Properties of Hycar 1072—a Carboxylic Nitrile Rubber

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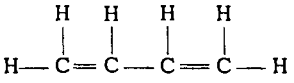
Butadiene-acrylonitrile copolymers have found increasing application because of the many unique properties built into the polymer chain by the nitrile group. These properties include oil and solvent resistance, abrasion resistance, heat resistance, low gas permeability, compatibility with phenolic resins, and compatibility with poly(vinyl chloride) resins. Through the use of carboxylic acid-bearing monomers with butadiene and acrylonitrile an active carboxyl group has now been added to the basic nitrile rubber polymer (*3*) to produce a commercial polymer with new and unusual properties (*1*). This paper presents some of the reactions and properties that have been demonstrated by Hycar 1072, a carboxylic nitrile polymer.

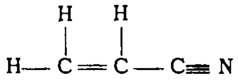
POLYMER STRUCTURE

The carboxylic polymer discussed here is basically a nitrile polymer to which carboxyl groups have been added during polymerization. The basic building units for this type of polymer are butadiene, acrylonitrile, and one or more unsaturated acids.



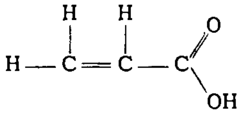
$\mathrm{H-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-H}$

Butadiene

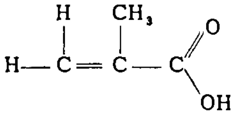


$\mathrm{H-\overset{H}{C}=\overset{H}{C}-C\equiv N}$

Acrylonitrile



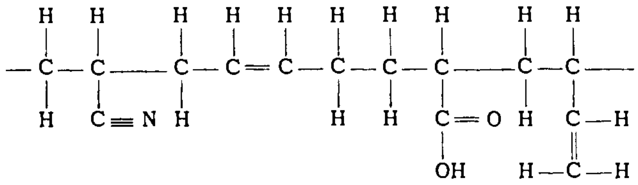
Acrylic acid



Methacrylic acid

The polymerization of these monomers produces a polymer chain containing the carboxyl group distributed along the chain in addition to the nitrile group distribution associated with standard nitrile polymers.

Representation of a Carboxylic Nitrile Polymer Structure



$\mathrm{-\underset{H}{\overset{H}{C}}-\underset{C\equiv N}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\underset{OH}{C=O}}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\underset{H-C-H}{\overset{\|}{C-H}}}{\overset{H}{C}}-}$

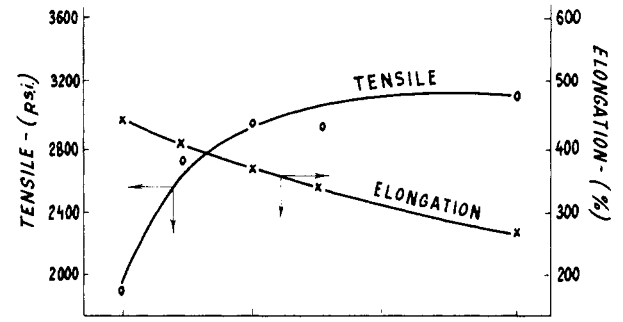
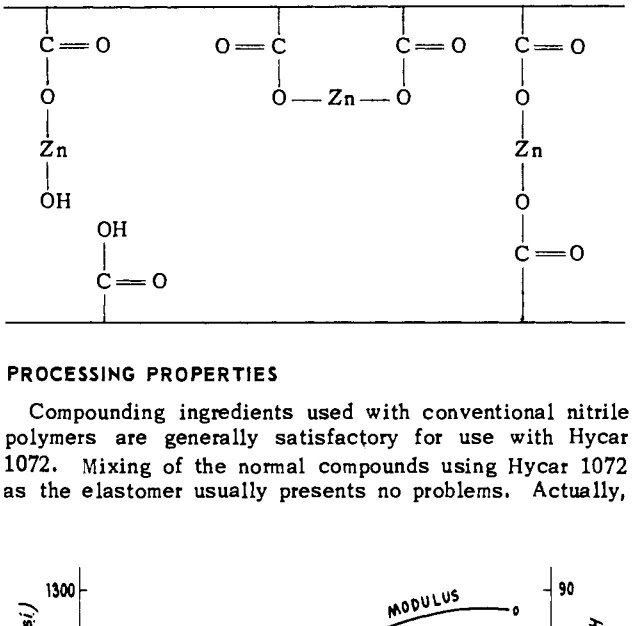


Figure 1. Tensile and elongation changes of the Hycar 1072 vulcanizate resulting from increasing sulfur content in a typical nitrile recipe

This simplified diagram should not be construed as representing the molecular structure of the polymer presented in this study, but used as a guide to the molecular segments which may be present in the polymer and which explain the behavior of the polymer toward several classes of cross-linking agents.

VULCANIZATION MECHANISM

Unsaturated copolymers of the nitrile rubber type are capable of vulcanization with sulfur and related agents because of the presence of the double bond and the effects associated with it. However, the presence of the carboxyl groups in Hycar 1072 provides this polymer with an additional active site for cross-linking reactions which standard nitrile polymers do not enjoy. Vulcanization through the active hydrogen of the carboxyl groups may occur in the presence of polyvalent metal oxides or their salts. Although the bulk of the data obtained has involved the use of zinc oxide, other inorganic compounds such as magnesium oxide, calcium silicate, sodium aluminate, sodium phospho aluminate, and litharge have been found to produce a cross-linking effect on the carboxyl containing polymer. The following possible linkages due to the interaction of the carboxyl groups on the chain and zinc oxide have been postulated (*2*).



PROCESSING PROPERTIES

Compounding ingredients used with conventional nitrile polymers are generally satisfactory for use with Hycar 1072. Mixing of the normal compounds using Hycar 1072 as the elastomer usually presents no problems. Actually,

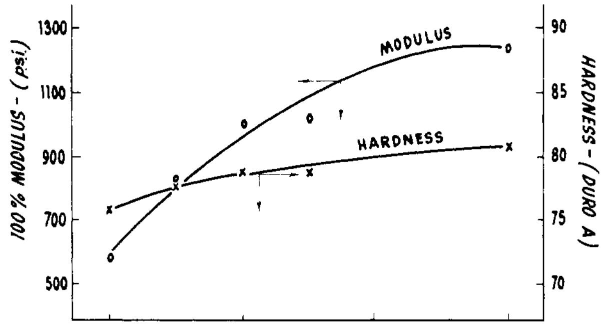


Figure 2. Change in hardness and modulus of the carboxylic vulcanizate related to sulfur content changes from 0 to 3 parts

in most cases, the batch mills better and smoother because of the more plastic nature of the elastomer when warm. As two types of polymer cross-linking reactions occur simultaneously when sulfur and zinc oxide are milled into the carboxyl polymer, the scorch tendency of Hycar 1072 has been checked thoroughly. Laboratory mill-mixed batches of Hycar 1042, a normal nitrile polymer, and Hycar 1072 showed that the Mooney scorch tendency of the carboxylic polymer is greater than the standard nitrile polymer when tetramethylthiuram monosulfide (TMTM) is used as the accelerator. However, the scorch time of the carboxylic TMTM system is still considerably longer than that of the noncarboxylic tetramethylthiuram disulfide (TMTD) system. With a TMTD cure system, both polymers are very nearly equal in Mooney scorch time.

In the case of the 6 x 16 inch laboratory mill batches the zinc oxide was added as the last pigment on the mill. This precaution was taken for the same reason that accelerators are usually added to nitrile polymers late in the mixing cycle—to reduce the possibility of early, unwanted cure. Actually, however, Hycar 1072 batches have been treated with much less regard for the scorch tendency due to the metallic oxide cure. In one case, laboratory Banbury (size 00) mixes were made in which the zinc oxide was added after 2 minutes of mixing, the batches being dropped after a total of 8 minutes of mixing at final internal batch temperatures of 265° to 310°F. No sign of scorch was found on the sheet-off mill nor was there a sign of scorch on remilling after 2 months of bin aging of the stock. It is recommended, however, that the usual practice of adding accelerators on the sheet-off mill be followed and that in the case of Hycar 1072 the metallic oxide be added on the mill also.

Sixty-inch mill batches of Hycar 1072 have been made with no observed scorch during milling. In one case the

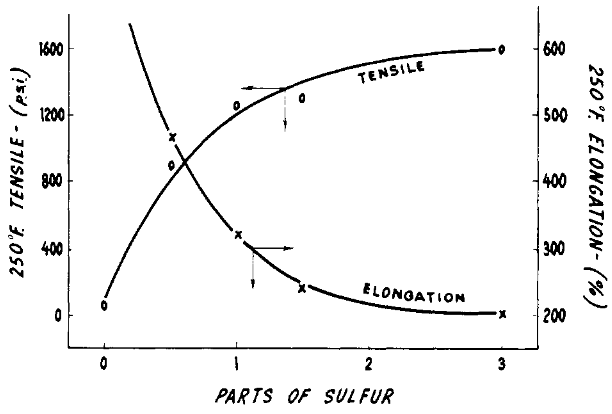


Figure 3. Stress-strain of Hycar 1072 measured at 212°F. related to sulfur content changes

Table I. Sixty-Inch Production Mill Batches

Recipe		
Hycar 1072	100.0	
Zinc oxide	5.0	
Stearic acid	1.0	
FEF black[a]	40.0	
TMTD[b]	3.5	
Zinc oxide addition	Last	First
Mooney scorch at 250°F., small rotor, ASTM D 1077–49T		
Scorch time (Δ 5), min.	16	12
Cure time (Δ 30), min.	25	21½
Garvey die extrusion rating	12½	13½
All cures 30 minutes at 310°F.		
Modulus at 300% elongation, p.s.i.	3080	3020
Ultimate tensile strength, p.s.i.	3340	3410
Ultimate elongation, %	360	390
Hardness (Duro A)	83	81

[a] Philblack A
[b] Methyl Tuads

Table II. Pure Gum Strength of Hycar 1072

Recipe		Hycar 1072 100 Stearic acid 1 Zinc oxide 10 Total 111			Hycar 1042 100 Steraic acid 1 Zinc oxide 5 Sulfur (1) 1.5 TMTM (2) 0.4 Total 107.9 (1) Blackbird (2) Unads	
Minutes cured at 310°F.[a]	15	30	45	15	30	45
Modulus at 300% elongation, p.s.i.	1010	980	960	390	420	430
Ultimate tensile strength, p.s.i.	5100	5480	5320	540	550	520
Ultimate elongation, %	540	540	520	370	370	350
Hardness (Duro A)	71	71	71	53	54	55
Tear, die C, with grain, lb./inch		210			81	
Tested at 250°F.						
Ultimate tensile strength, p.s.i.		130			100	
Ultimate elongation, %		1200			180	
Tear, die C, with grain, lb./inch		30			5	
Compression set, ASTM Method B						
22 hours at 158°F., %			91			10
Lupke rebound, %			44			48
Abrasion resistance, NBS ZZR601a		1830			...	...
Low temperature brittleness, ASTM D 746 pass (°F.)		−95			...	
ASTM oil 1—70 hours at 212°F.						
Ultimate tensile strength, p.s.i.		5280			550	
Ultimate elongation, %		490			350	
Hardness (Duro A)		70			51	
Volume change, %		−0.1			+0.3	

[a] Hycar 1072 compound press cooled.

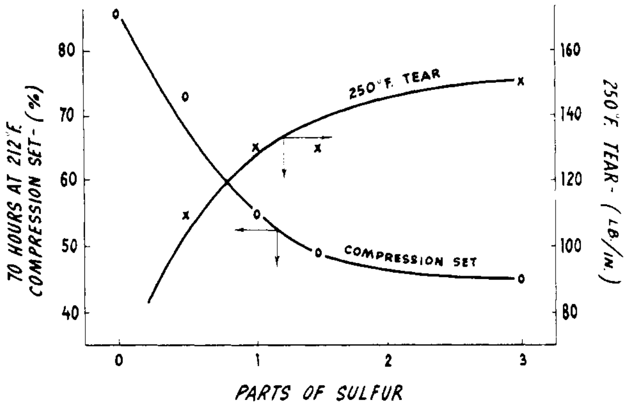


Figure 4. Relationship of tear measured at 250° F. and compression set to increasing sulfur content of a carboxylic nitrile recipe

zinc oxide was added as the last ingredient while in another it was added as the first pigment. The properties obtained from the 60-inch production mill batches are given in Table I.

Scorch time was reduced slightly by the early addition of zinc oxide, but considerable margin still exists in this normally scorchy compound and physical properties and extrusion characteristics were excellent.

In some recipes, Hycar 1072 has shown a tendency to scorch after a number of weeks of bin aging of the stock. This tendency can be reduced and Mooney scorch time increased by the use of increased amounts of stearic acid in the compound. The use of stearic acid provides a cheap, effective antiscorch agent for the metallic ion cross-linking reaction when needed for extreme processing conditions or unusually long room temperature bin aging.

PHYSICAL PROPERTIES OF HYCAR 1072 VULCANIZATES

Gum Strength. Nitrile polymers have one property in common with the most widely used synthetic polymers—a low pure gum tensile strength. The inclusion of carboxyl groups in the nitrile polymer chain has provided a site for a type of cross linking which is capable of developing high gum strengths. The only curing agent required is zinc oxide, although stearic acid may be valuable as a cure regulator. The data in Table II were obtained on a Hycar 1072 pure gum stock.

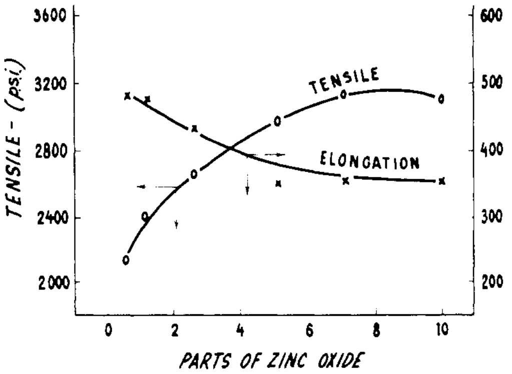


Figure 5. Tensile and elongation changes which occur as zinc oxide content of Hycar 1072 recipe is increased

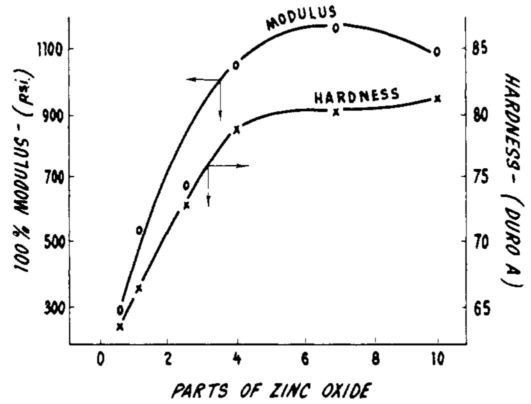


Figure 6. Modulus and hardness of Hycar 1072 vulcanizates related to changing zinc oxide content

The most startling feature is the fact that whereas normal nitrile polymers have a gum tensile strength in the range of 600 p.s.i. and an ultimate elongation of approximately 350%, the carboxylic nitrile polymer gum vulcanizate has a tensile strength of 5480 pounds per square inch and an elongation of 540%. Another unusual feature is the apparent thermoplasticity of the zinc cross link as evidenced by the values of the properties determined at 250° F. and the high compression set. The abrasion resistance is phenomenal; however, some of this apparent abrasion resistance may be due to a tendency to gum up the abrasion wheel. Equally outstanding is the excellent low temperature brittleness. All samples passed the ASTM D 746 test at −95 °F., the lowest temperature at which this particular test could be run in this laboratory.

Table III. Peroxide Cures of Hycar 1072

Recipe						
Hycar 1072	100.0			100.0		
Stearic acid	1.0			1.0		
FEF black	40.0			40.0		
Dicumyl peroxide[a]	1.75			1.75		
Zinc oxide	...			5.0		
Total	142.75			147.75		
Original Properties, all cures at 310°F.						
Minutes cured	15	30	45	15	30	45
Modulus at 100% elongation, p.s.i.	360	255	360	750	1320	1875
Ultimate tensile strength, p.s.i.	2805	2550	2875	3525	4470	4610
Ultimate elongation, %	430	390	400	320	320	250
Hardness (Duro A)	65	65	67	78	85	87
Compression set, ASTM method B 70 hours at 212 °F., %			25			35

[a] Di-cup, Hercules Powder Co.

CARBOXYL CROSS LINKS VS. DOUBLE BOND CROSS LINKS

Because Hycar 1072 contains the unsaturation of normal nitrile polymers and also carboxyl groups, it can be cured by cross links involving the double bonds, by cross links involving the carboxyl groups, or by a combination of the two types of systems. It is difficult to isolate the effect of a cure involving the polymer unsaturation only because the conventional cures depend upon the presence of at least some metallic oxide for good sulfur vulcanization. The presence of the oxide thus obscures the effect due to the sulfur cross link alone by adding cross links through the carboxyl group. The results given in Table III indicate that the use of dicumyl peroxide (*4*) allowed the determination of the physical characteristics of a good Hycar 1072 cure in the complete absence of metallic oxide.

The absence of the metallic oxide cure results in decreased tensile, increased elongation, decreased compression set, and decreased hardness.

In most commercial vulcanizates, however, a combination of a sulfur cure and a zinc oxide cure will ordinarily be present in the carboxyl containing polymer. The relationships which were found to exist as the Hycar 1072 was compounded in an SRF black reinforced recipe with 0.4 part of a TMTM accelerator using varying amounts of sulfur from 0 to 3 parts while holding the zinc oxide level at 5 parts and then varying the zinc oxide from 0.5 to 10 parts while holding the sulfur at 1.5 parts are shown in Figures 1 through 8. Examination of the graphs leads to the conclusion that optimum values of the properties tested should be obtained at a sulfur level of about 1.5 parts and a zinc oxide level of approximately 7 parts. These levels are in such close agreement with the levels of 1.5 parts of sulfur and 5 parts of zinc oxide which are customarily used with nitrile polymers that it has been concluded that conventional nitrile recipes need little or no modification of the cure system to obtain a satisfactory combination metallic oxide-sulfur cure of Hycar 1072. Subsequent investigations reported are based on the premise, therefore, that formulations found to give optimum results with a normal nitrile polymer will also produce satisfactory results with the carboxylic variation.

COMPARISON OF VULCANIZATES OF NITRILE AND CARBOXYLIC NITRILE POLYMERS

As it has been established that the sulfur and zinc oxide concentrations used in many nitrile rubber recipes are very nearly those needed for optimum properties in Hycar 1072, a direct comparison of the carboxylic acid polymer with a normal nitrile polymer using the same basic compound may be made. Such a comparison of the original properties of Hycar 1072 and a normal nitrile counterpart, Hycar 1042, is presented in Figures 9 through 15. The two polymers were compared in a simple recipe.

Polymer	100.0
Zinc oxide	5.0
FEF black	40.0
TMTD	3.5
Stearic acid	1.0

There are many differences between the properties of the carboxylic nitrile and the nitrile vulcanizates when the two are compared in identical recipes. The tensile strength of the carboxylic polymer is higher than that of the normal nitrile polymer and the elongation is lower. The modulus and hardness of the carboxylic polymer are appreciably higher. Tensile strength and elongation are both higher for the Hycar 1072 vulcanizate than the Hycar 1042 vulcanizate when the measurement is made at temperatures of 212° F. or higher. Tear strength of the carboxyl polymer vulcanizate is higher at both room temperature and elevated temperature. Compression set of the carboxylic acid-containing polymer is not so low as that of the standard nitrile polymer. An advantage exists in low temperature brittleness for the carboxyl polymer. The abrasion resistance of the carboxylic acid-containing polymer is many times that of the normal nitrile polymer according to the laboratory abrasion test employed.

Hycar 1072 behaves in a manner similar to normal nitrile polymers in its resistance to oils, fuels, solvents, and hot air. Table IV compares the resistance of Hycar 1072 vulcanizates with Hycar 1042 vulcanizates. The most striking

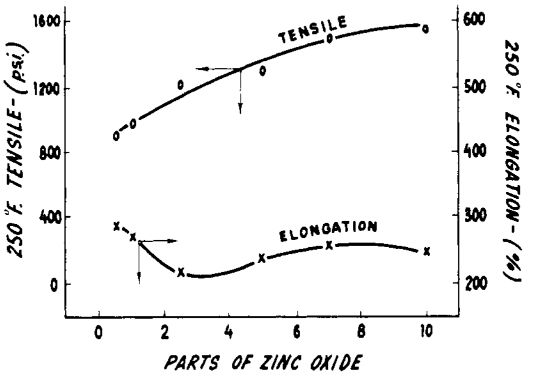


Figure 7. Stress strain measured at 250° F. related to zinc oxide content of carboxylic vulcanizate

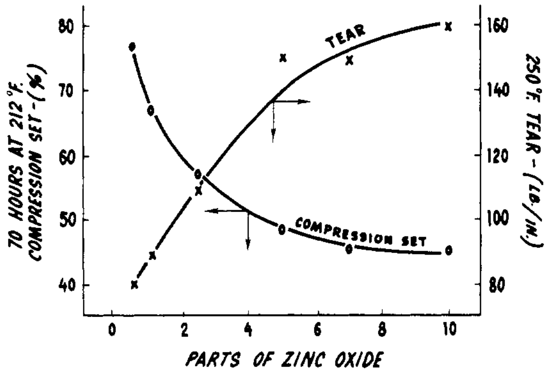


Figure 8. Relationship of hot tear and compression set to zinc oxide content of carboxyl polymer vulcanizate

Table IV. Immersion Properties of Hycar 1072

Recipe	
Polymer	100.0
Zinc oxide	5.0
FEF black	40.0
TMTD	3.5
Stearic acid	1.0

	Original Properties					
Polymer-Hycar	1072			1042		
Minutes cured at 310°F.	15	30	45	15	30	45
Modulus at 300% elongation, p.s.i.	2960	3100	3050	1100	1320	1380
Ultimate tensile strength, p.s.i.	3730	3740	3850	3000	3120	3290
Ultimate elongation, %	400	400	410	660	630	620
Hardness (Duro A)	81	80	80	64	65	65

Properties after immersion, all cures 30 minutes at 310°F.

Fluid	ASTM Oil, 70 × 250° F.				Reference Fuel, 70 × R. T.				Ethylene Glycol 70 × 212° F.		Methanol, 70 × 148° F.		Distilled Water 70 × 212° F.		Air Test Tube, 70 × 250° F.	
	Oil 1		Oil 3		Fuel A		Fuel B									
Hycar	1072	1042	1072	1042	1072	1042	1072	1042	1072	1042	1072	1042	1072	1042	1072	1042
Ultimate tensile, p.s.i.	4070	2480	3800	2180	2830	2020	2000	1090	2120	1400	1920	1670	2900	2150	3500	2720
Tensile change, %	+9	−21	+1	−30	−24	−35	−47	−65	−43	−55	−49	−46	−22	−31	−6	−13
Ultimate elongation, %	280	480	300	480	320	510	340	350	230	310	300	370	320	470	190	320
Elongation change, %	−30	−24	−25	−24	−20	−19	−15	−44	−42	−51	−25	−41	−20	−25	−52	−49
Hardness (Duro A)	90	67	80	55	80	65	65	45	80	60	58	44	80	63	90	70
Hardness change (points)	+9	+2	−1	−10	−1	0	−16	−20	−1	−5	−21	−21	−1	+2	+9	+5
Volume change, %	−2	0	+16	+20	+3	+3	+30	+31	+3	+6	+20	+24	+3	+7	....	....

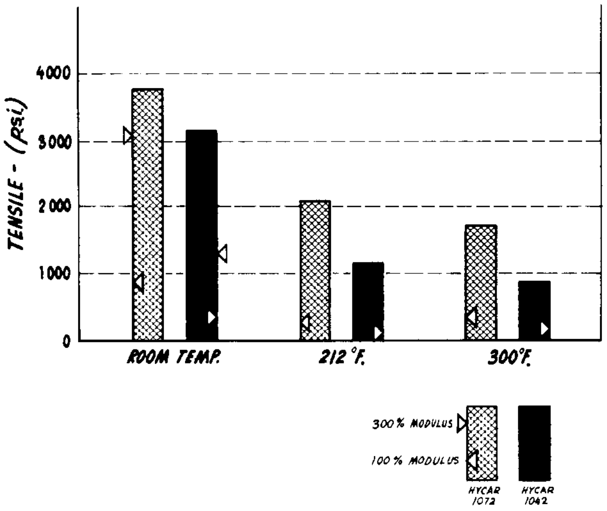


Figure 9. Comparison of ultimate tensile strengths of Hycar 1072 and 1042 vulcanizates at room and elevated temperatures

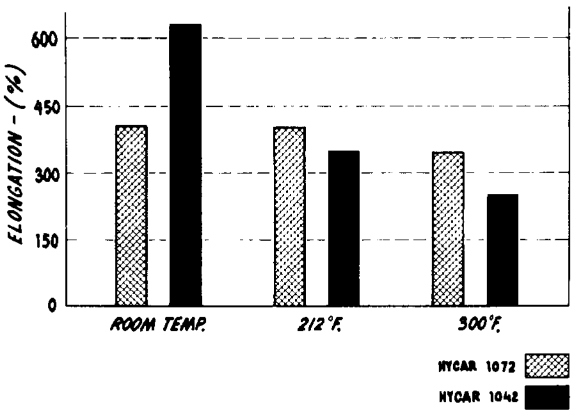


Figure 10. Ultimate elongation of Hycar 1072 and 1042 vulcanizates tested at room and elevated temperatures

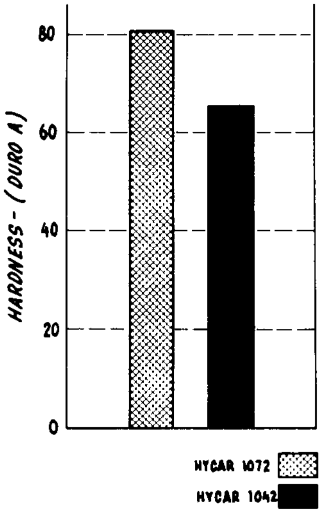


Figure 11. Comparison of carboxylic nitrile and normal nitrile vulcanizate hardness

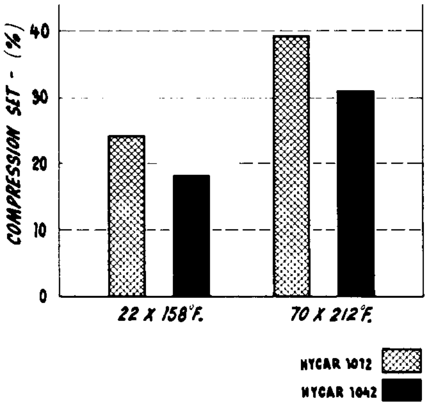


Figure 13. Comparison of compression set results from vulcanizates of Hycars 1072 and 1042

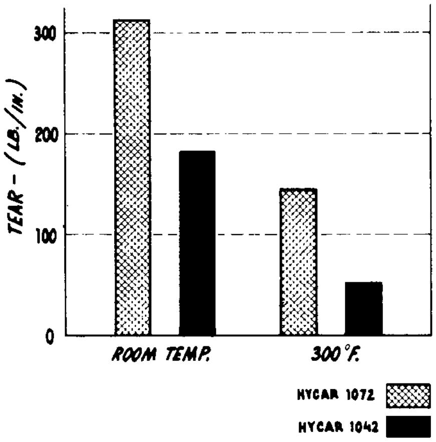


Figure 12. Tear strength of carboxylic and noncarboxylic nitrile vulcanizates

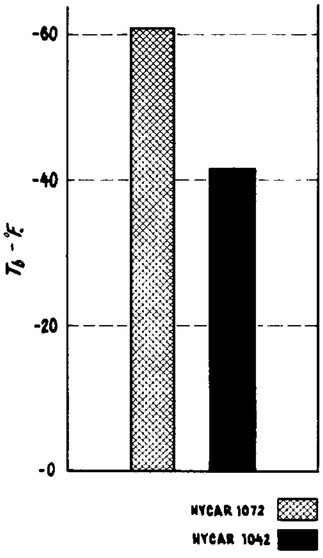


Figure 14. Low temperature brittleness of vulcanizates of carboxylic and noncarboxylic nitrile polymers

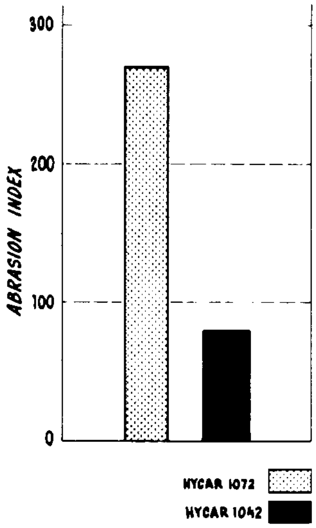


Figure 15. Resistance to abrasion of carboxyl nitrile and normal nitrile vulcanizates

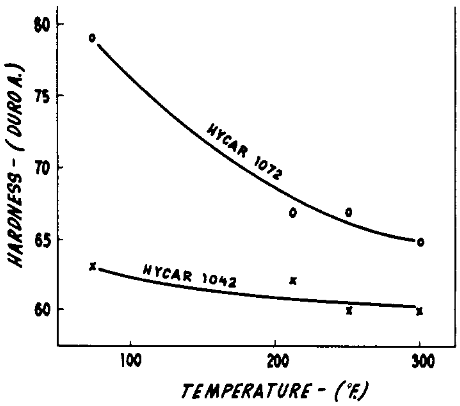


Figure 16. Hardness change as vulcanizates of Hycars 1072 and 1042 increase in temperature

Table V. Effect of Softeners on Hycar 1072 Vulcanizates

Recipe						
Polymer	100.0					
Zinc oxide	5.0					
Sulfur	1.5					
FEF black	40.0					
Softener	Variable					
TMTM	0.4					
Stearic acid	1.0					
Polymer, Hycar	1072	1072	1072	1072	1072	1042
Softener, type	ODN[a]	DBS[b]	DEHA[c]	S300[d]	DOA[e]	None
Softener, parts	19	29	25	25	28	0
All cures 30 minutes at 310°F.						
Modulus at 300% elongation, p.s.i.	2020	1950	2170	1810	1730	2400
Ultimate tensile strength, p.s.i.	2950	2620	2880	2760	2480	3180
Ultimate elongation, %	420	380	400	450	390	400
Hardness (Duro A)	70	68	70	68	65	70
Tear resistance, ASTM D 624, die C with grain lb./inch	190	200	150	170	170	220
Properties measured at 212°F.						
Ultimate tensile strength, p.s.i.	1280	....	1310	1380	....	1210
Ultimate elongation, %	400	....	340	550	....	190
Tear, die C, with grain, lb./inch	120	....	100	120	....	110
Properties measured at 250°F.						
Ultimate tensile strength, p.s.i.	1250	1170	....	....	1080	1040
Ultimate elongation, %	310	300	....	....	310	180
Tear, die C, with grain, lb./inch	120	110	....	....	110	110

[a] ODN, Octadecene nitrile.
[b] DBS, Dibutyl sebacate.
[c] DEHA, Di-2-ethylhexyl azelate.
[d] S300, Santicizer 300.
[e] DOA, Good-rite GP-233.

Table VI. Effect of Low Black Loading on Hycar 1072 Vulcanizates

Recipe		
Polymer	100.0	
Zinc oxide	5.0	
FEF black	Variable	
TMTD	3.5	
Stearic acid	10.	
Polymer, Hycar	1072	1042
Black, parts	10	40
Original Properties, all cures at 310°F.		
Cure time, minutes	30	30
Modulus at 300% elongation, p.s.i.	1020	1320
Ultimate tensile strength, p.s.i.	2940	3120
Ultimate elongation, %	510	630
Hardness (Duro A)	70	65
Low temperature brittleness, ASTM D 746		
Pass, °F.	−90	−55
Fail, °F.	−95	−60
Tear resistance, ASTM D 624, die C with grain, lb./inch	100	180
Properties measured at 212°F.		
Ultimate tensile strength, p.s.i.	830	1180
Ultimate elongation, %	500	350
Tear, die C, with grain, lb./inch	50	100
Block cured 45 minutes at 310°F.		
Compression set, ASTM Method B, 70 hours at 212°F., %	37	31
Immersions, samples cured 30 minutes at 310°F.		
ASTM oil 3, 70 hours at 350°F.		
Ultimate tensile strength, p.s.i.	1180	1080
Tensile strength change, %	−60	−65
Ultimate elongation, %	230	220
Elongation change, %	−55	−65
Hardness (Duro A)	64	52
Hardness change, points	−6	−13
Volume change, %	+21	+25

difference between vulcanizates of the two polymers after immersion is the tendency of Hycar 1072 toward a larger hardness increase, or no hardness decrease, in the hot oils.

VULCANIZATE HARDNESS AND HARDNESS CHANGES

One of the basic differences between the carboxyl-containing nitrile polymer and normal nitrile polymers is the hardness increase which results due to the interaction of the carboxyl group and a metallic oxide. One of the first questions which arises, however, is the effect of operating temperature on the relative hardness of carboxyl and noncarboxyl vulcanizates. Figure 16 illustrates that although the Hycar 1072 vulcanizate hardness was 16 units higher at room temperature than that produced by Hycar 1042 in an identical recipe, as the temperature at which the hardness test was run was increased the hardness of the two vulcanizates approached each other. A nitrile rubber part operating at 250° F., therefore, would be only 6 units higher in hardness if made from the carboxyl polymer than from the usual nitrile polymers, assuming the polymers to be used in identical recipes.

COMPOUNDING FOR REDUCED HYCAR 1072 HARDNESS

Virtually all rubber specifications are set up on the basis of an original room temperature hardness and therefore means of reducing the hardness of Hycar 1072 vulcanizates have been investigated. The most popular hardness level for nitrile vulcanizates appears to be in the 65 to 70 Durometer A range and this level was chosen as one of those on which to concentrate with Hycar 1072.

The hardness of Hycar 1072 vulcanizates can be reduced to the 65 to 70 Durometer level by three basic techniques. The first simply involves using no zinc oxide or other metallic oxide in the compound. This approach eliminates the metallic cross link which produces the increased vulcanizate hardness, but this is not practical with the usual sulfur and accelerator systems. With the elimination of

Table VII. Physical Properties of Hycar 1072-PVC Blends

Recipe				
Hycar 1072	50.0	....	50.0	....
Hycar 1042	....	50.0	....	50.0
Geon 101EP	50.0	50.0	50.0	50.0
Stabilizer[a]	5.0	5.0	5.0	5.0
Zinc oxide	....	....	5.0	5.0
Stearic acid	....	....	1.0	1.0
Sulfur	....	....	....	.75
Benzothiazyl disulfide	....	....	....	1.0
Garvey die extrusion rating, 26 r.p.m., 200° F.				
Total	14	10	14½	10½
Temperature of press, ° F.	345	345	310	310
Time of cure, minutes	5	5	30	30
Modulus at 100% elongation, p.s.i.	1200	1090	2150	1470
Ultimate tensile strength, p.s.i.	2370	1770	3450	3690
Ultimate elongation, %	260	400	350	360
Hardness (Duro A)	88	93	94	94
Low temperature brittleness, ASTM D 746				
Pass, ° F.	−50	−30	−80	−40
Fail, ° F.	−60	−40	−90	−50
Tear resistance, ASTM D 624, die C with grain, lb./inch	250	390	420	400
Taber abrasion, H22 wheel, 1000-g. wt.-5000 rev., weight loss, grams	0.032	0.031	0.022	0.030
Compression set, Method B, 22 hours at 158° F., %	81	69	95	37

[a] Dythal

the metallic cross link, other unusual properties of the carboxyl polymer vulcanizate disappear.

The second possibility for reducing hardness is the inclusion of efficient softeners or plasticizers in the compound. Using this method an 80 hard Hycar 1072 stock can be reduced to the desired 65 to 70 range with the addition of as little as 20 parts of softener. This approach can be valuable; however, at times problems of extraction will arise and, in addition, the tensile strength is almost invariably lowered slightly below that of a normal nitrile vulcanizate in the same hardness range. Table V shows examples of Hycar 1072 vulcanizates which would ordinarily have a hardness of 80, that have been softened to the 65 to 70 range, and compares these vulcanizates with an unplasticized Hycar 1042 vulcanizate.

A third method for reducing the hardness of carboxyl-containing vulcanizates is the obvious expedient of reducing the amount of reinforcing agent present. This move would produce a corresponding tensile strength decrease if employed with ordinary nitrile polymers; however, the carboxyl-containing nitrile retains a reasonable tensile strength, an effect associated with the excellent gum tensile exhibited by this polymer. Table VI shows some of the basic properties of a Hycar 1072 vulcanizate which has a hardness near 70 Durometer A by virtue of the drastically reduced black loading employed. The most impressive features of these results are the good tensile strength obtained despite the low black loading and the extremely low brittleness value of −95° F.

HYCAR 1072 BLENDS WITH VINYL

The presence of the carboxyl group in the nitrile polymer appears to influence the character of the blends of the polymer with poly(vinyl chloride) resins. For example, Hycar 1072-Geon blends make up in a Banbury much more rapidly than Hycar 1042-Geon blends. A poly(vinyl chloride) blend with the carboxyl-containing polymer reached a 320° F. dump temperature in a Banbury in one third the time required for a normal nitrile-poly(vinyl chloride) blend. The Hycar 1072-Geon blends so produced give measurably smoother extrusions than are obtained from the usual nitrile rubber blends with Geon resin. Extrusion rating data along with other pertinent data concerned with some blends of Hycar 1072 with Geon are shown in Table VII.

The most obvious differences which can be attributed to the presence of the carboxyl group in the blend are, in addition to those already noted, a much improved low temperature brittleness, an improved abrasion resistance, and a greater thermoplasticity.

HYCAR 1072 BLENDS WITH PHENOLIC RESINS

Nitrile polymers are sometimes used in small amounts with certain tailored phenolic molding resins because of the increase in impact strength which results. It is possible also to use these same phenolic resins as the reinforcing agent or stiffening agent in nitrile rubber vulcanizates.

Table VIII. Resin-Rich Hycar—Phenolic Blends

Recipe			
Hycar 1072	30.0	30.0	....
Hycar 1042	....	.....	30.0
Durez 12687	70.0	.....	70.0
G. E. 12316	....	70.0	....
Stearic acid	2.0	2.0	2.0
All cures 15 minutes at 325° F.			
Ultimate tensile strength, p.s.i.	5330	4450	3790
Ultimate elongation, %	2.4	2.0	2.1
Hardness (Duro D)	76	80	77
Izod impact ASTM D 256-54T, ft. lb./inch	0.32	0.38	0.40

Hycar 1072 produces higher tensile strength in the resin-rich blends and considerably higher tensile strength and stiffening in the rubber-rich blends. Such conditions are shown in Tables VIII and IX.

The appearance, milling, and processing characteristics of the rubber resin blends indicated that Hycar 1072 exhibits greater compatibility with the resin than the normal nitrile counterpart, Hycar 1042. Limited experience in the laboratory also indicated that Hycar 1072 is more compatible and gives better properties than Hycar 1042 when blended with cheaper phenolic resins of the more general-purpose type.

Table IX. Rubber-Rich Hycar—Phenolic Blends

Recipe			
Hycar 1072	100.0	100.0	.....
Hycar 1042	.....	.....	100.0
Durez 12687	25.0	50.0	50.0
Stearic acid	2.0	2.0	2.0
Zinc oxide	10.0	10.0	5.0
TMTD	.....	.....	3.5
All cures 30 minutes at 310°F.			
Ultimate tensile strength, p.s.i.	3700	3970	2350
Ultimate elongation, %	420	190	490
Hardness (Duro D)	42	58	39
Tear resistance, ASTM D 624, die C with grain, lb./inch	440	620	470
Low temperature brittleness, ASTM D 746			
Pass, °F.	−60	−25	−25
Fail, °F.	−70	−35	−35
ASTM oil 3, 70 hours at 300°F., vol. change, %	+23	+17	+19

CEMENTS

Hycar 1072 is readily soluble in the usual solvents used in making cements from nitrile rubbers. The possibility of a zinc oxide cure of a Hycar 1072 cement suggests a method of obtaining a tough, highly abrasion-resistant, unloaded film. Cements made from mixtures of Hycar 1072 and phenolic resins have shown good adhesion to metals. The presence of the reactive carboxyl group may suggest unique applications as protective coatings, caulking materials, or adhesives.

SUMMARY

The building of carboxyl groups into a nitrile polymer has changed many of the characteristics of the basic polymer from which it was built. Comparison of the carboxyl containing polymer with a similar nitrile polymer devoid of carboxyl groups leads to the following conclusions:

1. The oil and fuel resistance of the polymer is not harmed by the presence of the carboxyl groups, in fact, volume change on immersion in such materials is decreased slightly.
2. The inclusion of carboxyl groups in the nitrile polymer has produced a high gum tensile strength rubber with high oil resistance.
3. Recipes used for standard nitrile polymers are generally satisfactory with Hycar 1072.
4. When a standard nitrile polymer is compared with the carboxylic nitrile polymer in identical recipes, the carboxyl containing polymer exhibits a higher tensile strength, modulus, hardness, compression set, tear, not tensile, hot elongation, hot tear, and abrasion resistance. At the same time elongation and rebound are lower and low temperature brittleness is improved.
5. The hardness of a Hycar 1072 vulcanizate decreases more rapidly than a normal nitrile as the operating temperature rises above room temperature.
6. The use of plasticizers or reduced loading are effective methods for reducing the hardness of Hycar 1072 vulcanizates.
7. In the presence of low amounts of reinforcing agent Hycar 1072 vulcanizates retain satisfactory properties and in addition possess low temperature brittleness values near −95°F.
8. The carboxyl containing nitrile polymer shows unusual properties in blends with poly(vinyl chloride) and phenolic resins.

The properties observed suggest application in fields requiring high hardness compounds at no sacrifice in other properties; use in such items as oil well parts, shoe soles, and belting where higher abrasion resistance would be valuable; application in such lines as adhesives, protective films, and prosthetics where a high gum tensile in addition to other properties of a highly oil resistant polymer are valuable; use in conjunction with resins of various kinds of which poly(vinyl chloride) and phenolic types are typical; and adaptation to parts exposed to shock and oil or fuel at very low temperatures.

Hycar 1072 (B. F. Goodrich Chemical Co.), the carboxyl containing polymer described, is available commercially.

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Some Properties of Lignite Creosote

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The present study concerns an evaluation of properties of creosote derived from Saskatchewan lignite. Additional properties to those reported by Prostel (*8*) for North Dakota lignite have been measured. These include creosote toxicity, the effect of chlorination on the toxicity, and the rate of evaporation of the preservative.

At Bienfait, Sask., lignite is treated by the Lurgi low temperature carbonization process (*1,9*). The maximum temperature in the retort is 1290° to 1380°F. The lignite tar is condensed from the gas stream and is distilled at atmospheric pressure in batches. The fraction distilling between approximately 425° and 710°F. is collected as creosote. Two specimens were considered in the present study. The first was a representative stream sample from the distillation. The second was taken from a commercial shipment supplied to Northern Wood Preservers (Sask.) Ltd., Prince Albert, Sask.

Except as noted, the standard methods of the American Wood-Preservers' Association (*4*) were used in obtaining the data presented. Toxicity measurements were made by the agar flask method (*5*) as modified by Finholt (*7*). *Polyporus tulipiferus* (Madison 517) between 12 and 15 days old was the fungus used for inoculations.

In the initial stages of the work fractionations by distillation were made both at atmospheric pressure and under vacuum. However, as later work showed that distillation at atmospheric pressure did not adversely affect the toxicity of the preservative, vacuum distillation was discontinued.

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