Grafting Starch Xanthate with Vinyl Monomers and Hydrogen Peroxide in Foam Rubber Production

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Synopsis

Starch xanthate with degrees of substitution (D.S.) ranging from 0.12 to 0.56 reacted with vinyl monomers (acrolein, acrylamide, acrylic acid, acrylonitrile, methyl acrylate, or styrene) and hydrogen peroxide to form aqueous gels of starch–polyvinyl monomer graft copolymer. The same reactions conducted in a rubber latex medium resulted in a self-acidifying, self-heating, and self-foaming coagulation to give a foam rubber. Such products were formed from several synthetic latices (NBR, SBR, polyisoprene, and polychloroprene types) and natural rubber latex; noted for each were the effects of the D.S., of monomer and peroxide concentrations, and of starch:elastomer ratios. The dried foams were evaluated by standard strength tests. Foam rubber of acceptable extensibility and enhanced tensile strength (up to 110 psi) was obtained with 0.12–0.15 D.S. xanthate and with proper balance of vinyl monomer, peroxide, and starch:elastomer ratio. Resilience was fair to good, but compression set was rather poor compared to most foam rubbers of general use.

INTRODUCTION

Recent reports have described the novel reaction of xanthates (dithiocarbonate derivatives of alcohols) with vinyl monomers. Acrylonitrile has been grafted onto cellulose in an aqueous redox system consisting of cellulose xanthate–hydrogen peroxide.[1,2] Also styrene has been grafted similarly to cellulose.[3] We have now applied the graft polymerization reaction to the aqueous redox system of completely soluble starch xanthate–hydrogen peroxide. We find that it proceeds by a self-acidification to form an insoluble polyvinyl monomer (PVM) grafted starch. As we have previously reported, the reaction between starch xanthate (SX) and polyethylenimine (PEI) gives a product that can be precipitated by bringing the pH to less than 7.[4] Furthermore, this precipitation can be a coprecipitation with rubber latices, resulting in a rubber–solid product blend of enhanced physical properties.[5] To continue the study of compounded rubbers, we have investigated the SX–vinyl monomer reaction in the presence of rubber latices and found the process to yield a foamed coprecipitate having potential utility.

EXPERIMENTAL

Materials

Acrolein, acrylamide, acrylic acid, and styrene were reagent grade and acrylonitrile and methyl acrylate were practical grade organic chemicals from Eastman Organic Chemicals, Distillation Products Industries, Rochester, New York.

Hydrogen peroxide was reagent grade, 30% aqueous solution from Merck & Co., Inc., Rahway, New Jersey, or J. T. Baker Chemical Co., Phillipsburg, New Jersey. These chemicals were used as received.

SX samples were prepared from commercial, pearl corn starch (from CPC International, Inc., Argo, Illinois) by either a continuous "Ko-Kneader" process[6,7] or a "Roto-Feed" operation.[8] They were stored at 5°C as aqueous solutions of the sodium salt, pH 11.5. Because SX decomposes somewhat significantly in degree of substitution (D.S.) after several weeks storage under these conditions, the solutions were used before that time. All xanthate solutions were analyzed for starch by a cuprimetric method and for xanthate groups by an acidimetric method.[6,7] From these data, sodium starch xanthate (NaSX) content and D.S. were calculated, based on the anhydroglucose unit (AGU).

Latices and suppliers were NBR 236, Goodyear Tire and Rubber Co., Akron, Ohio; NBR N-251, Firestone Tire and Rubber Co., Akron, Ohio; PCP 571, E. I. duPont de Nemours and Co., Wilmington, Delaware; SBR 2105 (made by Goodyear Tire and Rubber Co.); PIP 700 (made by Shell Chemical Corp., Torrance, California); and Natural Rubber, Testworth Laboratories, Inc., Addison, Illinois. The International Institute of Synthetic Rubber Producers, Inc. has established detailed specifications describing these materials.[9a] They were used as received. All rubber compounding chemicals were obtained from Testworth Laboratories.

Preparation of PVM Grafted Starch

The essential reaction may be demonstrated in the absence of latex as follows. A weighed amount (ca. 15 g) of NaSX solution of known concentration (from ca. 10% to 14%) was dissolved in 50 ml of water. Then a mixture of pipetted volumes of acrylonitrile (AN) and the 30% H_2O_2 was stirred in rapidly. The total mixture was permitted to stand at room temperature in a beaker covered with a watch glass. Reaction was rapid and in 0.5–1 hr the entire content of the beaker became a white gelatinous mass which had some tendency to coalesce and exude liquid. The reaction was mildly exothermic and effervescent, more so with higher D.S. xanthate.

Coprecipitation of PVM Grafted Starch and Elastomer

The general procedure was as follows. To a weighed volume (usually 50 or 100 ml) of latex, a weighed amout of NaSX solution was added and uniformly dispersed. This mixture became a thick, smooth, yellowish cream, the thickness increasing somewhat as the xanthate D.S. increased, that maintained consistency and general appearance for several days. To the fresh cream, a mixture of the desired amounts of monomer and 30% H_2O_2 was added and dispersed with rapid stirring, with continued mixing until the suspension began to warm, thicken slightly, or show signs of effervescence.

The mixture was poured quickly into a casting vessel—a larger beaker, a small pan, a 150-mm Petri dish, or a graduate—the choice depending on type of solid cast shape wanted—cylinder, pad, thin sheet, or long core. In the graduate, the volume change was noted as reaction time progressed. Effervescence and expansion was very rapid, even with the lowest D.S. xanthate. The foaming re-

action was allowed to continue until judged complete as evidenced by cooling, cessation of effervescence, and constancy of volume. This point was reached in only 0.5–3 hr, but most casts were allowed to stand covered overnight before processing.

The spongy, solid masses, which were loose from the walls of their containers but had not shrunk, were easily removed. They were drained on a funnel into the exuded liquid; the total volume of milky exudate was measured and its pH determined. The sponges were rinsed in cold water until the rinse was clear and were dried to constant weight in a room temperature draft hood.

Physical Testing

Specimens were cut with a drill die tool from appropriately sized cylinder casts for determination of compression set by ASTM D 1055-62[9b] and ASTM D 395-67, method B.[9c] Some compression set values were found using room temperature (77°F) for the test period. An Instron (model TT-C) unit was used for tensile testing of dumbbell specimens (die C) from the thin sheet casts (1–3 mm thick) by ASTM D 412-66 procedure.[9d] The tension set was calculated. The static fatigue test was made as per ASTM D 1055-62[9b] with smaller than normal foam sheet sizes. Rebound was measured by the vertical drop method of ASTM D 2632-67.[9e] Equipment was not at hand for making indentation and flexing tests. Nitrogen determinations were made with the micro-Kjeldahl method.

RESULTS AND DISCUSSION

Grafting Reaction in Rubber Latex Media

It is known that H_2O_2 in alkaline solution will remove sulfur from a number of classes of sulfurous compounds, forming sulfate and carbonate salts.[10] This reaction has been projected to xanthates as follows[11]:

$$ROCSSNa + 8H_2O_2 + 5NaOH \rightarrow 2Na_2SO_4 + Na_2CO_3 + ROH + 10H_2O.$$

However, if there were a deficiency of alkali in relationship to the peroxide the reaction could be

$$ROCSSNa + 8H_2O_2 + NaOH \rightarrow 2H_2SO_4 + Na_2CO_3 + ROH + 6H_2O.$$

The sulfuric acid and the carbonate would then give rise to the gas CO_2 and a remaining mole of sulfuric acid to account for the effervescence and pH change that we observed. Some decomposition of H_2O_2 by alkali to give gaseous O_2 may occur, but that reaction decreases as pH decreases, and also would be a minimum because the oxygen has to be used to produce the sulfate and carbonate. Previous investigators of the xanthate—hydrogen peroxide redox system for graft polymerization have not indicated gas formation. At the time the above overall reaction is taking place to account for the salts and gas formations, grafting takes place, presumably by the free radical mechanism wherein RO· has been formed in the above equation in place of ROH.[2,3] Thus,

$$RO\cdot + (n + 1)CH_2{=}CHR' \rightarrow RO(CH_2CHR')_n CH_2CH_2R'$$
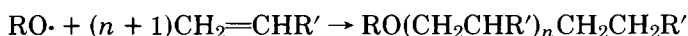
A rubber latex medium does not diminish the effervescent effect in most cases;

TABLE I

Effect of D.S., Monomer, and Hydrogen Peroxide Levels in SX–Vinyl Monomer–Hydrogen Peroxide–Rubber Latex Foam Reaction

Run No.	Reaction mixture ingredients[a]				Maximum foam gain		Exuded liquid		Foam dry solids wt., g
	Elastomer[b]	Starch wt., g; Starch/elastomer wt. %	Vinyl monomer; amount[c,d]	30% H_2O_2, ml	Vol., %	Time, min	ml	pH	
1	SBR 2105	1.65; 5.8	AA; 5.31	7.0	e		10	2.9	31.0
2	SBR 2105	1.65; 5.5	AC; 4.21	7.0	67	20	5	3.8	42.0
3	SBR 2105	1.65; 5.8	AM; 5.00	7.0	210	20	5	7.3	34.3
4	SBR 2105	1.65; 5.8	MA; 6.28	7.0	100	30	5	6.7	32.0
5	SBR 2105	1.65; 5.8	AN; 5.0	7.0	179	15	5	6.8	34.8
6	NBR 236	1.56; 7.6	ST; 3.0	5.0	f		25	7.6	—
7	NBR 236	1.24; 6.8	AN; 5.0	2.5	45	225	37	7.0	—
9	NBR 236	1.24; 6.8	AN; 5.0	7.0	49	60	40	7.0	—
10	NBR 236	1.24; 3.4	AN; 10.0	14.0	28	120	60	6.9	—
11	NBR 236	2.50; 6.8	AN; 10.0	14.0	50	120		7.0	
12	NBR 236	3.76; 10.2	AN; 10.0	14.0	75	120	—	7.0	
13	NBR 236	1.43; 7.2	AN; 5.0	7.0	—	—			21.3
17	NBR 236	0.98; 2.6	AN; 10.0	14.0	60	75	55	6.9	35.2
18	NBR 251	0.98; 2.4	AN; 10.0	14.0	96	45	30	6.9	36.5
19	SBR 2105	0.98; 2.3	AN; 10.0	14.0	>163	15	4	7.3	32.2g
21	PCP 571	0.98; 2.2	AN; 10.0	14.0	88	5	0		50.2
23	NBR 236	2.92; 7.9	AN; 10.0	14.0	35	180	15	7.1	44.0

24	NBR 236	3.41; 9.2	AN; 10.0	14.0	24	180	5	7.0	45.0
25	NAT	1.34; 7.0	AN; 5.0	7.0	320	2	70	—	—
26	NAT	4.90; 24.5	AN; 26.0	30.0	220	5	30	5.4	22.0
27	NAT	1.29; 5.0	ST; 3.0	5.0	>200	5	<5	7.8	—
28	SBR 2105	1.29; 4.5	ST; 3.0	5.0	f	—	5	7.8	30.5
29	NBR 236	1.29; 6.3	ST; 3.0	5.0			5	7.5	20.9
30	NAT	5.00; 25.0	AN; 26.0	30.0	220	5	5	3.0	42.0[h]
31	NBR 236	1.17; 3.2	AN; 10.0	14.0	28	120	55	6.8	—
32	NBR 236	1.76; 4.8	AN; 10.0	14.0	24	120	35	6.7	—
33	NBR 236	1.17; 6.4	AN; 5.0	14.0	22	180	35	5.9	—
34	NBR 236	1.17; 6.4	AN; 5.0	7.0	0	180	10	6.4	—
35	SBR 2105	50.0; 25.0	AN; 160.0	225.0	36	15	120	3.0	362
37	NBR 236	0.51; 2.8	AN; 5.0	7.0	0	180	17	5.4	—

[a] Runs 1–5 had 0.10 degree of substitution (D.S.) starch xanthate (SX); runs 6–16, 0.12–0.13; runs 17–29, 0.15–0.16; runs 30–35, 0.23–0.25; run 37, 0.55.
[b] NBR 236 = 45% AN:55% butadiene copolymer; NBR 251 = 24% AN:76% butadiene; SBR 2105 = 25% styrene:75% butadiene; PIP 700 = 100% isoprene polymer; PCP 571 = 100% chloroprene polymer; NAT = 100% natural rubber.
[c] AA = acrylic acid, AC = acrolein, AM = acrylamide, AN = acrylonitrile, MA = methyl acrylate, ST = styrene.
[d] In runs 1–4, the amount of monomer figure represents grams. In all other runs, all with AN or ST, the volume is given. Five ml of AN weighs 3.985 g; 3 ml of ST, 2.721.
[e] Solids "ball" immediately and swell, but volume increase was not measurable.
[f] Effervescence is slow to develop; it takes several hours to reach a foaming condition. Coprecipitation occurs over an 18-hr period.
[g] High mechanical loss.
[h] Yield weight indicates a 75%–80% polymerization, at the low final pH, of the AN added.
—, No datum.

in fact, the effect seems to be enhanced somewhat with the lower D.S. xanthates, 0.12–0.15. As the latices are themselves highly alkaline, they undoubtedly add a better alkali level to the low D.S. xanthates, which have lower alkali content than the higher D.S. materials. The final pH seems buffered to near neutrality below the 7.5–8.0 area at which most latices have their gelling point. The higher the D.S., the lower was the final exuded liquid pH (runs, 9, 34, 37, Table I).

Several vinyl monomers were used comparably, but AN was chosen for detailed investigation of parameters in the coprecipitation reaction. After mixing with AN and H_2O_2, NBR latices provided an induction period of 5–10 min followed by a steady foaming rate. SBR foam deposited solids initially, then continued to increase in foam volume in the supernatant without producing additional solids. The chloroprene latex foamed in stages more rapidly than the SBR—in just several minutes to a maximum volume, which then diminished about 80% and slowly regained to about 66% in a second stage, forming a core which held its liquid. Mixing with SBR or PCP latices had to be very rapid in order to cast. Natural latex foamed so quickly and profusely that it was unmanageable in castings, and the solids it produced were too soft and mushy to be handled. Polyisoprene did not foam and the solids it yielded had no cohesive strength.

For 0.12 D.S. xanthate, increasing the starch content in the NBR 236 latex foaming mixture, while keeping the AN–H_2O_2 amounts constant, increased the amount of foam and the amount of exuded liquid (runs 10 and 11). At 0.15 and 0.24 D.S., the reverse results were observed (runs 17, 23, 24, 31, and 32). In the data of Table I, one notes the interplay of magnitude of xanthate D.S. and quantities of AN of H_2O_2 in establishing the amount of foaming, pH, and exuded liquid. The use of too little H_2O_2 in relation to AN (runs 7, 11, 33, and 34) resulted in too high pH and a very fragile or no foam cast; too small an amount of AN–H_2O_2 mixture (run 9) resulted in a foam cast with irregular voids as compared to one from an adequate amount of AN–H_2O_2 (run 11); and too small an amount of SX in relation to AN–H_2O_2 resulted in no foam cast. In general, the casts with 0.24 D.S. derivative yielded comparatively small, compact, solid cores that had few voids or pores and were stiff. Xanthate of 0.55 D.S. reacted so quickly and formed such lumpy aggregates that it was very difficult to adequately stir them and cast them before they stiffened; the foams had large, rough, less-evenly dispersed voids or irregular running cracks. As in the SX graft copolymerization reaction alone, the 0.04 D.S. level seems inadequate. At a starch: elastomer ratio of 6.0 with SBR, a broader range of AN–H_2O_2 than that which gave satisfactory result in foaming, pH, and solid cores with a 0.10 D.S. xanthate did not produce a pH lower than 8.1 or any solid coprecipitation with the 0.04 D.S., even though considerable foaming occurred.

Physical Character of Elastomer–Starch–PVM Rubber

Dry foam cores with evenly distributed, uniformly small-sized pores were obtained with 0.12–0.15 D.S. xanthate. The structure was more open-celled than closed-celled, so the appearance was spongelike. The higher the percentage of starch in the reaction mixture, the larger was the size of the wet and dry cores. In a systematic series using 0.25 D.S. xanthate and NBR 236, wherein the amount of AN and H_2O_2 was regulated so as to vary the final pH, the precipitated product character when dried varied: pH 7.2, tan and hard; pH 6.6, creamy yellow and

friable; pH 5.2, off-white and powderable; pH 2.2, most easily powdered and white. There was little shrinkage on drying. Based on diameter measurements for disk casts and height measurements for cylinder casts, cores containing NBR 236 shrank about 15%; NMR 251, about 10%, SBR 2105, about 8%; and PCP 571, about 14%.

The recovery of dry solids was high. While attempts to recover more solids by adding acid to reaction mixtures of 0.13 D.S. xanthate and NBR 236 latex (run 13 recipe, Table I) did result in some pH drop and perhaps an indication of slightly more precipitation, the foam casts became fragile when as little as 6 ml of $0.1N$ sulfuric acid had been added and were not processable. The nitrogen content (10.29%) of the core made with NBR 236 (run 13) was consistent with a starch graft copolymer (containing 20% of the AN used) in admixture with a 40% AN:60% butadiene elastomer composition in the NBR 236. The analyses on other cores (runs 18, 19, and 21) provided a calculated AN conversion of 7% in the case of PCP 571 (0.34% N); 10%, in SBR 2105 (0.52% N); and 21%, in NBR 251 (6.88% N). Dimov and Pavlov projected a 20% or less polymerization of AN in making cellulose graft copolymer at pH 6–7.[2] With these extents of AN polymerization in the graft copolymer formation, the solid recoveries were 93% for PCP 571, 80% for SBR 2105 (mechanical loss in casting), 95% for NBR 251, and 96% for NBR 236. When the final pH was in the 2–3 range, the percent polymerization was much higher (runs, 2, 30, and 35); for example, in run 35 with SBR 2105 the yield and 6.39% N content were consistent with a 63% polymerization of AN.

The foamed solid isolates from polychloroprene–latex mixtures were dark brown, whereas those from the other elastomers were white to light tan. None had a noticeable odor. The compression set values were not particularly good for a general type foam rubber. In part this may be due to their relatively high apparent densities as foamed, 24–40 lb/ft^3, as compared to the 4–20 lb/ft^3 range found for many common foam rubbers.[12] The compression set at 77°F was a little lower than that at the test standard 158°F. The styrene–butadiene copolymer and polychloroprene elastomers had the best compression behavior (Table II).

The compression set dropped slightly as the starch derivative content was raised, but when the 10% level of derivative was reached the set increased (runs 10–12, 17, 23, and 24). The rebound similarly fell, but the rise at the end of the starch range was not noted. Both compression set and rebound decreased upon increasing acid addition in attempts to raise solid yields, but other strength characters were stable until the aforementioned acid addition point was reached. Improved resilience by butadiene in copolymers was noted in the rebound values of runs 18 and 19 that utilized 76% diene as compared to run 17 with 55% butadiene copolymer. Glycerol as a plasticizer, added to the latex (NBR 236) in amounts equal to the weight of starch incorporated, had no effect on these physical properties, nor did rapid drying and curing at 230°F in an air draft oven for 4 hr. Blank coagulated solids of the elastomer were similarly not affected and possessed similar test values.

The elongations at break were in general within the ranges given for foam rubbers from a number of synthetic elastomer latices.[12] They are, of course, less than those of natural rubber. The tensile strengths at break have been enhanced greatly by the starch addition over the concentration range used. Again, perhaps

TABLE II
Strength Characteristics of SX–Vinyl Monomer–Hydrogen Peroxide–Rubber Latex Foam
Reaction Products

Run No.	Compression set Ch, %		Elong. at break, %	Tension set, %	Load at break, kg	Tensile strength, kg/cm^2	Rebound, %
	77°F	158°F					
6	—	—	700	25	0.69	5.49	—
10	—	47.3	—	—	—	—	15
11	—	44.9	—	—	—	—	12
12	—	49.0	—	—	—	—	10
13[a]	—	—	265	7	0.65	3.80	—
14	—	—	710	18	1.35	6.00	—
15	—	—	420	6	1.25	7.10	—
17	43.9	48.0	230	0	0.42	1.40	12
18	43.7	50.0	422	6	0.35	1.00	40
19	24.9	47.9	715	22	1.06	3.25	42
21	30.5	43.5	>870	75	1.23	7.75	18
23	33.3	—	—	—	—	—	11
24	41.2	—	—	—	—	—	12
28	—	47.4	—	—	—	—	55
29	—	51.1	305	13.9	0.66	3.27	—
31	—	45.9	—	—	—	—	13
32	—	45.8	—	—	—	—	13

[a] Run 13 repeated with 0.35 g of alkylated diphenylamine (Agerite Stalate S) anitoxidant and 0.2 g of mercaptobenzothiazole (Captax) accelerator mixed into the latex before xanthate addition, or with those additives plus 0.4-g powdered sulfur, produced foams and solids essentially the same as in run 13.
—, No datum.

the relatively high apparent density level plays some part in the high strengths found. The tension sets are acceptable, but it may be noted that with the more extensible blends the tension set mounts. The dry foams with the different elastomers, as exemplified by runs 17–21, passed the static fatigue test.

The addition of antioxidant, accelerator, and vulcanizer did not change the physical strength (see run 13). While antioxidant- and accelerator-containing foams appeared homogeneous, those made with dry sulfur appeared heterogeneous due to formation of globular sulfur particles. Emulsified or dispersed forms of additives should alleviate heterogeneity. The high temperature developed in the latex–starch graft copolymer reaction and coprecipitation, up to 190°F, may provide vulcanization and the sulfurous nature of the xanthate may furnish acceleration.

Potential Uses of Elastomer-Starch-PVM Rubber

The properties suggest that the materials warrant utility considerations in the general areas of foam rubber use, except where the higher starch contents could bring a problem under high-moisture environments. Most particularly they would seem suitable for poured-in-place foams or moldings. They could serve as insulators and sound or shock absorbers or vibration dampers, and in this regard as supportive or restraining media if loads are not excessive. Since compression set is not good, they would seem best suited under conditions which would apply the load as a stretch. Compression shock absorbers that need not

return completely to previous state may be an application. Shaping and cavitating might improve the compression set. The suppleness and tensile properties indicate that in thin sheets a use might be in linings, and in thicker pads in carpet application. Since the foaming and coagulation proceed so rapidly and a skin forms on the surface readily, some type of continuous casting and sheeting operation would be feasible.

Several patents cover various means and aspects of incorporating starch and starch derivatives into rubber.[13-19] The processes and products described in this paper overcome some shortcomings of, and extend the concepts of, the previous incorporations of starch; furthermore, they provide a method of nonmechanical foaming of rubber latices and a potential method of making a powderable rubber composite. A patent has been issued[20] and some fundamental aspects of the grafting reaction *per se* are reported elsewhere.[21]

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