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Polyhydroxybutyrate - a Biodegradable Plastic and its Various Formulations

Sabbir Ansari[1], Tasneem Fatma[2]

Research Scholar, Department of Biosciences, Jamia Millia Islamia, New Delhi, India [1]

Professor, Department of Biosciences, Jamia Millia Islamia, New Delhi, India [2]

Abstract: Plastic waste is increasing every year and the precise time needed for biodegradation is unknown. Environmental awareness has driven the development of new biodegradable materials, especially for single use plastic items. Polyhydroxybutyrate (PHB), biodegradable thermoplastic polyester is emerging out as a boon to overcome the problem of plastic waste accumulation. However, it has some drawbacks like moreover, it is still much more expensive and lacks mechanical strength compared with conventional plastics, high crystallinity, stiff and brittle, thereby resulting in poor mechanical properties with a low extension at break, which limits its range of applications. Here we report some PHB based blends which improved the quality of plasticizers.

Keywords: Polyhydroxybutyrate, biodegradable thermoplastic polyester, crystallinity, plasticizers

I. INTRODUCTION

In the past decades, an enormous market for biologically compatible products evolved. In this context, biologically degradable polymers are still rather underdeveloped. Although well known in principle, application of these materials has been limited to only specialized usage in medicine. However, there is without doubt great commercial potential of biodegradable plastics as substitute for polyolefin commodities like polypropylene (PP) and polyethylene (PE), but currently the high costs and the limited availability of these materials stand in the way of a broad introduction to a ready market [1] [2].

One of these promising materials is poly[(R)-3-hydroxybutyric acid (PHB). PHB has been the subject of extensive studies as an environmentally friendly polymeric material. Polyhydroxybutyrate (PHB) is a polyhydroxyalkanoate (PHA), a polymer belonging to the polyesters class that are of interest as bio-derived and biodegradable plastics [3]. The poly-3-hydroxybutyrate (P3HB) form of PHB is probably the most common type of polyhydroxyalkanoate, but other polymers of this class are produced by a variety of organisms: these include poly-4-hydroxybutyrate (P4HB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), polyhydroxyoctanoate (PHO) and their copolymers.

Poly (hydroxyalkanoates) (PHAs) belongs to a family of natural polyesters having a structure with the same three-carbon backbones and differing alkyl groups at b or 3 positions [4]. Such materials become more attractive when their mechanical properties compare favorably with those of commercial polymers. This is well illustrated by the estimate that consumption of biopolymers will grow to approximately 100 million metric tons/year by 2020 in Europe, while the perspective for 2008 also shows a growing market for biodegradable polymers [4].

Polyhydroxybutyrate (PHB) offers many advantages over traditional petrochemically derived plastics. In addition to its complete biodegradability, PHB is formed from renewable resources. It possesses better physical properties than polypropylene for food packaging applications and is completely nontoxic. The poor low-impact strength of PHB is solved by incorporation of hydroxyvalerate monomers into the polymer to produce polyhydroxybutyrate-co-valerate (PHBV), which is commercially marketed under the trade name Biopol. Like PHB, PHBV completely degrades into carbon dioxide and water under aerobic conditions [5].

PHB is produced by microorganisms (such as *Ralstonia eutrophus* or *Bacillus megaterium*) apparently in response to conditions of physiological stress; mainly conditions in which nutrients are limited. The polymer is primarily a product of carbon assimilation (from glucose or starch) and is employed by microorganisms as a form of energy storage molecule to be metabolized when other common energy sources are not available. Current production employs Alcaligenes eutrophus because it grows efficiently on glucose as a carbon source, accumulates PHB up to 80% of its dry weight, and is able to synthesize PHBV when propionic acid is added to the feedstock [5].

PHB is a partially crystalline polymer with a high melting temperature and a high degree of crystallinity, then it is brittle and has limited applications [6]; moreover, it is still much more expensive and lacks mechanical strength compared with conventional plastics. If the properties of the PHB can be further improved by the addition of a small quantity of an environmentally benign material, this polymer will find applications in more special or severe circumstances; in this case, it will be also necessary to know its behavior to degrade in similar to the real disposal waste. Because of its high crystallinity, PHB is stiff and brittle, and this results in very poor mechanical properties with a low extension at break, which limits its range of applications. Until now, there has been no large commercial production of PHB products because of its higher cost with respect to commercial polymers, high brittleness, and difficult processing.

During the last two decades, the great interest in the reduction of environmental impact caused by food packaging and their indiscriminate use, have increasingly received the scientist attention specially focused in the development of new biodegradable materials as a way to reduce the petroleum-based plastic residue. There are reports in which PHB is blended with several other plastics thereby yielding a better quality of plastic. Here are the some reports enclosed.

II. RELATED WORK

Poly(lactic acid) (PLA):

In this sense, poly(lactic acid) (PLA) is becoming increasingly popular as a biodegradable plastic owing to its high mechanical strength, superior transparency and easy processability compared to other biodegradables polymers [7]. Nowadays, PLA is an economically feasible material [8] derived from renewable resources [9], in particular from sugar and starch [10], chemically synthesized, commercially available with good performance characteristics as a packaging material [11] that is currently being used for many short term applications, such as disposable cutlery (plates, cups, lids and drinking straws), bags and film packages [12].

Moreover, its waste is suitable to be used in pyrolysis facilities to produce green energy [13] and also it is a compostable material [14]. Therefore, the PLA is suitable for food packaging applications [9]. Nevertheless, the use of PLA for food packaging is limited because of PLA has lower water vapor permeability, poor mechanical and thermal properties, low ductility, and its thermal and oxygen barrier properties are quite poor compared with equivalent petroleum based polymers [15].

Moreover, although the addition of plasticizer increases PLA gas permeability, owing to its poor ductility PLA plasticization is required for film applications [16]. Polymer barrier properties are of fundamental importance for food packaging applications. For instance, there are many food products sensitive to oxidation and to overcome this trouble packages with reduced oxygen permeability are desirable. On the other hand, the water resistant is also important, particularly for materials intended for direct contact with high moisture foods as well as materials to be submitted under high humidity conditions during storage and/or transport [11]. PLA barrier properties are decided by the crystalline and molecular characteristics [17]. Thus, research on modifications of PLA has mainly focused on the increase of PLA crystallinity.

There are many studies focusing on PLA modification such as the addition of modifiers, copolymerization or blending. Blending PLA with another bio-based and/or biodegradable material allow to adjust some properties in wide range while legislation also favors completely compostable materials with minimal carbon-footprint [18], such as are those provided by the physical blend processing technology. In this sense, poly-hydroxybutyrate (PHB), another biodegradable thermoplastic, is the most common representative of Poly-hydroxyalkanoates (PHA) that has been proposed for short term food applications [19]. It is also a brittle polymer, as its enzymatic polymerization leads to the formation of macromolecules with highly ordered stereochemical structure, as a result large crystallinity [18]. One of the great advantages of PHB over many other biodegradable polymers is it biodegradability under both, aerobic and anaerobic conditions [20]. For this reason, PLA and PHB and their blends are biodegradable materials commonly investigated for food packaging applications [21–24]. One of the potential application fields of these materials is as a film. Bartczakwe et al., 2013 demonstrated that blending of PLA with atactic poly([R,S]-3-hydroxy butyrate) (a-PHB) leads to significant improvement of drawability and impact strength [25]. The blends of PLA with a-PHB are biodegradable, similarly to plain PLA, and can be considered as a potential material for packaging, especially for food. It has been reported that 25 wt% of PHB produced a reinforcement effect on PLA matrix [24] due to PHB could be used as a nucleating agent [23]. In this sense, Zhang and colleagues studied blends of PLA and poly(hydroxybutirate) (PHB) in different proportions and concluded that blending PLA with 25 wt% of PHB some interactions between both polymers matrices were observed. Furthermore, their results also showed improved mechanical properties [24]. However, PLA and PHB films are rigid and need to be modified. One common practice for film manufacturing is the plasticizers addition to increase the molecular mobility and consequently enhance the material flexibility. The composition of materials in contact with foodstuffs is tightly regulated, so food grade plasticizers are required. Furthermore, when consumers decide to purchase food products the aspect of packaging could influence the decision, and therefore high transparency in food packaging is required. Arrieta et al., 2013 blended poly(lactic acid) PLA, and poly(hydroxybutyrate) PHB, and plasticized with a natural terpene D-limonene (LIM) with the dual objective to increase PLA crystallinity and to obtain flexible films intended for food packaging applications [26]. The influences of plasticization process on the mechanical properties showed that D-limonene provoked an increase in elongation at break. Disintegrability under composting conditions was also investigated and it was observed that PHB delays the PLA disintegrability under composting while D-limonene speed it up. In brief, the best results regarding structural, thermal, barrier and mechanical properties were found for the ternary PLA–PHB–LIM film.

Abdelwahab et al., 2012, investigated blend of poly (lactic acid) (PLA) (75% by weight) and poly(3-hydroxybutyrate) (PHB) (25% by weight) with a polyester plasticizer (Lapol 108) at two different concentrations (5 and 7% by weight per 100 parts of the blends) [27]. They reported that the melting temperature of PLA and PHB blends mostly did not change with an increase in plasticizer content, and the thermal stability of PLA and PHB was not affected. Also, the elongation at break of the PLA/PHB blend was greatly improved with the addition of plasticizer. In addition, in preliminary biodegradation studies carried in natural compost neat PHB showed some biodegradation, whereas the samples containing PLA did not experience a substantial biodegradation.

Clays:

Montmorillonite is among the most commonly used clay because it is environmentally friendly and readily available in large quantities with relatively low cost [28, 29]. Addition of nanoparticles such as nanoclays to form nanocomposites [30, 31] has provided the means to improve materials performance including biodegradation. One advantage of clay nanocomposites is their capacity to improve polymer barrier properties retaining the flexibility and optical clarity of the pure matrix [32, 33]. Incorporation of an organic modifier onto the clay surface, to mediate between the polarity of the hydrophilic clay surface and that of the more hydrophobic polymer, has been widely adopted for compatibilization and for easy exfoliation of the clay platelets into the polymer matrix during processing. Thus, as expected, the organoclay dispersibility within a polymer matrix has been found to depend on factors such as type and quantity of surfactant, type of clay, as well as on the processing conditions. It is reported that with only a few percent of clay, PHB exhibits greatly improved mechanical, thermal and barrier properties compared with the pristine polymers [34]. Puglia et al.,2014 prepared polymer nanocomposites, based on a bacterial biodegradable thermoplastic polyester, poly(hydroxybutyrate) (PHB), and unmodified montmorillonite Cloisite Naþ (CNa) and chemically modified Cloisite 15A and 93A (C15A and C93A),through a solution route. XRD results suggest a better dispersion for C15A and C93A based nanocomposites that present also a more surface hydrophobic nature respect to PHB matrix and PHB nanocomposite loaded with unmodified Cloisite. This result is in accord with disintegrability behavior of PHB nanocomposites. Visual observation, chemical, thermal and morphological investigations proved that the disintegration in composting conditions was faster for PHB_4CNa respect to the systems loaded with modified clays suggesting the possibility to modulate the disintegrability capacity of PHB selecting a specific filler [35].

Others:

Baltieri et al.,2008 studied the influence of four types of plasticizers, dioctyl phthalate (DOP), dioctyl adipate (DOA), triacetyl glycerol (TAG) and polyadipate (PA), in the thermal and mechanical properties of Poly(3-hydroxybutyrate) (PHB) [36]. These plasticizers were introduced alone or mixtures of them, using concentrations that varied from 5 to 30% wt. Their influence in some important polymer parameters as Tg, Tm and degree of crystallinity, and on its mechanical behavior, elongation and tensile strain were investigated. The best results were obtained for the sample with 30% TAG and that one using a binary mixture of plasticizers PA 20% and TAG 10%.

Wang et al.,2008 plasticized PHB with DOP, dioctyl sebacate (DOS), and acetyl tributyl citrate (ATBC). From the differential scanning calorimetry measurements, they concluded that only the addition of ATBC leads to an obvious decline in Tg and improves other thermal characteristics of PHB. However, it does little to improve the mechanical properties. Blending with poly(3-hydroxybutyrate-co-4-hydroxybutyrate) [P(3/4HB)] improves the mechanical properties of PHB with a good elongation at break obtained. The MFI test revealed that the addition of stabilizer antioxidant 1010 and the addition of poly(3-hydroxybutyrate-co-hydroxyhexanoate) [PHBHHx] and P(3/4HB) enhanced the thermal stability of PHB and stabilized the MFI value [37]. Therefore, the combination of ATBC, antioxidant 1010, and PHBHHx or P(3/4HB) could widen the PHB processing window.

III. CONCLUSION

Poly(3-hydroxybutyrate) (PHB), a renewable and bacterially synthesized, completely biodegradable, highly hydrophobic thermoplastic polyester material. However due to its high crystallinity, PHB is stiff and brittle, and this results in very poor mechanical properties with a low extension at break, which limits its range of applications. However, these drawbacks of PHB can be overcome by preparing PHB-based blends with other polymers or plasticizers. Here we reported some of the important PHB based blends which improved its physical as well as chemical properties. This compiled data will further help the researchers in better understanding the topic as well as applying better and new approaches targeting PHB based blends.

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