Biobased and Biodegradable Plastics

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Abstract

Because of the increasing environmental issues, the world has moved to the greener side, i.e., on zero or low emission side. The same case has been followed in the case of the composites development. Green composite is the main answer to this problem, as the name itself tells that the composite which is fabricated by reinforcing the natural fibers in the polymer matrix, which may be thermoset or thermoplastics. But if we want to make this composite as a fully biodegradable type, then we will have to use polymers derived from the cereals such as starch,

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Soy, PLA (poly lactic acid). These biopolymers degraded with respect to time so named as biodegradable type. In this chapter, we described a brief introduction of these biopolymers and their mechanical and morphological studies. Some of the applications of these biocomposites have also been described in this chapter.

Keywords

Biopolymer · Bio-plastic · Green composite material · Mechanical properties · Morphological studies

Introduction

Biopolymers are generally produced by living species. Biopolymer's molecular structures are made up of repeating units of saccharides, nucleic acids, and numerous additional chemical side chains which also take part in their functionalities. Biopolymers are extracted from the polysaccharides and can be produced from biomonomers by utilizing the conventional chemical processes or by genetically modified the organisms such as polyhydroxyalkanoates. It has been found that the genetically modified microorganisms have a great potentiality with properties generally suitable for biomedical applications like tissue engineering, etc. The main applications of the biopolymers are found in foods, clothes, decoration, or furniture, etc. It has been observed that the fossil fuels are the main or primary source for the production of the plastics which can be considered as a commercial product and are utilized in huge amounts in various applications. But these fuels are in of limited amount and also affect the environment, as it (plastic) being considered as a pollutant. At present, we must think of about the sustainable development which means that the products can be degradable with time cycle or period. By following that theme, the renewable energy became the most attractive theme nowadays. Biopolymers are cost effective and have great functionality as compare to the polymers derived from fossil fuel. The reason behind this is well known as the cost of the fuel or oil is very high as compared to the cost of available feedstocks such as starch; also the main advantage of using biopolymer is their biodegradability, which is utmost important from the environmental point of view [1]. The bionanocomposites justifies a special recognition because they involve different areas such as biology, materials science, and nanotechnology altogether. It is generally noticed that the polymer nanocomposites are the outcome of the addition of inorganic/organic fillers into polymers at the nanoscale. The tremendous properties of these new materials come from the available variety of biopolymers and fillers available, for example, clays, metal nanoparticles, natural fibers. [2]. It has been observed that the nanofillers reinforcement in the polymer matrix ultimately enhances the mechanical properties of the nanocomposites because of the superior interaction of the filler with the matrix [3]. The main advantage of bionanocomposite is that they are biocompatible or biodegradable in nature. The process involves in their degradation is due to hydrolysis or metabolic processes. So the main application of the nanocomposites generally comes under biomedical technologies, for example, tissue engineering, implants, dental applications. However, natural fibers may assume to be a new challenge for nanoclays filler that is being used as a conventional nanofillers for various applications [4], as these are now produced on an industrial scale.

Biopolymers Classification: A Brief Overview

Figure 1 shows a general classification of bio-based polymers. It has been observed that depending upon contents and the environment, the biopolymers may or may not be biodegradable. There are various reasons available for the utilization of the biopolymers in present time. This reason may be pertaining to the development of the new materials by using biopolymers, utilizing the waste for the development of these materials, environmental aspects, i.e., low emission of harmful gases such as carbon dioxides and the last but not least the useful utilization of the agricultural waste which is a big problem now a days. Waste disposal problem has been solved by the utilization of these biopolymers. However, the biopolymers were intentional to be utilized in various common applications such as packaging, farming, medical with lesser strength requirements. But the main disadvantages of these biopolymers are their very high cost. This high cost of biopolymers (in comparison to conventional plastics) is not because of the cost of raw materials which are generally used for biopolymer synthesis but because of the low volume of

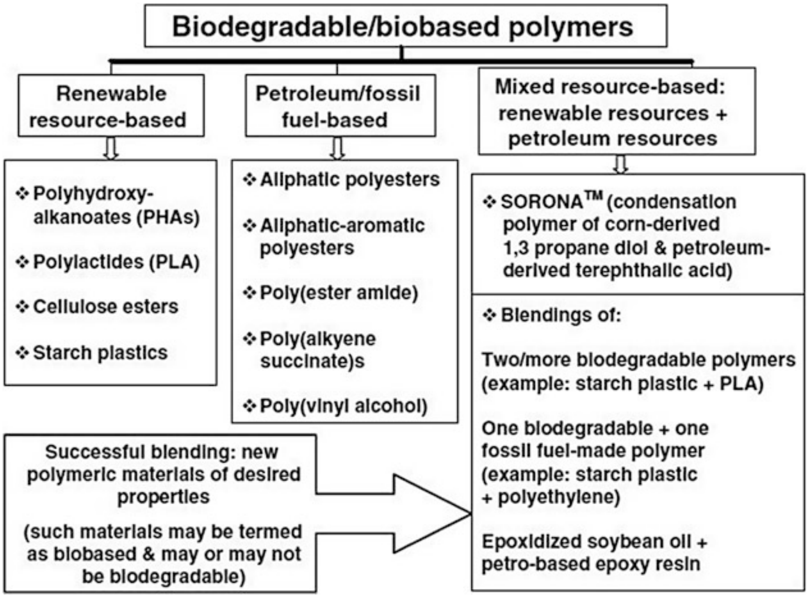

Fig. 1 Classification of bio-based polymers [5]

production. The main aim for the development of biopolymers is their stability during storage and life cycle assessment. Biopolymers reinforced with natural fibers ultimately produced green composites which can replace the conventional or synthetic fiber reinforced composites [5].

PLA (Poly Lactic Acid)

PLA (Poly Lactic Acid) is a distinctive polymer that mostly acts not only similar to PET but also behaves like polypropylene (PP). This is the polymer with the widest range of applications because of its ability of crystallization (stress or thermal). This polymer can be developed into films, fibers, and blow moldable to form the preforms of bottles just like PET [6]. The PLA has also considered being excellent for food packaging application. PLA can be processed by two processes, namely, direct condensation of lactic acid and by the ring-opening polymerization of the cyclic lactide dimer, as shown in Fig. 2. It has been observed that the direct condensation faced difficulties in the removal of the amounts of water in the later stages of polymerization which ultimately affects the molecular weight attained by this process. So ring-opening polymerization of lactide is found to be more suitable for processing. PLA has also found very much suitable as a matrix in natural fire composites or green composites. PLA generally has very good mechanical properties which are just similar to those of polystyrene [7].

Starch

Starches, which are generally used in different applications, are extracted from cereal seeds such as corn, wheat, rice, potato. Starches, extracted various sources, are chemically same [8, 9]. Starch generally consists of the polysaccharides amylose and amylopectin [8, 9]. It has been noticed that naturally occurred cereal starches consist of 72–82 wt% of amylopectin and 18–33 wt% of amylose. On the other hand,

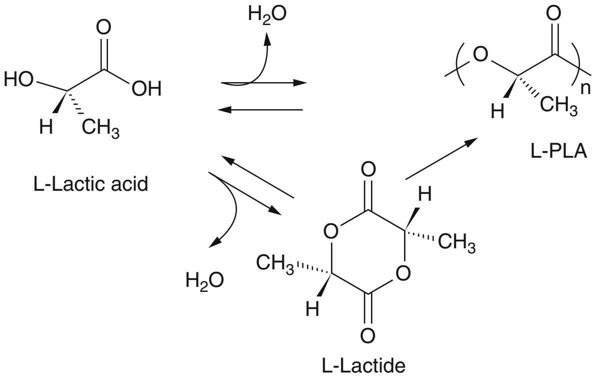

Fig. 2 Ring-opening polymerization of the cyclic lactide dimer [5]

modified genotypes, e.g., “waxy” starches, contain lesser than 1% of amylose, whereas high-amylose genotypes contain up to 70% amylose. The processing of starch granules can be done by heating in aqueous media, resulting in their gelatinization. The gelatinization results from swell up of the granules, which ultimately solubilize the starch as amylose filtered from the granules and made amylopectin fully hydrated which ultimately resulted in the loss of molecular order and the melting of the starch crystals [8, 10, 11].

In comparison to synthetic or conventional plastic, it has been observed that starch-based composites are inferior to moisture, brittleness. For the commercial applications, starch must be altered or modified by reinforcing it with materials (particulate or fiber), which ultimately enhances its properties and minimizes its water absorption capacity or sensitivity. Most of the researchers chemically modified the starch with other biopolymer resulted in the improvements in the properties of the material. Example of these polymers is chitin/chitosan [12], cellulose, poly(lactic acid) (PLA), and poly(vinyl alcohol) (PVOH) [13–15].

Soy

Soy protein, another alternative of the petroleum polymers, is used in the manufacturing of adhesives, plastics, packaging, and binders. Soy protein can be considered as the main co-product of soybean oil, is easily available and renewable, and also consists of functional properties as specifically needed by plastic industries. There are numerous applications of the soy protein, generally utilized to manufacture adhesives, coatings, lubricants, plastics, and other specific products. However, the soy protein plastic applications are also found in automobile industries and packaging industries to make automobile parts and packaging materials. As per environmental concerns, the main objective of the industries is to develop and utilize the green products which can be considered as an alternative to the petroleum-based chemicals or plastics. Soy-based products not only solve the environmental pollutions problems but also provide high-performance characteristics.

Soy Protein Plastics

The soy protein plastics generally should have good mechanical properties and water resistance properties and can be improved by plasticization process by using plasticizers like glycerol, ethylene glycerol, propylene glycerol, 1,2-butanediol, polyethene glycol, and sorbitol [16–29]. The mechanical properties and water resistance can be enhanced by adding zinc sulfate or formaldehyde, acetic anhydride, glyoxal, or a polyphosphate filler [29–34]. However, these properties can also be controlled and optimized by the adjustment of the different processing parameters, for example, molding temperature, pressure, and the initial moisture content [34–39].

Mechanical Properties of Biocomposite Materials: A Recent Study

Emad Omrani et al. (2015) developed bio-based carbon-fabric epoxy composites using liquid composite molding and compared their bending strength and modulus with pure bio-based epoxy composite and found that bending strength and bending modulus are improved with the addition of carbon layers in the composite. As carbon fiber volume fraction increases from 0% to 30% in the carbon-reinforced composites, bending strength also increases from 15 to 95 MPa. This enhancement is also observed in the bending modulus as it rises from 40 MPa in pure epoxy samples to 300 MPa in 30% fiber volume fraction carbon-reinforced composite [40] (Fig. 3).

H. Essabir et al. (2016) developed bio-based hybrid composites from waste coir residues and noticed a decrease of about 8–9% in tensile strength due to formation of high stress zones around fillers for all composites at 20% weight of natural fillers like coir and coir shell particles compared to neat Polypropylene. Authors also reported a gain of 29% and 24% in Young's modulus of binary and ternary composites, respectively, when coir shell particles (20 wt%) are added [41].

V. Paul et al. (2015) studied the mechanical properties of a bio-based composite derived from banana plant source and found that when a banana sap is added to the matrix an increase of about 18% in tensile stress takes place. The BSM (Banana Sap Matrix) composite failed at a mean stress value of 26.1 ± 1.14 MPa as compared to 22.2 ± 0.82 MPa of the control composite. Also a 25% improvement in flexural modulus was noted [42] (Fig. 4).

Pengju Pan et al. (2007) found that on addition of kenaf fibers (20 and 30 wt% KF), the tensile modulus of the PLLA (poly(L-lactide))/KF composites increased by 21% and 30%, respectively, when compared with the pure PLLA. However, the tensile strength as well as the fracture strain of the composites shows a decrease as

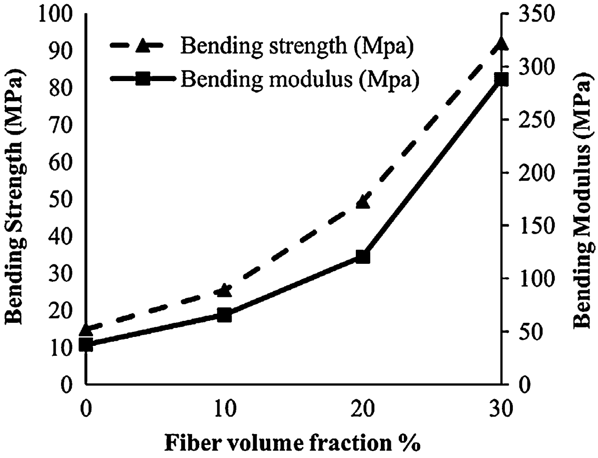

Fig. 3 Bending properties of the pure epoxy and carbon-reinforced composite specimen [40]

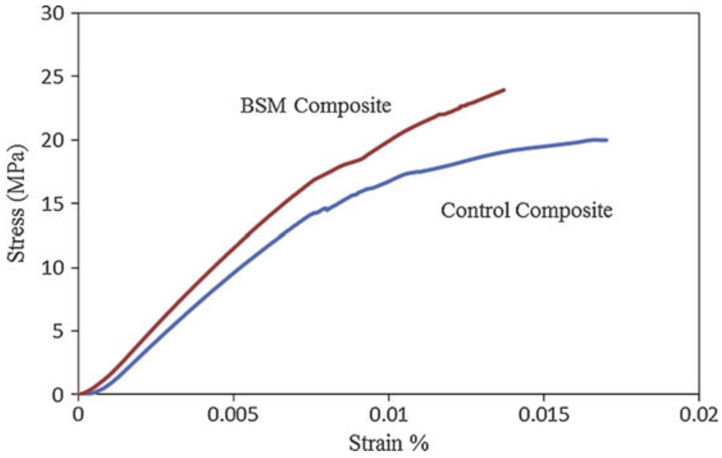

Fig. 4 Variation of tensile stress as a function of % strain comparing the BSM composite with the control composite using mean values. (Reprinted with permission from [42])

the Kenaf content increases. A possible explanation is inadequate adhesion between KF and PLLA [43].

Christos Mavrakis et al. (2008) incorporated MG (mastic gum) to gel matrices based on gelatin, egg white, or polysaccharides and observed that addition of MG particles at a concentration level of 6% resulted in an increase in gel elasticity and yield strength of white gels. A tremendous rise was observed in Young's modulus of elasticity. However, in the case of polysaccharide gels, addition of MG resulted in a considerable decrease in the gel resistance to compression. Mechanical strength of the polysaccharide gels also decreased with an increase in MG content [44].

Xiaomei Ma et al. (2017) demonstrated that by reinforcing calcium alginate (with nanocrystalline cellulose) in biopolymer matrix, the tensile strength of both CNC (cellulose nanocrystals) and OCNC (oxidized derivative of CNC) – modified alginate fibers – changes in the following manner: first it increases with increase in the nanocrystal's content, reaches a maximum at 0.5 wt.% loading, and then decreases if the loading is increased anymore [45] (Fig. 5).

H. Dahy (2017) synthesized two composites RA shell from agro-fibers, cereal straw short fibers color, coconut fibers of reddish brown and Plant CULTURE (biocomposite composed of agro-fibers compounded by a bio-based thermoplastic matrix (PLA bioplastic)) and compared their tensile strength among themselves and with a reference material. He found that Plant CULTURE had the maximum Ultimate Tensile Strength followed by reference material and TRA shell, respectively [46] (Fig. 6).

Runguo Wang et al. (2016) developed bio-based TPVs (Thermoplastic vulcanizates) from polyester elastomer and PLA by an in situ dynamical cross linking and mixing method. With an increasing BPE (Bio-based polyurethane) elastomer content, a decrease in tensile strength (17.8–7.4 MPa) and hardness (97–86°) was observed [47] (Fig. 7).

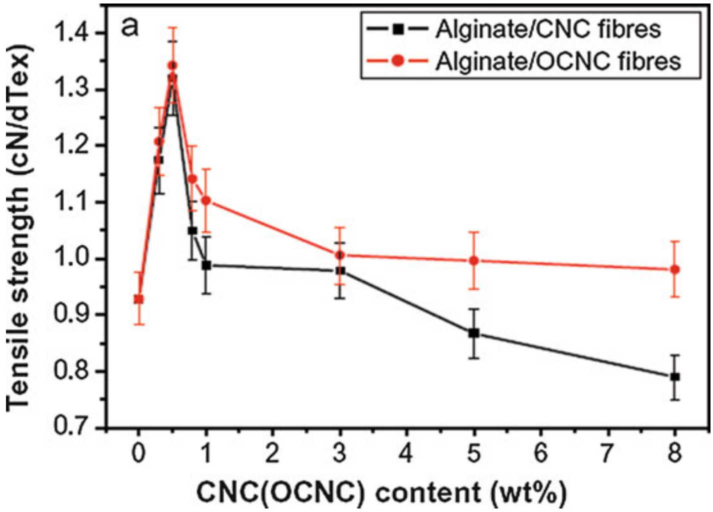

Fig. 5 Effect of the nanocrystal's content on (**a**) the tensile strength, (**b**) elongation at break, and (**c**) work at break of the nanocomposite fibers. (Reprinted with permission from [45])

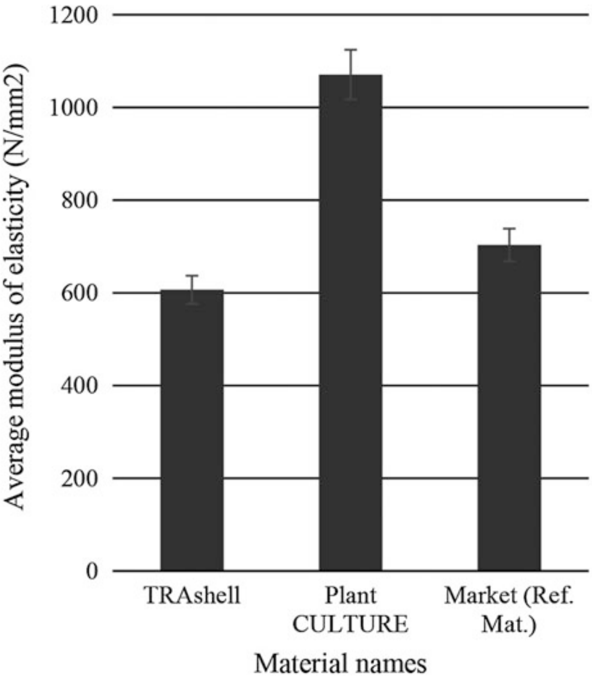

Fig. 6 The average modulus of elasticity of the developed green biocomposite cladding materials in comparison to the market reference material. (Reprinted with permission from [46])

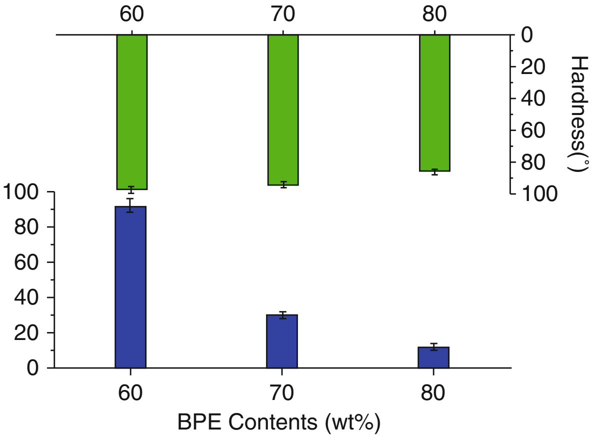

Fig. 7 (**a**) Strain-stress curves of bio-based TPVs with different blending ratios of BPE/PLA; (**b**) tensile set at break and hardness at different of BPE contents. (Reprinted from [47] by kind permission)

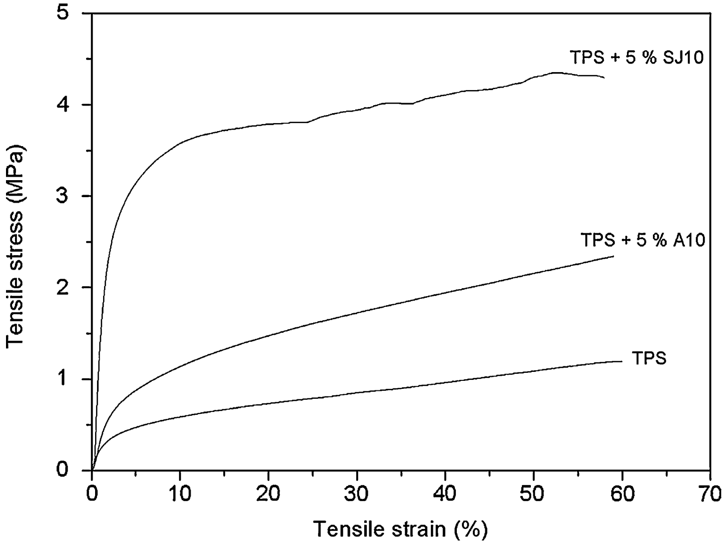

Fig. 8 Stress-strain curves of films based on TPS and bionanocomposites with 5% w/w of A10 and SJ10 talc particles. (Reprinted with permission from [48])

Luciana A. Castillo et al. (2015) found that incorporating talcs to thermoplastic starch (TPS) induced an increase in tensile strength as well as the elastic modulus. Figure 8 shows tensile test curves corresponding to TPS and composites with talc particles. Talc addition did not modify stress strain behavior of TPS films. In addition, the synthesized bionanocomposites thus obtained presented more resistant elastic deformation than neat TPS films. A10 stands for Australian

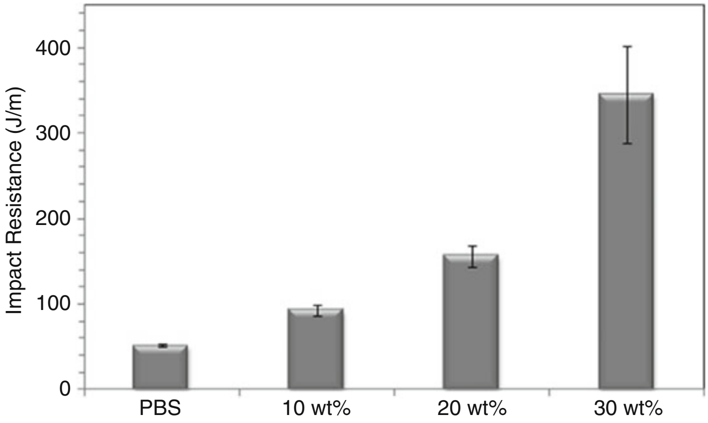

Fig. 9 Izod impact resistance of PBS reinforced with different curaua contents (10–30 wt%, 3 cm). (Reprinted with permission from [49])

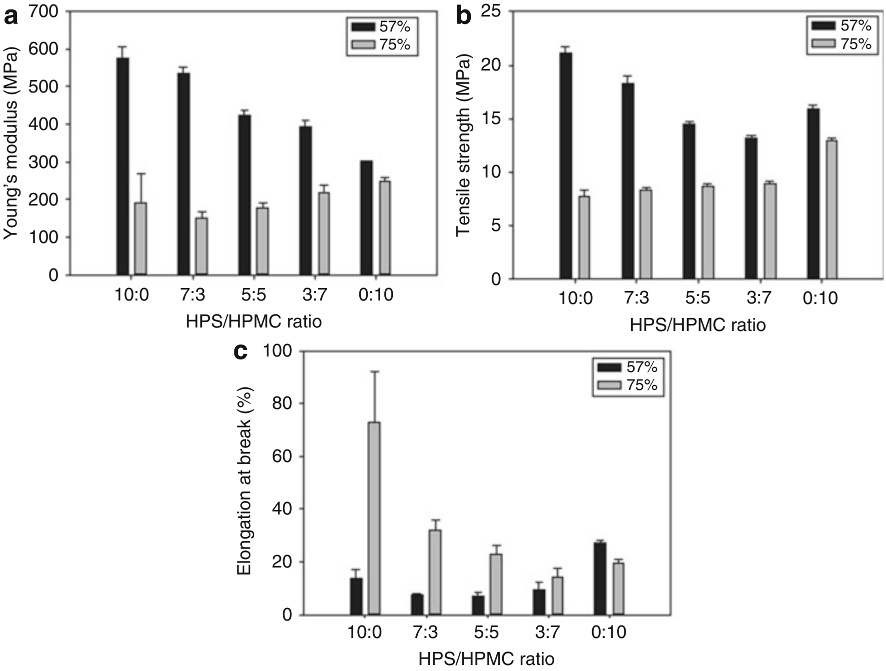

Fig. 10 Tensile properties of HPS/HPMC fibers with different HPS/HPMC ratios equibilized under different relative humidity conditions. (Reprinted with permission from [50])

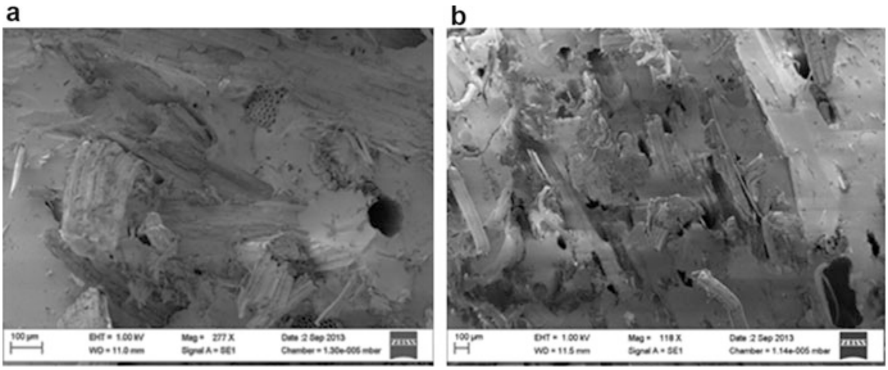

Fig. 11 SEM images showing tensile fracture surface of (**a**) BSM composite and (**b**) control composite. (Reprinted with permission from [42])

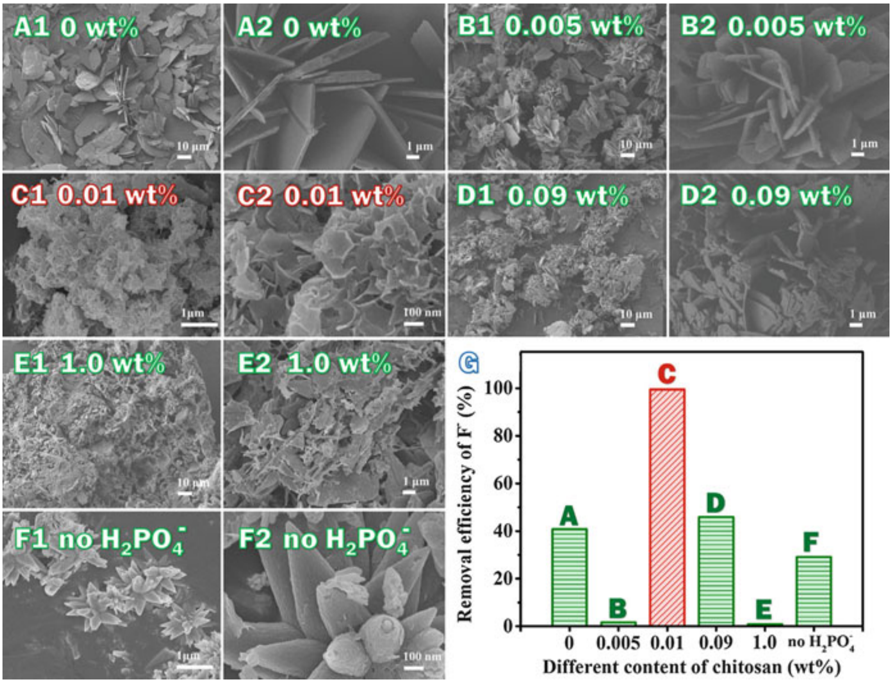

Fig. 12 (**a**–**f**) SEM images and (**g**) defluorination efficiency of brushite which prepared with different content of chitosan (initial concentrations 10 mg/L, 20 mL, adsorbent 0.05 g, pH = 6). (Reprinted with permission from [52])

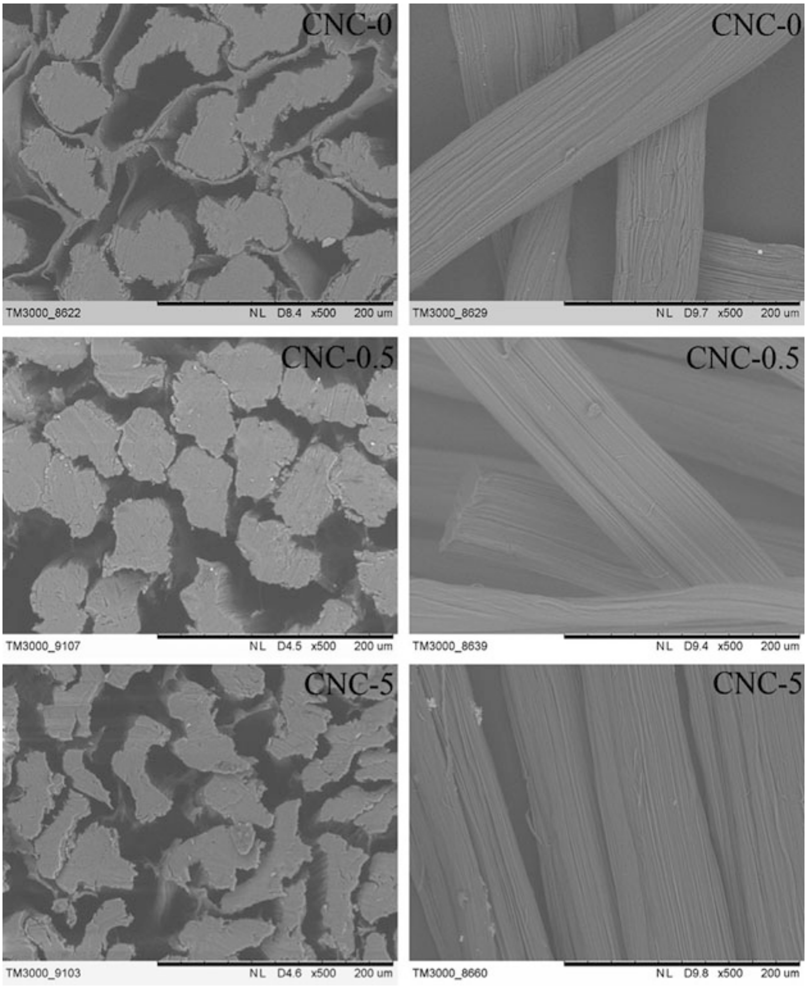

Fig. 13 SEM micrographs of Alginate/CNC nanocomposite fiber. (Reprinted with permission from [45])

talc with a purity degree of 98% w/w and SJ10 Argentinean talc containing up to 16% w/w of impurities [48].

Elisabete Frollini et al. (2015) synthesized composites based on poly(butylene succinate) (PBS) and curaua fibers and found that impact resistance of composites was not only greater than that of PBS homopolymers (approximately 52 Jm-1) but also noticeably increased with increase in the weight percentage of fibers, with the highest value for 30 wt% curaua fibers (345 Jm-1). The flexural strength repeated the trend, but in case of this property change up to 30 wt% of loading was not that great

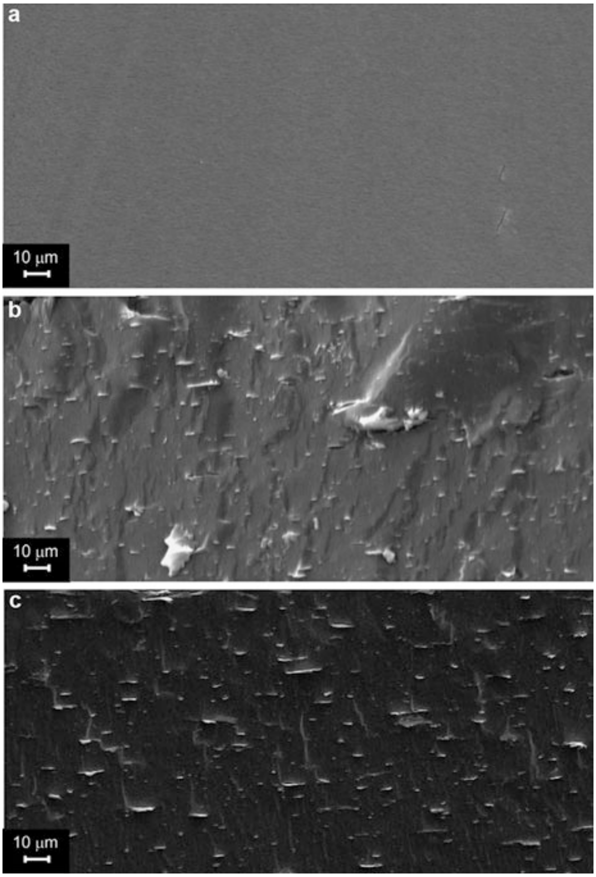

Fig. 14 SEM micrographs of films based on: (**a**) TPS; (**b**) and (**c**) bionanocomposites of TPS with 5% w/w of A10 and SJ10 talc particles, respectively. (Reprinted with permission from [48])

as in the case of impact resistance test. An increment of approximately 64% of curaua fibers weight is significant [49] (Fig. 9).

Yanfei Wang et al. (2016) synthesized blends of hydroxypropyl methylcellulose (HPMC) hydroxypropyl starch (HPS) and compared their tensile properties at 25 °C and equilibrated at 57% RH (Relative Humidity) and 75% RH conditions. Figure 5 shows the results regarding Young's modulus (E), tensile strength (st), and elongation at break (εb). At 57% RH, the pure HPS film had the highest E and st, while the pure HPMC film had the least values. In general it is observed that with increasing HPS content, E and st of the HPS/HPMC blend films also increased. It is known that εb of the pure HPS film was much lower than that of the pure HPMC film and that εb of pure films was greater than that of all blend films. When RH increased to (75%), E and st got reduced generally. On the other hand εb values increased for all materials. Pure HPS film, but εb was lower for the pure HPMC film [50] (Fig. 10).

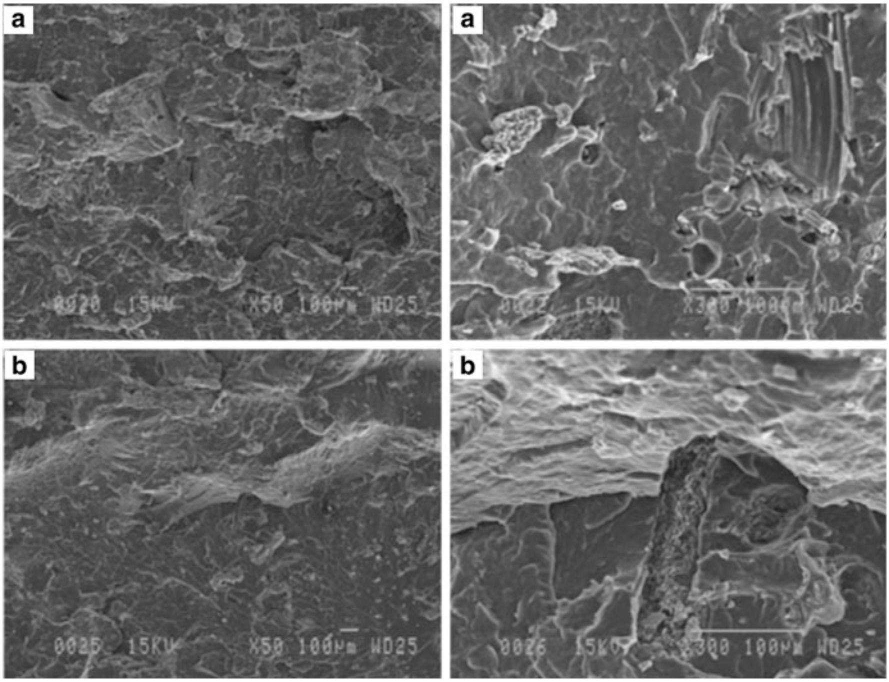

Fig. 15 Morphologies of hybrid composites (10:10) at low high and magnification: (**a**, **a′**) without compatibilizer and (**b**, **b′**) with compatibilizer (SEBS-g-MA). (Reprinted with permission from [41])

Zhilong Yu et al. (2017) synthesized biopolymer-based edible nanocomposite films using CNFs, corn starch, and chitosan and noticed that with increasing CNFs (Cellulose nanofibrils) content, the tensile strength of the films did not significantly alter. The elongation at break however decreased. It reduced by 39% at 100% of CNFs. However, the Young's modulus showed an increasing pattern at higher contents of CNFs ($\geq$60%) added to the films [51].

Morphological Studies of Bio-composites: An Overview

V Paul et al. (2015) performed SEM analysis of BSM composite and control composite shown in Fig. 11a and found that the morphology of the tensile fracture surface of (a) BSM composite and (b) control composite have cavities present in the composite material. Nevertheless, a fewer holes were present in Fig. 12a which implies that the banana fiber is physically well bonded to the matrix as compared to (b). The only difference between the two samples is the presence of banana sap in the matrix [42].

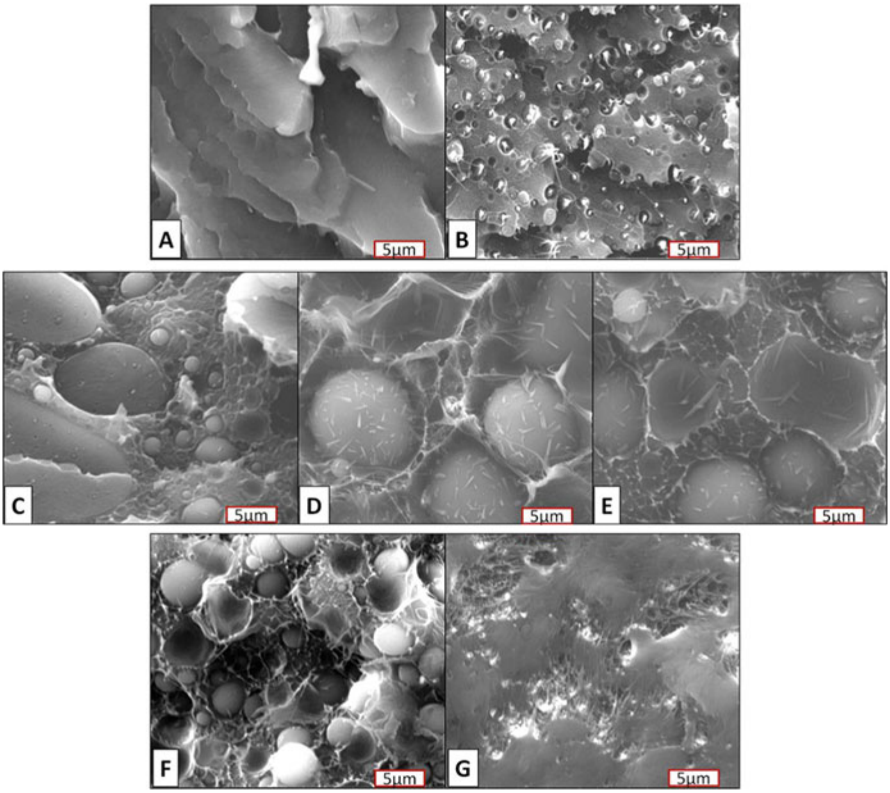

Fig. 16 SEM images of impact fractures of PTT, BioPE and their blends: (**a**) PTT/BioPE (100/0), (**b**) PTT/BioPE (80/20), (**c**) PTT/BioPE (60/40), (**d**) PTT/BioPE (50/50), (**e**) PTT/BioPE (40/60), (**f**) PTT/BioPE (20/80), (**g**) PTT/BioPE (0/100). (Reprinted with permission from [53])

Yanhong Chen et al. (2017) experimented on petal-like nanosheets of brushite by using chitosan as a regulator for adsorption of fluoride ions in the drinking water. They found the tremendous difference in the morphology of brushite which was prepared with different content of chitosan was shown in Fig. 12. It had been observed that structures were mainly controlled by the content of chitosan in the composites. In the absence of chitosan, brushite was in a typical large tabular habit (Fig. 12a1, a2), which was the most common crystal morphology of brushite. When the chitosan content in precursor was more than 0.09 wt% (Fig. 12e1, e2, f1, f2), the brushites were no longer uniform and the amorphous part like chitosan were found. Then, these composites were tested for defluorination efficiency by normal adsorption process (Fig. 12g). The sample that was prepared by the calcium precursor with 0.01 wt% chitosan displayed the best defluorination efficiency of 99.48 [52].

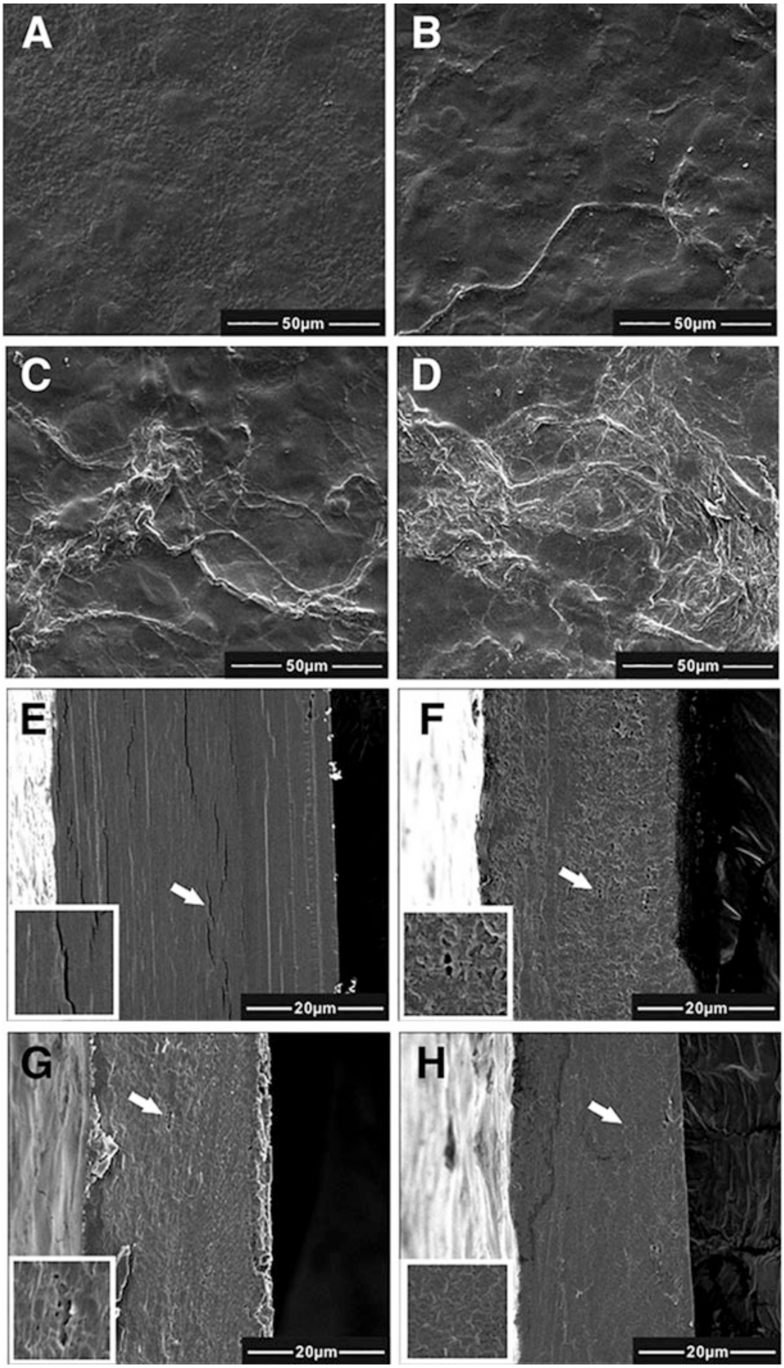

Fig. 17 (continued)

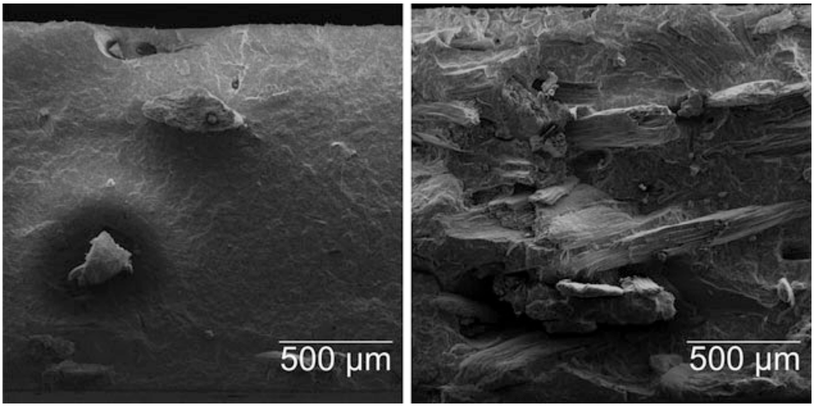

Fig. 18 SEM micrographs of fiber dispersion in PHB/agave (left) and P(HB-HV)/agave (right) composites. (Reprinted with permission from [54])

Xiaomei Ma et al. (2017) found in SEM analysis of sodium alginate that the cross-section of the prepared fibers is not uniformly round, but rather exists as a kidney-like shape. There are many grooves on the surface of the fibers. The kidney-like morphology is the special characteristic evolved from wet spinning, which can be attributed to the dehydration during the subsequent drying stage, leading to the shrinkage of the fibers. With the increase of the nanocrystal content, the composite fibers become flat (evidenced from CNC-5 and CNC-0.5). This can be attributed to the viscosity decrease of their respective spinning dope with the increase of the nanocrystal loading [45] (Fig. 13).

Luciana A. Castillo et al. (2017) analyzed talc nanoparticles distribution in TPS matrix, as well as homogeneity and appearance of the developed films, using SEM. This study was performed in a JEOL JSM-35 CF electron microscope (Japan), with a secondary electron detector. Films were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and being coated with a gold layer (~30 Å), using an argon plasma metallizer (sputter coater PELCO 91000). Thus, film surfaces and their cross-sections were satisfactorily observed [48] (Fig. 14).

H. Essabir et al. (2016) analyze the effect of hybridization and coupling agent on morphological properties polypropylene hybrid. In the composite, the distribution/dispersion of the fillers and the affinity (compatibility) between the fillers and the matrix are the two main factors that affects the final properties (structural, thermal, mechanical, and rheological). Micrographs of the fractured samples were been used to determine the degree of filler dispersion/distribution and their affinity with the

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Fig. 17 SEM observation of the surfaces (**a**: 0% CNFs; **b**: 20% CNFs; **c**: 60% CNFs; **d**: 100% CNFs) and cross sections (**e**: 0% CNFs; **f**: 20% CNFs; **g**: 60% CNFs; **h**: 100% CNFs) of nanocomposite films. The cross-sectional areas (**e**–**h**) pointed by the white arrows were magnified at the same ratio and displayed at the lower left corner of each micrograph. Scale bar: (**a**–**d**), 50 μm; (**e**–**h**), 20 μm. Magnification: (**a**–**d**), 1000×; (**e**–**h**), 2000. (Reprinted with permission from [51])

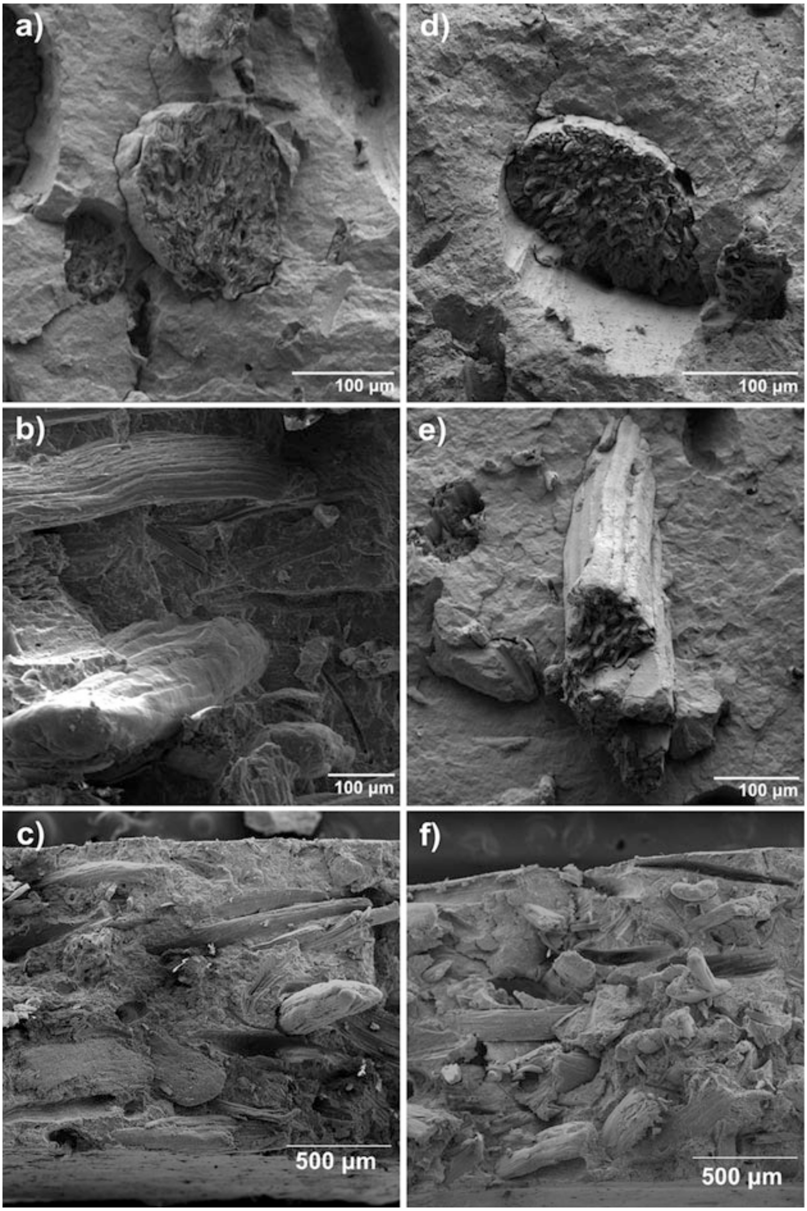

Fig. 19 SEM micrographs of PHB/agave (left column) and P(HB-HV)/agave (right column) composites prior deformation (**a**, **b**, **d**, **e**) and after tensile breakage. (Reprinted with permission from [54])

matrix. The hybrid composite (10:10) at low magnification has been illustrated in Fig.15a, b [41].

Eugene Enriquez et al. (2016) analyzed the morphological properties of poly (trimethylene terephthalate) and high density polyethylene. The SEM images of the impact fracture samples displayed in Fig. 8 illustrate the fractured surfaces of the virgin and blended materials. The SEM images display the brittle and ductile deformation mechanisms of the impact samples. The surface morphology of neat BioPE was relatively smooth comparatively to the neat PTT fracture surface, which produced more cracks throughout the surface [53] (Fig. 16).

Zhilong Yu et al. (2017) studied the effect of cellulose nanofibrils on the active functions of biopolymer-based nanocomposite films and developed the biopolymer-based edible nanocomposite films. It is mixed with edible films and can used for the purpose of food packaging. The results of the SEM photographs conclude that the CNFs shows good filling effect on the structure of biopolymers films which can also enhance the blocking of lights in the films, oxygen, and water vapor and also weakens the water trapping capability [51] (Fig. 17).

Erika V. Torres-Telloa et al. (2017) studied the agava fibers which are important waste of the tequila industry for the preparation of green composites made by two polymers named as polyhydroxybutyrate and its copolymer hydroxyvalerate.

Figures 18 and 19 present SEM micrographs of PHB/agave and P(HB-HV)/agave composites in which there are no significant surface differences in their appearance. Images at lower magnification (Fig. 18) show good fiber dispersion in both biopolymer matrices, which is very important in order to have an efficient stress transfer between the fibers and the matrix. Additionally, the fiber-matrix interface before any deformation can be observed in Fig. 18a, b, d, e. In the case of PHB/agave and P(HB-HV)/agave composites, it had been observed that some fibers were pulled-out after tensile tests (Fig. 19c, f) in spite of that it was found that the mechanical properties had not been reduced by the fiber addition [54].

Conclusion

The main aim for the development of biocomposites is to make a new class of fiber-reinforced plastics which has to be competitive with synthetic fiber-reinforced composites and is environmentally suitable or biodegradable in nature. So for that reason, natural fibers are selected which are biodegradable in nature, and by reinforcing these natural fibers into a biopolymer matrix, a renewable or recyclable biocomposite can be developed. Bioplastics and biocomposites easily replace the synthetic or petroleum-based plastics, which ultimately solves the environmental problems or issues. There is a great opportunity for developing novel bio-based products, but the main challenge is the design of these bio-based products. In this chapter, we mainly described the overview of the specific biopolymers and the mechanical and morphological properties of biocomposites.

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