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Review

What could be greener than composites made from polysaccharides?

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ABSTRACT

Composites prepared from several polysaccharides represent a new category of environmentally safe materials for applications to explore. Up to date synthetic polymers are predominantly used for composite preparation prior to polysaccharides. It is related to environmental problems due to use of organic solvents in the process as well as due to the crisis of petrochemical industry-related plastics. Materials produced in this way are not biodegradable and their production costs are high. If the constituents of composites could be solubilized and chemically bonded than the formed insoluble composite could be prepared from a single type of polysaccharide. Mixing of polysaccharides that are isolated from different sources is recommended. Cyclodextrin-based composites are also considered as member of polysaccharide-composite family. There is a need to compare properties of composites with differing polysaccharide composition to make an optimal choice. Economical aspects also speak for the choice of cheaper polysaccharides to reach comparable properties in relation to the more costly possibilities of composite production. Films, foams, gels, artificial tissues, drug components, building materials or components for civil engineering, medical, paper or food applications, are potential end products without environmental drawbacks.

1. Introduction

Composites are engineered materials made from two or more constituents with significantly different physical or chemical properties from their components, which remain separate and distinct within the finished structure. There are two types of constituent materials, which are known as matrix and reinforcement components. The matrix in the material surrounds and supports the reinforcement component by maintaining their relative positions. A synergism results in material properties, which are unique prior to used constituents. Names and descriptors arise from the respective experiences of different perspectives and experience. While different industries use different terms to describe the same things, the same term can be applied in vastly different contexts. In the case of polysaccharide constituents the final product properties requirements for composites could be fitted without keeping the separate classification for matrix and reinforcement components. Most of the literature published on composites deals with synthetic polymers. The present review is focused on composites prepared solely from polysaccharides or their sources. The sources are plant cell walls or some types of living organisms if it is not in conflict with ethical principles. Polysaccharides are environmentally friendly and could be degraded by microorganisms without further assistance. It is believed that their use could be profitable especially when they are by-products of other processes. As there are other natural polymers or related carbohydrate groups like proteins, lignin or cyclodextrins, which are used as constituents of polysaccharide-containing composites, their environmental impact is also covered. There is a lack of literature on standard procedures for quantitative biodegradation, which could be used for environmental evaluation and it is hard to evaluate the material on "green" basis (Kyrikou & Briassoulis, 2007). For some people it might be a part of "political vocabulary", especially if they came from the synthetic polymer community. Polysaccharides, lignin and proteins isolated from natural materials are more environmentally friendly than synthetic polymers as the amount of energy and environmental impact required for synthetic polymers production must be also taken into account (Clark et al., 2005; Shen & Patel, 2008). Except for plastics related to petrochemical polymers, there are also so-called biodegradable plastics like polylactic acid, but even those could be replaced by polysaccharides due to lower costs and better properties of final composite. Mixing of polysaccharide based materials with plastics means mixing hydrophilic and hydrophobic materials, which requires energy. The goal to replace only a part of the higher-cost plastics with lower-cost polysaccharides is not the best strategy (Rowell, 2007). The full replacement of plastics with polysaccharides for composites production is a part of the non-pollute environmental strategy.

2. Solvent

Water is the most important green solvent and the most suitable solvent for polysaccharides or proteins. By mixing water solu-

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ble and water insoluble polysaccharides, the insoluble ones could act as matrix while the soluble ones work as reinforcing part. As composites may contain, except polymeric components, also water soluble/insoluble compounds, polysaccharide swelling in water and water sorption is beneficial in relation to applications like drug-delivery, paper toils or similar possibilities. Combination of natural cellulose fiber with kaolin in the presence of sucrose results in nanocomposites (Fahmy & Mobarak, 2008). Cellulose nanocomposites loaded with silica nanoparticles were made, but it is not clear how homogeneously are they distributed (Yano, Maeda, Nakajima, Hagiwara, & Sawaguchi, 2008). Also cellulose microfibrils in starch-pectin blend form nanocomposite (Ort et al., 2005). The use of ionic liquids (IL) could affect the properties due to solubility and produce composites with much broader range of polysaccharide constituents (Zhu et al., 2006). By preparing soluble polysaccharide mixtures, the further properties change could be achieved by subsequent chemical modification in IL (Murugesan & Linhardt, 2005). Higher yields and recycling of IL will improve environmental standards (Earle & Seddon, 2000). This is an advantage in comparison with the use of synthetic polymers as composite constituents as their use is mostly connected with application of organic solvents and their environmental drawbacks. Although some synthetic polymers like polyvinyl acetate (PVA) or phenol-formaldehyde (PF) resin are soluble in water, they represent an environmental problem. Sugar beet cellulose nanofibril-reinforced composites should be prepared by applying cheaper polysaccharides, which could act in a same way as PVA or PF and replace those plastics (Leitner, Hinterstoisser, Wastyn, Keckes, & Gindl, 2007). In most applications the composite end product should not release components by mixing with water. To achieve this, the product might be covered with polysaccharide-based water insoluble film.

3. The choice of polysaccharide combination

Polysaccharides with the more regular structure will be always the predominant components responsible for mechanical strength. Cellulose from plants or microbially produced (Chiou et al., 2007) is the main candidate for the matrix/reinforcement constituent. By acetylation it could become soluble in water (Rakhmonberdiev, Sidikov, Yusupov, Zainutdinov, & Kazantseva, 1997). It could be combined with chitosan, xylan, starch, or pectin due to hydroxyl, amine or carboxyl interaction without a covalent linking between individual polysaccharides (Muzzarelli, Stanic, Gobbi, Tosi, & Muzzarelli, 2004). Composites could be formed by multilayer films consisting of layers of single type polysaccharides (Kim, Wang, & Chen, 2007). Modified pectin molecules can affect the growth of bone cells (Kokkanen, Ilvesaro, Morra, Schols, & Tuukanen, 2007) or can be a part of drug-delivery system (Liu, Fishman, Hicks, & Liu, 2005). Even more complicated polysaccharides like heparin could be used for preparation of composite fiber with anticoagulation properties containing also cellulose constituent (Viswanatham et al., 2006). It was done by electrospinning from room temperature IL solution into the ethanol solution. By simple mixing of heparin and cellulose solutions in IL and subsequent casting, films could be prepared and might be used as membranes for kidney dialysis (Murugesan, Mousa, Vijayaraghavan, Ajayan, & Linhardt, 2006). Heparin immobilization strategies might result in new approaches and applications (Murugesan, Xie, & Linhardt, 2008). This might be costly due to unique heparin structure so the replacement with cheaper strategy should be considered. Cellulose-based batteries using IL in nanoporous structure are in development (Pushpavaj et al., 2007). Also with the help of IL cellulose could be quaternized using choline chloride/urea as solvent and IL/quaternizing agent in presence of NaOH (Abbott, Bell, Handa, & Stoddart, 2006). Beside acetylation of cellulose (Abbott, Bell, Handa, & Stoddart, 2005) also starch (Biswas, Stogren, Stevenson, Willet, & Bhowmik, 2006) could be acetylated in IL. Perhaps better acetylation procedure could be developed for particleboard preparation from wood flakes and substitution of methylmelamine with cross-linking acylation procedure (Wagner, Schwarzinger, Leidl, Schmidt, & Endesfelder, 2007). For cellulose dissolution urea/$ZnCl_2$ (Abbott et al., 2005) or 1-methyl-3-butylimidazolium chloride (Heinze, Schwikal, & Barthel, 2005) were used. Chitosan is a very attractive constituent with amine group which could be used for CO_2 reversible sorption (Xie, Zhang, & Li, 2006). This is a nice example for replacing synthetic polymer with greener novel application of chitin and chitosan.

There are many ways to produce composite by cross-linking a single type of polysaccharide. Cross-linking and introduction of ion-exchanging group in one step results in materials, which could be considered as composites as their properties change so dramatically from those of substrate and the product is insoluble in water (Šimkovic, 1997, 1997a, 1999,; Šimkovic, Francis, and Reeves, 1997b; Šimkovic, Hricovíni, Šoltés, Mendichi, & Cosentino, 2000; Šimkovic & Laszlo, 1998). By using cross-linking compounds having different length and the water-in-oil cross-linking method spherical particles with defined dimensions were prepared from starch (Šimkovic, Hricovíni, Mendichi, & van Soest, 2004).

By solubilization of plant materials and simultaneous chemical modification of plant cell wall components in one step, new water soluble composite precursors could be prepared (Šimkovic, Mlynár, & Alföldi, 1990, 1992). Another method of solubilization of polysaccharides is a pretreatment with $ZnCl_2$ under acidic conditions (Šimkovic, Antal, & Alföldi, 1994). It might lead to pectin isolation procedure, when suitable plant source of agricultural residue could be chosen. Although it was mentioned before that IL could be used for fractionation of lignocellulose materials (Zhu et al., 2006), the behavior of non-cellulosic polysaccharides is unclear as cellulose seams to be extracted more selectively by this neoteric solvent (Fort et al., 2007). Hyaluronan was cross-linked with polyethylene glycol (PEG) bridges, which might remain as allergens in organism after drug releasing, because PEG is not biodegradable in the same manner as hyaluronan (Pike et al., 2006). Cross-linking with smaller bridges (Šimkovic et al., 2004) or ionic bonds (Leshchiner & Konowicz, 2005) is likely to be safer. Good example for an artificial extracellular matrix is cross-linking of chitosan and chondroitin with glutaraldehyde and calcium ions and subsequent co-cross-linked with other bifunctional reagent (Peng, Yu, Mi, & Shyu, 2006). This material demonstrated antibacterial capability, biocompatibility according to *in vitro* antibacterial test with possible scaffold-guided tissue-engineering application.

Wood boards modified with incorporated sulfur or silica represent another example of composites where the original wood structure is modified without destroying the matrix (Šimkovic, Martvoňová, Maniková, & Grexa, 2005, 2007). They could be used as flame-retarded building materials. The constituents were incorporated into the material by insolubilizing the inorganic compounds formed from water solutions. In the case of sulfur the effect was achieved by its crystallization inside the wood cell wall. It was formed from $Na_2S_2O_3$ or $Na_2S_2O_5$ under the acidic environment. Similar principle was used when alkali-soluble silicates were precipitated inside wood material after diffusion and subsequent acidification. The obtained products produced lower amounts of smoke than unmodified materials when burned under cone calorimer conditions.

Today many of the polysaccharide-polysaccharide composites are prepared by extruding their mixtures in presence of glycerol to form plasticized interactions probably due to thermal cross-linking (Averus, Fringant, & Moro, 2001). It is energy consuming and the process affects the mechanical properties and not all the negative environmental aspects of the product could be predicted. The processes are even more dramatical when wood-synthetic polymers composites are extruded (Burgstaller, 2007). For the case of cellulose-starch as well as other combinations a non-extruding composite preparation methodology might be possible and environmentally safer. For many food applications, films could be produced. Sources like the konjac glucomanan–gelan gum (Xu, Li, Kennedy, Xie, & Huang, 2007), cotton stalk xylan (Guksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007), pullulan (Singh, Sani, & Kennedy, 2008) or corn arabinoxylan-konjac glucomannan (Mikkanen, Yadav, Cooke, Willför, & Hicks, 2008) are selected examples. If the synthetic polymers are used in mixtures, they course immiscibility with polysaccharides resulting in holes in the film. It would be worth to try to prepare composite films by mixing the above polysaccharides and compare their properties. Also the role of polysaccharides as adhesives should be explored more in composite technologies.

4. Cyclodextrin-based composites

Cyclodextrin-containing composites have a green future as cyclodextrins can dramatically affect the solubility of polysaccharides and other compounds not soluble in water due to their hydrophilic side and hydrophobic cavity (Ramírez et al., 2006; Zhang, Chen, Li, He, & Zhon, 2007). As a constituent they behave similarly as polysaccharides and are chemical individums at the same time. Composites prepared by cross-linking of cyclodextrins without the presence of other constituents have a potential as adsorbents (Tang et al., 2006). By bonding to silica they could function as stationary phases for reversed-phase liquid chromatography (Fujimoto, Maekawa, Murao, Jinno, & Takeichi, 2002). The specific inclusion complex causes the chirality effect (Gubitz & Schmid, 2001). Also by grafting cyclodextrin to polysaccharide the prepared composites can act as materials with adsorbing properties (Zhang, Wang, & Yi, 2004). Hydroxypropyl chitosan-graft-carboxymethyl-β-cyclodextrin (HPCH-g-CM β-CD) was synthesized by grafting CM β-CD onto HPCH using water soluble condensing agent (Prabaharan & Mano, 2005). Due to the presence of hydrophobic β-CD rings on the HPCH backbone, this composite could be used as matrix for controlled drug release. Also hydroxybutenyl-β-CD was used for drug solubilization (Buchanan, Buchanan, Edgar, & Ramsey, 2007).

5. What about protein or lignin constituents?

There are known fish gelatin films (Avena-Bustillos et al., 2006) and gels (Chiou et al., 2007) with possible applications related to reducing water loss from encapsulated drugs and refrigerated or frozen food systems. Other types of proteins like collagen could be amidated with hyaluronic acid to be applied in tissue-engineering (Bakoš, Soldan, & Hernández-Fuentes, 1999; Park, Park, Kim, Song, & Suh, 2002; Reháková, Bakoš, Vizárová, Soldan, & Juríková, 1996). The disadvantage of proteins in comparison to polysaccharides is their lower swelling effect and water adsorption as well as low stability towards elevated temperatures, quicker biodegradability and other environmental factors. This alters the structure and properties of the final composites. Proteins could be solubilized in IL (DiCarlo, Compton, Evans, & Laszlo, 2006). This must be considered as environmental drawback for IL use as they are toxic for fish and other organisms living in water.

Lignin can also be considered as potential composite constituent (Park, Doherty, & Halley, 2008). It should not be considered only as partial substitution of phenol-formaldehyde (PF) resins but also an environmentally safer alternative. PF products must be completely eliminated from industrial production due to their formaldehyde production in the product ageing process. Lignin could be also used as filler for rubber-based composites (Košíková, Gregorová, Osvald, & Krajčovičová, 2007) or in antioxidant applications (Vinardell, Ugartodo, & Mitjans, 2008). Negative impact of lignin on environment is formation of aromatic procarcinogens in the process of thermal degradation, however on the presence of these compounds in composites improves their flame-retarding properties. Also desirable component property is lignins hydrophobicity and ability to interact with fibers. Such properties are required in some paper composite applications (Antonsson, Henriksson, Johansson, & Lindström, 2008). The environmental difference due to using plant materials instead of pure polysaccharides could be neglected when lignin is stored at the landfill. During the process aromatic structures from lignin transfer in soil and form similar products like humic substances formed from polysaccharides. It is due to the fact that lignin structures are more stable than polysaccharides, as they are transferred to more condense aromatics as they form soil organic matter (Schulten, Leinweber, & Theng, 1996).

6. Conclusions

According to amounts and costs of multi-saccharide composite materials produced in certain applications, the most important applications seam to be paper – and health – related ones. Every application requires individual economical assessment and in the end one could be as green as the economy allows it. The prices of natural polymers increase from plant polysaccharides like cellulose, starch, hemicelluloses, pectin and algae polysaccharides, to polysaccharides from living species like chitosan, hyaluronan, heparin, chondroitin sulfate to proteins and enzymes. That is why it would be beneficial to compare multicomponent composites made from polysaccharides from the point of view of their properties in relation to economical possibilities. Every research group needs an economical supervisor for every step of a chemical reaction to occur. It is evident that composites with predominantly carbohydrate content are fulfilling all the discussed aspects of a green material. The life without them at present is impossible.

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