Tensile Strength of Gum and Reinforced EPR and SBR Vulcanizates*

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Synopsis

The tensile strength and elongation at break of EPR and SBR gum vulcanizates were determined as a function of network chain density. A large viscous contribution to the tensile force was found at low crosslink density, and the maximum in the tensile strength versus chain density curve decreased as more nearly equilibrium conditions were approached. The rate dependence of tensile strength of black-filled EPR was studied by creep rupture experiments. The temperature dependence of the tensile strength of filled EPR and SBR was studied and compared. The same limiting degree of cure was obtained for both filled and gum vulcanizates of EPR.

In this report, the relation between degree of crosslinking and tensile strength for ethylene–propylene and styrene–butadiene gum vulcanizates was investigated. This was done to check the results of Epstein and Smith,[1] which showed that the maximum in the degree of crosslinking versus tensile strength curve for styrene–butadiene vulcanizates was a viscous phenomenon and to provide more data on which to base a comprehensive theory of the tensile strength of elastomers.[2] Carbon black-reinforced vulcanizates were studied in an attempt to elucidate the important variables responsible for the large drop in tensile strength which occurs when temperature is increased.

EXPERIMENTAL

Materials

Ethylene–Propylene Terpolymer (EPR). DuPont's ECD-330 was used. This rubber contains about 53 mole-% ethylene[3] and a small amount of unsaturation to provide sites for vulcanization.

Styrene–Butadiene Copolymer (SBR). The low molecular weight fraction was removed from Philprene 1502 for use in a portion of this work.

This material is referred to as an extracted SBR in this report. Thirteen per cent of the lower polymeric material in the SBR was removed by fractional precipitation from a benzene solution, methanol being used as nonsolvent. The viscosity-average molecular weight of the extracted SBR was 280,000 g./mole.

Procedures

Compounding Recipes. The compounding recipes for EPR stocks have been given elsewhere, as have vulcanization and swelling techniques.[3] Recipes for SBR stocks are given in Table I.

TABLE I

| | Parts by weight | | | | |
	A	B	C	D	E
Philprene 1502 (extracted)	100	100	—	—	—
Philprene 1502	—	—	100	100	100
Philblack 0	—	—	—	—	30 or 100
Zinc oxide	—	—	—	—	5
Methyl tuads	4.86	13.3	4	16	4
Altax	—	—	—	—	1
PBNA	1.18	1.18	—	—	—

SBR gum compounds were prepared by adding the curing agents to a solution of SBR in benzene. The benzene was then removed under vacuum. Vulcanization was carried out at 305°F.

Tensile Strength Measurements. The tensile strengths of gum vulcanizates were determined at 25°C. with an Instron testing machine. Three crosshead separation speeds were employed, usually 20, 2.0, and 0.2 in./
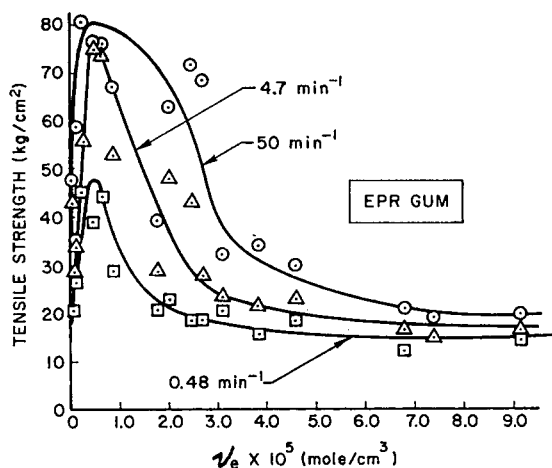

Fig. 1 Tensile strength as a function of chain density for EPR gum vulcanizates.

min. Dumbbell samples of gauge length 0.94 cm. and width 0.159 cm. were cut from vulcanized sheets with a die. Sample cross sections varied between 8 and 15×10^{-3} cm.[2]. The average of at least five determinations was recorded. Only samples which broke sharply in the test region were considered valid. The tensile strength was based on the original cross sectional area of the sample. The average deviation from the mean for all the determinations was about 12%. The extension ratio at break was obtained by following bench marks on the sample with a pair of dividers.

At temperatures higher than room temperature, tensile strengths were determined with the apparatus described previously.[3] A crosshead speed of 0.3 in./min. was used. The samples were allowed 12 min. at temperature before the experiment was started which was found to be sufficient to establish thermal equilibrium.

RESULTS AND DISCUSSION

Tensile Strength as a Function of Chain Density for EPR and SBR Gum Vulcanizates

Vulcanizates of EPR and SBR of different degrees of crosslinking were prepared by varying the temperature and time of cure. The tensile strengths of these vulcanizates were determined at 25°C. at three strain rates.

The results obtained for EPR vulcanizates are shown in Figure 1, where tensile strength is plotted against the effective number of chains in the vulcanizates. The degree of crosslinking was determined by equilibrium swelling methods, heptane being used as solvent.[3] The strain rates reported are average values. The rate of elongation was not constant, since dumbbell test specimens were used.

The general shape of the tensile strength versus ν_e curves is the same as reported by Taylor and Darin[4] and Epstein and Smith.[1] The maximum in the curve decreases as the strain rate decreases. The position of the maximum appears to be independent of strain rate. It occurs at a ν_e of about 0.5×10^{-5} mole/cm.[3] for EPR gum vulcanizates.

In Figure 2 the logarithm of the extension ratio at break is plotted against log ν_e. The extension ratio at break seems to decrease very slightly with decreasing strain rate. A straight line fits the experimental data at degrees of crosslinking higher than that at the maximum in the tensile strength curve. However, deviations from the linear relationship occurs at low crosslink densities where experimental difficulties were observed. The test specimens were observed to neck down at the failure point just prior to rupture for the lightly crosslinked vulcanizates and it was not possible to get the specimen to break sharply.

The tensile test specimens were investigated for permanent set. They were allowed to swell for 8 hr. in benzene vapor to preclude extraction of any of the sample. After the removal of benzene in a vacuum oven, the
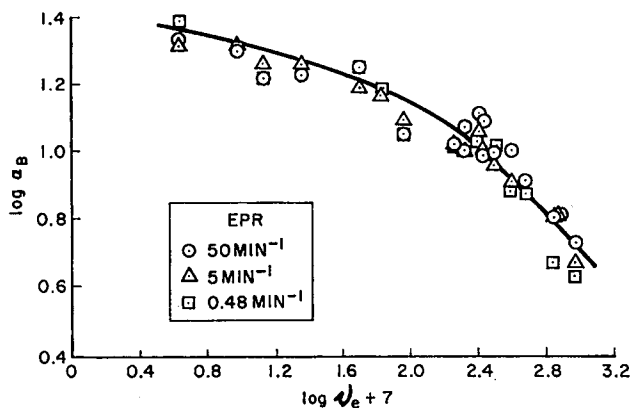
Fig. 2. Extension ratio at break as a function of chain density for EPR gum vulcanizates.

distance between the bench marks was measured and compared with the original distance. Within experimental error no permanent set was found for any of the EPR vulcanizates. This means that viscous flow did not occur during the time necessary for a tensile strength experiment.

The tensile strength versus ν_e curves for SBR vulcanizates are given in Figure 3. The value of μ reported by Berry, Cayré, and Morton[5] for SBR in benzene at 25°C., $\mu = 0.33 + 0.24\ V_r$, was used to compute ν_e from swelling data. In Figure 3 the curves for strain rates of 50 min.$^{-1}$ and 0.48 min.$^{-1}$ were obtained with the SBR polymer which had been extracted to remove a fraction of low molecular weight polymer. An unextracted SBR was used to obtain the data for the 5.0 min.$^{-1}$ curve.

The unextracted SBR curve has a maximum at a ν_e of about 1.3×10^{-5} mole/cm.^{3}. The data of Epstein and Smith,[1] which were obtained at a higher strain rate, gave a maximum at a ν_e of 1.7×10^{-5} mole/cm.^{3} and the tensile strength values at high degrees of crosslinking were about 18 kg./
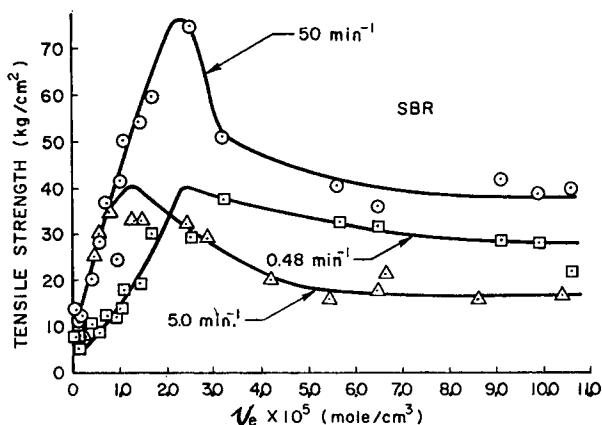

Fig. 3. Tensile strength as a function of chain density for SBR gum vulcanizates.

cm.[2], in agreement with our results for unextracted SBR. The extracted SBR material gave anomalous results. The maximum in the extracted sample curves occurred at higher crosslink densities, and the tensile strengths at high crosslink densities were much higher than observed for the unextracted samples.

The extension ratios at break for the SBR gum vulcanizates are plotted as a function of chain density in Figure 4. The plot is similar to that obtained with EPR. At low strain rates and low crosslink densities it was not possible to get the test specimens to break sharply as was the case with EPR. The SBR vulcanizates also showed no evidence of permanent set.
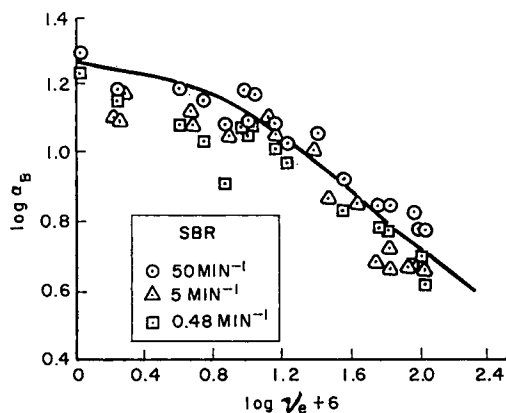

Fig. 4. Extension ratio at break as a function of chain density for SBR gum vulcanizates.

A theoretical explanation for the rate dependent maximum in the tensile strength versus degree of crosslinking curve has been given.[6] It is due to the fact that a greater fraction of chains, which have been extended to their limit of extensibility, is present at the moment of break in lightly crosslinked vulcanizates. A rate dependent non-affine deformation of the network junction points comes into play at these chain elongations approaching full extension and provides a molecular mechanism to explain the results.

An attempt was made to obtain vulcanizates of higher cross-link densities in the case of EPR by adding sulfur and more curing agent to the compounding formula. However, a limiting state of cure ($\nu_e \cong 92 \times 10^{-6}$ mole/cm.[3]) was obtained, probably due to the limited amount of unsaturation present in ECD-330. If the initial molecular weight of the ethylene–propylene terpolymer is taken as 70,000 g./mole and it is assumed that all the polymer double bonds are used up in the vulcanization reaction to produce the above chain density, then the crosslinking index, $\gamma = M_n/M_c$, is calculated to be about 7. This means that, on the average, each molecule of the ethylene–propylene copolymer would contain about 7 double bonds. Hence, the molecular weight between crosslink sites, M_c, would be about 10,000 g./mole.

Time-to-Break Under Constant Load for Reinforced EPR

A method of studying the rate dependence of tensile strength is to determine the time necessary to break a sample under constant load at different temperatures,[7] sometimes called creep rupture experiments. These measurements under various constant loads have been made on an EPR + 30 HAF black vulcanizate (recipe E) cured for 60 min., at 150°C. When the data were plotted as load versus log t, the curves for data taken at

vaous temperatures were found to superpose when shifted along the log t axis. This was also the case with the previously studied SBR systems.[7] In Figure 5 the composite curve obtained by shifting the data to effect superposition on the 43°C. curve is shown.

A plot of the logarithm of the shift factor, log a_T against $1/T$ gives a straight line as shown in Figure 6. From the slope of this line,[7] the activation energy for the process was found to be 43 kcal./mole. This is the same as the value of 44 $\pm$ 2 kcal./mole obtained for three SBR systems,[7] a sulfur-cured SBR + 30 HAF, a peroxide-cured SBR + 30 HAF, and a
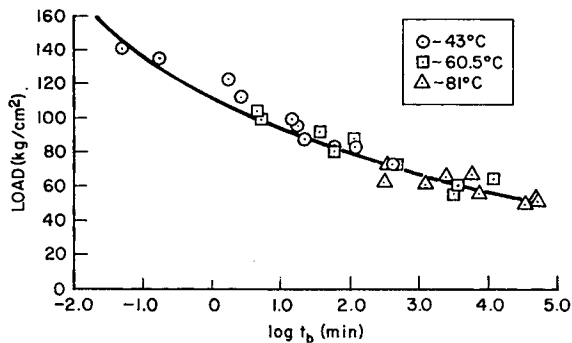

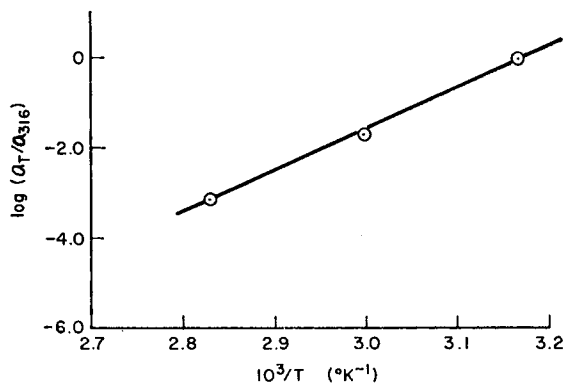Fig. 5. Time-to-break under constant load reduced to 43°C. for EPR + 30 HAF.

Fig. 6. Log (a_T/a_{316}) vs. $1/T$ for the rate process involved in creep rupture experiments with EPR + 30 HAF.

sulfur-cured SBR + 50 HiSil 233. From the study of the SBR systems it was concluded that the temperature dependence of the strength of carbon black- and silica-filled SBR is a function of neither the filler type nor the vulcanization system. This work with EPR indicates that it is also essentially independent of the rubber matrix at least for these two systems.

Tensile strength measurements in vacuum on EPR showed that the presence of air had no measureable effect on strength at high temperatures. A tensile strength of 47 ± 3 kg./cm.^{2} was obtained at 120°C. for the EPR + 30 HAF vulcanizate in vacuum or in air. In contrast, the tensile strength of SBR at high temperatures was found to decrease markedly in the presence of oxygen.[7]

Since filled SBR and EPR show the same temperature dependence of tensile strength, it is concluded that oxidation reactions have only minor importance as far as the mechanism responsible for this decrease in strength is concerned at least below a temperature of 120°C. Also, a decrease in filler–rubber adhesion with increasing temperature has already been ruled out by "Mullins effect" studies[7] as a possible mechanism to explain the decrease in tensile strength.

Tensile Strength of Filled SBR and EPR as a Function of Strain Rate at 25°C. and 86°C.

The tensile strength of SBR + 30 HAF (recipe E) and EPR + 30 HAF vulcanizates has been determined at three strain rates at 25 and 86°C. The results are summarized in Table II.

TABLE II

Tensile Strength at Three Strain Rates for Reinforced SBR and EPR at 25°C. and 86°C.

Elastomer	Strain rate, min.$^{-1}$	Tensile strength, kg./cm.^{2}	
		25°C.	86°C.
SBR + 30 HAF[a]	22.0	316	112
	5.0	295	89
	0.48	230	65
EPR + 30 HAF[b]	22.0	260	95
	5.0	256	86
	0.48	220	69

[a] Cured 30 min. at 290°F.
[b] Cured 60 min. at 290°F.

At 25°C. the dependence of tensile strength on strain rate is not great for the filled EPR and SBR studied. However, at the higher temperatures the effect of strain rate appears to become relatively more important.

Tensile Strength as a Function of Temperature

The temperature dependence of the tensile strength of the EPR + 30 HAF compound, which was cured for 60 min. at 305°F., at a strain rate of 0.8 min.$^{-1}$ is shown in Figure 7. Also shown in the figure are data obtained
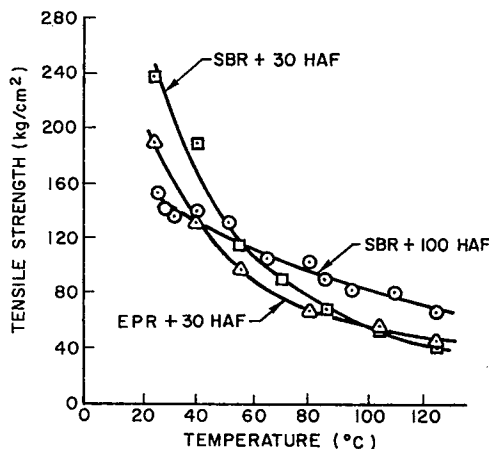
Fig. 7. Temperature variation of tensile strength measured at a strain rate of 0.8 min.$^{-1}$ for EPR and SBR containing the indicated amount of HAF black.

for SBR vulcanizates containing 30 and 100 phr of HAF black at the same strain rate. The SBR compounds (recipe E) were cured for 30 min. at 305°F. The chain densities of the vulcanizates were determined by equilibrium swelling methods and are reported in Table III.

TABLE III
Chain Density for Filled SBR and EPR

Elastomer	$\nu_e \times 10^4$, mole/cm.^{3}
EPR + 30 HAF	0.89
SBR + 30 HAF	1.60
SBR + 100 HAF	4.23

The tensile strengths of EPR and SBR both containing 30 phr of HAF are seen to exhibit similar dependence on temperature. The EPR vulcanizate starts at a lower tensile strength at room temperature and appears to cross the similarly loaded SBR curve at about 100°C. The tensile strengths of the two elastomers are nearly the same at temperatures between 85 and 125°C. This is the case even though the chain density of the EPR vulcanizate as measured by swelling is about half that of the SBR vulcanizate. However, the deleterious effect of oxygen on SBR tensile strength at high temperature must be separated before any valid conclusions concerning chain density and tensile strength of these filled elastomers can be made.

The highly loaded SBR containing 100 phr of HAF black shows a smaller dependence of tensile strength on temperature. The room temperature tensile strength was lower but the tensile strength at 125°C. was 67 kg./cm.^{2} as compared to about 43 kg./cm.^{2} for the vulcanizates containing 30 phr of HAF black.

SBR compounds prepared by ball milling[8] the compounding ingredients and carbon black with a solution of SBR in benzene gave the same tensile strength versus temperature curves at the same crosslink density. Thus, dispersion of black does not seem to be a major factor in determining tensile strength at elevated temperatures.

Limiting Chain Density in Filled EPR

The chain density for the EPR vulcanizate containing 30 phr of HAF black was found to be about 8.9×10^{-5} mole/cm.[3] for a 60 min. cure at 150°C. After 10 hr. post-cure at 125°C. the chain density increased slightly to 9.8×10^{-5} mole/cm.[3]. This limiting degree of cure was nearly the same as was found for the gum vulcanizates. Hence, it appears that the number of crosslinks formed in the HAF-filled system is also controlled by the number of double bonds in the polymer. This means that double bonds are involved in the formation of bonds between carbon black and polymer for this curing system.

CONCLUSION

The maximum in the tensile strength versus chain density curves for EPR and SBR gum vulcanizates is strongly dependent on strain rate. The maximum becomes less evident as true equilibrium conditions are approached. It occurs at a ν_e of about 0.5×10^{-5} mole/cm.[3] for EPR and a ν_e of about 1.3×10^{-5} mole/cm.[3] for SBR.

The activation energy obtained for the process operating in creep rupture experiments with black filled EPR was the same as previously obtained for several SBR systems. Hence, the mechanism responsible for the decrease in strength is probably the same for both elastomer systems. The presence of oxygen had no deleterious effect on the tensile strength of filled EPR at 120°C.

The temperature dependence of the tensile strength at constant strain rate of filled EPR and SBR is similar up to about 80°C., where oxidation becomes important in the SBR system.

The same limiting state of cure was obtained for both gum and filled ECD-330 vulcanizates. Hence, it appears that a limited number of polymer double bonds participate in the formation of filler–polymer bonds in the curing system used.

References

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Résumé

On a déterminé la résistance à la traction et l'élongation à la rupture des gommes vulcanisées d'EPR et de SBR en fonction de la densité des réseaux de chaînes. On trouve une grande contribution de la viscosité à la résistance à la traction à faible densité de ramification et le maximum dans la courbe de la résistance à la traction en fonction de la densité des chaînes diminue au fur et à mesure que l'on s'approche des conditions d'équilibre. On a étudié la dépendance de la vitesse de la résistance à la traction de l'EPR contenant du noir comme charge par des expériences de rupture au fluage. On a étudié et comparé la dépendance de la température de l'EPR et de l'SBR chargé. On a obtenu le même degré limite de post-traitement pour l'EPR chargé et pour la gomme vulcaniseé d'EPR.

Zusammenfassung

Die Zugfestigkeit und Bruchdehnung von ungefüllten EPR- und SBR-Vulkanisaten wurde in Abhängigkeit von der Netzketten-Dichte bestimmt. Bei niedriger Vernetzungsdichte wurde ein grosser viskoser Beitrag zur Zugkraft gefunden und das Maximum in der Kurve, Zugfestiekeit gegen Kettendichte, nahm bei Annäherung an die Gleichgewichtsbedingungen ab. Die Geschwindigkeitsabhängigkeit der Zugfestigkeit von Russ-gefülltem EPR wurde anhand von Kriech-Bruch-Versuchen untersucht. Die Temperaturabhängigkeit der Zugfestigkeit von gefülltem EPR und SBR wurde untersucht und verglichen. Für gefüllte und ungefüllte EPR-Vulkanisate wurde der gleiche Grenzvulkanisationsgrad erhalten.