

The Preparation of Powdered EPDM Rubber from Solution

INTRODUCTION

It has been predicted¹ that by the year 1980, one fifth of all domestic extruded rubber will be made from a dry blend of powdered elastomer and compounding ingredients. Recently, a simple and inexpensive technique has been developed for producing powdered rubber from various latices (styrene-butadiene rubber, natural rubber, nitrile rubber, and polybutadiene rubber).² This method, wherein a small percentage of starch xanthide (as low as 3 phr) is used as a partitioning agent, is an extension of earlier work in which starch xanthide at much higher loading levels was incorporated into various elastomers as a reinforcing agent.³⁻⁵ The coprecipitation of starch xanthide with various rubbers is accomplished by first dispersing the rubber latex in a starch xanthate solution at a pH near 12. Acidification of this mixture under oxidizing conditions brings about coprecipitation of the rubber and starch, the rubber coming down encased in crosslinked starch xanthide.

This procedure for preparing powdered rubber has now been adapted to solution polymers such as ethylene-propylene terpolymer (EPDM) elastomers. In adapting the coprecipitation technique to EPDM solution polymers, a difficulty exists because of the immiscibility of the hexane/EPDM solution and the water solution of the starch xanthate. This problem can be overcome by emulsifying the hexane/EPDM solution in aqueous starch xanthate. The organic solvent is removed by vacuum distillation and/or steam stripping, the latter being carried out intermittently. The EPDM is then in latex form in the starch xanthate solution and the mixture can be coprecipitated by acid addition in the presence of sodium nitrite.

EXPERIMENTAL

Starch xanthate was prepared from pearl corn starch and carbon disulfide as a 10% solution in aqueous base, as described by Abbott et al.² At high starch xanthide loading levels of 20 to 40 phr, starch xanthate with a degree of substitution (D.S.) of 0.08 was used in preparation of samples; and for production of 5 phr starch xanthide/EPDM powdered elastomers, the starch xanthate had a D.S. of 0.35. T. P. Abbott of the Northern Laboratory has found that a D.S. of 0.35 is optimum for the preparation of powdered elastomers containing a small percentage of starch xanthide as a partitioning agent.

The EPDM solution polymer was Royalene 521 EPDM cement provided by Uniroyal Chemical. The polymer solution contained 5.85% solids and was used as received. The emulsifying system was a combination of water-soluble Dresinate 562 (potassium rosin soap), hexane-soluble Span 85 (sorbitan trioleate), and Span 20 (sorbitan monolaurate). This combination does not necessarily represent an optimum emulsifying system, because the emulsion as prepared in the next paragraph begins to separate if left standing for more than 16 hr.

The procedure for preparing starch xanthide/EPDM powdered rubber is as follows: A quantity of EPDM polymer solution containing the desired weight of polymer is made 0.22% by weight in Span 85 and 0.44% by weight in Span 20. To this polymer/emulsifying agent/hexane solution is added an equal volume of 1% aqueous potassium rosin soap solution containing the desired amount of starch xanthate and sufficient sodium nitrite to crosslink the starch xanthate to starch xanthide. The mixture is then Waring blended for 5 min, after which the resulting emulsion is placed in a resin kettle and the hexane is removed by evaporation at room temperature and reduced pressure. After solvent removal is completed, the EPDM latex/starch xanthate mixture is then coprecipitated through the rapid addition of a 10% sulfuric acid solution to pH 3.0. The finely divided starch xanthide/EPDM coprecipitate is washed once in distilled water and thrice with absolute ethanol before it is vacuum oven dried for 16 hr at 65°C.

Experimental starch xanthide loading levels were 5, 10, 20, 30, and 40 phr. At the higher starch xanthide loadings of 20 to 40 phr, it was found that the organic solvent could be removed either before or after coprecipitation by acid addition; but when the starch xanthide loading

levels were below 20 phr, solvent removal prior to coprecipitation yielded the more acceptable product. It is also possible to remove the solvent by steam stripping of the EPDM in hexane/starch xanthate in water emulsion. The steam is applied only intermittently both to control foaming and to prevent overheating and consequent decomposition of the starch xanthate which even decomposes, though gradually, at room temperature.

Vulcanizates were prepared from several of the starch xanthide/EPDM powdered elastomers according to a cure recipe given in the *Vanderbilt Rubber Handbook*.⁶ A 5-phr starch xanthide/EPDM powdered rubber was mill blended with 50 phr of an HAF Black (N-339) and cured. A 40-phr starch xanthide/EPDM powdered elastomer was cured without any additional reinforcing agents. The physical properties of these vulcanizates were determined in accordance with ASTM procedure D-412.

RESULTS AND DISCUSSION

A hexane solution of EPDM can be emulsified with aqueous starch xanthate by employing a combination of hexane-soluble and water-soluble emulsifying agents. This approach has been successfully used in the development of latex paints.⁷ However, unlike the instances using paints where all nonionic emulsifying agents can be utilized to produce quite stable latices after the organic solvent is removed by vacuum distillation, the starch xanthide-rubber latex coprecipitation procedure requires a latex that can be destabilized by acidification. In the system described herein, it appears that the suspended EPDM polymer particles tend to precipitate before the starch xanthide. This conclusion is based on several initial trials in which the acid addition was done dropwise and the resulting products consisted of a viscous mass of EPDM and rice-shaped particles of starch xanthide which were easily separated manually from EPDM mass. Rapid addition of the acid avoids this problem. The resulting product regardless of starch xanthide loading level is a finely divided starch xanthide/EPDM coprecipitate.

The starch xanthide/EPDM powdered elastomers prepared by the modified coprecipitation procedure had particle sizes in the range of about 1 to 4 mm. At a 5-phr starch xanthide loading level, 65% of the particles passed the 8-mesh size screen. At a 40 phr starch xanthide loading level, 70% of the particles passed the 12-mesh size screen.

The physical properties of the vulcanizates are given in Table I. The ultimate tensile strength, 300% modulus, and per cent elongation of the 5-phr starch xanthide/EPDM powdered rubber compounded with 50 phr HAF black were found to be comparable to values which would be expected had the test vulcanizates been prepared from slab rubber.

The tensile properties of the 40-phr starch xanthide-reinforced EPDM vulcanizate are inferior to the properties shown by a carbon black-reinforced material, but no effort was made to optimize the reinforcement effects of the starch xanthide.

Starch and starch xanthide are both susceptible to swelling in the presence of water. Atmospheric water has little effect either on the powdered rubber properties or on vulcanizate characteristics. If the starch xanthide is to be used only as a partitioning agent to produce

TABLE I
Physical Properties of SX/EPDM^a Vulcanizates

Sample identification	Ultimate tensile strength, psi	300% Modulus, psi	Elongation, %
5 phr SX/EPDM compounded with 50 phr HAF black (from powder)	2800	1230	590
40 phr SX/EPDM, no black (from powder)	1600	1400	400
50 phr HAF black/EPDM (from slab)	2800	1250	425

^a SX/EPDM = Starch xanthide/ethylene-propylene terpolymer.

powdered rubber at low phr loading levels, the effect of water on subsequent vulcanizate properties is negligible. If the starch xanthide is also to be used as a reinforcing filler at high loading levels, immersion in water does have a deleterious effect on both modulus and ultimate tensile strength. This problem of water sensitivity of starch xanthide-reinforced elastomers can be readily overcome by several methods as described by Bagley and Dennenberg,¹⁰ Dennenberg and Bagley,¹¹ and Buchanan et al.¹²

CONCLUSIONS

The advantages of processing powdered elastomers as opposed to baled elastomers have been shown by Woods⁸ and Abbott.⁹ Preparation of powdered EPDM rubbers from a hexane solution by the starch xanthide coprecipitation procedure shows promise for starch xanthide levels from 40 phr down to a low level of 5 phr. A comparison of the tensile properties of EPDM slab rubber compounded with a highly reinforcing carbon black and a 5-phr starch xanthide EPDM powdered rubber compounded similarly shows no significant difference in physical properties. At the higher (40 phr) starch xanthide loading levels, appreciable reinforcement is achieved without addition of conventional reinforcing agents.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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