Hydrophobic Modification of Agro-Based Polymers: A Selected Review

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Agro-based polymers are found in nature and comprise a broad range of polymeric substances with different chemical structures and properties. These polymers tend to be biodegradable, sustainable, readily available, and mostly inexpensive. As a result, they have attracted increasing attention from researchers in recent years. As part of our work on the utilization of agricultural materials, we have modified several of these biopolymers with hydrophobic moieties. In this work, a review is given of selected hydrophobically modified biopolymers, based on the work done at USDA Agricultural Research Service. The biopolymers covered include starch, cellulose, carboxymethyl cellulose, xylan, cashew gum, and zein. Most of these polymers are hydrophilic, and the addition of the hydrophobe imparts additional properties that may extend the utility of these polymers for different applications.

Introduction

Hydrophobically modified polymers represent a distinct family of polymeric additives that can impart useful rheological, interfacial, or surfactant-like behavior to aqueous polymer formulations and dispersions (1, 2). In general, they contain a water-soluble polymer grafted with hydrophobic side chains or terminal groups. The hydrophobic groups can self-associate in water, leading to a shear-thinning rheological behavior, which is valuable in paint, personal care, enhanced oil recovery, and other applications. Several of these polymers have been commercialized, including hydrophobically

modified hydroxyethyl cellulose (HMHEC) (*3*, *4*), hydrophobically modified ethoxylated urethanes (HEUR) (*5*, *6*), and hydrophobically modified alkali swellable emulsions (HASE) (*7–9*).

Biobased polymers (or biopolymers), e.g., polysaccharides and proteins, have recently received a lot of attention from people engaged in research and product development because they are frequently agriculturally based, sustainable, biodegradable, non-toxic, and environmentally friendly. Their use as replacements for synthetic polymers and plastics is especially attractive in view of the increasing public awareness of plastic waste (*10*, *11*) and microplastics (*12–14*) and the fluctuating prices of petroleum and natural gas. Polysaccharides, in particular, have often been subjected to many chemical modification reactions, and quite a few hydrophobically modified polysaccharides have been reported (*3*, *4*, *15*, *16*). Rheological properties have often been studied (*17*, *18*).

Prior to their current affiliation with USDA, some of the present authors have been involved with earlier research done on hydrophobically modified polymers; these earlier studies have been reviewed in prior volumes of the ACS Symposium Series (*19*, *20*) and elsewhere (*21*). For example, hydroxyethyl cellulose (HEC) was grafted with polycaprolactone through lipase-catalyzed ring-opening polymerization (*22*). Another approach involved the lipase-catalyzed reaction of vinyl stearate with polysaccharide, which grafted the stearate ester onto the polysaccharide with acetaldehyde as a byproduct; this approach was used for HEC (*19*) and cationic guar (*20*, *23*). Another approach entailed the reaction of a polysaccharide with an alkyl ketene dimer via heat or enzyme catalysis; this reaction was applied to HEC (*24*), cationic guar (*24*), and starch (*25*). Other approaches included the syntheses of hydrophobically modified poly(ethylene glycol) (*26*) and poly(aminoamides) (*27*).

At USDA Agricultural Research Service (ARS), one of the thrusts of research and development involves the utilization of agro-based materials, particularly biopolymers, in order to expand their applications and upgrade their value. Working with collaborators, the present authors have modified several of these biopolymers with hydrophobic moieties. In this article, we have reviewed selected hydrophobically modified biopolymers, based on the work done at USDA-ARS. In the past, hydrophobically modified polymers are often used to produce associative thickeners, emulsifiers, and materials with surfactant-like properties. Likewise, our hydrophobically modified biopolymers show many of these same properties and may be considered useful additions to this family of polymeric additives.

Starch Derivatives

Among all biobased materials, starch is one of the most commonly studied. An easy way to produce a hydrophobic starch is to acetylate it. This is done commercially through the reaction of an aqueous suspension of starch granules with acetic anhydride and sodium hydroxide (*28*, *29*). At USDA, microwave has been employed (*30*) together with high temperature and pressure to speed up the acetylation of corn starch up to a degree of substitution (DS) of 0.1–1.5. The procedure involved heating in a sealed microwave reactor a mixture of corn starch, acetic acid and acetic anhydride. Reaction conditions included 150–160 °C temperature, 4–7 min time, and >90% reaction efficiency. A product with DS 0.4-0.9 obtained at 160 °C was over 90% water-soluble at ambient temperature, with 70% of the acetate found at the C6 position of the anhydroglucose. Acetylation at 120 °C produced products (DS 0.2–0.3) that were water insoluble but highly swellable.

Another major development was a solvent-free process for the preparation of acetates of polysaccharides with the use of iodine as a catalyst (Figure 1) (*31*, *32*). The method is simple, rapid, and characterized by a high conversion ratio. A variation was the combination of microwave heating

and iodine-catalyzed acetylation of starch via acetic anhydride (*33*). After only 2 min at 100°C with a low level of iodine (0.16-2.5 mol%, relative to starch), significant amounts of acetylation occurred. The DS increased as iodine/starch and acetic anhydride/starch ratios increased. However, molecular weights decreased as iodine levels increased.
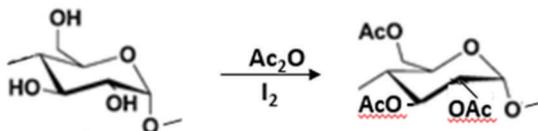

Figure 1. Acetylation of starch via the use of iodine and acetic anhydride; no solvent was needed. AcO refers to acetoxy.

A further improvement was found that used metal chlorides instead of iodine as catalyst for acetylation of starch (*34*). Aluminum chloride, ferric chloride, zinc chloride, antimony chloride, tin chloride, cupric chloride, nickel chloride and cobalt chloride were attempted as catalysts at different temperatures (40-110°C), reaction time and acetic anhydride level. Iodine was also included for comparison. All the metal chlorides studied were found to be active as catalysts for the acetylation of starch. However, each metal chloride had a somewhat different reactivity with a different optimal temperature needed for the satisfactory reaction to take place. The molecular weight of the starch acetate products was reduced during the reaction. The reactivity trends among the metal halides seemed to correlate both with the ease of complexation between the halide and the substrate and with the acidity of the metal chloride.

The addition of the longer chain (and more hydrophobic) stearate to maltodextrin with DS of 0.07–2.40 was achieved by heating maltodextrin and vinyl stearate in the ionic liquid 1-butyl 3-methylimidazolium dicyanamide at 75°C (*35*). Stearates of low DS(0.07) were insoluble in water but formed a gel and absorbed over seven times their weight of water. Maltodextrin stearates of DS 0.6 showed intense birefringence resembling starch granules in DMSO while cholesteric liquid crystalline behavior was observed in toluene (reflected blue light). Blue light reflection disappeared on heating to >60–80°C then reformed on cooling. Stearates with high DS (2.4) were soluble in chloroform or toluene and had a high degree of swelling in hydrocarbons such as hexane. Films cast from maltodextrin stearates had contact angles of 84–93°, indicating a very hydrophobic surface. These starch stearates seemed interesting and may find potential applications as water absorbents, hydrocarbon/oil absorbents, water resistant coatings, and liquid crystalline materials.

Cellulosic Derivatives

Although cellulose has many hydroxy groups in its chemical structure, the cellulose fiber is insoluble in water because of its crystallinity and its extended network of hydrogen bonds in its physical structure. However, when cellulose is derivatized with methyl substituents, the resulting methyl cellulose is water soluble up to 55°C (*36, 37*). For acetyl substitution, the solubility of the resulting cellulose acetate depends on the DS; it is soluble in acetone, dioxane and methyl acetate for DS between 2.0-2.5, and soluble in methylene chloride for DS between 2.5-3.0 (*38, 39*). For DS between 0.4-0.9, it is water-soluble (*38*); this water-soluble cellulose acetate exhibits surface-active properties (*40*) and has been evaluated as a film coating (*41*) and sizing for cotton yarn (*42*). It has

been shown earlier that iodine-catalyzed acetylation can be utilized for cellulose acetate synthesis (*31*).

If a hydrophilic reagent is used for cellulose substituents, the resulting cellulose derivatives tend to be water-soluble, e.g., carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC). Several examples of hydrophobically modified HEC have been mentioned in the Introduction (*19*, *24*). The addition of an acetate group to CMC can also impart some hydrophobic character to CMC, and a study that converted agricultural residues to CMC and CMC acetate has been reported earlier (*43*).

Modifications of Xylan

Xylan is part of the hemicellulose family of biopolymers and serves as a plentiful, eco-friendly agro-based resource. As xylan is currently underutilized and undervalued, it is helpful to explore xylan derivatives for product development. A known derivative is xylan acetate, usually made with acetic anhydride and strong mineral acid (*44*, *45*). Earlier, iodine-catalyzed acetylation reactions (*31*, *32*) were reported for cellulose and starch. Later, Ren et al. (*46*) combined iodine catalysis together with ionic liquid solvents to acetylate xylan.

We have extended this approach (*47*) by looking at the acylation of xylan through the use of selected Lewis acids; in particular, five metal halides have been studied ($FeCl_3$, $ZnCl_2$, $AlCl_3$, $SbCl_3$, and $SnCl_2$) and compared to iodine as acylation catalysts. All the metal chlorides were found to be active catalysts for esterification, but their activities differ, particularly with respect to temperature. Through the choice of a suitable catalyst and temperature, xylan acetates with different DS values can be made. It has been noted (*48*, *49*) that xylan acetate has thermoplastic properties, and it can potentially serve as an eco-friendly and sustainable replacement for petroleum-based plastics in film, fiber, and laminate applications.

Whereas the acetate substitution inserts a non-hydrophilic moiety to xylan, a higher degree of hydrophobicity can be achieved through the reaction of xylan with alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA). AKD and ASA are both commercially available sizing agents for paper applications (*50*, *51*). Each reagent contains an aliphatic long chain together with a reactive group (ketene dimer or anhydride) (Figure 2).
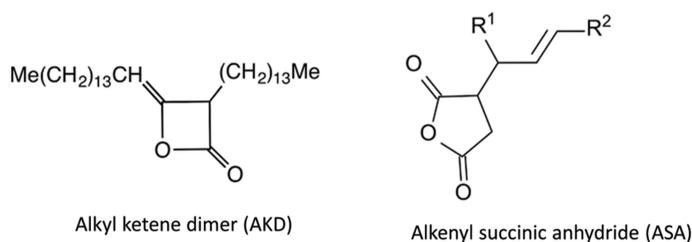

Alkyl ketene dimer (AKD)

Alkenyl succinic anhydride (ASA)

Figure 2. Structures for AKD and ASA; R^1 and R^2 are aliphatic chains.

The reactive group can undergo a reaction with a biopolymer to form the hydrophobically modified biopolymer. The xylan-AKD derivatives have been made (*52*) at 90°C, using dimethyl sulfoxide as solvent and 4-dimethylamino-pyridine as promoter. Samples with DS up to 0.006 have been produced. For the xylan reaction, 2-octenyl succinic anhydride (OSA) was used as the ASA (with R^1 = H, R^2 = C_5H_{11}). The xylan-OSA derivatives have been synthesized (*52*) at 120°C

in dimethyl sulfoxide with DS up to 0.105–0.135. The structures of these products have been confirmed with NMR and FT-IR spectroscopy. These xylan derivatives increase the structural diversity of xylan and provide additional options for people seeking to use hydrophobically modified polysaccharides in their applications.

Modified Cashew Gum

Cashew gum (CG) is obtained from the bark exudate of the cashew tree (*Anacardium occidentale L.*). It is a hydrophilic, branched high-molecular-weight polysaccharide comprising 72% β-D-galactopyranose, 14% α-D-glucopyranose, 4.6% α-L-arabinofuranose, 3.2% α-L-rhamnopyranose, and 4.5% β-D-glucuronic acid (*53, 54*). This biopolymer has been previously modified with different functional groups (*55, 56*), but only recently have two publications reported the attachment of long-chain hydrophobes. For hydrophobic modification with alkyl ketene dimer (AKD) (*57*), the reaction was conducted at 90 °C, using dimethyl sulfoxide as solvent and 4-dimethylaminopyridine as a promoter (Figure 3). Samples with DS up to 0.016 were made; the higher DS samples tended to be insoluble. This was due to the large hydrophobe on AKD; similar results were found earlier for AKD-starch derivatives (*25*).
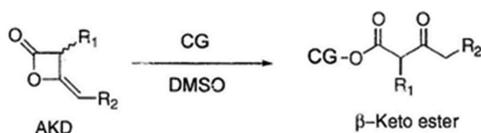

Figure 3. Reaction of cashew gum (CG) with AKD.

CG has also been modified with two types of ASAs (OSA and tetrapropenyl succinic anhydride) (*58*). The reaction product for CG-OSA adduct is shown in Figure 4. Reactions were conducted at 120 °C using dimethyl sulfoxide as a solvent, with conversions better than 88%. Samples with degrees of substitution (DS) between 0.02 and 0.20 were made.
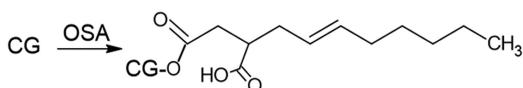

Figure 4. Reaction of cashew gum (CG) with OSA.

The addition of the hydrophobe decreased the affinity of cashew gum for water absorption. Hydrophobically modified polysaccharides are often used as polymeric emulsifiers, thickeners, and compatibilizers; we anticipate that these new hydrophobically modified CGs may be used for the same applications.

Derivatives of Zein

Zein refers to the alcohol-soluble storage proteins of corn/maize seeds and has been much studied and used for a variety of industrial and food applications (*59, 60*). For example, it can be used as a film for food packaging, where it exhibits high gloss, microbial resistance, and edibility.

However, zein-cast films tend to be stiff and brittle, and the mechanical strength is reduced as it absorbs moisture (*61*). An approach to mitigate this moisture issue was to derivatize zein with the acetyl group (*62*). Another approach was to modify zein with OSA (*61*). This was achieved in dimethyl formamide in a microwave reactor, where the reaction time was 5 min. The reaction occurred between the anhydride in OSA and the OH and amine functionalities in zein to form ester and amide linkages, respectively (Figure 5). The zein and the OSA-modified zein had comparable mechanical properties.
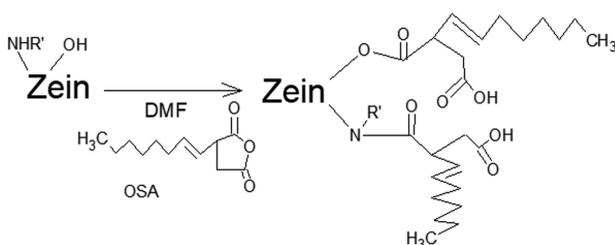

Figure 5. Reaction of zein with OSA.

An alternative method to reduce water absorption and surface wetting behavior of zein was to react the surface of zein with OSA and AKD (*63*). The method entailed applying the zein surface with a coating of AKD or OSA and baking it at about 100°C. The modified surface exhibited reduced water absorption and increased contact angle relative to the unmodified zein surface.

Yet another approach to enhancing the hydrophobicity of zein was to modify zein with several isocyanates and diisocyanates in solution (*64*). The major reaction pathways were identified with the help of NMR and FTIR. For all the isocyanates and diisocyanates employed, the surface free energy of the modified zein was found to decrease, indicating reduced hydrophilicity. The moisture uptake was also decreased with isocyanate and diisocyanate modifications. Gel electrophoretic patterns showed that the diisocyanate cross-linked a portion of zein to generate higher molecular weight species. DSC data showed single glass transition temperatures in all cases, indicating that homogeneous blends were formed during the reaction. The mechanical properties of modified zein were either similar to unmodified zein or reduced in some cases.

Conclusions

It is clear from this review that hydrophobic modifications of biopolymers represent an important and useful opportunity for innovation and product development. A summary of the reactions is given in Table 1. A number of biopolymers have been studied as substrates for the hydrophobic reaction, including polysaccharides (starch, cellulose, xylan, cashew gum), polysaccharide derivative (CMC), and protein (zein). The hydrophobe varies in size from acetate to stearate, alkyl esters and amides. Thus, these reactions show quite a range of diversity in substrates, reagents, and product structures. It may be noted that the substrates are all agro-based and readily available commercially. The reactions consist of one or two steps and should be relatively inexpensive to do. Thus, the hydrophobically modified biopolymers should be attractive as economical and sustainable materials for further commercial development.

Table 1. Summary of Different Hydrophobic Modification Reactions

approach	reagent(s)[a]	substrate	product
microwave, high temp/pressure	Ac_2O/HOAc	starch	acetate
heat (microwave)	Ac_2O/iodine	starch; cellulose. CMC	acetate
heat	Ac_2O; metal Cl	starch; xylan	acetate
heat	vinyl stearate	starch	stearate
heat	AKD/DMP	xylan; cashew gum	alkyl β-keto ester
heat (microwave)	ASA	xylan; cashew gum; zein	alkyl ester
heat	isocyanate; diisocyanate	zein	alkyl ester/amide

[a] HOAC = acetic acid. DMP = 4-dimethylamino-pyridine.

Acknowledgments

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