microbes either convert the carbon in the polymer chains to carbon dioxide or incorporate it into biomolecules [309]. However, this entire process is very slow, and it can take 50 or more years for plastic to fully degrade [311]. This is not aided by the fact that the photodegradative effect is significantly decreased in seawater due to the lower temperature and oxygen availability and that the rate of hydrolysis of most polymers is insignificant in the ocean [309].

### 6.3 Conclusions

Biobased polymers are becoming a widespread technology due to environmental concerns and the realization that global petroleum resources are finite. In the last decades, impressive progress has been made in the field of environmentally friendly biodegradable polymers and composites. Polymer biocomposites are not only replacing the existing polymers in a number of applications, new combinations of properties for new applications are also obtained from them. Nowadays, polyethylene/polyhydroxyalkanoates-based biocomposites and bionanocomposites are commonly found in many applications, from basic to hi-tech commodities, due to advancements in biotechnologies and public awareness. Due to the great number of properties of PE/PHAs-based biocomposites and bionanocomposites they are mainly considered for a wide range of applications such as paper and packaging, structural, military, coating, optical, fire retardant, and aerospace. Biomedical applications are also being considered.

## Abbreviations

CC	carbonaceous char
CMC	cellulose derivative
CNF	carbon nanofiber
CNTs	carbon nanotubes
COD	carbon oxygen demand
CS	chitosan
CS/PEG/G	chitosan/polyethylene glycol/gelatin
DBD	dielectric barrier discharge
DMA	dynamic mechanical analysis
DNS	Dika nutshell powder
DSC	differential scanning calorimetry
EPR	epoxy resin
ESR	electron spin resonance
EVA	ethylene-vinyl acetate
GAOs	glycogen accumulating organisms
HDPE	high-density polyethylene
IDT	increase of thermal resistance
KC	kenaf cellulose
LDPE	low-density polyethylene
MAO	methylaluminoxane
MDPE	medium-density polyethylene
MRE	meals ready to eat
MTM	montmorillonite clay
MWCNTs	multi-walled carbon nanotubes
NC	nanoclay
NFC	nanofibrillated cellulose
NMR	nuclear magnetic resonance
OA	orotic acid
OI	oxidation index
OMMT	organically modified montmorillonite
OTR	oxygen transmission rate
PBAT	poly(butylene adipate-co-terephthalate)
PCL	polycaprolactone
PEG	poly(ethylene glycol)
PEG-co-CA	poly(ethylene glycol-co-citric acid)
PEO	polyethylene oxide
PEP	polyethylene-alt-propylene
PHAs	polyhydroxyalkanoates
PHB-co-HHx	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)



PHBs	polyhydroxybutyrates
PHO	polyhydroxyoctanoate
PHBV	poly(hydroxybutyrate-co-hydroxyvalerate)
PI	polyisoprene
PINCs	polymer inorganic nanocomposites
PLA	polylactic acid
PMMA	polymethyl methacrylate
RH	relative humidity
RIF	rifampicin
RWF	recycled wood fiber
SBS	styrene-butadiene-styrene
SEM	scanning electron microscopy
SMKS	silane-modified kaolinite/silica core-shell nanoparticles
SWCNTs	single-walled carbon nanotubes
TEM	transmission electron microscopy
UMWPE	ultrahigh molecular weight polyethylene
VFAs	volatile fatty acids
WPCs	wood-plastic composites
XRD	X-ray diffraction

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