

Chapter 13

Biodegradable Copolyester-Based Natural Fibers–Polymer Composites: Morphological, Mechanical, and Degradation Behavior



Jyoti Giri and Rameshwar Adhikari

Abstract Random disposal and accumulation of commodity plastics in the open environment after their end use is an issue that has triggered a lot of concerns both in public and academic debates owing to their seemingly high contribution toward the environmental pollution and potential impacts on biota and human health. Thus, finding the greener solution to this problem has got immense socio-economic and ecological significance. As a result, there is an increasing trend of using biodegradable or compostable polymeric materials. It has been demonstrated that the incorporation of plants-based reinforcing fillers into biodegradable polymers to construct composite materials have proved benefits in various applications. A great deal of research has been performed in order to develop novel sustainable polymeric materials having tailored physical properties over a wide range. As a consequence, by using bio-based fillers, new composite materials have been developed and commercialized. In this chapter, initially, the attention will be made on the review of different methods of extracting microcrystalline (MCC) and nanocrystalline (NCC) celluloses from different agro-based wastes using a series of thermo-mechanical and chemical processing routes. After a quick review on the structure-properties correlation of the micro- and nanocomposites of copolyesters, we shed light on biodegradable *green* composites with special emphasis on their morphological studies and correlations to deformation and degradation behavior. On the ground of the results obtained from our laboratory complemented by literature works, the structure-property correlations of copolyester-based composites have been discussed. Finally, the chapter concludes highlighting the new trends, major challenges, and opportunities relevant to the related research field.

J. Giri · R. Adhikari (✉)

Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal
e-mail: nepalpolymer@yahoo.com

J. Giri

Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, Kathmandu, Nepal

R. Adhikari

Research Centre for Applied Science and Technology, Tribhuvan University, Kathmandu, Nepal

Keywords Biodegradable polymer · Copolyester · Microcrystalline cellulose (MCC) · Nanocrystalline cellulose (NCC) · Gel permeation chromatography (GPC)

1 Introduction

One of the recent trends in materials science and engineering is to use polymers in different high-tech applications taking into account for their safe disposal after use. Polymers are being used extensively from the very early days of twentieth century, and nowadays, we can hardly imagine any fields in everyday life where the polymers are completely absent [1–6].

As most of the synthetic polymers we use today originate from raw materials based on fossil fuels, which is going to be used up quite quickly that, in the near future, we would not have alternative sources. Therefore, we need to think about the alternatives of synthetic polymers and at the same time, think for the lesser use of the polymers introducing enhanced functionality and recyclability into the conventional polymers [1, 6]. Nowadays, scientists are trying to develop renewable resources-based fillers such as microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC), hemicelluloses, lignin, chitosan, proteins as well as the inorganic fillers, namely layered silicates, silica, calcium carbonate, carbon black, graphene, multiwalled carbon nanotube (MWCNT), etc. [2–13]. Depending upon the nature and compatibility of the fillers with polymers, the property of the composite materials can be modulated. Such composites find applications in aerospace engineering, medical devices, tissue engineering, and in designing the smart drug delivery systems [10, 14–21].

Moreover, inorganic fillers used in polymer composites on disposal after their utility into the open environment usually may give hazardous impacts to life. Many of them are toxic for living beings human health as the chemicals used for compatibilization as well as for fire retardancy (such as brominated polystyrene, tetrabromophthalic anhydride, and decabromophenyl oxide) are proved to pose threat to the natural environment [22, 23].

As an alternative, the greener methods have been introduced by using regenerated natural resources (such as cellulosic fibers) which give similar or even more advanced properties than the reinforcement effects in the conventional composites with inorganic fillers [3, 10]. It has been known that the cellulose fibers are stronger than several mineral-based fibers, have a high volume-to-weight ratio, and can be easily dispersed homogeneously into polymer matrices via common processing techniques [4, 7]. On the other hand, the renewable resources have the advantages of being inexpensive, regenerative, and local availability [2, 4, 8]. These may reduce significantly the use of fossil fuel by-products and promote green economy and smart materials development [17, 24–26].

Thus, the bio-based and biodegradable plastics are emerging as reliable alternatives to conventional commodity plastics [27, 28]. Several of them, however, have generally the problem of poor mechanical properties, difficulty in tuning crystallization behavior, high manufacturing costs, and reduced ease of processing. Currently,

biodegradable polyesters such as polybutylene adipate-*co*-terephthalate (PBAT), polyethylene terephthalate (PET), polylactic acid (PLA), polybutylene succinate (PBS), polycaprolactone (PCL), and polyglycolic acid (PGA) are being investigated [8–11, 25]. Among them, completely biodegradable blends and composites based on PBAT, PCL, PLA, and PHB are becoming quite popular [27–29]. Irrespective of the materials chosen for technical applications, it is a key issue to control the morphological details of the material at different length scales to design the tailored properties profile [10, 13, 25, 27]. As a consequence, a comprehensive understanding of the correlation between morphology, mechanical properties, and degradation behavior of such systems is required.

This chapter aims at discussing the structure and properties of a biodegradable copolyester-based composite materials with special attention to their mechanical, morphological, and biodegradation behavior. A brief introduction about the filler preparation and corresponding characterization techniques will be followed by an overview of natural fibers-based polymer composites. Then, the detailed discussion on the structure-properties correlation of the copolyester–natural fibers composites will be presented. The degradation behavior of the composites under soil burial condition will be discussed with an emphasis on molecular weight reduction and degradation mechanism. Finally, the chapter will be concluded highlighting some new trends and challenges in developing completely biodegradable and compostable composite materials.

2 Preparation and Characterization Techniques

The preparation of fillers for composites fabrication and the characterization of polymer interface as well as the morphology of the composite are some important aspects of tailoring the properties profile of the materials.

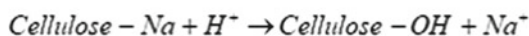
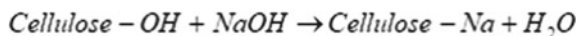
2.1 Preparation of Micro-and Nanocrystalline Cellulose

The common sources of MCC and NCC are the plant-based natural fibers such as sisal [30, 31], kenaf [32, 33], castor oil plant [34], bamboo [35–37], jute [2], pineapple leaf [38], cotton [39, 40], and ramie [41]. There are many processes to extract MCC and NCC from the bioresources which can broadly be classified as chemical, mechanical, and bacterial ones [5, 42–45].

2.1.1 Chemical Method

After preliminary treatments such as washing, drying, chopping, pulverizing, and sieving, the raw plant fibers are subjected to strong alkali treatment. The process is

Scheme 1 Mercerization of cellulose fiber with NaOH followed by acid treatments to microfibrillate the cellulose macrofibers [35]



Scheme 2 Oxidative bleaching of cellulose microfibers by sodium hypochlorite (NaClO) solution for synthesis of white crystalline MCC [6]



called as *mercerization* and causes the fibers to undergo fibrillation and delignification [35, 38]. Usually, alkali solutions used for this process are from caustic soda or caustic potash [38, 46] whereby the optimization of alkali concentration and processing temperature are important issues to consider [47]. The *mercerization* further involves the addition of Na⁺ groups into the cellulosic molecular segments which can later be removed by treating with acids (Scheme 1) [35]. The treatment with acids such as (COOH)₂, HCOOH, CH₃COOH, dilute H₂SO₄, and HCl also acts to dissolve the amorphous regions in the cellulose [48].

The raw fibers are converted to white shining crystals on bleaching with chemicals such as NaClO, NaCl, NaClO₃, NaClO₂, and H₂O₂. These usually produce nascent chlorine or oxygen to bleach the fibers and at the same time also dissolve hemicelluloses and amorphous regions exposing neat cellulose crystallites [6, 38, 46, 49–52]. Scheme 2, for instance, shows the bleaching action of the NaClO.

Cellulose fibers then easily give rise to the production of MCC. Further disintegration into the nanosized crystals can be achieved by controlled hydrolysis with strong acids under constant and vigorous stirring and sonication. The chemical disintegration is quite challenging in term of purification of the cellulosic fiber as a lot of mass loss may occur. Acid treatments leading to the formation of the NCC have been reported by several authors [53–55] by variation of acid concentration, time of treatment, temperature, and freeze-drying procedures. As a result, the NCC crystalline aggregates having several tens of nanometers width and up to several hundred nanometer lengths can be obtained.

2.1.2 Mechanical Method

(a) Compression and roller mechanical technique

In compression mechanical method, cellulosic fibers are placed between beds of two metal plates at high force of 10 ton for 10 s, whereas in roller mechanical technique, fibers are passed between two rollers in which one is mobile while the other is fixed. These techniques were used to fibrillate wood dust and corn stover into cellulose nanofibers [54, 55].

(b) Homogenization

In this technique, cellulose fibers are passed through a narrow valve at very high pressure and released suddenly to normal pressure which acts as the shear force to

explode the inner fibers. The basic concept of this technique is to release all binding forces initially applied to the nanofibers while forming macroscopic fibers. Usually raw and mercerized fibers are employed for homogenization. This technique was used for nanofibrillation of hard and softwood pulps, banana peels, and sugar cane baggage [45, 46, 56, 57].

(c) *Ultrasonication*

Ultrasonication is an electro-mechanical process of disintegrating macrocellulose into the NCC. Sound energy of more than 20 kHz is used to agitate particles present in the aqueous cellulose suspension which leads to the microscopic disintegration followed by breakage of intermolecular bonds [49, 58]. Besides the energy of the ultrasonic waves, the treatment time, temperature, and presence of impurities can significantly alter the yield, morphology, and hence the properties of the NCC.

2.1.3 Bacterial Synthesis

One of the most important features of the bacterial cellulose is its chemical purity, which distinguishes it from the cellulose extracted from higher plants, usually associated with hemicelluloses and lignin, removal of which involves several steps. Due to their unique ultra-fine and uniformly reticulated structure, the bacterial nanocellulose find wide applications in paper, textile, food, and cosmetics industries as well as in tissue engineering and medicine [59].

Bacteria such as *Acetobacter xylinus*, *Rhizobium*, *Agrobacterium* *Escherichia coli*, and *Sarcina* have been found to biosynthesize cellulose nanofibers with highly crystalline texture [60, 61]. Further, NCC and MCC fibrils can be synthesized by bacteria in the presence of glucose, oxygen, nitrogen, and micronutrients. In this process, various carbon compounds in the nutrition media are utilized by the microorganisms to polymerize their molecules into a single, linear β -1, 4-glucan chains and secrete outside the bacterial cell. First, nascent β -1,4-glucan chains are produced. Then, a number of such chains combine to form interwoven microfibrils to give a thick gelatinized network of the fibers [59]. The amount and nature of bacterial cellulose production vary, besides the nature of the microorganisms with the type of carbon sources (such as glucose, mannitol, glycerol, fructose, sucrose, and galactose) [62].

2.2 Preparation of Polymer Composites

There is a vast number of references available for fabrication of polymer composites involving biodegradable polymers and natural fibers. In brief, the common processing route involves the physical mixing of the components in a drum, followed by agitation inside an internal mixture under inert atmosphere and palletization. The samples fabricated during melt compounding of the pellets are then subjected to molding

by various means such as compression, blowing, casting, injection and spinning, calendaring, blowing, and printing [4, 6–9, 11, 13, 14, 25, 35, 36, 41].

2.3 Characterization Techniques

There are wide varieties of techniques that characterize the specific properties of the polymeric materials. The choice of the techniques depends primarily on the nature of the properties that are relevant for the particular application. For the degradable materials intended for packaging, insulation and other low load-bearing fabrications, the stability against thermal and mechanical stress as well as the structural details linked to those properties are of particular interest. In this section, we briefly highlight the techniques used for such characterizations. For the detailed information on those issues, the readers are referred to specific monographs and reviews [63–68].

2.3.1 Structural Characterization by Microscopy

Morphological characterization of materials is generally performed by microscopic (optical as well as electron microscopy) and X-ray diffraction techniques. These methods provide a wide range of information on different length scales. The structural details of fibers and polymer composites ranging from a few Angstroms up to over 100 mm can be evaluated by these tools [7] (Fig. 1).

The optical microscopy (OM) offers the overview imaging of the microscopic structures which are a few microns up to a few millimeters in dimension. Polarizing

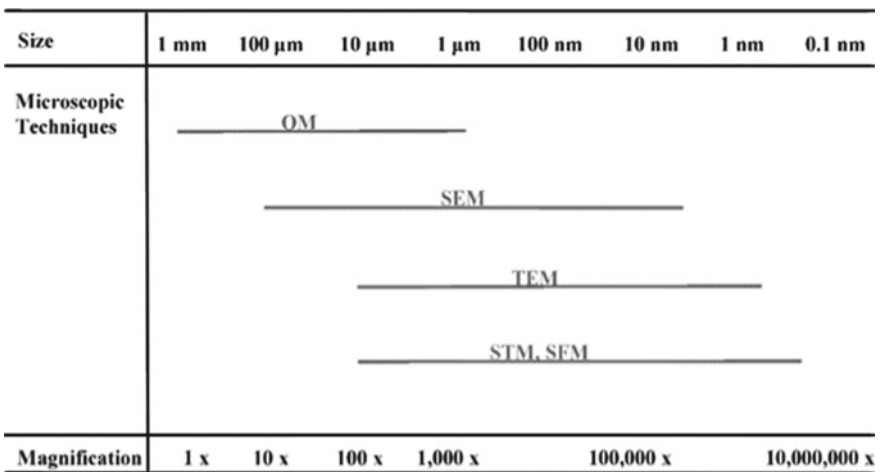


Fig. 1 Resolution ability of different microscopic tools [69]

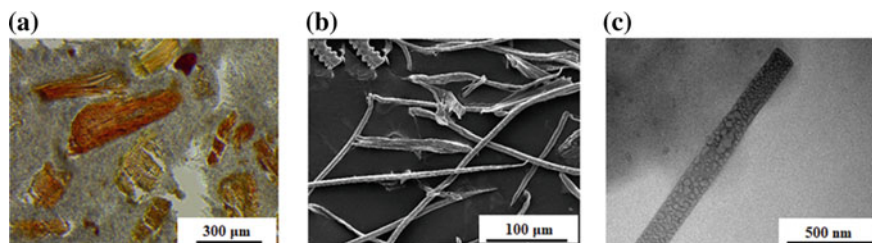


Fig. 2 Micrographs showing morphology of natural fibers at different length scales: **a** optical photograph of the fibers embedded in a polymer matrix, **b** microcrystalline cellulose (MCC), and **c** nanocrystalline cellulose obtained from the MCC [71]

optical microscopy (POM) gives, in most cases, the clear idea about the microscopic dimension as well as information about the structural heterogeneity of the materials including macroscopic crystalline textures [66, 70].

Scanning electron microscopy (SEM) [6, 71–74] and transmission electron microscopy (TEM) [56, 71, 74–76] offer the resolution of up to individual nanofibers illuminating the insight into the polymer–fiber interface. The SPM including scanning tunneling microscopy (STM) and scanning force microscopy (SFM) can easily go into atomic resolution domain of materials characterizations [62–68]. Thus, it can be easily followed that the scanning probe techniques and electron microscopy (EM) possess the central position among the modern nanoscale characterization tools for detailed characterization of the polymeric materials.

As illustration, Fig. 2 shows the morphology of cellulosic fibers on different length scales as observed by POM, SEM, and TEM. The overview of the natural fibers along the longitudinal axes is presented in Fig. 2a in which the grayscale of birefringence in the fiber surface represents the crystalline texture of the fibers. The field emission SEM imaging of the chemically processed MCC fibers illustrated in Fig. 2b depicts quite uniformly distributed cellulosic fibers while the micrograph in Fig. 2c shows the structure of individual nanofiber obtained from the same stuff as presented in Fig. 2b via strong acid treatment [71]. It should be, nevertheless, admitted that the information obtained by microscopic tools is limited to very local structural details. For more integral structural details of the materials, diffraction and spectroscopic techniques are required.

2.3.2 X-Ray Diffraction and Spectroscopic Characterization

Many polymeric materials, including natural polymers and fibers, are semicrystalline in nature and their crystalline behavior can be well revealed by X-ray diffraction (XRD). In this method, the intensity of the peaks along with the 2θ values precisely signifies the crystalline behavior. The diffractogram can be used to calculate the crystallinity index, determine the nature of crystals as well as quantify the d-spacing (practically the distance between two crystalline layers) [66, 77, 78]. The crystallinity

index can be calculated as [77]:

$$\text{Crystallinity index (\%)} = \frac{I_{200} - I_{\text{am}}}{I_{200}} \times 100\%$$

where

I_{200} Intensity value for crystalline cellulose, and
 I_{am} intensity value for amorphous cellulose.

It can be concluded that the cellulosic fibers depict the crystalline peaks at the 2θ values between 12° and 25° of the diffractogram [38, 46, 71, 79, 80]. For instance, the XRD patterns of banana peel MCC fibers obtained by a series of mechano-chemical processing steps are presented in Fig. 3. The size of the nanocrystals was manipulated by allowing the cellulosic nanomaterial through the homogenizer for 3, 5 and 7 times which resulted in the decrease of the particle size in the same order (which have been designated as N3, N5, N7, respectively in Fig. 2 [46]. The figure shows an increasing trend of the crystallinity on decreasing the particle size of NCC.

In the similar manner, the crystallization behavior of polymers and composites with natural fibers can be determined by XRD [81, 82]. The method allows the observation of influence of filler incorporation in nucleation of crystalline phases, of the polymer matrix.

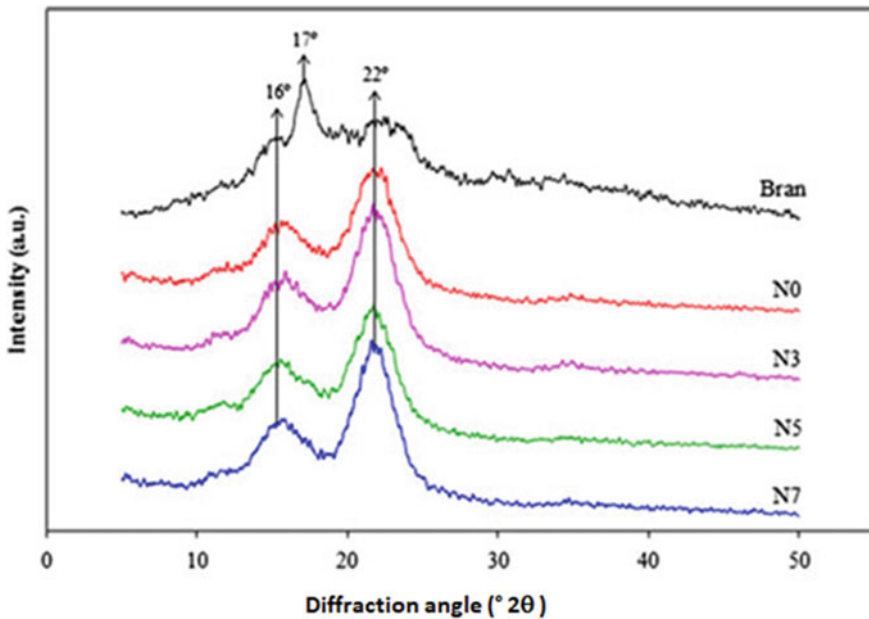


Fig. 3 XRD patterns for banana peel (Bran), NCC (N0) and the NCC passing through homogenizer for 3 (N3), 5 (N5) 7 (N7) times [46]

Spectroscopic techniques such as Fourier transform infrared (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS) can be utilized in order to access molecular-level information on the interaction between different phases, nature of the interface, etc. In particular, in FTIR spectra, the spectral positions on wavenumber scale are directly linked to different functional groups and thus may signify the interaction at the interfacial region. The information can be later linked with the resulting physico-chemical properties of the materials [36, 83–85].

We illustrate the application of spectroscopy in characterization of polymer composites comprising biodegradable copolyester, the PBAT, and 5 wt% each of micro-(M5) and nanocrystalline (N5) celluloses, see Fig. 4. Let us first examine the peaks corresponding to the copolyester. The small peaks located at $1460\text{--}1354\text{ cm}^{-1}$ [86] give IR absorption for vibrational stretching of C–H bond in the CH_3 group of PBAT. Moreover, the peak at 1099 cm^{-1} indicates the presence of C–O–C stretching vibration of the ester bond of the PBAT. Similarly, the peak centered at 723 cm^{-1} represents the aromatic ring present in the polymer [87].

Figure 4 further shows the absorption spectra of the M-5 composites which are exactly similar in pattern as of the PBAT [85]. The PBAT, M-5, and N-5 all show absorption peaks at $2959\text{--}2845\text{ cm}^{-1}$ (corresponding to C–H stretching) [32, 88], the

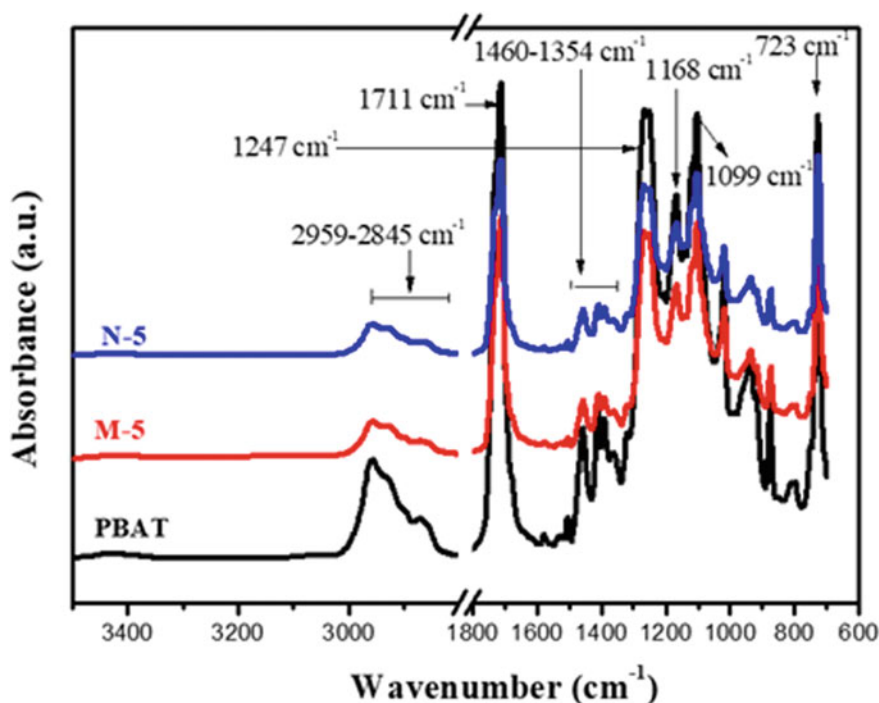


Fig. 4 FTIR absorption spectra of the PBAT compared to that of M-5 and N-5 composites [85]

intense peak at 1711 cm^{-1} (representing C=O stretching), and another intense peak at 1247 cm^{-1} (corresponding to C–O stretching of carbonyl group) [47, 85, 89].

In the spectra of the composites surfaces, there are no peaks corresponding to the MCC and the NCC. The presence of the only peaks corresponding to the PBAT in both the composites indicates the dominance of PBAT toward the surface of the composite films. The FTIR spectra further illustrate that, in spite of good compatibility between MCC as well as NCC with the PBAT, there is no significant bonding of chemical nature, also supporting the notion of microscopic results [85]. In brief, the spectroscopic data act as signature for chemical identity of the materials also illustrating the presence of any chemical interaction in the interfacial region and preference of any components toward the surface.

2.3.3 Mechanical, Thermal, and Degradation Behavior

Mechanical properties of polymeric materials and fibers can be determined by different methods such as tensile as well as compression, impact, and dynamic mechanical testing [68]. On the other hand, thermal and degradation behavior can be measured by various techniques as well [67]. These measurements not only provide the materials specific properties profile of the substances but also record the signature of various chemical treatments and interfacial modifications. Here, we present as an example of the effect of micro- and nanofibrillation of the cellulosic fibers on their thermostability [85].

The plot in Fig. 5 illustrates of thermogravimetric analysis of MCC and NCC [85]. Both show two-step degradation processes. The MCC shows an initial weight loss of up to 7% at around $120\text{ }^{\circ}\text{C}$ which corresponds to the removal of water and other volatile substances. The MCC itself starts to degrade at $225\text{ }^{\circ}\text{C}$, the major degradation occurring at T_{max} of $373\text{ }^{\circ}\text{C}$. The complete thermal degradation of the MCC takes place at around $400\text{ }^{\circ}\text{C}$ [85].

Similarly, NCC losses its weight by 10% due to the removal of water and other volatile substances at around $120\text{ }^{\circ}\text{C}$ while its degradation starts at $231\text{ }^{\circ}\text{C}$ followed by the major degradation occurring at T_{max} of $300\text{ }^{\circ}\text{C}$. The complete degradation of the NCC occurs at $408\text{ }^{\circ}\text{C}$ leaving the residual mass of 22.16% in the form of char after combustion at $600\text{ }^{\circ}\text{C}$. Thus, on comparing thermal behavior, one can observe that the MCC is found to be more thermally stable than the NCC [85].

Thus, the thermogravimetric measurements allow the comparison of the thermostability of the materials at hand, irrespective of whether the materials are the natural fibers or their blends or the composites with polymers.

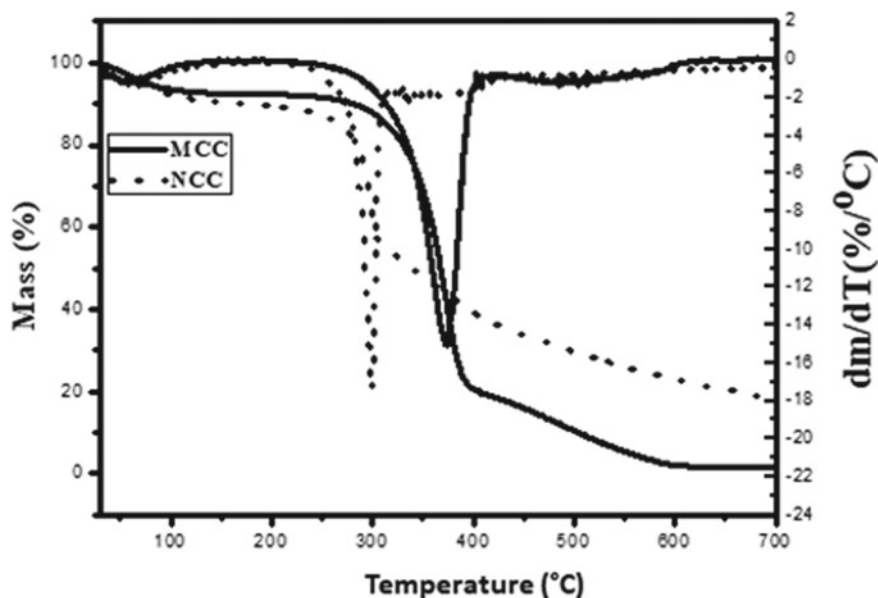


Fig. 5 TGA thermograms of MCC and NCC extracted from WS [85]

3 Natural Fibers and Degradable *Green* Composites

3.1 Natural Fiber Composites

It has been pointed out that the common fillers of both scientific and economic interests have been derived from wood flour [90–96], rice husks [96, 97], and other natural resources such as flax, sisal, kenaf, kraft, and jute. [98–101]. Particular attention has been paid in many previous studies on the use of agricultural and carpentry wastes (such as rice husks, cotton rests, and saw dusts. [90–92, 102]) as reinforcing filler to prepare the novel composite materials. A large volume of scientific data concerning the processing, properties, and morphological aspects of natural fillers in polyolefins [91, 102], polyesters [103], and thermosetting resins [104] can be found in the literature. Aiming at the study of the thermal, mechanical, and morphological properties of the composites of commodity plastics such as polypropylene (PP) and polyethylene (PE), the former was blended with carpentry waste of the wood *Shorea robusta* and investigated for morphological, mechanical, and thermal properties of the composites [105]. The morphological results are presented in Fig. 6.

Figure 6a is the SEM image of fracture surface of neat PP/60 wt% wood flour composite. There are sharp ridges at the interfacial region, formed by incompatibility between the components [105]. Figure 6b presents the SEM micrographs of the corresponding sample as presented in Fig. 6a but containing 5 wt% maleic anhydrides grafted PP (PP-g-MA) as a compatibilizer in the polypropylene matrix. The fracture

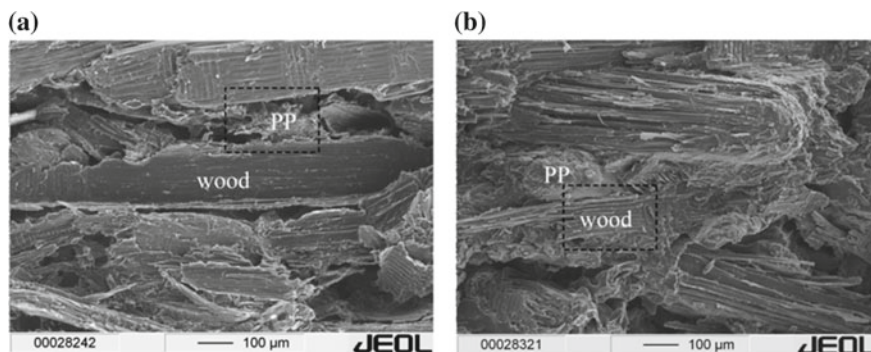


Fig. 6 SEM images of composites containing 60 wt% wood flour in PP matrix; **a** no compatibilizer and **b** with compatibilizer [105]

surface morphology of the composite presented is quite similar to that presented in Fig. 6a with typical structures of the wood fibers and the surrounding polypropylene matrix. However, the wood structures in Fig. 6b appear rougher and have no cracks at the boundaries with the matrix. The filler particles further keep their basic morphology, but exhibit coarser surface textures implying the presence of good bonding between the particles and matrix [105].

Such morphological behavior is typical of hydrophobic polymers with hydrophilic natural fibers. There is generally a clear indication of role of compatibilizers in the morphological properties of the composites [10].

The results so far outlined in this section help to illustrate the basic morphology of natural fibers composites and the effect of compatibilizer on morphology and thus on resulting properties of the materials [105]. The presence of natural fibers in contact with commodity plastics may facilitate the weathering process of the polymer. However, it should be kept in mind that these composites are unable to spontaneously biodegrade. In the next section, the structure and properties of some completely degradable composite materials will be illuminated.

3.2 Degradable Polymer Composites

Biodegradable polyesters and copolyesters [30, 106–108] have been recently used as a matrix to prepare new materials. Among the biodegradable polymers, PLA and polybutylene succinate (PBS), aliphatic–aromatic copolyesters, etc., have got particular commercial attention due mainly to their biodegradability and sustainability [28, 29, 36, 52].

Thus, aiming at the development of completely biodegradable composite materials based on locally available low-cost bamboo flour (BF) as filler, structure-properties correlations in the composites of the aliphatic–aromatic copolyester (a commercial

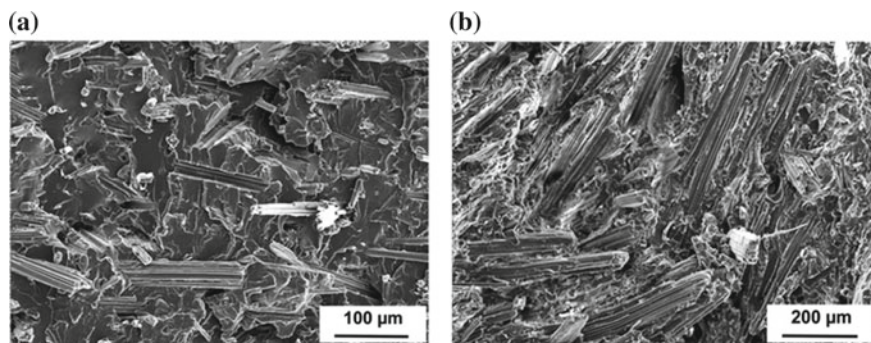


Fig. 7 Scanning electron micrographs of the Ecoflex/BF composites: **a** 20 wt% BF and **b** 60 wt% BF; cryo-fractured surface of the specimens [36]

product, the PBAT, called as Ecoflex) and BF were studied. For instance, the SEM micrographs of the fracture surfaces of two different composites (having 20 and 60 wt% of alkali-treated bamboo flour) are presented in Fig. 7 [36].

In the composites with 20 wt% BF (Fig. 7a), both the matrix and filler can be easily recognized. At several locations, BF which have been pulled-out from the matrix can be observed. Also, the holes formed by the pulled-out fibers are visible on the micrographs [36].

At high BF content, the matrix fraction practically disappears on the micrographs as it functions only as binding materials for the BF. In the composite with 60 wt% BF (Fig. 7b), the fibers are as randomly and uniformly distributed as in the case of low filler content composite. The fibers have no preferential orientation. It is indeed very interesting to note that a very large amount of BFs can be dispersed into the polymer matrix without using any compatibilizer [36].

For gaining closer insight into the morphology of the Ecoflex/BF composites, the compression-molded samples were studied by wide-angle X-ray scattering (WAXS) using reflection modes which provided the information on the structure of materials on the surface as well as bulk of the specimens. The results are presented in Fig. 8 [36]. In the pure Ecoflex, several peaks corresponding to the semicrystalline framework of the matrix could be ascertained. The Ecoflex crystalline reflections of the composites observed at values of 2θ 17.3°, 20.2°, and 23° progressively disappeared, implying that the structure of the matrix was gradually destroyed by the presence of BFs. As a result, in the composites with 40% BF or more, the structure of the BFs predominated, and the diffractogram of cellulose appeared [36].

It was demonstrated that quite high amount of BF could be easily incorporated quite homogeneously into the biodegradable polymeric matrix. The filler weakly adhered to the matrix as demonstrated by the pulling-out of BFs on the electron micrographs, which was further attested by thermogravimetric analysis [36].

The tensile mechanical properties of Ecoflex/BF composites are presented in Fig. 9 [36]. The results illustrate that the pristine polymer exhibits large plastic deformation, accompanied by yielding, cold drawing, and strong strain-hardening

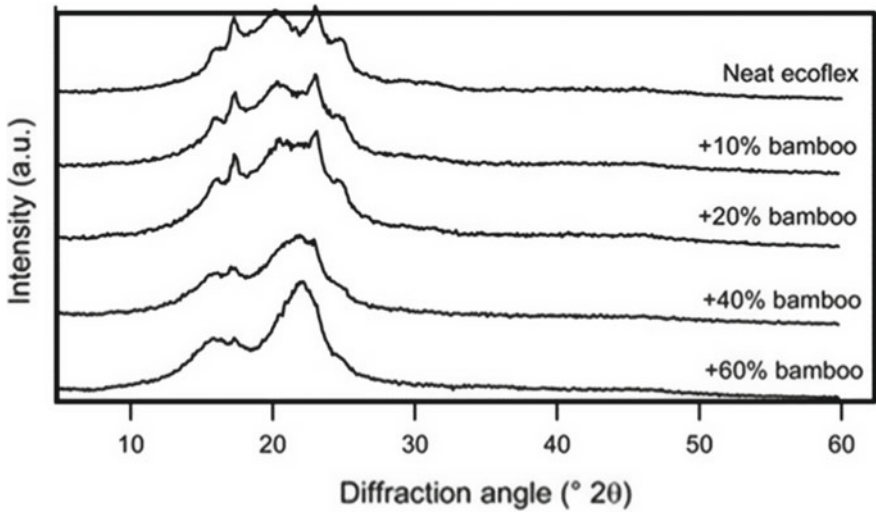


Fig. 8 WAXS patterns of Ecoflex/BF composites containing various amount of BFs recorded in reflection mode [36]

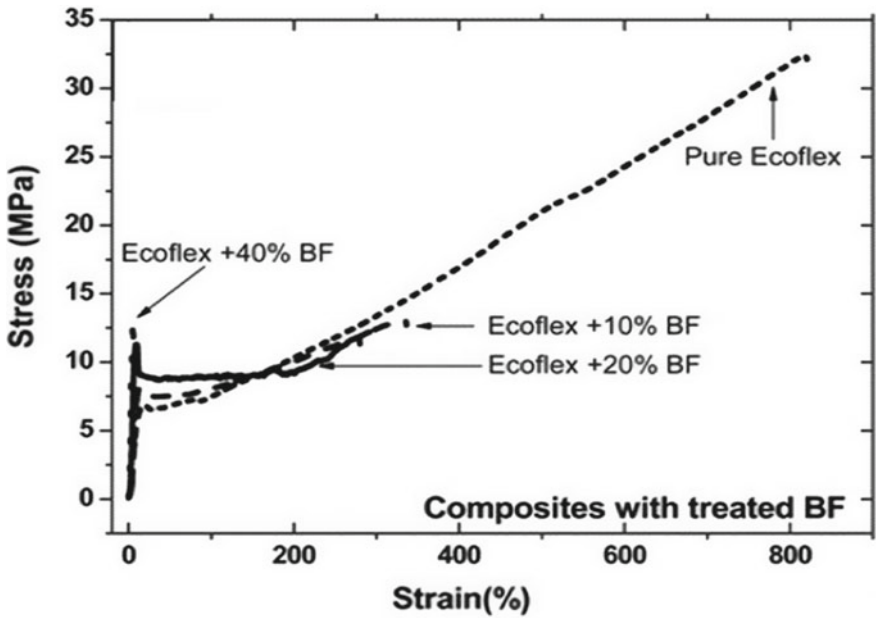


Fig. 9 Tensile stress–strain curves of Ecoflex/BF composites having various BF concentrations [36]

phenomena showing elongation at break of 800% and tensile strength of over 30 MPa. The addition of 20 wt% of the filler BF results in a drastic reduction in both strain at break and tensile strength. Nevertheless, the yield strength of the composites increases with filler content. The composites were thus reported for being suitable for low load-bearing applications [36].

In spite of the matrix being degradable, such materials (as the composites based on PLA, PHB, Ecoflex, etc.) may not be termed as completely degradable as the filler and matrix remain intact due to the presence of compatibilizers at the filler/matrix interface [30, 36, 103]. In the next section, we will deal with the composite materials using micro- and nanocrystalline celluloses derived from agricultural wastes and also shed light on the degradation behavior of such materials.

3.3 Completely Degradable Green Polymer Composites

The completely degradable *green* composites are those in which the polymers are derived from green sources. Besides, all the constituents of the composites must undergo degradation under soil composting conditions. Such composites are indeed the need of the present situation. Degradable polymers with aromatic ring usually do not go biodegradation or composting process as breakage of such ring needs high energy, and in the soil, there are no microbes which can enzymatically deteriorate the aromatic rings to convert the polymers into simpler forms [14]. Polymers containing simple hydrolysable chemical bonds (such as ester, ether bonds) get easily decomposed under soil burial conditions and attacked by microorganisms and minerals [30, 109]. Thus, PLA, PHA, PHBV, and their composites with bio-fillers such as MCC, NCC, starch, hydroxyapatite, lignin, chitin, and chitosan are used to prepare completely green composites [36, 83, 85]. These composites even due to the presence of the biogenic fillers undergo early degradation. There are many research reports on evaluating the effect of filler nature and duration of soil burial on the biodegradation of polymeric materials [2, 83, 85, 110–112].

3.3.1 Introduction to Biodegradation

Polymers comprise giant molecules which may undergo degradation when their bonds break. The later process can be induced by exposure of the materials to light (such as UV radiation), environmental weathering, and soil composting or microbial incubation [29, 42, 112–114].

Incubating the polymeric materials with specific microorganisms may break the macromolecules during their metabolic activity. The bacteria produce primary and secondary metabolites or some specific enzymes which have the capacity to break the stereospecific and stereoselective bonds. *Bacillus subtilis*, *Aspergillus niger*, *Streptococcus aureus*, *Candida*, and *E. Coli* are some of the organisms which are been proved as potential agents for degradation of polymeric materials [16, 78, 109,

113–115]. Besides the nature of microbes, the types, and dimension of biogenic filler and the surrounding environment in terms of pH, temperature, and presence of different ions affect the degradation process [62, 70, 87, 90, 94, 109, 110, 116, 117].

Soil offers a natural environment in the upper layer of earth crust the habitat for different organisms such as bacteria, virus, fungi, insect, small rodents, reptile, and mammals. Usually, we expect the good degradation process when the soil contains a large population of microorganisms, acidity and the corrosive minerals contents [27–29].

Turning toward the renewable flora-based resource of the nature, either from agriculture or from the forest products, it can be observed that major part of the plant bodies is made up of macromolecular cellulosic materials [6, 33, 38, 41, 43, 44, 46–48]. After end use of the products, a large part of agricultural and forest residues become wastes. Thus, it is wise to utilize such wastes as renewable resources to prepare MCC and NCC, which is in line with principles of green chemistry signifying the conversion of waste to value-added products [28, 117–121].

3.3.2 Morphological Characterization

In this section, among different kinds of biodegradable polymer composites, we focus on the structural characterization of some PBAT-based composite materials. An agricultural waste, the wheat stalk, was used for the extraction of MCC and NCC by thermo-chemical and mechanical treatments. The MCC and NCC were then compounded with the PBAT via melt mixing. For example, the lower (top) and higher (bottom) magnification SEM micrographs depicting the internal morphology of the composite comprising 40 wt% MCC (i.e., the sample M-40) are shown in Fig. 10 [85].

The micrograph with lower magnification (Fig. 10a) shows that there are regions with relatively smoother as well as rougher textures. The smoother areas represent the less deformed parts, whereas the rough areas stand for not deformed ones during fracture surface preparation. Nevertheless, at the first glance, it can be observed that

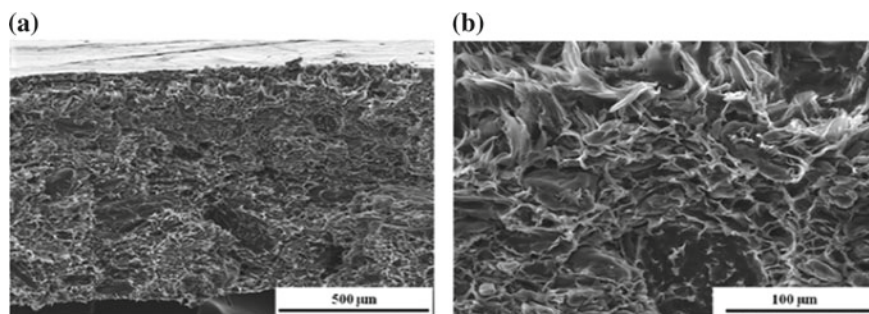


Fig. 10 Lower (top) and higher (bottom) magnifications of SEM micrograph of cryo-fractured surface of PBAT composite 40 wt% of MCC [85]

the composite is a quite homogeneous mixture of the polymer and the MCC. The average thickness of the MCC fibers is $5\ \mu\text{m}$ while the average length is about $100\ \mu\text{m}$ [85].

A closer look in Fig. 10b reveals further that there is a quite strong physical interaction between the polymer matrix and filler although there is no specific chemical bonding [85].

The properties of the composites were evaluated via soil composting tests, contact angle as well as water absorption measurements, scanning electron microscopy (SEM), and gel permeation chromatography (GPC) [85]. The cellulosic filler was found, as per SEM results, to uniformly disperse in the polymer matrix forming a quite homogeneous composite which visibly degraded completely within a few months under soil composting and showed high water absorption, these properties being enhanced with the filler content [85]. Compared to the neat PBAT, the composites showed enhanced surface hydrophilicity thereby increasing the vulnerability of degradation. In spite of the seemingly remarkable decrease in mechanical stability of the polymers under soil burial for several months, no substantial lowering of the molecular weight was observed [85].

These results are in consistence with the conclusions drawn in similar works reported in the literature including blends and composites with chitosan [122], starch [123], clay [124], and other systems comprising polylactides and other degradable systems [45, 53, 125].

For the sake of comparison, in Fig. 11, we present the morphology of a nanocomposite of the PBAT comprising 5 wt% of the NCC [85]. Indeed, the nanofiller content that brings the significant effect of large surface areas on the properties of the nanocomposites lies in the range of 1–5 wt% [126–128]. Thus, it makes sense to present the results comprising a lower amount of the nanofiller.

The dispersion of the NCC in the polymer matrix is uniform, with no noticeable tendency of agglomeration of the filler into the polymer matrix. The agglomeration tendency of the nanofiller into the polymer is a sign of the incompatibility of the filler with the adhering matrix [129]. The micrographs presented in Fig. 11 depict

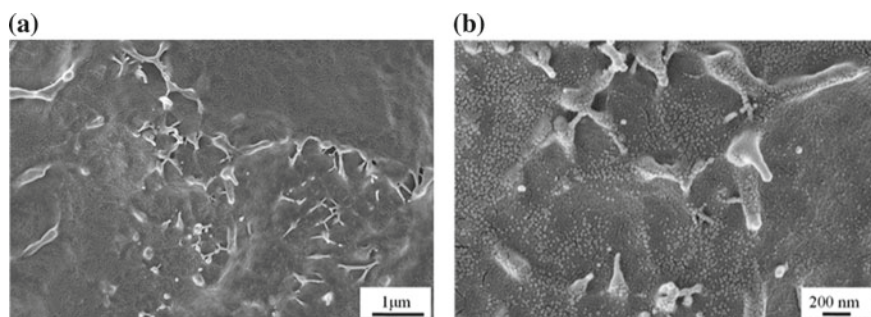


Fig. 11 Lower (top) and higher (bottom) magnifications SEM micrographs of PBAT composite comprising 5 wt% of NCC [85]

a reasonable PBAT/NCC compatibility, which is also supported by the presence of cylinder shaped fillers with the thickness in the range of 40–80 nm [85].

Looking at the thickness of individual nanocrystals and corresponding microcrystals, the average number of the nanocrystals per microcrystal bundle can be estimated to be approximately 100. Thus, it can be concluded that the nanofibrillation could bring, in case of cellulosic materials, an increase in the surface area by about 100 times. Hence, the nanocomposites can be considered to be much more effective than the conventional ones [85].

3.3.3 Surface Properties

The surface property of the composites, particularly the hydrophilicity, also correlates with their susceptibility toward biodegradation. The nature of the surface determines how the material responds with highly polar substances such as water. During contact angle measurements, generally, the water droplets form the angles with interacting surfaces whose dimension depends upon hydrophilicity or hydrophobicity of the substrate. Higher contact angle represents hydrophobicity, whereas the lower contact angle stands for hydrophilicity [85, 130, 131].

Figure 12 shows spontaneous contact angles formed by water droplets on the surfaces of pure PBAT and two different composites [85]. At first glance, the contact angle on the PBAT surface looks slightly larger (implying slightly higher hydrophobicity) than on that of the composites. Indeed, the contact angles measured for the surfaces of PBAT, M-5 and N-5 composites are 83.3°, 77.1°, and 70.1°. The decreased hydrophobicity of the composites surfaces compared to the pure PBAT can be attributed to the presence of the hydrophilic cellulosic fractions [132]. The fact, that the spontaneous contact angles of both M-5 and N-5 composites are similar, further illustrates that the hydrophobicity of the specimens primarily depends not only on the chemical nature but also on the dimensional nature (micro- or nanoscale) of the bio-. The results imply that the lower the particle size of the hydrophilic fillers, the higher would be the ease of filler dispersion in composites and thus higher would be the interaction with water. The result is consistent with literature work [131].

The results from surface contact angle measurement, however, suggest that there is some segregation of the cellulose toward the sample surface that attracts water onto it although there was no clear evidence of surface segregation of the filler as per spectroscopic and microscopic data [133].

In summary, the wetting behavior can be correlated with the degradation susceptibility of the composites at hand, the nanocomposites being more susceptible to water absorption and thereby providing higher ease of degradation under soil burial conditions (to be discussed in the next section) [85, 134, 135].

The composites dealt with in Figs. 10, 11, and 12 have been found to possess excellent water absorption tendencies, thereby increasing the ease of hydrolysis and bond cleavage under microbial attack.

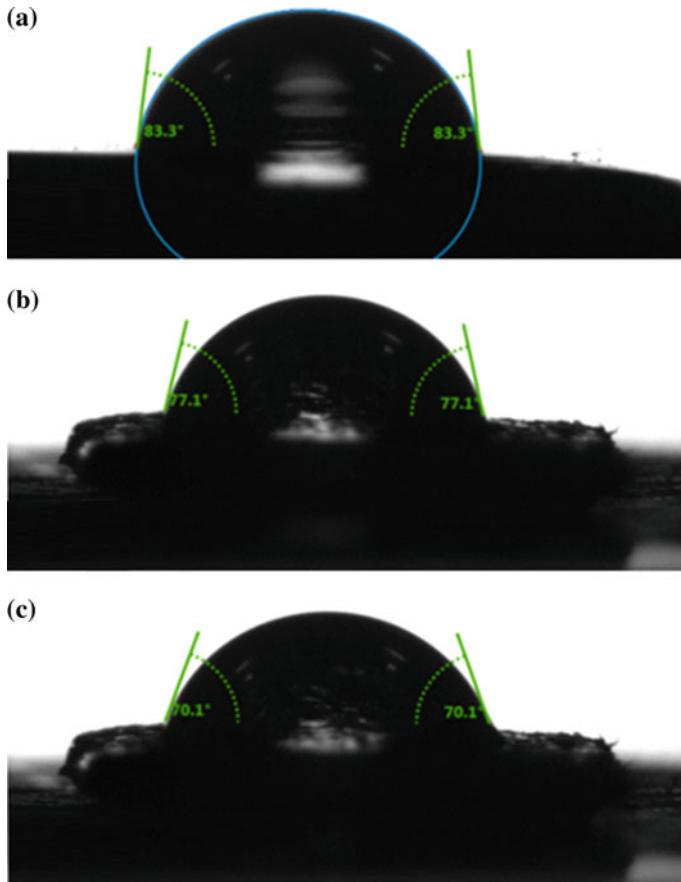


Fig. 12 Photographs showing spontaneous contact angles of water droplets on the PBAT surfaces of **a** pure PBAT, **b** composite comprising 5 wt% of MCC, and **c** composite comprising 5 wt% of NCC [85]

3.3.4 Degradation Under Soil Burial Conditions

Morphological investigations of the materials subjected to degradation under soil burial conditions were carried out. Thus, the information on the physical states upon various stress conditions was obtained. The structural features of the samples after the experiments are presented in Fig. 13 [85].

The photographs in Fig. 13 show that compared to the highly ductile nature of the PBAT, on soil composting, both the PBAT as well as its composites became quite brittle [85]. The surface of the composites was found to be attacked by the microbes. After 4 months of composting, the samples turned very brittle, the fragility of the specimen is more pronounced for the composites having a higher amount of the MCC [85].

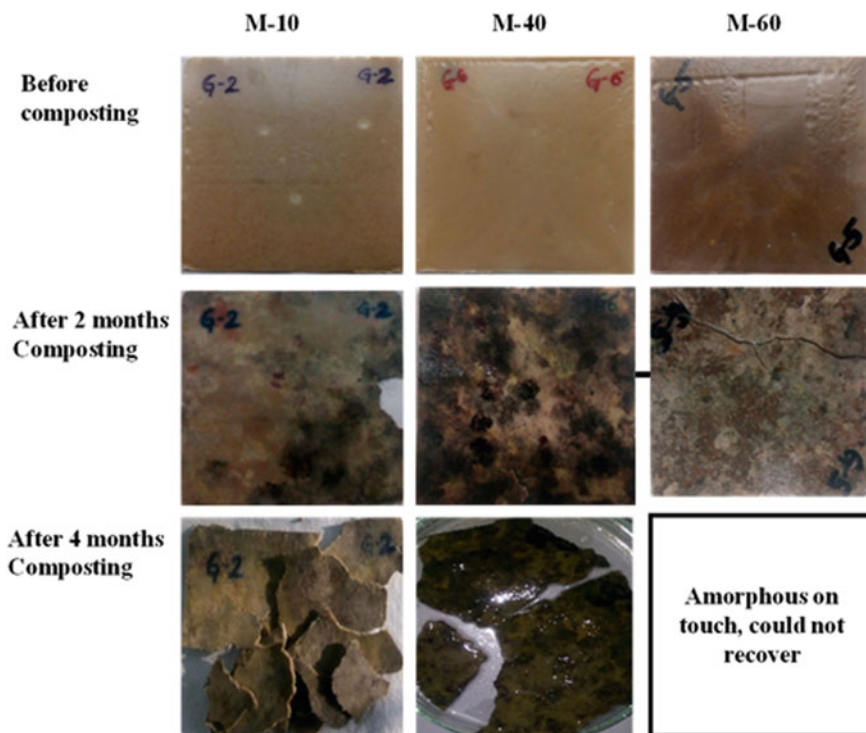


Fig. 13 Photographs of different PBAT/MCC composites subjected to soil burial for different periods of time as indicated [85]

Among the results presented in Fig. 13, morphological features of the composite M-20 were further studied in detail by scanning electron microscopy. In the beginning of the degradation, the voids of various diameters appeared on the samples surfaces, as a result of consumption of the filler particles as nutrients, by the microbes. With increasing soil burial period, the fillers content decreased which completely vanish after 4 months.

It can be expected that the degradation process of the composites materials under soil burial condition is accompanied by a drastic reduction in the molecular weight (M_w) of the polymers which finally would lead to embrittlement of the polymeric materials. Thus, the molecular weight of the polymers after the various interval of soil burial was analyzed [136–138].

The variation of the molecular properties of the PBAT in neat form and in the form of composites was investigated by gel permeation chromatography (GPC) using PS standard [85].

It was found that, under soil burial conditions, the M_w values of the pure PBAT decreased from 48.62–21.60 kg/mol in 4 months. In the case of the composite comprising 40 wt% of MCC, the M_w values decreased in same way [85]. Molecular

weight lowering was also observed on soil composting of poly(butylene sebacate) [110].

The PBAT showed significant ease of degradation in molecular weights under soil burial conditions which was further enhanced by the presence of the cellulosic filler. However, it was stressed that the polymer chains did not completely degrade but rather turned into smaller fragments that might be present for longer times as microscopic particles in the soil forming a sort of microplastics aggregates [85].

4 Biodegradation Mechanisms

Usually, any kind of degradation starts from the points of weak bonding in the heterogeneous materials. It is known that the chemical linkages, such as with ester, ether, amide, and hydrogen bonds are susceptible to hydrolysis that are easily attacked by chemicals and microbes [139–141].

The degradation process may proceed with the action of some kinds of acids or enzymes on those weak active sites thereby fragmenting the giant molecules into smaller entities including the liberation of some gases. The polymeric materials can even undergo photolytic degradation on long exposure to sunlight, microwaves, or UV-radiations and generate free radicals [42].

The biodegradation is a complex process which has been considered to take places in three basic stages [139]: biodeterioration, biofragmentation, and assimilation, in which also the influence of the abiotic factors cannot be undermined. The biodiversity of the microorganisms and their efficacy toward the formation of complex biofilm and their catalytic abilities transform the degraded substances to the nutrients represent highly sophisticated natural phenomena [62, 115].

The biodeterioration stage can be pretty well assessed by thermal and microscopic methods while the fragmentation stage can be monitored by evaluating the changes in the molecular characteristics. The production of carbon dioxide gas is a simple signature of the bioassimilation process which, of course, involves the formation of various kinds of metabolites and microbial biomass [59–62, 115, 116]. The terminal groups and gaseous substances, as well as the biofilms produced during the degradation processes, can be analyzed by different spectroscopic techniques [30, 109, 114, 139].

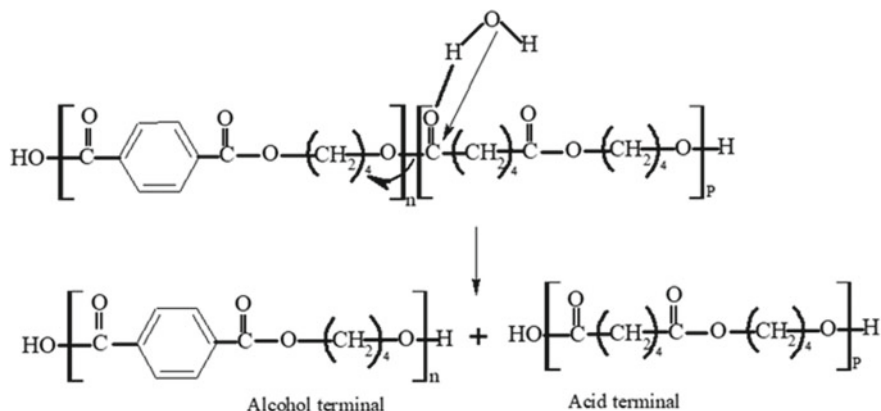
In case of polyesters and copolyesters, which have been primarily dealt with in this work, two important biodegradation mechanisms have been found effective; see Schemes 3: and 4: [139].

I. *Hydrolytic mechanism*

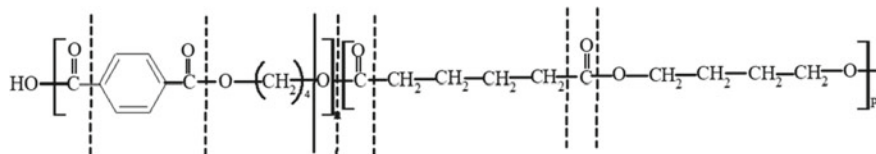
See Scheme 3.

II. *Main chain scission*

See Scheme 4.



Scheme 3 P BAT degradation *via* hydrolytic attack on carbonyl group of ester to liberate free -COOH and -OH groups; the letters “ p ” and “ n ” refer to the degree of polymerization of respective segments



Scheme 4 PBAT degradation by chain scission at different positions of the macromolecular skeleton under different conditions

5 Summary, Trends, and New Opportunities

In this chapter, we attempted to offer an overview, with recent research outputs and applications, the structure-properties correlations of biodegradable copolyesters-based polymer composites. The results can be summarized as follows.

- The lignocelluloses based micro- and nanofillers can be synthesized by various chemical, mechanical, and bioinspired (or biosynthetic) methods and be evaluated in terms of their structural and molecular characteristics via spectroscopic, microscopic, and scattering and chromatographic techniques.
- The MCC and NCC fillers can be incorporated up to a pretty high weight fraction, easily into the biodegradable copolyester matrix even without the use of compatibilizers. However, the practical applications of such composites are limited for low load objects fabrication.
- The copolyester-based composite materials undergo rapid fragmentation process under soil burial conditions leading to highly brittle materials. The molecular weight degradation has been, however, found to be not that significant within a few months duration.

There is a trend of utilizing the copolyesters and their composites for biomedical applications [9, 10, 21], for smart packaging films [14, 16, 106] and functional coatings and for flexible conducting materials [15]. These strategies are achieved by introducing different functional groups via grafting onto the natural polymer chains and then making graft and block copolymers with synthetic polymers. The challenge will be then to find suitable routes for biodegradation as the latter is a complex process and a single microbial strain would not be sufficient for the targeted biodegradation. In this case, microbial communities can be employed.

There are several biodegradation pathways for polymeric materials including degradable copolyesters which have been successfully employed. However, the routes for controlled degradation processes leading to the solution to the fundamental environmental problems are yet to evolve. In our Nepalese context, due to the presence of large microbial biodiversity in the region, and proven opportunities to design the microbial communities via uncomplicated genetic manipulation, there are unparalleled opportunities. The thermophilic and cold-loving bacteria might offer great potential in terms of degradation of the polymers, in general, which still needs to be explored.

Acknowledgements JG thanks the Indian National Science Academy (INSA) and Nepal Academy of Science and Technology (NAST) for providing the fellowship to visit IIT Guwahati and for providing PhD Research Fellowship, respectively. She further acknowledges the German Science Foundation (DFG) for providing her financial support for research stays in Germany.

References

1. Gross RA, Kalra B (2002) Biodegradable polymers for the environment. *Science* 297:803–807. <https://doi.org/10.1126/science.297.5582.803>
2. Abraham E, Elbi PA, Deepa B, Jyotishkumar P, Pothen LA, Narine SS, Thomas S (2012) X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose. *Polym Degrad Stab* 97:2378–2387. <https://doi.org/10.1016/j.polymdegradstab.2012.07.028>
3. Malho JM, Laaksonen P, Walther A, Ikkala O, Linder MB (2012) Facile method for stiff, tough and strong nanocomposites by direct exfoliation of multilayered graphene into native nanocellulose matrix. *Biomacromol* 13:1093–1099. <https://doi.org/10.1021/bm2018189>
4. Cho MJ, Park BD (2011) Tensile and properties of nanocellulose-reinforced poly(vinyl alcohol) nanocomposites. *J Ind Eng Chem* 17:36–40. <https://doi.org/10.1016/j.jiec.2010.10.006>
5. Frone AN, Panaitescu DM, Donescu D (2011) *UPB Sci Bull, Ser B: Chem Mater Sci* 73:133–152. https://www.scientificbulletin.upb.ro/rev_docs_arhiva/full20599.pdf
6. Rajan KP, Veena NR, Maria HJ, Rajan R, Skrifvars M, Joseph K (2010) Extraction of bamboo microfibrils and development of biocomposites based on polyhydroxybutyrate and bamboo microfibrils. *J Comp Mater* 45:1325–1329. <https://doi.org/10.1177/0021998310381543>
7. Lee SY, Mohan DJ, Kang IA, Doh GH, Lee S, Han SO (2009) Nanocellulose reinforced PVA composite films: Effect of acid treatment and filler loading. *Fibers Polym* 10:77–82. <https://doi.org/10.1007/s12221-009-0077-x>
8. William GE, Ballerini A, Zhang J (2005) Polymer nanocomposites: synthetic and natural fillers a review. *Maderas: Clencia Tecnologia* 7:159–178. <https://doi.org/10.4067/s0718-221x2005000300002>

9. Morouco P, Biscaia S, Viana T, Franco M, Malca C, Mateus A, Moura C, Ferreira FC, Mitchell G, Alves NM (2016) Fabrication of poly(ϵ -caprolactone) scaffolds reinforced with cellulose nanofibers, with and without the addition of hydroxyapatite nanoparticles. *BioMed Res Int Article ID 1596157*:1–10. <https://doi.org/10.1155/2016/1596157>
10. Ozkoc G, Kemaloglu S, Quaedflieg M (2010) Production of poly(lactic acid)/organoclay nanocomposites scaffolds by microcompounding and polymer/particle leaching. *Polym Compos* 31:674–683. <https://doi.org/10.1002/pc.20846>
11. Fukushima K, Wu MH, Bocchini S, Rasyida A, Yang MC (2012) PBAT based nanocomposites for medical and industrial applications. *Mater Sci Eng C32*:1331–1351. <https://doi.org/10.1016/j.msec.2012.04.005>
12. Rasyida A, Fukushima K, Yang MC (2017) Structure and properties of organically modified poly(butylene adipate-co-terephthalate) based nanocomposites. *IOP Conf Ser Mater Sci Eng* 223:012–023. <https://doi.org/10.1088/1757-899x/223/1/012023>
13. Chivrac F, Kadlecová Z, Pollet E, Avérous L (2006) Aromatic copolyester-based nanobiocomposites: elaboration, structural characterization and properties. *J Polym Env* 14:393–401. <https://doi.org/10.1007/s10924-006-0033-4>
14. Dhar P, Bhardwaj U, Kumar A, Katiyar V (2014) Cellulose nanocrystals: a potential nanofiller for food packaging applications—food additives and packaging. In: ACS symposium series, chap 17. American Chemical Society: Washington, DC, pp 197–239. <https://doi.org/10.1021/bk-2014-1162.ch017>
15. Gopakumar DA, Pai AR, Pottathara YB, Pasquini D, Morais LCD, Luke M, Kalarikkal NK, Grohens Y, Thomas S (2018) Cellulose nanofiber-based polyaniline flexible papers as sustainable microwave absorbers in the X-band. *ACS Appl Mater Interfaces* 10:20032–20043. <https://doi.org/10.1021/acsami.8b04549>
16. Moustafa H, Kissi NE, Abou-Kandil AI, Abdel-Aziz MS, Dufresne A (2017) PLA/PBAT bionanocomposites with antimicrobial natural rosin for green packaging. *ACS Appl Mater Interfaces* 9:20132–20141. <https://doi.org/10.1021/acsami.7b05555>
17. Cotana F, Brinchi L, Gelosia M, Coccia V, Petrozzi A (2012) Nanocrystalline cellulose from lignocelluloses biomass: applications and future prospects. In: 20th European biomass conference and exhibition, Italy, pp 1182–1194. <https://doi.org/10.1016/j.carbpol.2013.01.033>
18. Grüneberger F, Künninger T, Zimmermann T, Arnold M (2014) Nanofibrillated cellulose in wood coatings: mechanical properties of free composite films. *J Mater Sci* 49:6437–6448. <https://doi.org/10.1007/s10853-014-8373-2>
19. Leung ACW, Lam E, Chong J, Hrapovic S, Luong JHT (2013) Reinforced plastics and aerogels by nanocrystalline cellulose. *J Nanoparticles Res* 15:1–24. <https://doi.org/10.1007/s11051-013-1636-z>
20. Lu Y, Tekinalp HL, Eberle CC, Peter W, Naskar AM, Ozcan S (2001) Nanocellulose in polymer composites and biomedical applications. *Tappi J Nanocellulose* 13:47–54
21. Sgarioto M, Adhikari R, Gunatillake PA, Moore T, Malherbe F, Nagel MD, Patterson J (2014) Properties and in vitro evaluation of high modulus biodegradable polyurethanes for applications in cardiovascular stents. *J Biomed Mater Res B Appl Biomater* 102B:1711–1719. <https://doi.org/10.1002/jbm.b.33137>
22. Dasaria A, Yub ZZ, Caic GP, Maic YW (2013) Recent developments in the fire retardancy of polymeric materials. *Prog Polym Sci* 38:1357–1387. <https://doi.org/10.1016/j.progpolymsci.2013.06.006>
23. Sjödin A, Carlsson H, Thuresson K, Sjölin S, Bergman A, Östman C (2001) Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environ Sci Technol* 35:448–454. <https://doi.org/10.1021/es000077n>
24. Saba N, Jawaid M, Othman YA, Paridah MT (2015) A review on dynamic mechanical properties of natural fibre reinforced polymer composites. *Const Build Mater* 106:149–159. <https://doi.org/10.1016/j.conbuildmat.2015.12.075>
25. Su SK, Wu CS (2011) Polyester biocomposites from recycled natural fibers: characterization and biodegradability. *J Appl Polym Sci* 119:1211–1219. <https://doi.org/10.1002/app.32808>

26. Chauhan YP, Sapkal RS, Sapkal VS, Zamre GS (2009) Microcrystalline cellulose from cotton rags (waste from garment and hosiery industries). *Int J Chem Sci* 7:681–688
27. Banerjee A, Chatterjee K, Madras G (2014) Enzymatic degradation of polymer: a brief review. *Mater Sci Technol* 30:567–573. <https://doi.org/10.1179/1743284713y.0000000503>
28. Leja K, Lewandowicz G (2010) Polymer biodegradation and biodegradable polymers— a review. *Polish J Environ Stud* 19:255–266. http://yunus.hacettepe.edu.tr/~damlacetin/kmu407/index_dosyalar/2.%20makale.pdf
29. Shah AA, Hasan F, Hameed A, Ahmed S (2008) Biological degradation of plastics: a comprehensive a review. *Biotechnol Adv* 26:246–265. <https://doi.org/10.1016/j.biotechadv.2007.12.005>
30. Palisikowski PA, Kuchnier CN, Pinheiro IF, Morales AR (2017) Biodegradation in soil of PLA/PBAT Blends compatibilized with chain extender. *J Polym Environ* 26:330–341. <https://doi.org/10.1007/s10924-017-0951-3>
31. Mostafa HM, Sourell H, Blockisch FJ (2010) The mechanical properties of some bioplastics under different soil type for use as a biodegradable drip tubes. *Agric Eng Int* 12:12–21. <http://cigrjournal.org/index.php/Ejournal/article/view/1497/1270>
32. Han YH, Han SO, Cho D, Kim HI (2008) Dynamic mechanical properties of natural fiber/polymer biocomposites: The effect of fiber treatment with electron beam. *Macromol Res* 16:253–260. <https://doi.org/10.1007/bf03218861>
33. Chan CH, Chia CH, Zakaria S, Ahmad I, Dufresne A (2013) Production and characterization of cellulose and nano-crystalline cellulose from kenaf core wood. *BioResources* 8:785–794
34. Vinayak DL, Guna VK, Madhavi D, Arpitha M, Reddy N (2017) *Ricinus communis* plant residues as a source for natural cellulose fiber potentially exploitable in polymer composites. *Ind Crops Prod* 100:126–131. <https://doi.org/10.1016/j.indcrop.2017.02.019>
35. Das M, Chakraborty D (2008) The effect of Alkalization and fiber loading on the mechanical properties of bamboo fiber composites, part 1: polyester resin matrix. *J Appl Polym Sci* 112:489–495. <https://doi.org/10.1002/app.29342>
36. Adhikari R, Bhandari NL, Causin V, Le HH, Radusch HJ, Michler GH, Saiter JM (2012) Study of morphology, mechanical properties, and thermal behavior of green aliphatic-aromatic copolyester/bamboo flour composites. *Polym Eng Sci* 52:2296–2303. <https://doi.org/10.1002/pen.23335>
37. Batalha LAR, Colodette JL, Gomide JL, Barbosa LCA, Maltha CRA, Gomes FJB (2012) Dissolving pulp producing from bamboo. *Bioresources* 7:640–651
38. Cherian BM, Leao AL, de Souza SF, Coata LMM, Olyveira GMd, Kottaisamy M, Nagarajan ER, Thomas S (2011) Cellulose nanocomposites with fibres nanofibres isolated from pineapple leaf fibers for medical applications. *Carbohydr Polym* 86:1790–1798. <https://doi.org/10.1016/j.carbpol.2011.07.009>
39. Morais Teixeira E, Correa AC, Manzoli A, Leite FDL, Oliveira CRD, Mattoso LHC (2010) Cellulose nanofibers from white and naturally colored cotton fibers. *Cellulose* 17:595–606. <https://doi.org/10.1007/s10570-010-9403-0>
40. Satyamurthy P, Vigneshwaran N (2013) A novel process for synthesis of spherical nanocellulose by controlled hydrolysis of microcrystalline cellulose using anaerobic microbial consortium. *Enzym Microbial Technol* 52:20–25. <https://doi.org/10.1016/j.enzmictec.2012.09.002>
41. Yu T, Li Y (2014) Influence of poly(butylenes adipate-co-terephthalate) on the properties of the biodegradable composites based on ramie/poly(lactic acid). *Composites: Part A* 58:24–29. <https://doi.org/10.1016/j.compositesa.2013.11.013>
42. Nagata M, Inaki K (2011) Biodegradable and photocurable multiblock copolymers with shape-memory properties from poly(ϵ -caprolactone) diol, poly(ethylene glycol) and 5-cinnamoyloxyisophthalic acid. *J Appl Polym Sci* 120:3556–3564. <https://doi.org/10.1002/app.33531>
43. Giri J, Adhikari R (2013) A brief review on extraction of nanocellulose and its application. *BIBECHANA* 9:81–87. <https://doi.org/10.3126/bibechana.v9i0.7179>

44. Sanjay MR, Arpitha GR, Naik LL, Gopalakrishna K, Yogesha B (2016) Applications of natural fibers and its composites: an overview. *Sci Res* 7:108–114. <https://doi.org/10.4236/nr.2016.73011>
45. Siro I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 17:459–494. <https://doi.org/10.1007/s10570-010-9405-y2890-2895>
46. Pelissari FM, Sobral PJDM, Menegalli FC (2014) Isolation and characterization of cellulose nanofibers from banana peels. *Cellulose* 21:417–432. <https://doi.org/10.1007/s10570-013-0138-6>
47. Ibrahim NA, Hadithon KA, Abdan K (2010) Effect of fiber treatment on mechanical properties of kenaf-fiber-Ecoflex composites. *J Reinf Plast Compos* 29:2192–2198. <https://doi.org/10.1177/0731684409347592>
48. Reddy JP, Rhim JW (2014) Isolation and characterization of cellulose nanocrystals from garlic skin. *Mater Lett* 129:20–23. <https://doi.org/10.1016/j.matlet.2014.05.019>
49. Dai D, Fan M (2010) Characteristic and performance of elementary hemp fibre. *Mater Sci Appl* 1:336–342. <https://doi.org/10.4236/msa.2010.16049>
50. Rosli NA, Ahmad I, Abdullah I (2013) Isolation and characterization of cellulose nanocrystals from *Agave angustifolia* fibre. *BioResources* 8:1893–1908
51. Cesar NR, Marcelo A, da-Silva P, Botaro VR, Menezes AJD (2015) Cellulose nanocrystals from natural fiber of the macrophyte *Typha domingensis*: extraction and characterization. *Cellulose* 22:449–460
52. Yan FY, Krishniah D, Rajin M, Bono A (2009) Cellulose extraction from Palm Kernel cake using liquid phase oxidation. *J Eng Sci Technol* 1:57–68
53. Liu DY, Yuan XW, Bhattacharyya D, Eastal AJ (2010) Characterizations of solution cast cellulose nanofibre- reinforced poly(lactic acid). *eXPRESSPolym Lett* 4:26–31. <https://doi.org/10.3144/expresspolymlett.2010.5>
54. Shaheen TI, Emam HE (2018) Sono-chemical synthesis of cellulose nanocrystals from wood sawdust using acid hydrolysis. *Int J Biol Macromol* 107:1599–1606. <https://doi.org/10.1016/j.ijbiomac.2017.10.028>
55. Chen X, Kuhn E, Wang W, Park S, Flanagan K, Trass O, Tenlep L, Tao L, Tucker M (2013) Comparison of different mechanical refining technologies on the enzymatic digestibility of low severity acid pretreated corn stover. *Bioresource Technol* 147:401–408. <https://doi.org/10.1016/j.biortech.2013.07.109>
56. Stelte W, Sanadi AR (2009) Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood. *Ind Eng Chem Res* 48:11211–11219. <https://doi.org/10.1021/ie9011672>
57. Li J, Wei X, Wang Q, Chen J, Chang G, Su LKJ, Liu Y (2012) Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization. *Carbohydr Polym* 90:1609–1613. <https://doi.org/10.1016/j.carbpol.2012.07.038>
58. Oksman K, Etang JA, Mathew A, Jonoobi M (2011) Cellulose nanowhiskers separated from a bio-residue from wood bioethanol production. *Biomass Bioenergy* 35:146–152. <https://doi.org/10.1016/j.biombioe.2010.08.021>
59. Czaja W, Krystynowicz A, Bielecki S, Brownjr R (2006) Microbial cellulose—the natural power to heal wounds. *Biomaterials* 27:145–151. <https://doi.org/10.1016/j.biomaterials.2005.07.035>
60. Bielecki S, Krystynowicz A, Turkiewicz M, Kalinowska H (eds) (2005) *Bacterial cellulose: biotechnology of polymer: from synthesis to patents*. Munster, Germany. Wiley-VCH, Verlag GmbH pp 381–434
61. Iguchi M, Yamanaka S, Budhiono A (2000) Review bacterial cellulose—a masterpiece of nature’s arts. *J Mater Sci* 35:261–270
62. Mikkelsen D, Flanagan BM, Dykes GA, Gidley MJ (2009) Influence of different carbon sources on bacterial cellulose production by *Gluconacetobacter xylinus* strain ATCC 53524. *J Appl Microbiol* 107:576–583. <https://doi.org/10.1111/j.1365-2672.2009.04226.x>
63. Michler GH (2008) *Electron microscopy of polymers*. Springer, Berlin. <https://doi.org/10.1007/978-3-540-36352-1>

64. Thomas S, Chan CH, Pothan LA, Rajisha KR, Maria H (eds) (2013) Natural rubber materials. Blends and IPNs
65. Thomas S, Stephen R (eds) (2010) Rubber nanocomposites: preparation, properties, and applications. Springer Publisher, Heidelberg, Germany. ISBN 978-0-470-82345-3
66. Sawyer LC, Grubb DT, Meyers GF (eds) (2008) Polymer microscopy. Springer Publisher, Heidelberg, Germany. <https://doi.org/10.1007/978-0-387-72628-1>
67. Guo Q (2016) Polymer morphology: principles, characterization, processing. Wiley. ISBN-13: 978-1118452158
68. Grellmann W, Langer B (eds) (2017) Deformation and fracture behaviour of polymer materials. Springer, Berlin. ISBN: 978-3-319-41879-7
69. Adhikari R, Michler GH (2009) Polymer nanocomposites characterization by microscopy. *Polym Rev* 49:141–180. <https://doi.org/10.1080/15583720903048094>
70. Bandera D, Sapkota J, Josset S, Weder C, Tingaut P, Gao X, Foster EJ, Zimmermann T (2014) Influence of mechanical treatments in the properties of cellulose nanofibers isolated from microcrystalline cellulose. *React Funct Polym* 85:134–141. <https://doi.org/10.1016/j.reactfunctpolym.2014.09.009>
71. Giri J, Lach R, Sapkota J, Susan MABH, Saiter JM, Henning S, Katiyar V, Adhikari R (2019) Structural and thermal characterization of different types of cellulosic fibers. *BIBECHANA* 16:177–186. <https://doi.org/10.3126/bibechana.v16i0.21650>
72. He J, Tang Y, Wang SY (2007) Differences in morphological characteristics of bamboo fibres and other natural cellulose fibres: studies on X-ray diffraction, solid state ¹³C-CP/MAS NMR, and second derivative FTIR spectroscopy data. *Iran Polym J* 16:807–818
73. Okubo K, Fujii T, Yamamoto Y (2004) Development of bamboo-based polymer composites and their mechanical properties. *Compos Part: A* 35:377–383. <https://doi.org/10.1016/j.compositesa.2003.09.017>
74. Bozzolz JJ, Lonnie D, Jones R (1992) Electron microscopy, principals and techniques for biologists, 2nd edn. Bartlett Publish
75. Yang J, Ye DY (2012) Liquid crystal of nanocellulose whiskers grafted with acrylamide. *Chin Chem Lett* 23:367–370
76. Rosa MF, Medeiros ES, Malmonge JA, Gregorski KS, Wood DF, Mattoso LHC, Glenn G, Orts WJ, Imam SH (2010) Cellulose nanowhiskers from coconut fibers: effect of preparation conditions on their thermal and morphological behavior. *Carbohydr Polym* 81:83–92. <https://doi.org/10.1016/j.carbpol.2010.01.059>
77. Mathew AP, Oksman K, Pierron D, Harmand MF (2012) Fibrous cellulose nanocomposite scaffolds prepared by partial dissolution for potential use as ligament or tendon substitutes. *Carbohydr Polym* 87:2291–2298. <https://doi.org/10.1016/j.carbpol.2011.10.063>
78. Herrera MA, Mathew AP, Oksman K (2012) Comparison of cellulose nanowhiskers extracted from industrial bio-residue and commercial microcrystalline cellulose. *Mater Lett* 71:28–31. <https://doi.org/10.1016/j.matlet.2011.12.011>
79. Mathew AP, Oksman K, Sain M (2005) Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *J Appl Polym Sci* 97:2014–2025. <https://doi.org/10.1002/app.21779>
80. Maiti S, Ray D, Mitra D, Sengupta S, Kar T (2011) Structural changes of starch/polyvinyl alcohol biocomposite films reinforced with microcrystalline cellulose due to biodegradation in simulated aerobic compost environment. *J Appl Polym Sci* 122:2503–2511. <https://doi.org/10.1002/app.34377>
81. Nam JY, Ray SS, Okamoto M (2003) Crystallization behavior and morphology of biodegradable polylactide/layered silicate nanocomposite. *Macromolecules* 36:7126–7131. <https://doi.org/10.1021/ma034623j>
82. Mandal A, Chakrabarty D (2014) Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse. *J Ind Eng Chem* 20:462–473. <https://doi.org/10.1016/j.jiec.2013.05.003>

83. Pokhrel S, Lach R, Le HH, Wutzler A, Grellmann W, Radusch HJ, Dhakal RP, Esposito A, Henning S, Yadav PN, Saiter JM, Heinrich G, Adhikari R (2016) Fabrication and characterization of completely biodegradable copolyester-chitosan blends: I spectroscopic and thermal characterization. *Macromol Symp* 366:23–34. <https://doi.org/10.1002/masy.201650043>
84. Giri J, Lach R, Le HH, Grellmann W, Susan MABH, Saiter JM, Henning S, Adhikari R (2019) Compostable composites of wheat stalk microcrystalline cellulose and Poly(butylenes adipate-co-terephthalate): structural, thermal and mechanical properties. Submitted
85. Giri J, Lach R, Grellmann W, Susan MABH, Saiter JM, Henning S, Katiyar V, Adhikari R (2019) Compostable composites of wheat stalk microcrystalline cellulose and Poly(butylene adipate-co-terephthalate): surface properties and degradation behaviour. *J Appl Polym Sci*, Submitted
86. Lee KY, Blaker JJ, Bismarch A (2009) Improving the properties of nanocellulose/poly lactide composites by esterification of nanocellulose. Can it be done?
87. Kramer F, Klemm D, Schumann D, Heßler N, Wesarg F, Fried W, Stadermann D (2006) Nanocellulose polymer composites as innovative pool for (bio)material development. *Macromol Symp* 244:136–148. <https://doi.org/10.1002/masy.200651213>
88. Paula MPD, Larcerda TM, Frollini E (2008) Sisal cellulose acetates obtained from heterogeneous reaction. *eXPRESS Polym Lett* 2:423–428
89. Teeri TT, Brumer H, Daniel G, Gatenholm P (2007) Biomimetic engineering of cellulose-based materials. *Trends Biotechnol* 25:299–306. <https://doi.org/10.1016/j.tibtech.2007.05.002>
90. Demir H, Atikler U, Balkose D, Tihminlioglu F (2006) The effect of fiber surface treatments on the tensile and water sorption properties of polypropylene–luffa fiber composites. *Compos A* 37:447–456. <https://doi.org/10.1016/j.compositesa.2005.05.036>
91. Beg MDH, Pickering KL (2008) Mechanical performance of Kraft fibre reinforced polypropylene composites: influence of fibre length, fibre beating and hygrothermal ageing. *Compos Part A: Appl Sci Manufact* 39:1748–1755. <https://doi.org/10.1016/j.compositesa.2008.08.003>
92. Beg MDH, Pickering KL (2008) Reprocessing of wood fibre reinforced polypropylene composites. Part II: hygrothermal ageing and its effects. *Compos Part A: Appl Sci Manufact* 39:1565–1571. <https://doi.org/10.1016/j.compositesa.2008.06.002>
93. Sanadi AR, Caulfield DF, Jacobson RE, Rowell RM (1995) Renewable agricultural fibers as reinforcing fillers in plastics: mechanical properties of Kenaf fiber-polypropylene composites. *Indus Eng Chem Res* 34:1889–1896. <https://doi.org/10.1021/ie00044a041>
94. Rana AK, Mandal A, Mitra BC, Jacobson R, Rowell R, Banerjee AN (1998) Short jute fiber-reinforced polypropylene composites: effect of compatibilizer. *J Appl Polym Sci* 69:329–338. [https://doi.org/10.1002/\(sici\)1097-4628\(19980711\)69:2%3c329:aid-app14%3e3.0.co;2-r](https://doi.org/10.1002/(sici)1097-4628(19980711)69:2%3c329:aid-app14%3e3.0.co;2-r)
95. Nachtigall SMB, Cerveira GS, Rosa SML (2007) New polymeric-coupling agent for polypropylene/wood-flour composites. *Polym Test* 26:619–628. <https://doi.org/10.1016/j.polymertesting.2007.03.00>
96. Smits V, Chevalier P, Deheunynck D, Miller S (2008) A new filler dispersion technology. *Reinfor Plast* 52:37–43. [https://doi.org/10.1016/s0034-3617\(08\)70406-5](https://doi.org/10.1016/s0034-3617(08)70406-5)
97. Sanadi AR, Young RA, Clemons C, Rowell RM (1994) Recycled newspaper fibers as reinforcing fillers in thermoplastics: part i-analysis of tensile and impact properties in polypropylene. *J Reinfor Plast Compos* 13:54–67. <https://doi.org/10.1177/073168449401300104>
98. Bledzki AK, Reihmane S, Gassan J (1996) Properties and modification methods for vegetable fibers for natural fiber composites. *J Appl Polym Sci* 59:1329–1336. [https://doi.org/10.1002/\(sici\)1097-4628\(19960222\)59:8%3c1329:aid-app17%3e3.0.co;2-0](https://doi.org/10.1002/(sici)1097-4628(19960222)59:8%3c1329:aid-app17%3e3.0.co;2-0)
99. Martí-Ferrer F, Vilaplana F, Ribes-Greus A, Benedito-Borrás A, Sanz-Box C (2005) Flour rice husk as filler in block copolymer polypropylene: effect of different coupling agents. *J Appl Polym Sci* 99:1823–1831. <https://doi.org/10.1002/app.22717>
100. Yang HS, Wolcott MP, Kim HS, Kim S, Kim HJ (2006) Properties of lignocellulosic material filled polypropylene bio-composites made with different manufacturing processes. *Polym Test* 25:668–676. <https://doi.org/10.1016/j.polymertesting.2006.03.01>

101. Yang HS, Kim HJ, Son J, Park HJ, Lee BJ, Hwang TS (2004) Rice-husk flour filled polypropylene composites; mechanical and morphological study. *Compos Struct* 63:305–312. [https://doi.org/10.1016/s0263-8223\(03\)00179-x](https://doi.org/10.1016/s0263-8223(03)00179-x)
102. Ichazo M, Albano C, González J, Perera R, Candal M (2001) Polypropylene/wood flour composites: treatments and properties. *Compos Struct* 54:207–214. [https://doi.org/10.1016/s0263-8223\(01\)00089-7](https://doi.org/10.1016/s0263-8223(01)00089-7)
103. Sreekumar PA, Joseph K, Unnikrishnan G, Thomas S (2007) A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Compos Sci Technol* 67:453–461. <https://doi.org/10.1016/j.compscitech.2006.08.025>
104. Satapathy A, Patnaik A, Pradhan MK (2009) A study on processing, characterization and erosion behavior of fish (*Labeo rohita*) scale filled epoxy matrix composites. *Mater Des* 30:2359–2371. <https://doi.org/10.1016/j.matdes.2008.10.033>
105. Adhikari R, Bhandari NL, Le HH, Henning S, Radosch HJ, Michler GH, Garda MR, Saiter JM (2012) Thermal, mechanical and morphological behavior of poly(propylene)/wood flour composites. *Macromol Symp* 315:24–29. <https://doi.org/10.1002/masy.201250503>
106. Pal AK, Katiyar V (2017) Thermal degradation behavior of nanoamphiphilic chitosan dispersed poly(lactic acid) bionanocomposite films. *Int J Biol Macromol* 10:1267–1279. <https://doi.org/10.1016/j.ijbiomac.2016.11.024>
107. Kitagawa K, Ishiaku US, Mizoguchi M, Hamada H (2005) Bamboo-based ecomposites and their potential applications. In: Mohanty AK, Misra M, Drzal LT (eds) *Natural fibers biopolymers, and biocomposites*. CRC Press, Boca Raton, USA
108. Lee SH, Ohkita T, Kitagawa K (2004) Eco-composite from poly(lactic acid) and bamboo fiber. *Holzforschung* 58. <https://doi.org/10.1515/hf.2004.080>
109. Pinheiro IF, Ferreira FV, Souza DHS, Gouveia RF, Lona LMF, Morales AR, Mei LHI (2017) Mechanical, rheological and degradation properties of PBAT nanocomposites reinforced by functionalized cellulose nanocrystals. *Euro Polym J* 97:356–365. <https://doi.org/10.1016/j.eurpolymj.2017.10.026>
110. Pereda M, Amica G, Racz I, Marcovich NE (2011) Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. *J Food Eng* 103:76–83. <https://doi.org/10.1016/j.jfoodeng.2010.10.001>
111. Ochi S (2008) Mechanical properties of kenaf fibers and kenaf/PLA composites. *Mechan Mater* 40:446–452. <https://doi.org/10.1016/j.mechmat.2007.10.006>
112. Kabir MM, Wang H, Lau KT, Cardona F (2012) Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview. *Compos Part B: Eng* 43:2883–2892. <https://doi.org/10.1016/j.compositesb.2012.04.053>
113. Novotny C, Erbanova P, Sezimova, H, Malchova K, Rybkova Z, Malinova L, Prokopova I, Brozek J (2015) Biodegradation of aromatic-aliphatic copolyesters and polyesteramides by esterase activity-producing microorganisms. *Int Biodeter Biodegrad* 97:25–30. <https://doi.org/10.1016/j.ibiod.2014.10.010>
114. Siotto M, Zoia L, Tosin M, Innocenti FD, Orlandi M, Mezzanotte V (2013) Monitoring biodegradation of poly(butylene sebacate) by gel permeation chromatography, ¹H-NMR and ³¹P-NMR techniques. *J Environ Manage* 116:27–35. <https://doi.org/10.1016/j.jenvman.2012.11.043>
115. Sharma S, Singh I, Viridi JS (2003) Apotential *Aspergillus* species for biodegradation of polymeric materials. *Curr Sci* 84:1399–1402
116. Esmaeli A, Pourbabae AA, Alikhani HA, Shabani F, Esmaeili E (2013) Biodegradation of low-density polyethylene (LDPE) by mixed culture of *Lysinibacillus xylanilyticus* and *Aspergillus niger* in soil. *PLOS One* 8:1–10. <https://doi.org/10.1371/journal.pone.0071720>
117. Carrasco GC, Miettinen A, Hendriks CLL, Gamstedt EK, Kataja M (2011) Structural characterization of Kraft pulp fibres and their nanofibrillated materials for biodegradable composite applications. In: John C (ed) *Nanocomposites and polymers with analytical methods*, chap 10, pp 243–260. ISBN: 978-953-307-352-1 <https://doi.org/10.5772/21580>

118. Saxena M, Morchhale RK, Asokan P, Prasad BK (2008) Plant Fiber- Industrial waste reinforced polymer composites as a potential wood substitute material. *J Compos Mater* 42:367–384. <https://doi.org/10.1177/0021998307087014>
119. Cho MJ, Park BD, Kadla JF (2012) Characterization of electrospun nanofibers of cellulose nanowhisker/polyvinyl alcohol composites. *Mokchae Konghak* 40:71–77. <https://doi.org/10.5658/wood.2012.40.2.71>
120. Wu CS (2012) Characterization of cellulose acetate-reinforced aliphatic-aromatic copolyester composites. *Carbohydr Polym* 87:1249–1256. <https://doi.org/10.1016/j.carbpol.2011.09.009>
121. Faguaga E, Perez CJ, Villarreal N, Rodriguez ES, Alvarez V (2012) Effect of water absorption on the dynamic mechanical properties of composites used for windmill blades. *Mater Des* 36:609–616. <https://doi.org/10.1016/j.matdes.2011.11.059>
122. Li L, Ding S, Zhou C (2003) Preparation and degradation of PLA/chitosan composite materials. *J Appl Polym Sci* 91:274–277. <https://doi.org/10.1002/app.12954>
123. Shi B, Shlepr M, Palfery D (2011) Effect of blend composition and structure on biodegradation of starch/Ecoflex-filled polyethylene films. *J Appl Polym Sci* 120:1808–1816. <https://doi.org/10.1002/app.33309>
124. Chieng BW, Ibrahim NA, Yunus WMZW (2010) Effect of organo-modified montmorillonite on poly(butylene succinate)/poly(butylene adipate-co-terephthalate) nanocomposites. *eXPRESS Polym Lett* 4:404–414. <https://doi.org/10.3144/expresspolymlett.2010.51>
125. Panaitescu DM, Frone AN, Ghiurea M, Spataru CI, Radovici C, Iorga MD (2011) Properties of polymer composites with cellulose microfibrils. In: Brahim A (ed) *Advances in composites materials-ecodesign and analysis*, vol 5, pp 103–122. ISBN: 978-953-307-150-3. <https://doi.org/10.5772/14682>
126. Cho J, Joshi MS, Sun CT (2006) Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles. *Compos Sci Technol* 66:1941–1952. <https://doi.org/10.1016/j.compscitech.2005.12.028>
127. Yang Y, Lan J, Li X (2006) Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Mater Sci Eng A* 380:378–383. <https://doi.org/10.1016/j.msea.2004.03.073>
128. Paul DR, Robeson LM (2008) Polymer nanotechnology: nanocomposites. *Polymer* 49:3187–3204. <https://doi.org/10.1016/j.polymer.2008.04.017>
129. Birinchi L, Cotana F, Fortunati E, Kenny JM (2013) Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. *Carbohydr Polym* 94:154–169. <https://doi.org/10.1016/j.carbpol.2013.01.033>
130. Dhakal HN, Zhang ZY, Bennett N (2012) Influence of fibre treatment and glass fibre hybridisation on thermal degradation and surface energy characteristics of hemp/unsaturated polyester composites. *Compos Part B Eng* 43:2757–2761. <https://doi.org/10.1016/j.compositesb.2012.04.036>
131. Spiridon I, Darie RN, Kangas H (2016) Influence of fiber modifications on PLA/fiber composites: behavior to accelerated weathering. *Compos Part B Eng* 92:19–27. <https://doi.org/10.1016/j.compositesb.2016.02.032>
132. Dai X, Xiong Z, Na H, Zhu J (2014) How does epoxidized soybean oil improve the toughness of microcrystalline cellulose filled polylactide acid composites? *Compos Sci Technol* 90:9–15. <https://doi.org/10.1016/j.compscitech.2013.10.009>
133. Michler GH, Balta-Calleja FJ (2012) *Nano- and micromechanics of polymers: structure modification and improvement of properties*. Hanser Verlag Munich. ISBN-13: 978-1569904602, ISBN-10: 156990460X
134. Hassan MM, Wagner MH, Zaman HU, Khan MA (2011) Study on the performance of hybrid Jute/Betel nut fiber reinforced polypropylene composites. *J Adh Sci Technol* 25:615–626. <https://doi.org/10.1163/016942410x525858>
135. Wan YZ, Luo H, He F, Liang H, Huang Y, Li XL (2009) Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. *Compos Sci Technol* 69:1212–1217. <https://doi.org/10.1016/j.compscitech.2009.02.024>

136. Tesfaye M, Patwa R, Dhar P, Katiyar V (2017) Nanosilk-grafted poly(lactic acid) films: Influence of cross-linking on rheology and thermal stability. *ACS Omega* 2:7071–7084. <https://doi.org/10.1021/acsomega.7b01005>
137. Singh B, Sharma N (2008) Mechanistic implications of plastic degradation. *Polym Degrad Stab* 93:561–584. <https://doi.org/10.1016/j.polymdegradstab.2007.11.008>
138. Liu Y, Li Y, Chen H, Yang G, Zheng X, Zhou S (2014) Water-induced shape-memory poly(D,L-lactide)/microcrystalline cellulose composites. *Carbohydr Polym* 104:101–108. <https://doi.org/10.1016/j.carbpol.2014.01.031>
139. Itry RA, Lamnawar K, Maazouz A (2012) Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym Degrad Stab* 97:1898–1914. <https://doi.org/10.1016/j.polymdegradstab.2012.06.028>
140. Dvorackova M, Stloukal P, Koutny M, Gregovska M (2011) Biodegradability of aliphatic-aromatic copolyester in aqueous anaerobic and aerobic environments. In: *Recent advances in environment, energy system and naval science—Proceedings of the 4th international conference on environmental and geological science and engineering*. TBU Publications, pp 141–146. ISBN: 9781618040329
141. Giri J (2019) Wheat stalk micro- and nanocellulose based degradable polymer composites: morphology, mechanical and degradation behaviour. Ph.D. thesis submitted to Institute of Science and Technology, Tribhuvan University, Kathmandu, Nepal