Ionically Bonded Filler–Elastomer Composites*

T. P. ABBOTT, C. JAMES, and F. H. OTEY, *Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

Tertiary amine-modified corn starches were converted to their basic or hydroxide form and combined with carboxylated butadiene–acrylonitrile copolymer and butadiene–styrene–sulfonic acid polymer to produce ionically bonded filler–elastomer composites. An increasing percentage of the elastomer fraction in the starch–elastomer composite is insolubilized as the starch-to-elastomer ratio increases. In addition to ionic bonding, a significant amount of elastomer is believed to be physically adsorbed onto the filler. The resulting composites are reprocessible, and some have sufficient tensile properties at room temperature for making rubber goods.

INTRODUCTION

Reinforcement of elastomers depends in part on physical attachment of the elastomer chains to reinforcing filler particles.[1] The qualitative interpretation of reinforcement on a molecular level includes slippage of chains from filler surfaces by breaking and making new physical bonds. This slippage allows relief from concentrated local stresses and prevents a premature break or catastrophic tear in the area of concentrated stress. Such an interpretation is appealing because it offers a molecular level explanation of both stress softening and reinforcement. For a more detailed explanation, the reader is referred to Boonstra[1] or Dannenberg.[2]

Others, notably Gessler,[3] have studied the physical properties of reinforced elastomers containing filler known to be covalently bonded to the elastomer. Generally, increasing the amount of covalent bonding does not improve the reinforcing properties of high-surface-area, small-particle-size fillers such as carbon black and silica but does improve dynamic properties of the cured product.

The molecular theory of reinforcement can be used to explain the lack of improved reinforcement by covalently bonded fillers. In areas of high local stresses such as at the tip of a cut or near a defect, chains will be more highly extended; some will be fully extended between their covalent filler attachments. Since the elastomer backbone is composed of covalent bonds of strength similar to the filler–elastomer bonds, a chain may break in the backbone as easily as at the filler surface. The chain end resulting from the fracture can no longer contribute significantly to the network's strength, unlike a chain which has not been broken but whose weaker physical attachment to the filler is temporarily disrupted. Thus, the work to break a physically bonded, vulcanized filler–elastomer composite is greater than the work to break a covalently bonded, vulcanized filler–elastomer composite.

Ionic crosslinking of elastomer chains has been studied by a number of workers,[4] but ionically linking filler particles to elastomers has not been investigated to our knowledge. However, ionic bonding of filler to elastomer in addition to ionic crosslinking may explain enhanced tensile properties observed by Brucksch[5] for butadiene–pyridine rubbers containing carbon black, silica, and "promotors" such as zinc chloride, zinc oxide, and lauryl bromide. Physical properties of ionically crosslinked elastomers give good evidence for a slippage of the ionic crosslinks similar to the slippage of physical bonds between filler and elastomer in the molecular theory of reinforcement. For the most part, elastomers used for ionic crosslinking contain sulfonic or carboxylic acid groups which are crosslinked by metallic bases. Characteristic of such crosslinked materials are high strengths, probably again due to local stress-relieving mechanisms, and high permanent set, probably due to slippage of mobile ionic crosslinks. A range of crosslink mobility is obtained depending on the metal cation used in the crosslink and presence or absence of carboxylic acid groups not bound to the elastomer. For example, Brown[6] found that the addition of stearic acid and other carboxylic acids not attached to the polymer chain would compete with metal ion crosslinks of the polymer and allow an ionically crosslinked elastomer to be reprocessed at lower temperatures. Further development of this idea and introduction of other novel ionic crosslink plasticizers have resulted in reprocessible or "thermoplastic" ionic elastomers such as "thionic polymers" at Exxon and another at du Pont.[7]

We believe that an alternate approach to achieving reinforcement is possible through ionically bonding fillers to elastomers so that no additional permanent crosslinking occurs at processing temperatures. Ionic links should be stronger than physical adsorption but not as strong as covalent bonding and should, therefore, improve reinforcement in sulfur-crosslinked to ionically bonded systems.

This paper describes our initial efforts to ionically bond starch filler to various elastomers with the ultimate goal of producing a quality, reprocessible elastomer composite. Starch is especially attractive for this study because it is known to reinforce elastomers[8] and because various crosslinking sites are easily attached onto the starch hydroxyls.

An acidic elastomer was reacted with a basic cationic starch to produce an ionic bond. Two elastomers were chosen: Hycar 1072, a carboxylated butadiene-acrylonitrile elastomer (NBR–COOH), because of its current uses and availability; and, in latex form only, an emulsifier-free styrene–butadiene polymer containing p-vinylbenzenesulfonic acid in the backbone (SBR–SO_3H). The starch was modified with tertiary amine groups which were then converted to the basic (hydroxide) form.

EXPERIMENTAL

Materials

The starch used was an unmodified pearl corn starch obtained from CPC International.

Cato 14, obtained from the National Starch Company, is a tertiary amine hydrochloride-modified corn starch, containing 13.6% water, 0.32% nitrogen (or 23 meq amine/100 g), and 0.5% chlorine.

Hycar 1570X19 latex, a carboxylated butadiene–acrylonitrile polymer emulsion equivalent to Hycar 1072 dry rubber, was provided by B. F. Goodrich Chemical Company in experimental quantities. The latex had total solids of 28.6% and a carboxy content, on a dry rubber basis, of 75 meq/100 g.

Styrene, stabilized with *tert*-butylpyrocatechol, from Eastman Organics Inc., was distilled at 50°C under vacuum and stored at 0°C until used.

1,3-Butadiene from Matheson, *p*-vinylbenzenesulfonic acid (Sty–SO_3Na) sodium salt from Polysciences Inc., and $K_2S_2O_8$, N,N-dimethyl-2-chloroethylamine hydrochloride, and hydroquinone were used as received.

Preparations and Procedures

Cato 14[OH]. Cato 14[HCl] was converted to the hydroxide form by conventional ion exchange procedures. In a typical preparation, 4.5 kg Cato 14[HCl] was mixed with $0.1N$ NaOH and the slurry fed into a Tohlbert basket centrifuge. The filter cake was washed with additional $0.1N$ NaOH until the effluent gave a negative Cl^- test with $AgNO_3$. The cake was then washed with water until the effluent was neutral and finally with ethanol to remove the water. After drying 12 hr at ambient conditions followed by 5 hr at 70°C in vacuo, the product contained 16.1 meq OH/100 g as determined by HCl titration, 0.32% nitrogen, and 0.01% chlorine.

[Starch–R_2NH]$^+$[OH]$^-$. A more highly substituted cationic starch than Cato 14 was prepared by heating at 50°C for 0.5 hr a solution containing 180 g (162 g dry basis) starch, 2 liters $0.5N$ NaOH, and 32 g N,N-dimethyl-2-chloroethylamine hydrochloride. The cationic starch was precipitated by adding 8 liters ethanol, filtering, and drying in vacuo. The product was then dispersed in 2 liters water and dialyzed against ten 10-liter aliquots of water over five days. Twenty grams NaOH was then added to the dialysis bag, and the dialysis was continued for another five days as described above. The product contained 40 meq OH/100 g of dry product as determined by HCl titration and 0.66% N (or 47 meq amine/100 g). Two other products made by the same procedure each contained 0.73% N (or 52 meq amine/100 g).

SBR–SO_3H. An emulsifier free butadiene–styrene–4-vinylbenzenesulfonic acid terepolymer (SBR–SO_3H) was prepared by a method similar to that of Jung and Krieger.[9] The 500-ml bottle polymerization recipe follows in order of addition: 264 ml H_2O, 16 ml $0.1M$ NaH_2PO_4, 12.8 ml $0.1M$ KOH, N_2 purge, 1.85 g Sty–SO_3Na, 13 ml styrene, 8 ml 3% $K_2S_2O_8$, and 41 g 1,3-butadiene.

The sealed bottles were tumbled in a polymerization bath at 65°C for $3\frac{1}{2}$ to 4 hr, which was calculated to yield 10% to 15% conversion. The bottles were then removed, pressure was released, and 3 ml of a 1% hydroquinone solution was added to shortstop the polymerization. Excess monomer was stripped off by steam distillation. The latex was then adjusted to pH 1.5 with $1M$ H_2SO_4. No coagulum was found when the latex was filtered through cheesecloth. The latex was then dialyzed against distilled water until the dialyzate was pH 5. The acidification and dialysis were repeated once. An infrared spectrum of the elastomer cast on Irtran II crystal was determined.

Elastomer–Filler Mixing. The Cato 14[OH] was combined with NBR–COOH or SBR–SO_3H by two methods. In the first, various amounts of a 10% aqueous solution of Cato 14[OH] at 80°C were mixed with Hycar 1570X19 latex. The latex–solution mixtures were then freeze dried.

In the second method, 36 g freeze-dried Cato 14[OH] was hand blended with 18 g water and then mixed with another 36 g Cato 14[OH] in the mixing chamber of a Brabender Plasticorder torque rheometer Type PL-V300. The mixing chamber was fitted with cam-style mixing blades and had a capacity of approximately 70 cm^3. The resulting paste was 80% Cato 14[OH], thermoplastic, and required a mixing torque in the Brabender at 60 rpm similar to that for solid baled Hycar 1072. The paste was mixed with Hycar 1072 in the Brabender mixing chamber at 100°C for 10 min at 60 rpm.

After the first 5 min of mixing, no additional water was given off from the mix, and the temperature rose slowly in most cases 5° to 10°C by the end of the 10-min cycle.

Gel contents were determined after freeze drying, after Brabender mixing, after 10 min milling, and after compression molding 30 min at 150°C. Tensile properties were determined on extruded and compression-molded samples.

Gel Determinations. Gel content was determined on samples sheeted 10 times through rubber mill rolls of the type described in ASTM D15-72, spaced 0.25 mm apart, and cut into strips 1 mm wide and approximately 1 cm long. Then 0.5-g samples of the strips were accurately weighed and placed on wire screens in 4-ounce bottles. Toluene (125 ml) containing 0.4 g/l. AgeRite Spar was pipetted into each bottle which was then capped and placed in a dark cabinet for at least 16 hr. The bottles were then shaken to ensure uniform solution. A 25-ml aliquot of soluble material was removed by pipet through a cotton plug, evaporated to dryness, and weighed.

$$\text{percent gel} = 100 - \text{percent solubles}$$

$$= 100 - \frac{500 \times (\text{weight of dry 25-ml aliquot} - \text{weight of blank})}{\text{original sample weight}}$$

Also the insolubles were filtered, washed twice with toluene, dried, and weighed to obtain the percent gel by an alternate method:

$$\text{percent gel} = 100 \times \frac{\text{gel weight}}{\text{original sample weight}}$$

The second method served as a check on the first gel determination. Percentages of elastomer that was insolubilized in the composites (E_I) were calculated by assuming that all of the cationic starch remained insoluble and that all of the solubles were elastomers (this was confirmed by infrared spectra of the gel and soluble portions):

$$E_I = 100 \times \frac{\% \text{ gel} - \% \text{ cationic starch in total composite}}{\% \text{ rubber in total composite}}$$

RESULTS AND DISCUSSION

Hycar 1072, either from 1570X19 latex or from a slab, is only partially soluble in toluene, possibly due to association of the carboxylic acid groups. However, when the NBR–COOH is combined with cationic starch, a significantly higher percentage of the elastomer becomes toluene insoluble. The increased insolubilization is caused by both physical adsorption on cationic starch and ionic bonding of the starch to elastomer. Data in Table I illustrate the effects on the

TABLE I
Toluene Solubility of Mixed Cationic or Pearl Corn Starch with a Carboxy-Nitrile Elastomer

Sample no.	Composition, %		Gel, %	Insolubilized elastomer E_I, %
	Starch-derived filler	Elastomer		
Cato 14 [OH] Mixed with Hycar 1570X19 (NBR–COOH) Latex and Freeze Dried				
1	0	100	20.9	20.9
2	4.5	95.5	57.6	55.7
3	16.7	83.3	68.2	61.8
4	25.0	75.0	75.3	67.1
5	33.3	66.7	78.1	67.2
6	50.0	50.0	83.0	66.0
7	66.7	33.3	92.7	78.0
Unmodified Starch Mixed with Hycar 1570X19 (NBR–COOH) Latex and Freeze Dried				
8	4.5	95.0	50.0	47.7
9	16.7	83.3	65.2	58.2
10	25.0	75.0	66.8	55.7
11	33.3	66.7	70.8	56.2
12	50.0	50.0	79.2	58.4
13	66.7	33.3	83.1	49.3
Cato 14 [OH] Paste Mixed with Slab Rubber (NBR–COOH) in Brabender				
14	20.0	80.0	69.7	62.2
15	33.3	66.7	74.5	61.8
16	50.0	50.0	81.9	63.8
17	66.7	33.3	88.3	65.0
Starch-$R_2NH^+OH^-$ Mixed with Hycar 1570X19 (NBR–COOH) Latex and Freeze Dried				
18	25.0	75.0	74.9	66.5
19	33.0	67.0	77.4	66.1
20	50.0	50.0	84.3	68.6
21	67.0	33.0	92.0	76.0

amount of toluene insolubles produced when increasing amounts of cationic starches were combined with an acidic elastomer (samples 1–7). The combination of unmodified pearl corn starch with NBR–COOH gives a significant amount of physically adsorbed gel as well (Table I, samples 8–13) but not quite as much gel as the combination of Cato 14[OH] and NBR–COOH. In Table I, the percentages of the total composites that are insoluble in toluene are listed as % gel.

The amount of elastomer insolubilized by combining Cato 14[OH] paste and slab rubber in the Brabender mixing head did not change appreciably with increasing starch-to-rubber ratio (Table I, samples 14–17). Although the Cato 14[OH] paste and NBR–COOH were equally viscous and appeared compatible during Brabender mixing, in some instances they tended to separate into two phases on the rubber mill. Apparently, the differing polarities were sufficient to overcome any chemical reaction of the acid and base groups. Even the freeze-dried samples had lower gel contents after intensive milling.

At high starch levels, the composites still contained an appreciable fraction of soluble elastomer apparently not attached to the starch. An attempt to increase the percentage of insoluble elastomer was made by replacing the Cato 14[OH] with a cationic starch (starch–$R_2NH^+OH^-$) that contains approximately twice the basic amine groups that Cato 14[OH] contains. Hycar 1570X19 latex and starch–$R_2NH^+OH^-$ were combined by the same procedure used for Cato

14[OH]. However, increasing the concentration of basic groups did not significantly improve the gel content over that gained from using Cato 14[OH] (Table I).

More of the elastomer was insolubilized by supplementing the filler–elastomer attachments with zinc or calcium ions (Table II). Specimens 22 to 25 in Table II were prepared by adding Cato 14[OH] in solution to Hycar 1570X19 latex (NBR–COOH) and freeze drying the mix. The metal oxides were added either into the latex before freeze drying or on the rubber mill after freeze drying as indicated in Table II. Samples 26 to 30 were made from mill-mixed slab Hycar 1072 (NBR–COOH) and metal oxides in various amounts. The dry mixes of samples 22 to 30 were subsequently heated 30 min at 150°C and then cooled, and gel contents were determined. The metal ions increased the amount of insoluble elastomer by 8% to 19% (samples 22–25, Table II) over that observed for a similar composite without metals (sample 4, Table I), but not significantly more than the metal ion crosslinking insolubilizes without added starch (compare E_I values of samples 22 and 23 to that for control sample 27 in Table II; also, compare the E_I value of sample 24 to that for sample 26 in Table II). Even at higher levels of metal oxide crosslinking, the NBR–COOH is not totally insolubilized, as shown in Table II (samples 28 and 29). This may partially explain the inability of basic starch filler to totally insolubilize the NBR–COOH.

Possibly the limiting factor in insolubilizing the elastomer is the amount of surface area of the latex particles and starch available to interact in the aqueous phase. First thoughts as to what is preventing total gelation turned to a probable interference from surfactant in the latex, but this was rejected since increased substitution on the starch did not compete more strongly for the NBR–COOH with surfactant and cause higher gels. Gel contents after freeze drying, milling, and compression molding demonstrate that the gelation is complete after starch solution–latex mixing and freeze drying. Since the reaction appears to take place in the latex–aqueous solution mix and does not increase with subsequent milling, the interaction must depend only on the area of contact in the original mixture. Both the starch, a highly branched, swollen colloidal particle, and the latex particle have obviously limited reaction surfaces. Little if any reaction appears to take place in the solid blend during mastication.

TABLE II
Toluene Solubility of Acidic Elastomer, Basic Strach, and Metal Oxide Composites

Sample no.	Composition, parts				Metal oxide added		E_I, %
	Cato 14[OH]	NBR–COOH	CaO	ZnO	On mill	To latex	
22	25	75	0.5	—		X	86.6
23	25	75	0.5	—	X		78.8
24	25	75	—	0.7	X		79.1
25	25	75	—	0.9		X	75.2
26	0	100	—	1.0	X		75.9
27	0	100	0.7	—	X		82.7
28	0	100	—	5.0	X		92.0
29	0	100	3.4	—	X		90.5

TABLE III
Physical Properties of Acidic Elastomer, Basic Starch, and Metal Oxide Combinations

Sample no.	Composition Elastomer, parts	Composition Starch, parts	Metal oxide type, parts	Tensile strength, MPa	At break Elongation, %	At break 10 min set, %	Stress at 300% elongation, MPa
			Hycar 1072 and Cato 14[OH]				
1	100	0	0	0.28	1000	150	0.4
5	67	33	0	2.8	340	10	1.6
22a	75	25	CaO, 0.5	9.7	660	20	6.4
31	100	0	CaO, 0.5	4.0	450	8	2.5
24	75	25	ZnO, 0.7	5.5	1000	140	3.9
32b	75	25	CaO, 0.5	11.9	600	37	—
33c	75	25	CaO, 9.5	10.0	480	20	5.2
			Hycar 1072 and Pearl Corn Starch				
11	67	33	0	1.8	400	10	1.8
34	67	33	CaO, 0.5	1.4	1000	150	1.4
			SBR–SO$_3$H and Cato 14[OH]				
35	67	33	0	10.3	350	—	9.3
36	100	0	0	3.7	360	—	—

[a] After mill mixing, sample 22 was extruded, cooled 24 hr, and physicals were determined.
[b] Same sample as 22, only compression molded 30 min at 150°C.
[c] Same sample as 32, only remilled after physicals run on 32 and re-formed in compression mold.
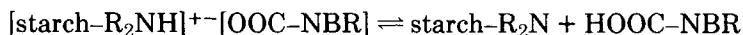
Physical Properties

Until the composites are optimized for reprocessibility, method of combination, and maximum gel contents, only the tensile properties of strength at break, set 10 min after break, elongation at break, and stress at 300% elongation are being determined. Tensile properties of several samples that have been extruded, molded, or remilled and remolded are given in Table III.

Sample 35 is a combination of SBR–SO$_3$H latex and Cato 14[OH] in aqueous solution that was freeze dried. The sample was not millable at 30–50°C but molded nicely at 150°C under pressure. Samples 35 and 22 have tensile strengths, elongations, and sets comparable to those of some commercial products, and they are reprocessible as demonstrated by samples 32 and 33 which retain properties similar to those of their original form, sample 22, after being re-formed. Physical properties of this magnitude were not obtained with the elastomer alone (samples 1 and 36), with the elastomer in combination with unmodified starch (sample 11), metal oxide (sample 31), or both (sample 34). Although Table III contains the results from only a preliminary study of the concept of ionically bound filler–elastomer composites, the results are encouraging and the composites appear to meet the standards for some commercial applications and are still reprocessible at high temperature and pressure.

CONCLUSIONS

Carboxylic elastomers are insolubilized by interaction with starch-containing basic or salt-forming groups. The basis of that interaction is believed to be primarily physical adsorption, but ionic salt formation between filler and elastomer probably does occur since the NBR–COOH or SBR–SO$_3$H latexes and cationic starch solutions neutralize each other rapidly. Although covalent bonds such as ester links are possible, they are less likely to occur than ionic links because of the slower reaction rate of most ester formations compared to strong acid–base reactions. Also, gel is formed rapidly with no heating necessary by merely mixing and freeze drying the basic starch and carboxylic polymer. On mixing the Cato 14[OH] solution and Hycar 1570X19 latex, the mixture thickens rapidly and in some cases coagulates in very small particles. In addition, the linkages are probably mobile since severe shear mixing such as hot rubber roll mixing for 20–30 min tends to phase separate the two components and decrease gel content. Such forces would tend to drive the equilibrium to the right in the equation

$$[\text{starch–R}_2\text{NH}]^{+-}[\text{OOC–NBR}] \rightleftharpoons \text{starch–R}_2\text{N} + \text{HOOC–NBR}$$

In any case, the physical properties of such composites (Table III) which have been extruded or compression molded are adequate to encourage further investigation, especially in light of the fact that no permanent crosslinks are used and the composites are reprocessible.

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