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Starch-Filled Polyvinyl Chloride Plastics—Preparation and Evaluation

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Starch was added as a filler to polyvinyl chloride (PVC) formulations to produce plastics that are potentially biodegradable. The most uniform and transparent plastics resulted when the filler was added either by coprecipitating a cross-linked starch xanthate-PVC emulsion or by concentrating a starch-PVC emulsion to produce a dry mixture of the two components. Physical properties of the plastics closely parallel those containing inorganic fillers, except for improved clarity. The starch-filled plastics were readily attacked by a mixture of microorganisms commonly occurring in soil.

Various techniques were studied for incorporating corn starch into polyvinyl chloride (PVC) formulations in a continuing effort to produce biodegradable plastics (Otey, *et al.*, 1972). Earlier studies demonstrated that starch and starch-derivatives can be used as reactive fillers in polyurethane plastics (Otey, *et al.*, 1969). Buchanan and associates (1968) developed methods for adding starch to rubber formulations by coprecipitating cross-linked starch xanthate and latex rubber. Three techniques evaluated here were coprecipitation of cross-linked starch xanthate with a PVC latex, co-concentration of a starch and PVC latex, and dry mixing of starch and PVC.

Experimental Section

Coprecipitation. In a 2-l. beaker mix 162 g (1 mol) pearl corn starch with 1200 ml of water. Add 250 ml of 2 N NaOH with good stirring to produce a uniform gel. Cool the starch gel to 20°C, add 6 ml (0.1 mol) of carbon disulfide with stirring, and store the suspension at 5 to 10°C for at least 2 hr. The product is a clear viscous solution containing about 0.07 xanthate group per anhydroglucose unit.

To 320 g (32 g dry basis) of the starch xanthate solution, add 300 ml of water and 135 g (76 g dry basis) of PVC latex (B. F. Goodrich Chemical Co. Geon 151) and stir for 30 min. Add 1.5 g of NaNO₂ and stir for 10 min. With good stirring add a water solution of 5% alum until the suspension maintains pH 4. Filter the resulting curd, wash three times with distilled water, and dry in a forced air oven at 40–50°C for 16 hr. Hammer mill the dry product (29.6% starch, 70.4% PVC) to a fine powder.

Co-Concentration. In a 1-l. beaker heat with stirring a mixture of 21.8 g of corn starch and 400 ml of water at 90°C for about 20 min. To the starch paste add 86.2 g (48.4 g dry basis) of Geon 151 and stir for 10 min. Pour the starch-PVC blend into a large glass tray and dry in a forced air oven at 40–50°C for 16 hr. Hammer mill the dry product (31% starch, 69% PVC) to a fine powder.

Dry Mix. Whole corn starch and commercial pregelatinized corn starch (A. E. Staley Manufacturing Co. Star-

amic 213) were each pin-milled to an average particle size of 20 μ , vacuum dried at 90°C, and then mixed with powdered PVC (Geon 126).

Plastic Formulation. Dry composites of starch-PVC, prepared as described above, were combined with dioctyl phthalate (DOP) and dibutyltin dilaurate stabilizer (2% of total mixture) and blended on a rubber mill at 250°F for 10 min. The mixtures were then molded in a 1 × 6 × 0.072 in. aluminum cavity at 140°C and 6000 psi for 10 min.

Test Methods. Plastics were tested by the following ASTM procedures: tensile strength and per cent elongation, D 638-64T; shore D hardness, D 1706-61; and fungi resistance, D 1924-70. The mixed fungus spore suspension contained *Aspergillus niger*, *Penicillium funiculosum*, *Trichoderma* sp., and *Pullularia pullulans*.

Per cent water absorption is the amount of water absorbed when the samples were soaked for 2 weeks at room conditions divided by original sample weight times 100. Clarity was determined with a Martin Sweets Co. color brightness tester, Model S2. Samples were placed over a beam of light and covered with a white background and then a black one. The reflectance values read for the black background divided by the reflectance for a white background times 100 are the reported clarity values. These values should be considered relative to the control only and not as having any numerical meaning. The method served as an alternative to visual observation. The lower the value the more transparent the specimen.

Results and Discussion

Properties of plastics formulated by the three methods used to incorporate three levels of DOP and various amounts of starch are recorded in Table I. Generally the addition of a starch filler to PVC systems lowered tensile strength and per cent elongation of the plastics and increased hardness in a pattern somewhat similar to inorganic fillers (Sarvetnick, 1969).

Strength properties were retained best when the starch was incorporated through coprecipitation or co-concentra-

Table I. Plastic Formulations and Properties

Diocetyl phthalate, PHR ^a	Starch		Tensile strength, psi	Elonga- tion, %	Specific gravity	Hardness, shore D	Water absorption, %	Fungi ^b resistance	Clarity ^c
	%	PHR							
Coprecipitate: Starch Xanthate-PVC (Geon 151)									
50	0	0	990	150	...	34	12
	10.5	18.1	1090	110	...	43	10
	21.5	42.4	1120	35	...	51	9
	25.5	52.7	1060	21	...	54	13
	29.3	64.0	850	11	...	52	29
25	0	0	2560	133	1.27	64	1.2	0	12
	12.3	18.0	2720	66	1.23	70	5.6	1	12
	24.7	42.4	2060	7	1.27	74	20.7	4	8
	32.9	64.1	2240	8	1.36	71	27.4	4	16
	38.0	79.6	2050	6	1.33	72	32.9	3	14
12.5	51.0	136.0	1920	5	1.35	73	37.5	3	20
	0	0	6690	3	...	79	8
	13.4	18.0	6030	1	...	80	13
	35.5	64.4	2870	1	...	81	23
	53.5	136.0	2810	1	...	82	30
Co-Concentrate: Starch-PVC (Geon 151)									
50	0	0	1180	150	...	35	9
	11.0	19.2	1160	88	...	44	17
	22.5	44.8	1570	59	...	51	15
	30.2	67.4	1730	28	1.26	54	20.9	3	15
	34.3	81.7	790	11	...	53	24
25	0	0	3650	140	...	59	13
	12.8	18.9	3220	44	1.24	65	6.5	1	16
	25.5	44.5	3350	22	1.32	70	15.3	1	19
	34.0	67.2	3360	13	1.31	71	21.5	4	15
	0	0	9930	10	...	77	11
12.5	20.7	30.4	7200	2	...	80	19
	36.5	67.5	4280	1	1.33	81	16.1	3	22
Dry Mix: Pregelatinized Starch-PVC (Geon 126)									
50	0	0	811	140	...	39	4
	11.5	20.0	592	120	...	45	8
	28.0	60.0	434	110	...	48	22
	39.4	100.0	342	110	...	50	38
	0	0	2600	150	1.25	70	1.7	0	6
25	13.4	20.0	2020	81	1.29	68	2.3	1	17
	31.7	60.0	1350	59	1.31	70	87	4	62
	43.6	100.0	1020	38	1.34	72	21.8	4	NG
	0	0	6910	8	...	81	9
	14.7	20.0	4640	3	...	81	40
12.5	34.0	60.0	2960	2	...	81	NG
Dry Mix: Whole Starch-PVC (Geon 126)									
50	11.5	20.0	657	120	...	43	23
25	13.4	20.0	2170	110	1.27	72	2.6	1	43
	23.6	40.0	1690	72	1.28	72	3.9	1+	75
	38.2	80.0	1370	31	1.30	74	8.4	4	85
	58.2	180.0	948	12	1.32	79	15.1	4	NG
	12.5	14.7	20.0	4860	7	...	79

^a PHR = parts per hundred parts polyvinyl chloride (PVC) resin. ^b ASTM D 1924-63; fungus growth: 0 = none; 1 = 10%; 2 = 10 to 30%; 3 = 30 to 60%; 4 = 60 to 100%. ^c By cursory observation those plastics with clarity values of less than 25 to 30 were as transparent as the controls that had no filler. NG = nonuniform and opaque.

tion. In fact, tensile strengths were somewhat higher than those for the controls when specimens contained 50% DOP and up to 30% starch.

Clarity of plastics was good when the starch was added by cocrecipitation or co-concentration. Those plastics having clarity values below 25 to 35 were transparent and uniform.

Water absorption increased with increasing amounts of starch and with the type of starch used. The most water was absorbed by cocrecipitated samples, and the least was absorbed by samples containing mechanically incorporated starch at any given level. Undoubtedly, higher moisture content increases susceptibility to microbial attack and reduces strength properties of the plastics. We interpret the low resistance to fungi and moisture as good indications that starch in such plastics would be readily attacked by microorganisms in disposal areas. Furthermore, the extensive degradation of starch filler would lead to erosion of the plastics through natural forces. Plastic

specimens made by dry mixing 13 to 52% clay with Geon 126 and DOP showed no mold growth when exposed to the fungi resistance test and absorbed 2.8 to 4.6% water.

Because starch has a low specific gravity of 1.5, its inclusion in PVC does not greatly increase the specific gravity of the plastic particularly when compared to most inorganic fillers.

Cocrecipitation and co-concentration techniques produce plastics with approximately equal properties. The slightly lower strength values for cocrecipitated samples are attributed to small losses of PVC during precipitation and washing. In contrast, the dry mixing techniques significantly reduce clarity and strength of the plastics. However, the use of pregelatinized starch does improve clarity, uniformity, and general appearance over those plastics made with whole starch. In addition to clarity, the most pronounced difference caused by formulating techniques was observed during tensile testing. Plastics made by dry mixing either whole or pregelatinized starch

and PVC developed crazes and color changes which were attributed to filler separation from the PVC resin, whereas those plastics made by coprecipitation or co-concentration remained clear and uniform during testing with no crazing or color change.

In summary, starch can be incorporated into PVC-DOP plastics in amounts of up to 100 parts of starch per 100 parts of PVC by weight with maintenance of strength properties nearly equivalent to those obtained with PVC containing conventional inorganic fillers. Of the techniques studied, the best for mixing starch into plastics were coprecipitation of starch xanthate-PVC latex or co-concentration of PVC-starch gel.

The starch-filled plastics are readily attacked by microorganisms commonly found in soil. This microbial attack should cause the plastics, upon disposal, to lose strength, become brittle, and be easily broken up by natural erosive forces into small particles that can become part of the soil.

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GENERAL ARTICLES

Dihydrochalcone Sweeteners: Preparation of Neohesperidin Dihydrochalcone

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A three-step batch preparation sequence for conversion of citrus-byproduct naringin to the intensely sweet neohesperidin dihydrochalcone was used to prepare product for pharmacological testing. The reaction sequence was cleavage of naringin to produce phloracetophenone 4'-neohesperidoside (PN), aldol condensation of PN with isovanillin to produce neohesperidin, and hydrogenation of neohesperidin to the dihydrochalcone. Reactions were successful in producing 220 lb of product at greater than 98% purity. An overall reaction yield of 10% was obtained. Caustic concentration, rate of addition of isovanillin, and catalyst condition were observed to be the critical variables controlling the reaction yields. Overall yields as high as 26% may be attainable.

Introduction

The dihydrochalcone derivatives of several flavanone glycosides obtained from citrus fruit are intensely sweet (Horowitz and Gentili, 1963, 1969) and have potential for use as nonnutritive sweeteners in foods where low sugar intake is desirable or necessary. This potential seems to be greatest for use in citrus flavored beverages, chocolate, and soft drinks. Non-food flavoring use in oral products such as toothpaste, mouthwash, and chewing gum can capitalize on the characteristic persistence and slow initial onset of the sweetness sensation.

Utilization of selected dihydrochalcones as food additives requires extensive animal feeding trials and certification by the Food and Drug Administration. Preliminary toxicology (Agricultural Research Service, 1968) indicated that neither naringin dihydrochalcone nor neohesperidin dihydrochalcone (100 and 1500× sweeter than sugar, re-

spectively) caused ill effects when fed to rats at levels up to 5% of the diet for 180 days. More extensive testing seemed appropriate but was prevented by the lack of sufficient quantities of the dihydrochalcones.

This paper details preparation data obtained at the Engineering and Development Laboratory of the Western Regional Research Laboratory, USDA, during the manufacture of neohesperidin dihydrochalcone for full-scale rat and dog feeding trials. Emphasis is placed on variables which have a critical effect on the rates of reaction, equilibria, and the obtainable yield.

The synthesis used was cleavage of naringin to phloracetophenone 4'-neohesperidoside (PN), followed by condensation of PN with isovanillin to neohesperidin, and concluded with catalytic hydrogenation of neohesperidin to neohesperidin dihydrochalcone (Horowitz and Gentili, 1969; Krbeček, *et al.*, 1968).