Bioresource Technology 101 (2010) 6843–6851

Contents lists available at ScienceDirect

Bioresource Technology

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

Development of corn starch based green composites reinforced with *Saccharum spontaneum* L fiber and graft copolymers – Evaluation of thermal, physico-chemical and mechanical properties

B.S. Kaith [a,*], R. Jindal [a], A.K. Jana [b], M. Maiti [a]

[a] Department of Chemistry, Dr B.R.A. National Institute of Technology, Jalandhar 144011, Punjab, India
[b] Department of Biotechnology, Dr B.R.A. National Institute of Technology, Jalandhar 144011, Punjab, India

ARTICLE INFO

Article history:
Received 30 November 2009
Received in revised form 20 March 2010
Accepted 24 March 2010
Available online 14 April 2010

Keywords:
Saccharum spontaneum L fiber
Graft copolymer
MMA
Corn starch
Green composites

ABSTRACT

In this paper, corn starch based green composites reinforced with graft copolymers of *Saccharum spontaneum* L. (Ss) fiber and methyl methacrylates (MMA) and its mixture with acrylamide (AAm), acrylonitrile (AN), acrylic acid (AA) were prepared. Resorcinol–formaldehyde (Rf) was used as the cross-linking agent in corn starch matrix and different physico-chemical, thermal and mechanical properties were evaluated. The matrix and composites were found to be thermally more stable than the natural corn starch backbone. Further the matrix and composites were subjected for biodegradation studies through soil composting method. Different stages of biodegradation were evaluated through FT-IR and scanning electron microscopic (SEM) techniques. *S. spontaneum* L fiber-reinforced composites were found to exhibit better tensile strength. On the other hand Ss-g-poly (MMA) reinforced composites showed maximum compressive strength and wear resistance than other graft copolymers reinforced composite and the basic matrix.

1. Introduction

The ever-growing environmental pressure caused by the widespread consumption of petroleum based polymers and plastics have spurred a thrust into the development of biodegradable or environmentally acceptable materials. Biopolymers derived from various natural resources such as protein and starch have been regarded as alternate materials. Biodegradable polymeric materials derived from renewable sources, are considered as the most promising materials because their easy availability and cost effectiveness. Starch is the major form of carbohydrate in plants (Zeppa et al., 2009). In packaging applications, starch based materials have received great attention. Biodegradable starch based polymers have been found to possess wide range of properties which find application in biomedical field like making bone plates and screws, in drug delivery carriers and tissue engineering scaffolds (Marquesa et al., 2002). Worldwide corn represents the major commercial source of starch. It is a semicrystalline polymer composed of a mixture of amylose, a linear polysaccharide and amylopectin, a highly branched polysaccharide (Avella et al., 2005). However, in the absence of plasticizers, films made from starch are very brittle therefore, starch is commonly pretreated with a plasticizer to make the films shatter resistant (Chen and Evans, 2005; Mali et al., 2004). Since, plasticized starch cannot meet all the requirements essential for packaging applications, as such water resistance and barrier properties, therefore, it is important to incorporate hydrophobic properties into the starch based materials (Dole et al., 2004; Mali et al., 2002; Yılmaz et al., 2004). Thus, the green composite concept could be a promising option using of crop-derived fibers and matrix materials. Considerable growth has been seen in the use of bio-composites in the automotive and decking markets over the past few decades (Shibata et al., 2008; Suharty et al., 2008). Some researchers have prepared biodegradable composites of cellulose diacetate and starch and examined their physical and thermal properties (Lee et al., 2006). Biodegradable thermoplastic composites were prepared by the reaction of aliphatic polyester and polybutylene succinate adipate (PBSA) with granular corn starch (Ratto et al.,1999). Morreale et al. (2008) synthesized corn starch based biodegradable polymer by adding wood flour in the form of short fibers with two different sizes (coarse and fine). Different types of corn starch based polymeric matrix composites are used in hard tissue replacement (Mano et al., 2004). Corn starch can be converted to corn starch plastic through extrusion with a suitable cross-linker. The corn starch matrix based composites reinforced with natural fibers have a poor moisture resistance and chemical

* Corresponding author. Tel.: +91 9780684883; fax: +91 181 2690320.
E-mail addresses: bskaith@yahoo.co.in (B.S. Kaith), jindal@nitj.ac.in (R. Jindal), ak_jana@yahoo.com (A.K. Jana), maiti.mithu@yahoo.com (M. Maiti).

0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.03.113

stability because of easy vulnerability of natural fibers towards moisture and corrosive environment. In order to enhance moisture, chemical and thermal resistance, natural fibers can be processed by chemical modifications such as etherification, esterification and grafting (Kaith et al., 2009a).

Graft copolymerization is the simplest tool in the hands of chemists to improve the properties of natural fibers. Modification of cellulosics through graft copolymerization provides a significant root to alter the physical and chemical properties of the fibers. Various workers have carried-out graft copolymerization onto different cellulosic back-bones using vinyl monomers through various chemical and radiation techniques (Joshi and Sinha, 2006; Li et al., 2006; Yanbin et al., 1999; Wang et al., 2008). Graft copolymerization of MMA onto different back-bones such as poly(butyl acrylate) (Valette et al., 2002), polymethyl acrylate, acrylic acid, polyvinylidene fluoride (Gallagher and Jakeways, 2003), glycol polymers (Haddleton and Ohno, 2000) and cellulose (Shen and Huang, 2004) resulted in increased hydrophobicity, chemical resistance and physical strength of the material.

Saccharum spontaneum L. grows as a wasteland weed and lowland eco-region at the base of the Himalayan range in India, Nepal, China and Bhutan. It is widely distributed plant and occurs at an altitude ranging from sea-level to 1000 m. It belongs to Poaceae family with Magnoliphyta division. Genus *Saccharum* has five extant species of which *S. spontaneum* L. is a wild species. *S. spontaneum*, like wheat, rice, corn and other grains, is of the grass family, characterized by segmented stems, blade-like leaves and reproduction by seed. It is a perennial grass, growing up to 3 m in height. Its ability to quickly colonize in disturbed soil has allowed it to become an invasive species that takes over croplands and pasturelands. It is used as valuable medicinal herb in traditional systems of medicine in India. It is a first growing biomass with flowers containing fibers. These fibers are distinctly different in appearance from other type fibers studied earlier such as cotton, jute, flax, ramie and hemp. These fibers are white/purplish silky and have better strength and fineness (Bhandari, 1990; Sastri and Kavathekar, 1990).

Chemical modification of *S. spontaneum* fibers for enhancement of moisture retardance, chemical resistance and thermal stability through graft copolymerization with MMA and binary monomer mixtures MMA + AAm, MMA + AA and MMA + AN were studied earlier (Kaith et al., 2009a, b). This was due to the fact that with grafting of these groups onto the hydroxyl and other functional groups present in natural fibers, the vulnerable sites were blocked.

In continuation of our earlier work the objective of the present work is to develop the corn starch matrix based green composites and enhancement of chemical, mechanical and thermal properties through reinforcement with different graft copolymers of *S. spontaneum* fiber. The composites have been found to possess better chemical and thermal stability in comparison to corn starch matrix. The composites prepared were further subjected for biodegradation evaluation so that the green composites prepared could be used as structural materials in building, cars, interior decorations, furniture, packagings and boxes.

2. Methods

2.1. Purification of materials

S. spontaneum L. was collected from the waste land weeds of National Institute of Technology campus, Jalandhar and the fiber was separated from the plant manually. It was purified through soxhlet extraction in acetone for 72 h (Kaith et al., 2009a). Corn flour, resorcinol, formaldehyde, and sodium hydroxide (s.d. fine Chemicals Ltd, Mumbai, India) were used as received.

Casting of composites was carried-out in an iron die with dimension: 250 mm × 50 mm × 5 mm (l × b × w).

2.2. Development of biodegradable matrix and composites

Resorcinol–formaldehyde (Rf) cross-linker was prepared by the mixing of specific molar ratio (1:0.8) of resorcinol and formaldehyde. Sodium hydroxide (50% aqueous solution) was added with 5% weight basis of resorcinol with constant stirring. Since the reaction is exothermic, temperature was maintained at 50 °C till resinification was attained (Ghosh, 2002).

Corn starch matrix was prepared by the addition of resorcinol–formaldehyde cross-linker in a specific w/w ratio at resinification stage to the thick slurry of corn starch in deionized water. The mixture stirred and maintained at 40 °C for 30 min. The resin was cast in an iron die and was kept for pre-curing at room temperature (28 °C) for 24 h. Finally, the sample was cured by hot pressing in a Carver hydraulic hot press at 90 °C for 30 min under the load of 178×10^3 N/m^2.

Corn starch matrix based composites were prepared by mixing of *S. spontaneum* fiber and its graft copolymers with semisolid corn starch matrix at w/w ratio (0.5:10). The mixture was transferred to water bath maintained at 40 °C and was thoroughly stirred for 30 min so as to obtain a thick paste. The paste was taken into an iron die and was pre-cured at ambient temperature (28 °C) for 24 h. The pre-cured composite specimen was hot pressed and was processed as per the method used in case of corn starch matrix preparation.

Though the mechanical strength of the composite was found to increase with increase in the concentration of the cross-linker used but at the same time it was found to reduce the biodegradability. In order to find out the optimum concentration of the cross-linker for optimal mechanical strength, samples were prepared using different concentrations of resorcinol–formaldehyde (2%, 4%, 6%, 8% and 10%) and evaluation of tensile strength and biodegradability was carried-out (Tables 1 and 2).

2.3. Tensile strength

The tensile strength was measured by Universal Testing Machine (model LR100 K, LLOYD) as per the ASTM D 638 standard. Strain rate was 10 mm per min and total extension range was 25 mm. Tensile stress was applied till the failure of the sample and the total extension per unit force was noted.

Table 1
Effect of cross-linker on tensile strength of corn starch based matrix.

Sample	Cross-linker (%)	Tensile strength (MPa)	Increase in tensile strength (%)	Extension (mm)	Strain (%)
Corn starch	2	07.31 ± 0.46	–	1.7 ± 0.05	8.9 ± 0.11
Corn starch	4	13.24 ± 0.52	44.7	1.5 ± 0.07	7.8 ± 0.14
Corn starch	6	16.75 ± 0.57	56.3	1.4 ± 0.04	6.7 ± 0.12
Corn starch	8	19.88 ± 0.61	63.2	1.3 ± 0.08	5.6 ± 0.17
Corn starch	10	20.38 ± 0.66	64.13	1.1 ± 0.03	5.6 ± 0.21

No. of replication was 3.