

# Modified Wheat Flour–Natural Rubber Blends. II

ARUN K. HOTA, *Materials Science Centre*, and MRINAL M. MAITI\* *Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India*

## Synopsis

Effect of cyanoethylation of starch on the properties of starch xanthide–NR vulcanizates has been studied. Significant improvements in compounding, tensile modulus, tensile strength, and retention of wet strength of the vulcanizates have been recorded. Equilibrium swelling of vulcanizates by water is also greatly suppressed. The role of cyanoethylation of starch in imparting such specific effects has been analyzed in the light of the polarity of the cyanoethyl group and its effect in lowering the critical yield stress of the modified starch for efficient dispersive mixing in NR matrix.

## INTRODUCTION

In recent years, efforts have been made to make use of starch as a filler for rubber<sup>1–9</sup>, which after suitable chemical modification, e.g., by forming starch xanthide or xanthate salts and adopting suitable method of incorporation into rubber matrix, e.g., by coprecipitating with rubber lattices, has been found to offer good strength properties to the vulcanizates and exhibit accelerating activity for sulfur vulcanization when incorporated as xanthide or xanthate salts.

So far, detailed studies are confined to starch–SBR and starch–NBR systems only. Only limited information<sup>1,2</sup> is available on the starch–NR system. Starch xanthide/xanthates reportedly offer relatively poor reinforcement in NR as compared to SBR or NBR systems. Our objective, however, was to study the starch–NR system considering that both the components are important agricultural products and are biodegradable. Also, better reinforcement may be expected to be obtained by increasing the starch–NR interactions by suitable chemical modification and/or by decreasing the starch particle size in the NR-filled stocks. With these ends in view, we have resorted to cyanoethylation of starch xanthate. The cyanoethyl group incorporated into starch is expected to act as an internal plasticizer within starch, which may enhance the disintegration of starch particles during milling. Smaller reinforcing starch particles are the expected result. Also, expected is a better adhesion of NR with cyanoethylated starch xanthide. Further, cyanoethylation of starch may offer certain other advantages. The reported drawbacks like poor wet strength and dimensional stability, higher susceptibility to microorganisms and acids of starch xanthide/xanthate–

\*To whom all correspondence should be addressed.

elastomer system<sup>10-13</sup> are expected to be overcome by cyanoethylation of starch xanthide, since cyanoethylation of cellulose is known to offer high resistance to microbial degradation, increased hydrophobicity, and enhanced resistance to degradation by heat and acids.<sup>14,15</sup> Additionally, this method of modifying starch has the unique advantage that both xanthation and cyanoethylation can be carried out simultaneously and easily using gelatinized starch in alkaline medium.

In this communication, we report the processability, cure characteristics, and vulcanizate properties as functions of degree of xanthation and cyanoethylation at constant starch loading (unmodified basis) of cyanoethylated starch xanthide-NR compounds.

## EXPERIMENTAL

### Materials

Stabilized natural rubber (NR) latex containing 60% total solids supplied by Indian Rubber Board, Kottayam, was used. Wheat flour (~80% starch content) was used as purchased from domestic processors. Sodium hydroxide (NaOH), carbon disulfide (CS<sub>2</sub>), acrylonitrile (AN), sodium nitrite (NaNO<sub>2</sub>), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were of analytical grade.

### Preparation of Cyanoethylated Starch Xanthide-NR Master Batches and Analysis of the Products

An aqueous alkaline wheat flour dispersion was subjected to xanthation followed by cyanoethylation, using standard procedures.<sup>5,14,15</sup> The cyanoethylated starch xanthate solution was mixed with NR latex and coprecipitated by acidifying the mixture under oxidizing conditions. The product was analyzed with respect to degree of xanthation/cyanoethylation of starch by determining the sulfur and nitrogen content of the products. The details of the experimental conditions for the preparation of the master batches and analysis of the products have been reported elsewhere<sup>16</sup> by the authors.

### Master Batch Formulations

Master batches have been prepared at a constant flour loading of 100 phr on a dry and an unmodified basis. Accurate level of starch loading was monitored from the results of starch recovery in some blank xanthation-cyanoethylation without NR latex, and confirmed from the N and S contents of both the master batches and the base NR obtained from latex. Various master batches of NR-cyanoethylated starch xanthide (designated as NCX) that have been tested in this investigation are listed in Table I. The master batches differed in the degree of substitution of the starch hydroxyl groups by xanthate (DS xanthation) and cyanoethyl (DS cyanoethylation) groups.

### Mix Formulation

Modified starch-filled NR compounds tested in the investigation are represented by a general recipe as given in Table II. The stocks have been numbered in correspondence to the number designation of the base master batch, NCX.

TABLE I  
DS Xanthation and DS Cyanoethylation of Starch and  
Percent Starch Recovery in Various Master Batches

Designation of the master batch	DS xanthation ( <i>X</i> ) per mol of AGU <sup>a</sup>	DS cyanoethylation ( <i>C</i> ) per mol of AGU <sup>a</sup>	Starch recovery (%)
NCX <sub>1</sub>	0.21	0	95.8
2	0.17	0.42	94.75
3	0.12	0.64	94.30
4	0.09	0.86	94.10
5	0.05	1.09	93.08
6	0.28	0	96.65
7	0.24	0.36	96.15
8	0.19	0.47	95.20
9	0.16	0.62	94.64
10	0.07	0.78	93.55
11	0.39	0	97.05
12	0.34	0.30	96.86
13	0.26	0.41	96.20
14	0.20	0.49	95.62
15	0.11	0.69	94.03

<sup>a</sup>AGU = anhydro glucose unit of starch.

TABLE II  
General Recipe<sup>a</sup> of the Modified Starch Filled NR Compounds

Ingredients	Parts by weight
Natural rubber (NR)	100
Modified starch (dry and unmodified basis)	40 <sup>b</sup>
Zinc oxide	5.0
Stearic acid	2.0
Sulfur	2.5
Benzothiazyl disulfide	1.0

<sup>a</sup>ASTM D15-66T (1968 f), 2A.

<sup>b</sup>The actual weight of the modified starch will be greater than 40 g by an amount dependent on the degree of substitution (DS) of the modified starch.

### Compounding

Dry master batches in the form of crumbs were subjected to milling on a laboratory two-roll mill (12 × 6 in.) for a maximum period of 30 min to effect phase inversion and homogenization until a smooth continuous band was obtained. An additional required amount of NR was then added and milled together for another 5 min for a homogeneous dispersion. Other ingredients were then added in prescribed sequence, and compounding was completed in a total time of 45 min.

### Cure Characterization

Curing of the compounds was followed on a Monsanto oscillating disc rheometer, R-100, at 140°C and at ±3°arc. Cure parameters of the compounds were determined from the respective rheographs.

### **Vulcanization**

Vulcanization of the compounds were effected in a hydraulic press (Carver laboratory press) at 140°C and for optimum time as ascertained from the individual rheograph of the compounds.

### **Physical Testing (Dry and Wet Conditions)**

Tensile testings of the vulcanizates, both dry and wet, were performed on an Instron tensile tester at room temperature and at a speed of 50 cm/min. Indentation hardness was measured in the IRHD scale.

### **Swelling Tests**

Equilibrium swelling in both water and benzene were measured after immersing the test specimens in those media for 7 days at room temperature (30°C).

## **RESULTS AND DISCUSSION**

### **Physical Appearance of the Vulcanizates**

All the vulcanizates were light brown to yellowish brown, differing in intensity and hue depending on the levels of xanthation and cyanoethylation of starch. Opacity or transparency of the vulcanizates also depended on the DS xanthation and cyanoethylation. In general, the vulcanizates with zero cyanoethylation are opaque. Transparency improved as the xanthation level was reduced or the degree of cyanoethylation was increased or both.

### **Milling Characteristics of the Master Batches**

Milling of master batches became progressively difficult with the increase in the xanthation level or decrease in the cyanoethyl level of starch. Table III summarizes the effect of xanthation and cyanoethylation levels on the minimum milling time required for the dry master batches to form a smooth continuous band on the mixing rolls. While milling time increased with the increase in the DS xanthation (stocks 1, 6, and 11), increase in cyanoethylation levels decreased the milling time considerably. It is also to be noted that milling was least difficult with stock 5 and most with stock 11. Clearly, xanthation (in the form of xanthide) induces resistance, while cyanoethylation facilitates the mixing.

The results deserve evaluation in the light of the existing theories of dispersive mixing. Initially, the dry NR-starch master batches were obtained as hard crumbs in which the modified starch constituted the matrix with NR as the dispersed phase. On milling, the starch matrix underwent fragmentation to particles of smaller dimension. The fragmentation takes place when the matrix experiences a minimum or a critical shear stress. As milling continues, the starch particles gradually decrease in dimension and at a certain stage a phase inversion takes place when NR constitutes the matrix resin.

It appears that higher degree of xanthation makes the particulate dispersion of starch more difficult because of increased compactness of the more

TABLE III  
Minimum Milling Time<sup>a</sup> at Various DS Xanthation/Cyanoethylation Levels

Stocks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
X/C <sup>a</sup>	0.21/0	0.17/0.42	0.12/0.64	0.09/0.86	0.05/1.09	0.28/0	0.24/0.36	0.19/0.47	0.16/0.62	0.07/0.78	0.39/0	0.34/0.30	0.26/0.41	0.20/0.49	0.11/0.69
Minimum milling time (min)	24	22	20	20	18	25	23	21	21	20	28	25	23	21	21

<sup>a</sup> Cold mixing: 12 × 6 in. rolls: speed ratio = 1.20. X = DS xanthation and C = DS cyanoethylation.

crosslinked starch solid. As a result, the critical yield stress required for complete phase inversion in the initial milling stage and in the subsequent dispersive mixing of the starch filler increases. The effects of an increased critical shear stress are an increase in milling time to arrive at a smooth and homogeneous band of the mix, and an increase in the average particle size of the dispersed starch.

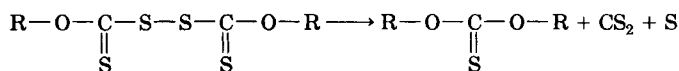
In cyanoethylated xanthated starch, the pendent cyanoethyl group, because of its bulk, reduces the compactness of the starch solid. It acts more like an internal lubricant, and thus greatly decreases the critical yield stress. This results in an easy disintegration and finer dimension of the starch particles.

### Cure Characteristics

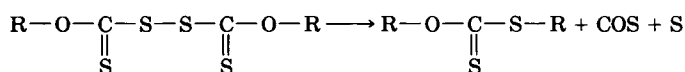
#### *Effect of Xanthation*

As evident from the rheometric data (Table IV), with increasing values of  $X$  (stocks 1, 6, and 11), initial and minimum rheometer torque decrease. The initial torque of the compounds provides a qualitative estimate of the interfacial interaction between the rubber phase and the starch xanthide filler particle. The greater the extent of interaction, the greater is the initial torque. Extent of such interaction depends on two factors. First is the total interfacial area which is larger with finer filler particles at the same loading. Second is the specific strength of interaction which is determined by the chemical identity of the filler surface. Referring to the data in Table III, it may be argued that the first factor is predominantly responsible for the observed trend in initial and minimum rheometer torque. In other words, it is the higher stiffness, and hence, higher critical shear stress required for fragmentation of the more xanthated starch, which is responsible for bigger particle size and wide size distribution of starch xanthide. This leads to the lowering of total area for interphase interaction and a reduction in the initial and minimum torques. Since polarity of starch xanthide increases with increasing degree of substitution which results in a reduced specific strength of interaction, both factors appear to have contributed to the decrease of the initial and minimum torques.

The observed decrease in scorch time, and increase in maximum torque, extent of cure, and cure rate index with increasing values of  $X$  are consistent with the reported coaccelerating activity of starch xanthide.<sup>1-9</sup> Increased crosslinking of the NR is reportedly caused by the release of elemental sulfur from the decomposition of xanthide groups:<sup>17</sup>



or



where R = starch moiety. Decrease in maximum cure time/optimum cure time and reversion time with the increase in the xanthation level may also be explained in the same light.

TABLE IV  
Cure Characteristics<sup>a</sup> of the Starch-NR Master Batches

Stock	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
X/C	0.21/0	0.17/0.42	0.12/0.64	0.09/0.86	0.05/1.09	0.28/0	0.24/0.36	0.19/0.47	0.16/0.62	0.07/0.78	0.39/0	0.34/0.30	0.26/0.41	0.20/0.49	0.11/0.69
Initial rheometer torque (dN m)	4.5	6.5	7.0	7.0	8.5	4.0	5.0	6.0	6.5	8.0	3.0	4.5	5.0	5.5	7.0
Minimum rheometer torque (dN m)	3.0	4.5	5.0	5.0	6.0	3.0	3.0	4.0	5.0	5.5	2.0	4.0	3.0	4.0	5.0
Maximum rheometer torque (dN m)	65.0	72.5	73.0	76.0	72.0	70.0	74.5	75.0	76.5	73.0	74.0	84.5	85.0	75.0	73.0
Extent of cure (dN m)	62.0	68.0	68.0	71.0	66.0	67.0	71.5	71.0	71.5	67.5	72.0	81.5	82.0	71.0	68.0
Time to maximum cure (min)	28.0	32.5	42.0	45.5	68.0	22.0	26.5	31.5	40.0	46.0	19.0	20.5	25.0	31.0	42.0
Scorch time (min)	4.0	5.0	5.0	5.5	6.0	4.0	4.0	5.0	5.0	6.0	3.0	3.5	4.0	5.0	5.0
Time to 90% cure (min)	20.0	21.5	22.0	30.0	32.5	16.0	18.5	22.0	27.5	31.0	14.5	16.0	18.0	21.0	22.0
Reversion time (min)	40.0	45.0	47.5	58.0	80.0	36.5	38.0	45.0	52.0	65.0	32.0	34.0	35.0	46.0	48.0
Cure rate (min <sup>-1</sup> )	6.25	6.1	5.9	4.0	3.7	8.3	7.4	5.9	4.5	4.0	8.7	8.0	7.1	6.25	5.9

<sup>a</sup> Monsanto R-100 rheometer,  $\pm 3^\circ$  arc, 140°C.

*Effect of Cyanoethylation*

Although the exclusive effect of cyanoethylation level of starch xanthide on cure characteristics cannot be established from the data of the Table IV, some information can be obtained by comparing the curing behavior of the individual pairs of stocks, 3 and 15, 2 and 9, 1 and 14, and 6 and 13, at almost comparable values of  $X$  but with varying values of  $C$ . In each of the pairs of stocks, an increase in cyanoethylation level is manifested in the increase in initial torque, minimum torque, maximum torque, and extent of cure. Scorch time registers only marginal increase, but cure rate index is lower to some extent. However, there are perceptible increases in maximum cure time/optimum cure time and time to reversion. These observations suggest that cyanoethylation of starch retards the vulcanization process to some extent, but not very significantly.

The increase in the initial and minimum torque with increase in cyanoethylation level is attributable to the reduced particle size and enhanced rubber-filler interaction of the more cyanoethylated starch. Sharp increase in both the maximum torque and the extent of cure is also attributable to the above two factors. Such an inference is drawn on the basis of the facts that cyanoethylation of starch apparently renders the vulcanization process slower, and has little effect on the equilibrium swelling of the NR matrix in benzene (discussed in a subsequent section).

**Mechanical Properties of Vulcanizates***Effect of Xanthation*

With increasing xanthation level of starch (stocks 1, 6, and 11) both the modulus at 200% elongation and hardness of the dry vulcanizates increase, while the breaking stress and the elongation at break decrease. The effects are consistent with an increase in crosslink density as would be expected at a higher level of xanthation.

Decrease in modulus and tensile strength of the wet vulcanizates is possibly due to an increased stress concentration at the starch rubber interface due to volume expansion of the particulate dispersed starch on being equilibrium swelled in water. Another reason may be the weakening of the NR-starch interfacial interaction due to imbibition of water between the phases. Assuming that the NR matrix as such is only a little swelled by water, the only plausible explanation for an increased elongation of the wet vulcanizates is the reduced wet strength of the starch solid. In this case, the imbibed water increases the free volume and decreases the cohesive energy of the solid starch, which result in a drastic reduction of its mechanical strength. In fact, the xanthated starch on oxidative coagulation is recovered wet as a rubbery (i.e., of low mechanical strength) mass during its preparation.

*Effect of Cyanoethylation*

Taking into consideration the individual pairs of stocks, 3 and 15, 2 and 9, 1 and 14, and 6 and 13, at comparable levels of xanthation ( $X = 0.12$  and  $0.11$ ,  $0.17$  and  $0.16$ ,  $0.21$  and  $0.20$ , and  $0.28$  and  $0.26$ , respectively), with varying



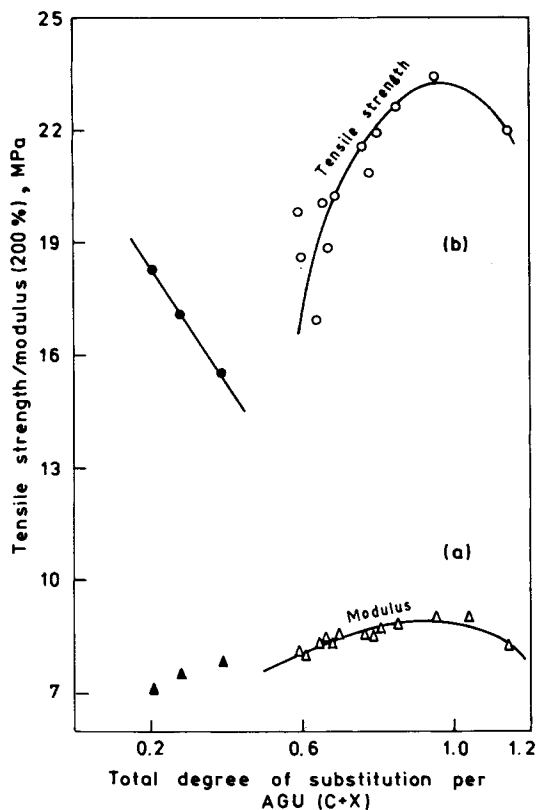


Fig. 1. Variation of tensile strength (○) and modulus (200%) (Δ) with total degree of substitution,  $(C + X)$  per AGU. Solid marks correspond to zero cyanoethylation.

levels of cyanoethylation ( $C = 0.64$  and  $0.69$ ,  $0.42$  and  $0.62$ ,  $0.0$  and  $0.49$  and  $0.0$  and  $0.41$ , respectively), we see that, with increasing values of  $C$ , tensile strength and modulus increase markedly. Elongation at break, however, suffers only a marginal increase with increasing cyanoethylation.

Thus, the effects of cyanoethylation of starch xanthide are those of true reinforcement. As discussed earlier in the context of cure characteristics of the NR-cyanoethylated starch xanthide compounds, the marked improvements in the modulus and tensile strength are attributable to finer particle dimension of the cyanoethylated starch xanthide or an enhanced interfacial interaction with NR or to both.

Modulus of the vulcanizates is increased with increase in both the xanthation and cyanoethylation levels, and it is worth while to see the resultant effect of total degree of substitution ( $C + X$ ) on starch. It is seen from Figure 1(a) that modulus increases monotonically with increase in  $(C + X)$ , and attains a maximum value at  $(C + X) \approx 0.95$ , beyond which it declines. At zero cyanoethylation (stocks 1, 6, and 11), however, the modulus values are not accommodated in this monotonic trend. Figure 1(b) shows a very similar interdependence between tensile strength and total degree of substitution with a maximum tensile strength at the same value of  $(C + X) \approx 0.95$ . It is to be noted that at the only available higher value of  $(C + X)$ , i.e.,  $1.14$ ,  $X$  is

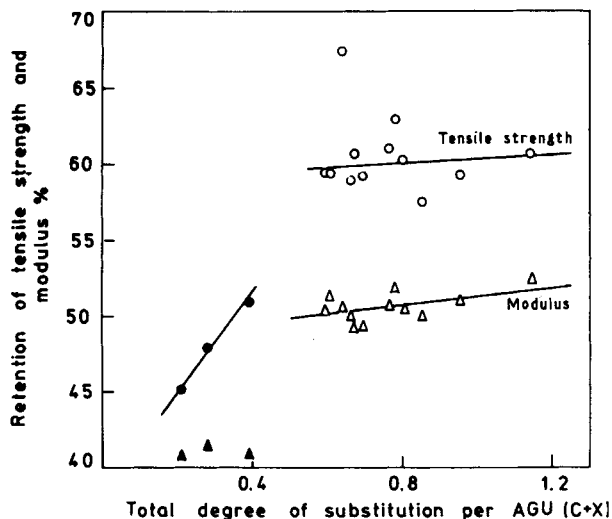


Fig. 2. Variation of percent retention of tensile strength ( $\circ$ ) and modulus (200%) ( $\Delta$ ) after 70 h water immersion with total degree of substitution,  $(C + X)$  per AGU. Solid marks correspond to zero cyanoethylation.

only 0.05. Such a low value of  $X$  may be responsible for the observed decline in modulus and tensile strength. The results lead to the inference that maximum reinforcement with respect to modulus and tensile strength can be attained at a total degree of substitution of around 0.95 and there exists a critical minimum xanthation level of around 0.09, which is necessary to impart sufficient compactness or mechanical strength of the particulates dispersed starch.

With the incorporation of cyanoethyl groups, the percent retention of tensile strength and modulus of wet vulcanizates are greatly improved. For both the properties, the changes are more pronounced at higher difference of cyanoethylation level. Figure 2 depicts the variation of percent retention of wet strength and modulus with total degree of substitution on starch. Clearly, the retention is higher in the case of tensile strength. The trends in the retention of these properties of the wet vulcanizates are, however, essentially the same. Between  $(C + X) = 0.6$  and 1.15, the retention of both tensile strength and modulus increases very slowly with cyanoethylation level. It appears that the same factors are responsible for enhanced retention of tensile strength and modulus.

### Swelling in Benzene ( $S_B$ )

Figure 3 illustrates the variation of benzene uptake per 100 g of rubber as function of  $X$ . A distinct linear correlation exists between  $S_B$  and  $X$ , the former decreasing with increase of the latter. This is quite expected in consideration of the accelerating activity of the starch xanthide groups. With increasing level of xanthation, the total accelerator content and the available sulfur from xanthide in the compounds increase; so does the efficiency of vulcanization or the crosslink density, which correspond to lower equilibrium swelling.

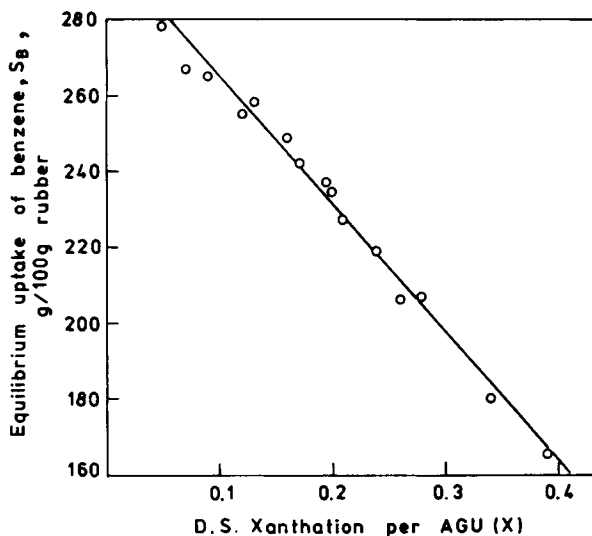


Fig. 3. Variation of equilibrium uptake of benzene,  $S_B$ , with DS xanthation  $X$  per AGU.

Figure 3 also leads to a general conclusion that level of xanthation,  $X$ , in NR-starch compounds predominantly or primarily controls the equilibrium swelling behavior of the vulcanizates.

Although no clear interdependence between  $S_B$  and  $C$  could be established, some information can be obtained from a critical analysis of the swelling data in Table VI. Referring to the swelling behavior of the individual pairs of stocks, 3 and 15, 2 and 9, 1 and 8, and 6 and 13, at almost comparable levels of xanthation but with varying levels of cyanoethylation, equilibrium swelling increases or remains virtually unchanged with increasing level of cyanoethylation. The effect is more pronounced at a lower level of xanthation and at a higher difference in the level of cyanoethylation between two compounds at comparable xanthation levels.

Effect of cyanoethylation level on equilibrium swelling in benzene, though very much subdued, deserves further consideration with regard to the role played by the former. Two possibilities may be explored. First, the cyanoethyl group itself may deter the efficiency of vulcanization to some extent and, thus, decreasing the crosslink density and increasing the equilibrium swelling. Second, the modified starch filler in the vulcanizates may itself absorb some benzene which is contributed by a much less polarity of the cyanoethyl group and/or less compact starch solid phase (increased free volume) due to the presence of bulky cyanoethyl pendent groups. In consideration of the data on scorch time, cure rate index, initial rheometric torque, and the minimum rheometric torque at 140°C, and the deliberations made in the preceding sections, both the above two possibilities appear to be responsible for enhanced benzene uptake on increasing the cyanoethylation level. However, the effects are only marginal and can be neglected.

### Swelling in Water

Similar to the benzene uptake behavior of the rubber component, the water absorption of the starch component decreases with increase in the xanthation

TABLE V  
Physical Properties of Vulcanizates

Stock no.	DS xanthation X	DS Cyanoethylation C	Hardness IRHD	Tensile strength (MPa)	Elongation at break (%)	Modulus (200%) (MPa)	After 70 h water immersion		
							Tensile strength (MPa)	Elongation at break (%)	Modulus <sup>a</sup> (200%) (MPa)
1	0.21	0	60	18.3	520	7.1	8.3 (45.4)	540	2.9 (40.9)
2	0.17	0.42	62	19.8	520	8.1	11.8 (59.6)	530	4.1 (50.6)
3	0.12	0.64	63	21.5	530	8.5	13.1 (60.9)	540	4.3 (50.6)
4	0.09	0.86	63	23.4	540	9.0	13.9 (59.4)	520	4.6 (52.1)
5	0.05	1.09	62	21.9	560	8.2	13.3 (60.7)	550	4.3 (52.4)
6	0.28	0	62	17.1	490	7.5	8.2 (48.0)	520	3.1 (41.3)
7	0.24	0.36	63	18.6	500	8.0	11.1 (59.7)	520	4.1 (51.3)
8	0.19	0.47	63	20.0	510	8.4	11.8 (59.0)	520	4.2 (50.0)
9	0.16	0.62	63	20.8	520	8.5	13.1 (63.0)	510	4.4 (51.8)
10	0.07	0.78	63	22.6	550	8.8	13.0 (57.5)	530	4.4 (50.0)
11	0.39	0	64	15.5	440	7.8	7.9 (51.0)	500	3.2 (41.1)
12	0.34	0.30	65	16.9	450	8.3	11.4 (47.5)	460	4.2 (50.6)
13	0.26	0.41	65	18.8	480	8.3	11.4 (60.6)	510	4.1 (49.4)
14	0.20	0.49	63	20.2	500	8.5	12.0 (59.4)	520	4.2 (49.4)
15	0.11	0.69	63	21.9	530	8.7	13.2 (60.3)	500	4.4 (50.6)

<sup>a</sup> Figures in parentheses denote % retention of dry strength.

TABLE VI  
Swelling Behavior of Starch-NR Master Batches

Stock no.	DS xanthation X	DS cyanoethylation C	Water <sup>a</sup> swelling (equilibrium), swelled $\frac{\text{wt}}{\text{dry wt}}$	Water uptake per 100 g starch (unmodified)	Benzene <sup>a</sup> swelling (equilibrium), swelled $\frac{\text{wt}}{\text{dry wt}}$	Benzene uptake per 100 g rubber
1	0.21	0	1.18	69.50	2.47	277
2	0.17	0.42	1.10	39.80	2.52	242
3	0.12	0.64	1.08	32.23	2.58	255
4	0.09	0.86	1.08	32.69	2.62	265
5	0.05	1.09	1.06	24.86	2.68	278
6	0.28	0	1.14	54.51	2.33	207
7	0.24	0.36	1.09	35.93	2.37	219
8	0.19	0.47	1.09	36.05	2.48	237
9	0.16	0.62	1.08	32.32	2.54	249
10	0.07	0.78	1.10	40.51	2.65	267
11	0.39	0	1.07	27.62	2.05	166
12	0.34	0.30	1.06	24.12	2.12	180
13	0.26	0.41	1.07	28.13	2.28	206
14	0.20	0.49	1.07	28.12	2.46	235
15	0.11	0.69	1.08	32.32	2.60	258

<sup>a</sup>Temperature 30°C.

level. Although the data in Table VI do not explicitly spell out this trend, the data at zero cyanoethylation level (Fig. 4) clearly maintains a linear correlation between the equilibrium water absorption by starch and its xanthation level  $X$ . At moderate to high levels of cyanoethylation, the data bear an impression, though not very distinct, of a decrease in water absorption with increase in xanthation. The decrement is, however, not so drastic as observed at zero cyanoethylation levels. It appears that both the xanthide and the cyanoethyl groups conjointly suppress the water absorption of the modified starch, and with the introduction of cyanoethyl group, the effect of xanthation become less and less pronounced.

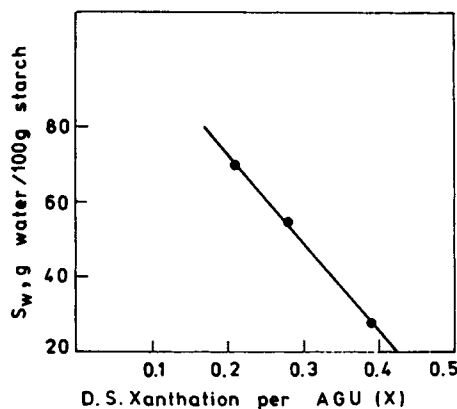


Fig. 4. Variation of equilibrium uptake of water,  $S_w$ , with DS xanthation  $X$  per AGU.

Effect of cyanoethylation level alone on equilibrium water absorption can be scanned out at any fixed level of xanthation. An analysis of the behaviors of the appropriate pairs of vulcanizates (i.e., 3 and 15, 2 and 9, 1 and 14, and 6 and 13) at comparable xanthation levels shows that equilibrium absorption of water by the vulcanizates sharply decreases with increase in cyanoethylation level. Role of cyanoethyl group in decreasing the water absorption may be explained in terms of its much lower polarity compared to the starch hydroxyl groups. This property of the cyanoethyl group has been advantageously used in reducing the moisture absorption and improving the crease resistance of cotton fabrics by partial cyanoethylation of the cotton cellulose.<sup>14, 15</sup>

### CONCLUSION

The present investigation shows that many of the reported drawbacks of starch-filled rubber vulcanizates can be overcome by simultaneous cyanoethylation-xanthation of starch. Specifically, the ease of milling could be substantially increased and the milling time greatly shortened by cyanoethylation. In regard to the cure characteristics of the NR-starch compounds, a great improvement in the extent of cure can be achieved. Scorch times and reversion times are, however, marginally improved, and the cure rate index is lowered to some extent. An appreciable improvement in tensile properties, particularly the modulus (200%) and tensile strength, without any significant change in maximum elongation, can be obtained with cyanoethylation of starch. The most notable effects of cyanoethylation are, however, a significant reduction in equilibrium swelling of the vulcanizates by water and an increased retention of the wet-strength properties.

The authors wish to thank the CSIR for its financial assistance in the form of a Junior Research Fellowship to A. K. H. for pursuing this study. Testing facilities provided by IEL are also gratefully acknowledged.

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Received July 13, 1987

Accepted October 24, 1987