

Controlling the Water Absorbency of Agricultural Biopolymers

Blending special bioabsorbable polyphosphate fillers, biodegradable soy protein isolate, plasticizer, and adhesion promoter in a high-shear mixer followed by compression molding resulted in a relatively water-resistant, biodegradable soy-protein polymer composite.

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Natural biodegradable polymers made from agricultural products, such as soy protein isolate and corn starch, have poorer water resistance than synthetic polymers derived from petrochemicals⁽¹⁻⁴⁾ and thus absorb more moisture. As a result, commercial exploitation of agriculturally derived materials has been very limited. The targeted applications for the natural biodegradable polymers require that the materials have sufficient stiffness and strength during their useful life but eventually biodegrade. Achieving this required combination of properties from the biodegradable polymers is very difficult because of their inherent water sensitivity and relatively low stiffness and strength, especially in moist environments.

To address these problems, the author recently initiated a long-range research project to develop affordable, stiff, strong bioabsorbable polyphosphate filler/soy-protein polymer composites, along with methods for making practical shapes from these products^(5,6,8). The research involves blending special bioabsorbable polyphosphate reinforcing fillers having low glass-

transition temperatures and the biodegradable soy-protein polymer⁽⁹⁾ using a single-screw (or twin-screw) extruder at temperatures above the polymer's melting point. The blended soy-protein polymer composite containing the required amount of the reinforcing fillers is then either injection molded or compression molded into articles of various shapes and sizes.

Blending the bioabsorbable polyphosphate reinforcing fillers and biodegradable soy-protein polymer enables the production of stiff, strong bioabsorbable filler/polymer composites with properties superior to those of pure soy-protein polymers.⁽⁶⁾ Both the filler and the polymer are nontoxic and bioabsorbable, making them excellent choices for such applications as medical/surgical devices and food packaging, and for other disposable food products that must safely biodegrade after their useful service life. The chemical nature of the filler (i.e., polyphosphates)^(8,10,11) and soy proteins [i.e., poly(amino acids)]⁽³⁾ indicates that recycled products made from these materials can be used as soil conditioners and/or animal nutrients, eliminating most of the problems of recycling or reusing synthetic polymers made from petroleum-based precursors.

Methods

Materials

The key composition of the special polyphosphate filler is $xM_2O + yZnCl_2 + zP_2O_5$, where M is mixed-alkali, and mole fractions $x = 0.37$, $y = 0.26$, and $z = 0.33$.^(8,10,11) The polyphosphate filler was ground and sieved through 200 mesh ($\leq 74 \mu\text{m}$ particle sizes). The glass transition temperature of the filler was found to be 219°C, using DSC at a heating rate of 10°C/min. The plasticizer (glycerol) and coupling agent (γ -

aminopropyltriethoxy silane) were analytical reagents that were used as received from the manufacturers. The soy protein isolate (PRO-Fam 646, Archer Daniels Midland, Decatur, Ill.) was used as received. The moisture content of the soy protein was measured by heating it to constant weight at 110°C, using a moisture analyzer (MA-30, Satorius Instruments, Inc.).

Materials Processing and Water Absorption Measurements

The desired amounts of polyphosphate filler (20 wt%) and the soy protein were mixed in a planetary-type mixer. The required amount of glycerol (10 wt% of the total batch formulation weight) was gradually added to the mixture with the mixer operating at low speeds. The soy-protein polymer composite batch (soy protein + polyphosphate filler + glycerol) was transferred into the mixing bowl of a Henschel high-speed mixer, and the composite batch was mixed at high speeds until all agglomerates were dispersed.

For the preparation of the coupled composite batch, two methods were used to apply the coupling agent. In the first method, 1 wt% (based on the total weight of the filler) was premixed with the required amount of the glycerol before its addition to the batch. In the second method, the fillers were treated with 0.5% aqueous solution of the silane by simple immersion for about 5 min. The excess water was decanted, and the pretreated filler was dried in a vacuum oven at 40°C for 24 hrs or until constant weight was achieved. The dried, pretreated filler was then mixed into the soy-protein polymer batch as before. The soy-protein/polyphosphate polymer composite batch was stored in a sealed plastic

Table. Moisture Content of the Biodegradable Soy-Protein Polymer and Composites After Conditioning at 50% Relative Humidity and 23°C for at Least 40 Hrs.

Material	Polyphosphate Filler, wt%	Moisture Content, wt%
Uncoupled	0	6.2
	20	5.0
Coupled (Method 1)	20	5.1
Coupled (Method 2)	20	5.1

Methods 1 and 2 are the two methods of applying the coupling agent described in the text.

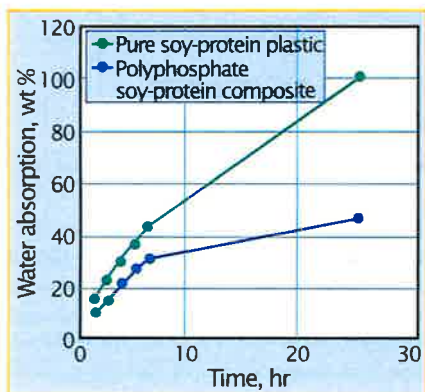


FIGURE 1. Time dependencies of water absorption of the materials showing effect of polyphosphate fillers.

bag until required for compression molding. The elapsed time between the batch preparation and compression molding was kept to a minimum (typically less than 1 hr). The coupled soy-protein/polyphosphate polymer composite batch containing 20 wt% filler (silane-treated) was prepared as previously described.

Type 1 ASTM standard tensile test specimens were compression molded, using a Wabash Metal Products compression molding machine under the following conditions: compression load = 8 tons; molding temperature = 150°C; molding time = 6 min; mold cooling time = 8 min. Typical dimensions of the specimen gauge section were 57 x 13 x 4 mm with an overall length of about 165 mm. These molding conditions were found to produce visually acceptable samples having reproducible properties. Subsequently, the compression-molded samples were conditioned at 23°C and 50% relative humidity for at least 40 hrs in a desiccator containing a saturated calcium nitrate salt solution.



FIGURE 2. A comparison of water resistance of soy-protein polymer and composite: Left to right, unfilled soy-protein polymer, uncoupled composite, coupled composite (method 1), coupled composite (method 2). The coupled and uncoupled composite contained 20 wt% polyphosphate filler, and the materials were immersed in water for 1 year.

The water absorption was measured according to standard ASTM D 570-95 method.⁽¹⁵⁾ A 4-g test specimen was cut from the compression-molded samples and totally immersed in water maintained at 23°C for 25 hrs. The percent of water absorbed was estimated from the difference in weights of the as-molded samples and the immersed sample.

Results

The water resistance of the unfilled soy-protein polymer can be dramatically increased by incorporating up to 20 wt% of the bioabsorbable, silane-treated filler into the pure soy-protein polymer. A possible chemical bonding model is used to explain the water resistance of the composites. As the mechanical properties of the polyphosphate/soy-protein polymer composite have been previously reported,⁽⁶⁾ the focus here is on the mechanisms of the observed water resistance. The work just described extends the usage of biodegradable polymers derived from natural renewable agricultural products to load-bearing applications, for which the currently available materials⁽¹⁻⁷⁾ are not adequate.

The *Table* shows the moisture content of the materials after they were conditioned at 50% relative humidity and 23°C for at least 40 hrs. The moisture content of the pure soy-protein polymer was reduced by about 1 wt% when the polyphosphate fillers were added. In this relatively dry state, the effect of the silane coupling agent was found to be insignificant.

Figure 1 shows the percent of water absorbed by the materials after immersion in water at 23°C for 25 hrs. A dramatic reduction in the inherent water absorption tendency of the soy-protein polymer by incorporating the polyphosphate fillers (especially after long immersion times) is clearly evident in this *Figure*. This reduction in water absorption of the composites was further enhanced by applying the coupling agent to the fillers, as described in the previous section. *Figure 2* shows a photograph of the soy-protein polymer and composite (20 wt%, coupled and uncoupled) immersed in water for 12 months under ambient conditions. The coupled composite can be seen in this *Figure* to be intact, while the other samples dissolved.

This ability to tailor the water resistance behavior of the soy-protein composite is desirable because it can be applied to the production of composites for load-bearing applications in both wet and dry conditions, not possible now with pure soy-protein polymer. Because the composite constituents are biodegradable

and nontoxic, the composite can be composted and returned to the soil as a nutrient after its service life.

These composites can perhaps also be used to make implantable surgical devices at polyphosphate-filler loading levels that the body can readily isolate, eliminating the residue after the device's service life. Blending the composite constituents with synthetic bioabsorbable polymers such as poly(lactic acid), poly(glycolic acid), and polycaprolactone may also provide polymer alloys and composites with enhanced properties for beneficial use in other applications. This is a matter for future investigation.

Figure 3 shows the proposed reaction mechanism for water resistance behavior of

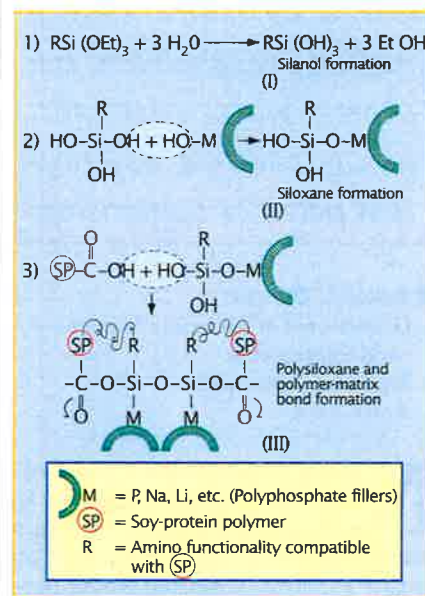


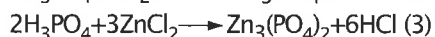
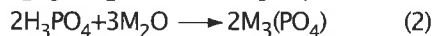
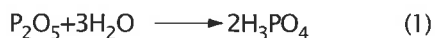
FIGURE 3. The interfacial chemical bonding mechanism for explaining the observed improvement in water resistance of the coupled composite.

the coupled composite. Initially, the silane coupling agent reacts spontaneously with water or with -OH groups of the glycerol to form silanols (I).^(6,12-14) This silanol can react with the -OH groups present on the surfaces of the fillers to form a siloxane (II) through hydrogen bonding and subsequent elimination of a water molecule. As *Fig. 3* shows, the siloxane is then capable of reacting with the -OH groups of the carboxylic functionality of the soy protein via hydrogen bonding to form the structure depicted in (III). Finally, this structure (III) can then undergo a condensation reaction leading to polysiloxane and polymer-matrix bond formation.

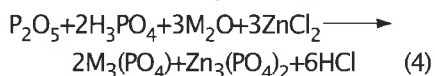
The covalently bonded structure in the

interface between the polymer and the fillers is resistant to water, leading to the observed water resistance behavior of the coupled composite.^(6,12-14) However, the alkyl group of the coupling agent must be chemically compatible with the soy-protein polymer matrix. Because soy protein is composed of poly(amino acids), γ -aminopropyltriethoxy silane was found to produce optimum results at very low levels. Scanning electron microscopic evidence (not shown) supports the proposed bonding mechanism.⁽⁶⁾

The possible reactions of the chemical constituents of the polyphosphate fillers with water are as follows:



Overall Reaction (Eqs 1+2+3)



The hydrochloric acid produced in the overall reaction above can reduce the available -OH groups in the system. This reduction in the -OH groups may be detrimental to the reaction of the coupling agent's dilute aqueous solution with the polyphosphate fillers (see the reaction scheme of Fig. 3). This explanation is consistent with the reduced mechanical properties of the coupled composite prepared by pretreating the polyphosphate fillers with an aqueous solution of the silane before its incorporation into the composite.⁽⁶⁾ In any case, pretreatment of conventional reinforcing fillers, such as borosilicate glass (E-glass), with aqueous silane solution is known to enhance the coupling reaction.^(6,13,14) The ability to change the interfacial conditions between the fillers and the matrix is important in tailoring the composites for specific, load-bearing applications, preventing premature part failure during use.

Conclusions

The results show that soy-protein polymer can be blended with bioabsorbable polyphosphate fillers to form water-resistant biocomposites for beneficial uses in moist environments where unfilled soy-protein polymer is unusable. How the adhesion promoter or coupling agent is applied determines the water resistance or time-controlled hydrolysis of the polymer. As noted by Scott,⁽¹⁶⁾ the future of biodegradable polymers will depend on the ability of users of plastics to view degrad-

ability as adding cost to their products; knowing how to control the inherent water absorbency of the plastics for broad applications is one key step in that direction. ■

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