BUTADIENE-FURFURAL COPOLYMERS

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The major source of the polymeric residue formed in the furfural extractive distillation method for purification of butadiene has been found to be due to a reaction of butadiene with furfural. A compound, a copolymer of two molecules of butadiene and one of furfural, has been isolated from plant residue and shown to be 2,3,4,5-bis-(Δ^2-butenylene)-tetrahydrofurfural. The same compound has been synthesized in quantity by direct reaction of furfural and butadiene under conditions simulating those in the plant. Proof of structure and data on the effect of various conditions on formation of this copolymer are presented.

FURFURAL has come into extensive use as a solvent in the extractive distillation processes for separation and purification of butylene and butadiene, particularly in the large butadiene plants operated for Office of Rubber Reserve as a part of the government synthetic rubber program (*1*).

To maintain the selectivity of the solvent and prevent fouling of heating surfaces, a small portion of the total stream is continuously redistilled in a purification unit to effect removal of the residue formed. The residue has varied from a black semisolid resin to a fairly fluid and lighter-colored liquid as conditions of operation of the main extractive distillation units as well as the redistillation units have varied.

The amount of residue (high boiling polymeric substances) made in the butadiene plants is only a minute fraction of the total furfural circulation. Polymerization is scarcely detectable on a once-through basis, but the gradual build-up in the recirculated solvent results in an appreciable polymer content. Solvent consumption varies over the range from about 0.005 to 0.02% of the circulation rate, depending on the individual plant system and conditions of operation. Because of the tremendous scale of operations, however, such losses become problems of considerable economic significance. Similarly, isolation of any pure chemical from this waste polymer would make it potentially available in fair supply by fine chemicals standards. For these reasons it was of interest to learn the source and nature of the polymer.

POSSIBLE SOURCES

The possible sources of the polymer include all the components of the systems used in the extractive distillation purifications of butenes and butadiene, as well as the materials from which the vessels, piping, pumps, and other auxiliaries are fabricated. The extractive distillation systems have been described in detail (*1*). Briefly, in butene purification, furfural containing about 5% water contacts a hydrocarbon stream comprising principally the 2-butenes and *n*-butane, although smaller amounts of 1-butene, isobutene, and butadiene may be present. In one modification used in some of the plants (*4*) an extractive distillation system is used to separate 1-butene from isobutane in a stream containing principally these two hydrocarbons. In butadiene purification, the principal components of the stream dissolved in the furfural-water solvent are 1-butene and butadiene, with lesser amounts of the butanes, 2-butenes, isobutene, and C_4 acetylenes. Some C_5 unsaturates also may be present. The furfural in the system is exposed to temperatures up to about 150° C. and in some reboilers may reach as high as 165° to 171° C. at times, for periods as long as 15 to 20 minutes in some cases. Pressures employed in the columns are generally in the range 40 to 80 pounds per square inch gage.

In the redistillation units, although designs differ somewhat, the furfural is subjected to distillation in contact with steam. Concentration of polymer in contact with furfural reaches a high level.

In circulating through the system, the furfural predominantly contacts carbon steel, although some chrome and chrome-nickel alloy steels are used. Many pump bodies are fabricated from acid-resisting bronze, and some cooling coils have been constructed employing antimonial-admiralty metal.

FURFURAL POLYMER

Furfural was first considered as the prime source of the plant polymer. As has been reported (*3*), furfural on exposure to oxygen undergoes autoxidation with resultant increase in color, acidity, and polymer content. Such changes, accelerated by heat, might be responsible for the amount of polymer encountered. However, the character of the polymer and more particularly the care which is exercised in plant practice to exclude oxygen precluded autoxidation of furfural from consideration. Nonoxidative polymerization of furfural, such as thermal breakdown (*2*) or acid catalyzed polymerization is known to occur (*9*) but as will be shown later could account for only a minor part of the polymer formation observed.

BUTADIENE POLYMER

A second possibility for the formation of polymer in these extractive distillation systems is from butadiene. Thermal polymerization of butadiene yields principally the dimer, 3-vinyl-1-cyclohexene (*7*, *8*), at rates which are known for various temperatures. Formation of the dimer does occur in the furfural extractive distillation systems as shown by its isolation from the hydrocarbon streams kettle bottoms. This compound distills at atmospheric pressure at 130° C., considerably lower than does furfural itself. Dimer therefore cannot account for the polymer isolated as a heavy residue in the furfural redistillation units, for it would all be flash-distilled overhead with the furfural. Higher boiling, oil-soluble polymers form at a much lower rate than dimer and need not be considered as sources of polymer of the magnitude found. Insoluble rubberlike polymer forms sometimes as an adherent deposit in certain lines carrying hydrocarbons of high butadiene content—namely, the well known popcorn polymer, but this type of polymer, of course, will not be encountered dissolved in the stream of furfural.

REACTION OF VARIOUS COMPONENTS OF SYSTEM WITH FURFURAL

The possibility was considered that interaction of furfural with one or more of the hydrocarbons in the system accounted for the excessive amounts of high boiling polymers encountered in the plants. To test this possibility, the rate of polymer formation in synthetically prepared samples of furfural saturated with each of the five hydrocarbons, *n*-butane, isobutene, 1-butene, the 2-butenes, and 1,3-butadiene, was determined at 126° C. and compared to the rate observed with the solvent (furfural-water) alone.

Portions of a sample of the wet furfural obtained from the circulating stream at one of the butadiene plants were added to a series of six small steel vessels. Weighed quantities of the pure hydrocarbons, sufficient to saturate the solvent at 126° C., were introduced into the cooled vessels through an inlet tube and valve provided on one end. The sealed steel tubes were placed in a thermostatically controlled oil bath maintained at 126° C. At intervals, small samples of the liquid phase were removed and analyzed for polymer content. The method employed comprised vacuum distillation in a small tared flask, removal of traces of volatile material from the residue by addition and distillation of small portions of acetone, and direct weighing of the residue. This procedure (*5*) developed for polymer determinations in the circulating furfural in the large butadiene plants has been used extensively for several years in their laboratories and in investigations on the effect of process variables, inhibitors, etc., on the rate of furfural polymerization. It has been shown to have a repeatability for one operator and apparatus of at least ±0.05% polymer and good absolute precision.

The results of this series of tests are shown in Table I.

It is apparent that furfural alone, under the conditions employed, forms a measurable amount of polymer. This amount is increased somewhat in the presence of butane or the butenes. However, with butadiene the order of magnitude is from five to ten times as great; therefore, this reaction must be considered as the major source of plant polymer. The values listed do not include the butadiene dimer which might have been formed as this is distilled off in the analytical procedure. From the chemical nature of butadiene and the change in the quality of the polymer to a lighter colored and much more fluid product, it seemed unlikely that the butadiene acted merely as a catalyst for furfural polymerization. The butadiene disappearance in the example given (two thirds of the total charge) is distinctly less than the increase in the quantity of polymer formed. The greatly increased rate of polymerization seems to result therefore from an actual condensation or copolymerization of 1,3-butadiene with furfural.

TABLE I. POLYMERIZATION OF PLANT FURFURAL[a] CONTAINING C_4 HYDROCARBONS

	C_4 Hydrocarbon Added[b], Wt. %	Hours at 126° C.	Polymer Formed, Wt. %	
			Total	Average rate, wt. %/day
None	...	24	0.17	0.17
	...	48	0.27	0.14
	...	72[c]	0.36	0.12
	...	91	0.43	0.11
n-Butane	1.6	24	0.34	0.34
	1.6	48	0.51	0.25
	1.6	72	0.62	0.21
1-Butene	2.2	24	0.29	0.29
	2.2	48	0.38	0.19
	2.2	72	0.52	0.17
2-Butenes	3.0	24	0.28	0.28
	3.0	48	0.39	0.19
	3.0	72	0.46	0.15
Isobutene	3.5	24	0.27	0.27
	3.5	48	0.40	0.20
	3.5	72	0.52	0.17
1,3-Butadiene	3.9	24	1.73	1.73
	3.9	48	2.91	1.46
	3.9[d]	72	4.07	1.36

[a] Furfural used contained 5.4% added water and had an initial polymer content of 0.88%.
[b] All were Phillips Pure Grade except isobutene which was Phillips Technical Grade.
[c] Value read from smoothed curve plotted through the 24-, 48-, and 91-hour points.
[d] Analysis by low temperature fractional distillation showed 1.3% butadiene remaining after 72 hours.

Further evidence of this condensation was obtained in another series of tests made with various furfural samples containing dissolved butadiene. Furfural circulating in the plant system contains polymer, traces of acids, inorganic solids in suspension, and other unknown materials; these might conceivably be involved in the increase in polymerization when butadiene is present. In Table II are shown the results of tests made with a series of different furfural samples in which any effect of impurities present was reduced or eliminated.

TABLE II. POLYMER FORMATION IN BUTADIENE-FURFURAL SYSTEMS

Furfural[a]	Butadiene, Wt. %		Hours at 126° C.	Pressure, Lb./Sq. In. Gage	Polymer Formed, Wt. %	
	Original	Final			Total	Rate/day
A	3.5	...	24	75	1.64	1.64
	3.5	...	48	55	2.73	1.36
	3.5	1.1	72	45	3.48	1.16
B	4.2	...	24	75	1.99	1.99
	4.2	...	48	55	3.10	1.55
	4.2	1.3	72	50	4.31	1.44
C	3.8	...	24	65	1.56	1.56
	3.8	...	48	45	2.59	1.30
	3.8	1.3	72	40	3.30	1.10
D	3.6	...	24	60	1.51	1.51
	3.6	...	48	35	2.56	1.28
	3.6	1.2	72	25	3.20	1.07

[a] A = Pure furfural steam distilled in glass; 5.0% water (0.02% polymer) B = Commercial grade new furfural as received; 5.0% water (0.65% polymer). C = Rerun furfural-overhead from butadiene plant redistillation unit; 4.7% water (0.24% polymer). D = Pure furfural, same as A with no water added.

These results indicate that the polymer is formed at a rate essentially uninfluenced by the purity of the furfural. The almost equal rate of formation with anhydrous sample D eliminates reaction of either component with water as a source of the polymer.

Inasmuch as these tests were conducted under conditions simulating those in the plant, it may be inferred that the major source of polymer is from a reaction between butadiene and furfural.

SYNTHESIS OF BUTADIENE-FURFURAL COPOLYMER

In order to make and isolate appreciable quantities of the butadiene-furfural polymer, reasonably favorable conditions for the synthesis were needed. Because the formation appeared to involve a condensation reaction, it was expected that such variables as concentration, temperature, pressure, and time would affect the quantity of product produced. An investigation of the effect of these factors was undertaken.

A series of tests was made using the technique described previously in which samples of wet furfural with varying quantities of butadiene were heated at several temperatures. The effect of butadiene concentration on the rate of copolymerization is shown graphically in Figure 1. The effect of temperature is shown in Figure 2. It is apparent that increase in either concentration or temperature increases the rate of copolymerization.

In some portions of the equipment in extractive distillation, furfural is in contact with butadiene streams at temperatures in the neighborhood of 71° C.; this allows the furfural to contain as much as 10 to 12 weight % butadiene. Tests made at 71° C. with the sample of furfural used in Table II with 11.0% butadiene added showed the formation of 0.41% polymer in 91

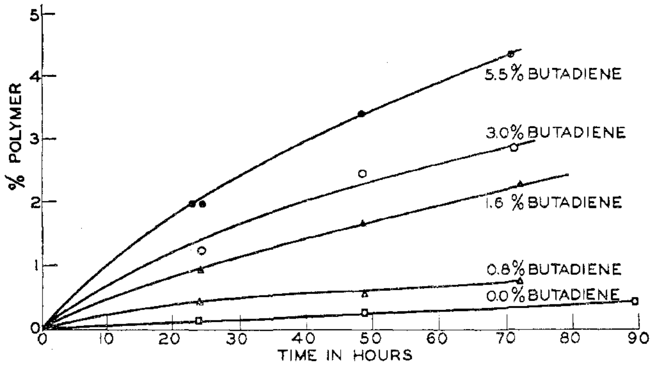

Figure 1. Effect of Butadiene Concentration on Butadiene-Furfural Copolymer

Furfural (5.4% water) heated at 126° C. in sealed tubes

hours, compared to 0.15% in the furfural alone. This temperature is evidently too low for rapid reaction with butadiene.

To determine whether pressure had any affect on the rate of condensation, a series of tubes was prepared containing the furfural and 3.0 to 4.2% butadiene. These were pressured with nitrogen to obtain a range of 60 to 100 pounds per square inch gage at 126° C. After heating at 126° C. and correcting to equivalent butadiene content the results showed that pressure within this low range had substantially no effect as might be expected.

These tests indicated that a synthesis of the copolymer should be favored by high butadiene concentration and temperature.

Table III. Properties of Butadiene-Furfural Copolymer

		Copolymer Isolated from Plant Residue	Copolymer Made by Synthesis
Boiling point		143° C. at 5 mm.	115° C. at 1.1 mm
Specific gravity 20/20		1.119	1.120
Refractive index 20/D		1.5225	1.5240
Iodine No.		250	253
Acetyl No.		0	0
Neutral equiv.		0	0
Saponification equiv.		0	0
Solubility			
Water		Insoluble	Insoluble
Dilute NaOH		Insoluble	Insoluble
Dilute HCl		Insoluble	Insoluble
Concd. H_2SO_4		Decomposes	Decomposes
Qualitative tests			
Flammability		Positive	Positive
Sulfur		Negative	..
Nitrogen		Negative	..
Halogen		Negative	..
Bromine absorption		Positive	Positive
Tollen's reagent		Positive	Positive
Aniline acetate		Negative	Negative
Heating with strong acid or alkali		Negative	Negative
Analysis, calculated for $C_{13}H_{16}O_2$			
%C	76.45	75.89	76.10
%H	7.84	7.81	8.03
Mol. wt. (Rast)	204	202	205
Derivatives			
Oxime			
Melting point		..	97.0–97.5° C.
Analysis, calcd. for $C_{13}H_{17}O_2N$			
%C	71.2	..	71.46
%H	7.82	..	7.88
%N	6.38	..	6.51
2,4-Dinitrophenylhydrazone			
Melting point (corrected)		153.4–153.8° C.	153.4–153.8° C.
Mixed melting point		153.7–154.2° C.	
Analysis, calculated for $C_{19}H_{20}O_5N_4$			
%C	59.3	..	59.35
%H	5.25	..	5.37
%N	14.68	14.59	14.3
Mol. wt. (Rast)	384	389	..
Corresponding acid (alkaline Ag_2O)			
Melting point (corrected)		89.7–90.0° C.	89.7–90.0° C.
Mixed melting point		89.9–90.2° C.	
Analysis, calculated for $C_{13}H_{16}O_3$			
%C	70.90	70.96	71.01
%H	7.27	7.21	7.55
Mol. wt. (Rast)	220	218	..

On the other hand, butadiene dimerizes at a rate which is proportional to temperature and concentration (7); extreme temperatures and concentrations might be expected to lead to formation of vinylcyclohexene in excessive amounts, thereby limiting or even decreasing the yield of desired product. This was confirmed experimentally.

Many syntheses of the desired copolymer were carried out. In one synthesis furfural (3800 grams), water (200 grams), and 15% by weight of butadiene were charged to a steel reactor and heated for 100 hours at 126° C. The fractionation of the material yielded a portion (250 ml.) boiling in the range 104° to 126° C. at 0.5 to 1.0 mm. of mercury. Redistillation, using a glass laboratory still with a 25-cm. column packed with glass helixes and with a silvered vacuum jacket, gave a fraction (from 10 to 85% of the distillate, 210 grams) boiling sharply at 115° C. at 1.1 mm. This represents a yield of 18.5%, based on the butadiene charged and on the theory that two molecules of butadiene copolymerize with one molecule of furfural (see section Structure of Copolymer). The product was a pale yellow oil having the properties given in Table III.

ISOLATION OF COPOLYMER FROM PLANT RESIDUE

A sample (204 grams) of the black resinous residue obtained from the butadiene plants was fractionated through a 25-cm. Vigreaux column at 15 mm. pressure. A pale yellow liquid fraction (31.7 grams) boiling at 165° to 173° C. was obtained. Refractionation through a 20-cm. column, packed with glass helixes, gave a constant boiling fraction (23.1 grams) with the properties shown in Table III.

Attempts to obtain higher boiling material by further distillation were unsuccessful owing to gaseous decomposition.

CONSTITUTION AND CHEMICAL PROPERTIES

The copolymer isolated from plant residue was characterized in one of the laboratories and independently of the characterization of the synthesized copolymer carried out in the other laboratory. Comparison of the results is shown in Table III.

Data in Table III prove the identity of the two products. In addition, certain conclusions as to the structure of the copolymer $C_{13}H_{16}O_2$ can be drawn:

One oxygen atom is present in an aldehyde group.

One oxygen atom is present as true ether, and not as a vinyl ether.

There is no active alpha hydrogen atom.

There are two double bonds in the molecule.

The double bonds are not conjugated with the aldehyde.

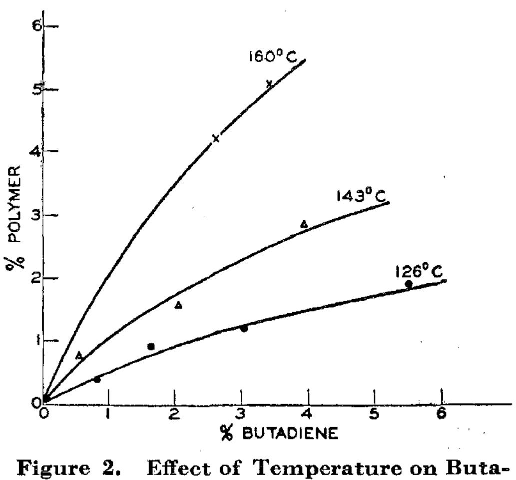

Figure 2. Effect of Temperature on Butadiene-Furfural Copolymer

Furfural (5.4% water) heated for 24 hours in sealed tubes

STRUCTURE OF THE COPOLYMER

The structure postulated for the condensation product is based on the condensation of two molecules of butadiene with one of furfural. This was first indicated by the material balance on butadiene consumed against polymer formed in the early synthetic experiments. The butadiene consumed was approximately half the weight of the product formed; this corresponds roughly to a ratio of two moles of butadiene to one of furfural.

Empirically, addition of two molecules of butadiene and one of furfural would give the formula actually possessed by the copolymer: $2(C_4H_6) + C_5H_4O_2 = C_{13}H_{16}O_2$

Since butadiene dimerizes readily to 3-vinyl-1-cyclohexene, and appreciable quantities of this material were found to be present in furfural-butadiene mixtures after heating, it seemed possible that the copolymer might be formed by reaction of one molecule of dimer with one of furfural.

Tests made on mixtures of the dimer with furfural showed that this is not the mechanism. Quantities of 1,3- and 5% of 3-vinyl-1-cyclohexene were added to samples of furfural and heated in sealed tubes at 126° C. The results are shown in Table IV.

Table IV. Butadiene Dimer–Furfural[a] Mixtures
(Heated 72 hours at 126° C.)

Dimer Added, Wt. %	Polymer Formed, Wt. %	
	Total	Rate per day
1.0	0.67	0.22
3.0	0.60	0.21
5.0	0.82	0.29

[a] Furfural used contained 5.4% water and 1.02% polymer.

The effect of increasing dimer concentration is negligible. Furthermore, the rate of polymer formation is markedly less than that found (1.36 wt. % per day as shown in Table I) with butadiene under similar conditions. Although the rate is somewhat greater than that with furfural alone (0.12 wt. % per day as shown in Table I) the increase can be accounted for by the partial depolymerization of butadiene dimer under conditions of the test.

If the copolymer under discussion were formed by reaction of the dimer with furfural, the rate of formation should have been greater in these tests than in those employing butadiene. As the contrary was found, dimer can be eliminated from consideration as one of the precursors of the copolymer.

PROBABLE MECHANISM OF FORMATION AND PROPOSED STRUCTURE OF COPOLYMER

The analytical data showing addition copolymerization and the character of the reactants (butadiene and furfural) indicated that the reaction of formation was of the Diels-Alder type. Butadiene can take either the acceptor or the donor role in the Diels-Alder reaction (*6*) as illustrated by its dimerization to form 3-vinyl-cyclohexene. In this reaction butadiene takes both roles, whereas with maleic anhydride, it is strictly a donor reactant. Furfural, on the other hand, fails to react as a donor even when treated with a strong acceptor, such as maleic anhydride (this is unlike furan and its homologs which form the expected adducts with maleic anhydride). Thus, furfural hardly can be expected to react as a donor with butadiene, which is a much weaker acceptor than is maleic anhydride. On the other hand, the decrease in electron density at the double bonds of furfural caused by conjugation with the aldehyde group might be expected to induce acceptor activity.

On the basis of this reasoning, it is believed that the initial reaction leading to formation of the copolymer is that of one molecule of butadiene and one of furfural to form two possible reaction products, formulas I and II as shown in Figure 3. The second molecule of butadiene would be more likely to react with I than with II since the former still has a double bond activated by the aldehyde group and the latter has not. Disregarding this for the moment, reaction of the second molecule of butadiene with I could give rise to formulas III and IV, and II on further reaction with butadiene could form IV and V.

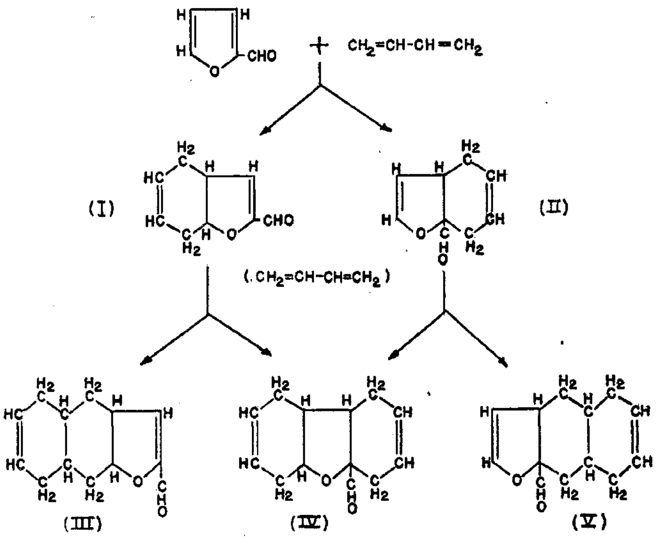

Figure 3. Proposed Structures of Copolymer

Inspection of formulas III, IV, and V shows that all of them have the requisite molecular formula: the one aldehyde group; the etheric oxygen; and the two double bonds. However, by consideration of the stability of the copolymer (Table III) to acid and alkali, two of the three formulas can be eliminated.

Formula III has a hydrogen atom activated by the aldehyde group through the conjugated double bond. Furthermore, it is an enol ether. On either score, III would be destroyed on exposure to hot aqueous acid or alkali. Although formula V has no active hydrogen atom, it is an enol ether and would be unstable in the presence of acid. By contrast, formula IV has neither an active hydrogen atom nor is it an enol ether. Thus IV would be expected to exhibit the stability which was found to be characteristic of the compound isolated. Therefore, IV is proposed as the structure of the butadiene-furfural copolymer, 2,3,4,5-bis(Δ^2-butenylene)-tetrahydrofurfural.

Formula IV could result from reaction through intermediates I or II but reaction through I seems more likely as it possesses an activated double bond; such a double bond would be required for further reaction with another molecule of butadiene to give IV. Thus, not only is IV the structure of the copolymer, but it is chemically the most probable product.

OTHER PRODUCTS OF BUTADIENE-FURFURAL POLYMERIZATION

As might be expected, 2,3,4,5-bis(Δ^2-butenylene)-tetrahydrofurfural is not the only product of butadiene-furfural polymerization. For instance, in the distillation of the plant residue, a small amount of an oil boiling intermediately between furfural and the copolymer was found. It was not identified but was furfural-free as shown by a negative aniline acetate color test. This may consist of some of the intermediate addition compounds from reaction of one molecule of butadiene and one of furfural. The undistillable material remaining in the distillation flask was a black tarry resin which was thermoplastic and could be ground at room temperature. It could be made infusible by heating with paraformaldehyde and an acid catalyst.

Similarly, unidentified products were obtained in the synthesis of the copolymer. Intermediate in boiling point between the copolymer and the black undistillable residue, there was obtained a red viscous oil often accompanied by white crystals. If not immediately present, the white crystals formed on long standing. A relatively sharp melting (130.7° to 131-2° C.) sample of the white crystals showed an elementary composition of 64.18% carbon, 7.38% hydrogen; neutral equivalent 192; molecular weight erratic due to low solubility. Test for aldehyde was negative. The viscous red oil appeared to be a mixture, giving a positive aldehyde test.

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Ultimate and Actual Tensile Strengths of Type III Latex Films

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A comparative study was made of the tensile strengths of raw polymer and gum vulcanizate films prepared from fifty-three Type III GR-S latices. The ultimate tensile strengths of the two types of films showed no correlation with one another when the calculations were based on the original cross-sectional areas. On the other hand, when the calculations were made on the actual areas at break, the tensiles of the raw polymer and vulcanizate films obtained from a given latex were found to be essentially the same. This identity of film tensiles obtained from a given latex indicates that here compounding and curing do not lead to any reinforcement of the polymer, nor to any change in the nature of the bonds involved in film rupture.

THE present practice for computing the ultimate tensile strengths of elastomeric films is to divide the breaking load by the cross-sectional area of the films before elongation. Such a calculation does not yield the actual force per unit area required to break the film, nor does it take into consideration the elongation of the film and the reduction in cross-sectional area which the film undergoes on stretching. The values for ultimate tensiles thus arrived at are not very indicative of the strength of the polymers involved, nor are the elongation measurements much more than numbers to accompany tensile results.

This difficulty was recognized as early as 1915 by Eaton and Grantham (*2*) when, in seeking to obtain a function dependent on both stress and strain, they expressed their results as a "tensile product"—i.e., the tensile calculated on the basis of cross-sectional area at break. Wiegand (*9*) and others (*1, 3, 8*) have also used the "tensile product" or "molecular tensile" to compare gum vulcanizates and loaded stocks to ascertain whether the use of fillers led to reinforcement of rubber and to what extent. A review of some of this work is given by Shepard (*6*) and by Shepard, Street, and Park (*7*).

During the past several years this laboratory has had the task of preparing satisfactory latex films and testing them for tensile strength. Involved have been films cast directly from straight latex and films of gum vulcanizates cast from compounded latices. During this work no connection could be established between the ultimate tensiles of uncompounded and compounded films when these were calculated on the basis of the original cross-sectional areas. On the other hand, when the tensiles were calculated on the basis of area at break—i.e., the force actually required to break a film per unit area—the tensiles of the uncompounded and compounded films, obtained from the same latex, were found to be essentially the same within the relatively large experimental errors involved in tensile testing.

The purpose of this paper is to present the film tensile results obtained on fifty-three Type III GR-S latices, both uncompounded and compounded, and to show that the tensiles, when calculated on the basis of the area at break, are unaffected by the compounding and curing processes.

CALCULATION OF ACTUAL TENSILE STRENGTH

Tensile strengths calculated on the basis of the original area will be referred to here as ultimate tensile strengths, T, and tensiles calculated on the basis of the area at break as actual tensile strengths, S.

Ordinary tensile measurements include the determination of the original area of the test specimen, A_o, the original length between bench marks, l_o, the load, L, at break, and the distance between bench marks at break, l_f. From these data the ultimate tensile strength is calculated as

$$T = L/A_o \tag{1}$$

and the percentage elongation, E, is taken as

$$E = \left(\frac{l_f - l_o}{l_o}\right)100 \tag{2}$$

From the same data it is possible to calculate the actual tensile strength of the specimens on the assumption that the volume between bench marks remains unaltered on stretching. That this assumption is justified for unloaded rubbers was shown by Schippel (*5*), who found that the change in volume of unloaded natural rubbers on stretching does not amount to more than about