Industrial Crops and Products 68 (2015) 60–79

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Green composites prepared from aliphatic polyesters and bast fibers

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ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form 8 August 2014
Accepted 19 August 2014
Available online 6 September 2014

Keywords:
Green biocomposites
Bast fibers
Biodegradable polymers
Aliphatic polyesters

ABSTRACT

In the recent years, the research about the use of natural cellulosic fibers as substitutes of the synthetic fibers (glass, aramid and carbon) used in the reinforcement of polymers, has been increased due to their biodegradability, lightness, reduced cost and favorable mechanical properties. Green composites are a particular class of biocomposites in which a biodegradable polymeric material is reinforced with natural fibers and represent a growing field in polymer technology. Such biodegradable polymers are usually aliphatic polyesters. The final properties of the composites are mainly depended on the kind of the fibers used, their aspect ratio, their volume fraction and orientation, and the adhesion strength on the fiber–matrix interface. Hence, one of the challenges that researchers face today is to achieve satisfactory interfacial bonding which will result in products with better mechanical properties. Such composites could find more industrial applications and consequently would have greater commercial acceptance. However, this is difficult due to the hydrophilicity of the fibers and the hydrophobicity of used polyesters. In the particular review the advances on the preparation of green composites with bast fibers and aliphatic polyesters are discussed. Emphases are given on the summary of the literature and presentation of the effect of the different kinds of bast fibers on the final products. The treatments used to improve the properties of the aliphatic polyesters in order for the final composites to perform advanced mechanical and thermal properties as well as biodegradability are also reviewed.

1. Introduction

Composite materials with fibers are widely explored, due to their easy processing, anisotropy and enhanced thermal and mechanical properties (Liu et al., 2009a,b). In the recent years, research about the use of natural cellulosic fibers as substitutes of synthetic fibers has increased, because of their biodegradability, reduced cost and sufficient mechanical properties. Currently, the most dominant reinforcing fibers for polymers are glass, aramid, and carbon fibers, and their applications are found in construction, automotive, aerospace, leisure and sporting industries. Their disadvantages – glass fibers have high density (2.5 g/cm^3) – and mainly their high cost production are the reasons that led the researchers to study the potential replacement of synthetic fibers by natural lignocellulosic fibers. Glass fibers are also hazardous materials during inhalation, can be difficult to recycle, need high energy consumption for their preparation. On the other hand, the most attractive advantages of natural fibers compared with glass fibers are their carbon dioxide neutrality and their biodegradable disposal (Wambua et al., 2003). Due to the above, natural fibers have gained rising research interest for the preparation of environment-ecofriendly materials to substitute the conventional non-degradable plastics.

Composite materials that are fully bio-based, meaning that both the matrix and the reinforcing agents originate from renewable sources, are named 'green composites' or biocomposites (Cheung et al., 2009; John and Thomas, 2008; Zini and Scandola, 2011; Signori et al., 2012). The conclusions of studies on eco friendly composites based on plant fibers and a variety of matrices decomposing in the environment, have been reported recently (John et al., 2007). Green composites are commercially produced, with biodegradable polymers like the aliphatic polyesters which can be degraded from enzymes like esterases. Trying to face problems caused by accumulation of plastic wastes, biodegradable aliphatic polyesters including polycaprolactone (PCL), poly(3-hydroxybutyrate) (PHB),

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http://dx.doi.org/10.1016/j.indcrop.2014.08.034
0926-6690/

polyhydroxyvalerate (PHV), and their copolymers, polylactide (PLA), polyglycolate (PGA), poly(butylene succinate) (PBSu), poly(propylene adipate) (PPAd) and their copolymers with different monomer ratios, poly(ethylene succinate) (PESu), etc., are used in various applications, for example bottles, packaging materials, fibers, mulch films and implants. Furthermore, the particular polymers can be synthesized from monomers that are derived from renewable sources (Flieger et al., 2003). So, these materials are potential alternatives for the replacement of fossil based thermoplastics in a wide range of uses.

Since 1990, researchers from both academic institutions and several industries have studied plant fibers, which have low density (1.5 g/cm^3), as alternative reinforcing agents and eco friendly substituents to glass fibers (Zini and Scandola, 2011). This resulted in an impressive growth of use of leaves from plants like flax, jute, hemp, pineapple and sisal prior to arrive to novel eco friendly composites, during last decade (Cheung et al., 2009). After cutting into fibers, leaves can be used as reinforcements (John and Thomas, 2008; La Mantia and Morreale, 2011).

The most important market for such composites is now the automobile industry, because new regulations from the European Union require new cars to be recyclable after 2015 at a level of 95% (Anandjiwala and Blouw, 2007). However, as fibers and polymers do not show the appropriate compatibility, such composites suffer from poor mechanical properties. Thus, the challenge about natural fiber reinforced polymer composites is to achieve satisfactory interfacial bonding. But as plant fibers and plastics show large differences in hydrophilicity, this cannot be easily achieved (John and Anandjiwala, 2008; Wambua et al., 2003). Low adhesion may cause low mechanical properties that lead to premature failure of the materials, because there are no interactions that will help transfer the stress from the matrix to the fiber (Pracella et al., 2006). Chemical modification of fibers can reduce their polarity and hydrophilicity. The use of interfacial additives is also a dominant way of achieving compatibility between filler and matrix (Li et al., 2007). The effect of these treatments on the behavior of the final composite materials will be discussed later on this chapter.

Green composites are advantageous materials as they completely decompose in the environment. They are also characterized by easy disposal or decomposition without any environmental impact, after closing their life cycle. In the present review the last evolution in biodegradable composites, which are consisted from fully biodegradable polymers like aliphatic polyesters and biobased fibers, is discussed in details.

2. Plant fibers

All plant fibers are lignocellulosic and are classified into 6 main categories, which are also consisted from subcategories and are presented in Fig. 1. Their main component is cellulose (40–90%) (Fig. 2), a hydrophilic polysaccharide consisting of a linear macromolecular chain of β(1 → 4) linked D-glucose units. The repeating unit is cellobiose, composed by two molecules of

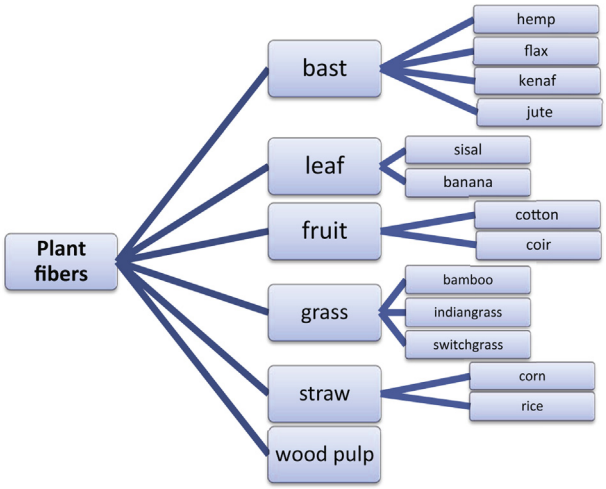

Fig. 1. Classification of natural fibers (reproduced with permission from Zini and Scandola, 2011).

glucose. The hydroxyl groups of glucose form hydrogen bonds in the molecule (intramolecular) and between different molecules of cellulose (intermolecular). The mechanical properties of cellulose are affected by its degree of polymerization, which varies. Cellulose has a good resistance in hydrolysis, even if all chemical processes degrade it in some extend (Heinze and Fischer, 2005). Cellulose of non-treated fibers has the crystal structure of cellulose I. Some treatments might change its crystal structure in cellulose II.

Apart from cellulose, other components exist in the plant cell walls like hemicellulose (2–20%) (Fig. 3), lignin (0.5–25%) (Fig. 4) and pectin (0.2–10%) (Summerscales et al., 2010). Hemicelluloses have smaller molecular masses compared to polysaccharides and are usually copolymers based on glucose or xylose, or even of mannose, glucuronic acid as well mannose. Hemicellulose can be degraded by both chemical and enzymatic hydrolysis. In contrast with cellulose, hemicelluloses are mostly branced molecules, and their degree of polymerization is 10–100 times lower.

Lignin fills the space and acts as glue between the cellulosic fibers. It is produced during the irreversible removal of water from sugars, mainly xylose. As the plant grows, more lignin is produced, providing mechanical stability (Sperry, 2003). It is resilient to most microorganisms, since its aromatic groups are resilient to anaerobic procedures, while its aerobic degradation is slow. The exact structure of lignin remains unknown since it is insoluble in any solvent.

Plant fibers contain also pectin, in a small amount. Pectin is the main component of the middle lamella, and it is a group of polysaccharides rich in galacturonic acid (Willats et al., 2001). Its exact structure is not entirely known, though it is believed that its three main components are homogalacturan and ramnogalacturan I and II, covalently bonded on the primary cell wall and on the middle lamella, forming a complicated pectin network.

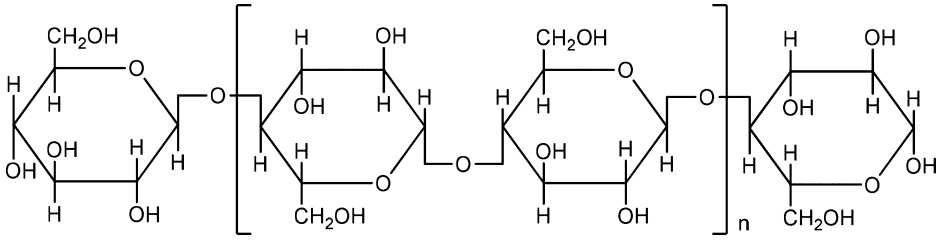

Fig. 2. Cellulose structure.