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BIODEGRADABILITY OF STARCH BLENDS- A REVIEW

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Abstract:

Degradation is a major delinquent across the world, due to the use of synthetic plastics. Ample efforts have been exerted to progress starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more pharmaceutical applications. The inherent advantages of synthetic polymers are obvious, but natural polymers accomplish diverse array with promising mechanical and barrier properties. At present and in the near future, effective strategies would be developed to strengthen starch blends as completely biodegradable polymers of appropriate biocompatibility, degradation rate. Due to it's inter and intra-molecular hydrogen bonding property, attempts have been made to blend materials like betacarotene, chitosan, molasses, fibre, polyvinylalcohol, wood, clay, o-phenyldiamine, metal oxides, polyaniline, hydroxyapatite etc., to form composites. This review emphasizes on studies like FTIR, SEM, TEM, XRD, TG-DTA and DSC, supportive to bring out the dimensional facts behind, to fetch it's the structural, functional applications, as an alternative to synthetics, thereby shielding the renewable resources on the landscape. These polymers could also extend their applications on the field of pharmaceuticals after proper clinical trials.

Keywords: Biodegradation, Starch, Polymer, Biocompatibility, Mechanical properties.

Introduction

The inherent necessity to reduce the environmental pollution caused by plastic and synthetics wastes has become a global concern, predominantly for bioremediation. Therefore, a focus on bio-based polymers as alternatives is been of recent trends in the field of polymer. Starch is an inexpensive, biodegradable, renewable natural polymers and abundant raw material, to produce thermoplastic starch (TPS) processed under high temperature, shear conditions and has attracted considerable attention since it can be modified toremove heavy metal ions and dyes.[1-8]Itcomprises hydrophilic character,

fast degradation rate and poor mechanical properties which made it suitable as a substituent for plastics. Its applications extends on advanced biomaterials field as tissue engineering scaffold, hydrogels for use as bone cements or drug-delivery carriers, protein immobilization, low cost adsorbent for dyeremoval, fabric desizing agent, erodible carriers for bioactivematerials and bio-coating.[9-18]There are many applications of starch based biodegradable blends in various fields such as in food industry, in agriculture, tissue engineering and drug delivery systems. Starch based polymers have three major applications in agriculture such as the covering of green house, mulch films and fertilizers.[19] However, starch is a hydrophilicmaterial, which does not well interact with commodity polymers suchas polyethylene due to its hydrophobic nature. Therefore, starch has gained great attention to blend with synthetic polymers because of its ability to accelerate biodegradation. Therefore, the popularity of starch/polymer blend as biodegradable material is greatly recognized. This review focuses on investigating the approaches that have been developed in order to improve compatibility of starch filled polarand non-polar synthetic polymers.

Structure and properties of starch

Starch [$C_6H_{10}O_5$] occurs naturally as discrete granules since the short branched amylopectin chains are able to form helical structures which crystallize. With a density of about 1.5 g/cm^3, their granules exhibit hydrophilic properties and strong inter molecular association via hydrogen bonding formed by the hydroxyl groups on the granule surface. There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked. *Tg*of native starch can be as low as 60 to 80°C when the weight fraction of water is in the range 0.12 to 0.14, which allows starch to be successfully injection moulded to obtain thermoplastic starch polymers in the presence of water. Evidently, starch is hydrophilic. The available hydroxyl groups on the starch chains potentially exhibit reactivity specific for alcohols.

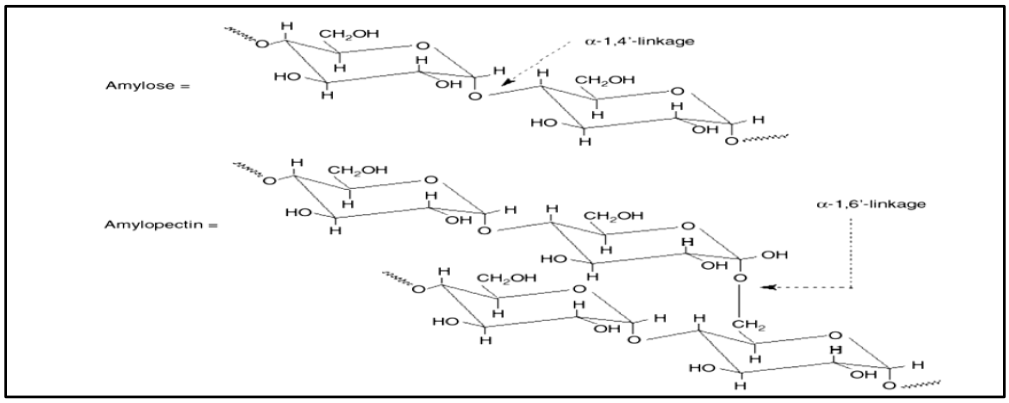

Figure1: Structure of Amylose and Amylopectin.

Starch is not a real thermoplastic, but in the presence of a plasticizer [water, glycerin sorbitol etc], at high temperature 90-80^{o}C and shearing, it melts and fluidizes, used in injection, extrusion and blowing equipment, those for synthetic polymers.

Starch/Polyaniline

Colocasiaesculenta corn starch/polyaniline composites have been synthesized by Saikia*et al*. using oxidative polymerization of PANI. Composites of 3 different concentrations were characterized by UV–Vis, FTIR, XRD, SEM [size ~2µm], and DSC analysis.[20]Remarkably, antioxidant [DPPH scavenging assay] and cytotoxic [haemolysis prevention assay] properties have been performed and found that the novel composite materials possessed tremendous potential for biomedical applications.

By *in situ* polymerization of aniline with starch, activated in acidic medium, starch/PANI composites were reported by NazarzadehZareh*et al.*[21] He improved the flexibility and mechanical properties by introducing polystyrene and studied the electrical conductivity of polyaniline/starch/polystyrene blends. FTIR analysis, UV-Vis, XRD and DSC, SEM studies demonstrated their biodegradability characteristics.

Starch/Wood

Reinforcement of Wood /TPS has been found to be advantageous for most application areas, substantially due to strong interfacial interactions and matrix properties. Petter Muller *et al.* worked on the shrinkage and interfacial adhesion properties of TPS/wood composites as debonding, fiber fracture with dimensional stability of 15–20 vol%, around10% of shrinkage. [22]

In 2014, Birnin-Yauri& Abbot projected the permeability of starch-wood composites with that of the synthetic adhesive urea-formaldehyde.[23] He plasticized this biocomposite with borax-glycerol systems and found an alternative to MDF due to its increased strength. These biocomposites were combined with MMT by ZhaofengLia*et al.* who explained the shear strength of that adhesive to be 5% in both wet and dry analysis with good thermal stability, using TGA analysis.[24] Interestingly, Ueberschaer*et al.*analyzed the micromechanical properties of starch biocomposites by passing X-rays, which supported the stability of amorphous/crystalline backbone of starch polymer.[25] Cross-linked polymer composites were prepared by Baishya and Tarun using MMT-grafted starch wood, whose mechanical strength, roughness, viscoelasticity, water-uptake were found to be significant using studies like FTIR, XRD, SEM.[26]

Starch/Hydroxyapatite

Yang Lei *et al.* synthesized biocompatible and bioactive nanohydroxyapatite through co-precipitation process using toxic-free, gelatinized starch matrix without any surfactants.[27] The efficacy of agglomeration and shape of crystals (aspectratio ~1 μm), showed much better than the reports of Sadjadi*et al.* and Fomin*et al*, who revealed large agglomerate sizes ~2 μm (SEM) and needle-like crystals with aspect ratio ~3 μm (TEM).[28,29] Castro-Cesena et.al studied the hydroxyapatite (HA)-starch blend to improve the blood-absorbing properties of collagen sponges in dentistry. The transversal section of the sponges showed that morphology changed with concentration of starch assimilated HA collagen, as compared to sponges prepared with starch by SEM image.[30] He analyzed the sponges of 1:0:0 and 1:4:0 (collagen:HA:starch by weight) that exhibited semi-spherical, irregular and interconnected pores between 150 and 200 μm, similar to those found in CollaPlug®. Pore size reduced to ~75 and ~25 μm in 1:4:5 and 1:4:10, with increasing starch concentration 100 to 200 mg/mL. Mohammad Shakira *et al.* coined Nano-hydroxyapatite/chitosan–starch nanocomposite in bone construction field with significant biocompatibility and cytotoxicity of the composite.[31]The cellular toxicity [MTT assay] study showed significant non-toxic nature of n-HA/CS–ST to both the cell lines even at higher concentrations (25–50 mg/ml) as compared to n-HA/CS at similar concentrations. He analyzed the hall effect of HA/CS–ST without interfering the cellular machinery over n-HA/CS which would be a promising candidate for bone tissue engineering in scaffold to be used as bone implant for orthopedic applications in mammals.

Starch/Clay

Slavutsky *et al.*prepared starch-MMT filmsby modifying the clay dispersion technique. The results showed that the addition of MMT using adequate methodology, improved the functional properties of the starch films due to the strong interaction between the MMT and glycerol/starch chains.[32] Water vapor solubility and permeability decreased with increasing montmorillonite content by the dispersion method. A decrease in film solubility, opacity and the improvement in water vapor barrier properties with the addition of nanoparticles below 10% were observed. Water diffusion was only dependent on the nanoclay content due to the increase in tortuosity of the diffusion path, caused by the nanoparticles. The similar polar and hydrophilic characters of the polymer matrix and the MMT led to strong adhesion between them via hydrogen bonding, leading to their potential for their application in the technology of biopolymer based films.

Chen and Evans examined nanocomposites of glycerol-plasticized starch, with untreated montmorillonite and hectorite.[33] Treated hectorite and kaolinite were added to produce conventional composites within the same clay volume. They used X-ray diffraction and transmission electron microscopy to confirm the type of composite. The natural smectite clays, montmorillonite and hectorite, readily formed nanocomposites with TPS as characterized by XRD, which showed wide (001) peaks and enlarged to 1.8 nm for the intercalated clay. The kaolinite indicates the conventional composites with TPS. TEM showed the untreated hectoritenanocomposites were partially exfoliated while the TPS–treated hectorite composites are conventional. Hence, those nanocomposites presented greater increases in modulus for a given volume fraction of clay, contributing to new class of biodegradable and environmentally acceptable materials. Nanocomposites of TPS/clay hybrids [Natural Na+MMT and organophylic Cloisite-30B], plasticized with glycerol, were prepared by melt-extrusion in a single-screw extruder by Bergaya*et al*. to investigate the hydrophilicity and crystallinity. Contact angle measurements and XRD results revealed that the increase in glycerol content led to materials with higher hydrophilicity and B-type crystallinity.[34] For materials plasticized with 25 wt% glycerol, XRD results revealed the appearance of the characteristic diffraction peak of intercalated Na+MMT with aging. The absence of the characteristic XRD peak, and the homogeneous matrix observed by SEM, suggested that the hybrids based on Cloisite-30B displayed a high degree of exfoliation. Results from soil burial tests showed that the addition of the organically-modified clay contributed to increase the biodegradation rate of nanocomposites, dependent on the relative crystallinity of the polymeric matrix, and on the sample hydrophilicity.

Chang *et al.*investigated the plasticized starch with rectorite clay [0 to 10 wt%] that exhibited decrease in water vapor permeability from 9.88 to $2.61\times10^{-10}gm^{-1}s^{-1}Pa^{-1}$.[35]The increasing bulk and surface hydrophobicities of TPS/Cloisite-Na/clay using SEM was explored by Fauze*et al.* which attributes to industrial application, predominantly in built-up of food ampules. Remarkably, Coativya*et al*. projected the interphase and confinement studies of starch-clay bionanocomposites by DSC, NMR, DMTA, who observed complex macromolecular dynamics behavior, increase the glass transition temperature.[36,37] He revealed that the high clay content (10%) slow-down the segmental relaxation due to confinement between the clay tactoids, while (3–5%). DSC measurements highlight an increase of the glass transition temperature for 10% clay which is shifted about 10◦C towards higher temperature compared to unreinforced starch. A significant modification of relaxation occurred due to interphase formation in the vicinity of clay coexisting with bulk

polymer. Microwave irradiation of potato starch-red clay based ceramics predicted by Angelie*et al.* shows the uniform distribution of solidified ceramic slurry as compared with the conventional counterpart by SEM fired at 1200°C.[38]Abreu*et al*. studied the starch-clay minerals from natural resources can competently persist the properties of bio-based materials.[39]

Applications

Starch-based polymers involve multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization. The starch basedbiodegradable polymers can be a possible alternative for food packaging to overcome these disadvantages and keep the advantages of traditional packaging materials. For instance, a starch/claynanocomposite food packaging material is developed, which can offer better mechanical propertyand lower migration of polymer and additives. Patel and Velikov studied starch-based edible films were odorless, tasteless, colorless, non-toxic, and biodegradable.[40] They can be used as the fertilizers controlled release matrices to release the fertilizers slowly or in controlled way. As a result, the loss of fertilizers and environment pollution can be avoided or reduced. Starch-based biodegradable polymers, in the form of microsphere or hydrogel, are suitable for drugdelivery.[41,42]There is no need for surgical removal of the device after drug depletion. They can be combined with bioactive particles, which allow new bone growth to be induced in both the interface of cement-bone and the volume left by polymerdegradation.[43] Starch-kaolinite interactions that allow269 better gliding of the starch chains and a basal orientation of the clay particles which are270 consistent with the increase plasticizing effect. Starch can serve as a potential adsorbent for the treatment reactive dyes and simulated dye bath effluent. Starch acetate- a hydrophobic starch ester, has been widely used to overcome the water solubility issues associated with extruded loose-fill packaging materials. In the domain of packaging application, plasticized starchcould help to deal with packaging waste associated with fossilbased packaging materials.[44]

Conclusion

With a burgeoning effort, the development of biodegradable starch impregnates, since the recent decade has extensively contributed towards the development of biodegradable materials with diverse applications on soil pollution. It endowed the synthesis of biocomposites with higher surface area, electro-activity, conductivity, hydrophilicity. Conversely, many shortcomings have been spread through the different characteristics of starch blends; therefore, reinforcement on

intermolecularinteractions shall be of interest. A focus on the principles behind the appropriate modifications topolymer system would induce the polarity of the biomaterials, which shall subsequently lead to the engagement of chitosan, cellulose, fibres, collagen etc, replacing the synthetics. Growth of bacteria/fungi on the starch blends drives researchers on such as *in-vitro* studies which may meet different requirements in industry. Applications of chemical and physical crosslinking methods for appropriatemodifications as deliberated in this review entertains the future perspectives on the extended starch blends using more than two polymers. A striving thirst on the natural polymers with biocompatibility to safeguard the environment against the carcinogenic plastics is fortified.

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