

A New Mechanism for Increasing Tear Strength and Cut-Growth Resistance of Elastomers

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SYNOPSIS

A new mechanism is presented for increasing the tear strength of noncrystallizing elastomers over a broad temperature range. It is shown that the incorporation, into elastomers, of a plastic filler with the proper yield strength can substantially increase tear strength by decreasing the excess stress that develops at the tip of a sharp cut in an elastomer strip under tension. To be effective at low aspect (length/diameter) ratio, the yield strength of the plastic must be of the same order of magnitude as the tensile strength of the elastomer to which it is added. The analysis is strictly valid only for very small deformations, where crack-tip blunting can be ignored, and for an applied stress sufficiently low that the plastic-yielding zone is very small relative to the crack length. It provides a useful model, at least, for the development of a new mechanism for increasing the tear strength of fluoroelastomers at sufficiently high temperatures, which is of significant practical importance. Examples of the use of a new fluoroplastic micropowder to provide over a fourfold increase in tear strength of several fluoroelastomers at high temperatures are given. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Certain physical properties of elastomers, such as tensile strength and tear strength, decrease rapidly with increasing temperature. This decline in properties is not too important for most elastomers, since their thermal stability usually limits their upper use temperature. Fluoroelastomers, such as vinylidene fluoride/hexafluoropropylene copolymers (VF₂/HFP, ASTM designation FKM) have excellent thermal stability, however, and are molded, cross-linked, and frequently used for long time periods above 200°C.

This article deals with techniques to improve the high-temperature tear strength of fluoroelastomers, although the techniques described are applicable to all elastomers at sufficiently high temperatures and to those elastomers at room temperature that do not undergo strain-induced crystallization. Some data on dynamic cut-growth resistance and abrasion resistance, which are closely related to tear strength,

are also presented. A review article¹ has been published on fluoroelastomers and should be consulted for details on the various types of commercially available fluoroelastomers and topics such as polymerization, compounding, processing, cross-linking, and physical properties.

Background

There have been a number of studies with the goal of improving the tear strength and cut-growth resistance of elastomers. The approach usually taken, for elastomers that do not undergo strain-induced crystallization, has been to find a reinforcing filler that would somehow dissipate energy during the tearing process. With few exceptions,²⁻⁴ this approach has not been very successful. Some improvements in tear strength have been realized in certain polymers, such as polyurethanes, by controlling polymer morphology.

Theories on cut growth usually attempt to explain how energy dissipation at the tip of a growing cut controls the cut-growth rate. It is the nature of these theories that they do not predict new mechanisms

for improving tear strength or do they lead to new solutions to the problem of the low tear strength of all elastomers at high temperatures. At the present time, there are no general procedures available for significantly improving the tear strength or cut-growth resistance of elastomers.

Tearing Energy and Tearing Test Methods

The first important advance in understanding the factors that control the growth of a crack in a brittle material was made by Griffith⁵ in 1921. He established a criterion for crack instability based on the principle of conservation of energy. Griffith calculated the elastic energy stored in the vicinity of a crack and compared the rate of decrease of this energy as the crack propagates with the energy needed to form new fracture surfaces.

Rivlin and Thomas⁶ extended the Griffith fracture hypothesis to the tearing of elastomeric materials. By taking into consideration the effects of viscoelasticity, they found that a criterion similar to the one proposed by Griffith is applicable to elastomers. The "tearing energy" is defined⁶ as the energy that is released during the tearing process and can be thought of as the driving force for crack propagation in an elastomer. It is not only a measure of the energy necessary to create a unit of new surface, but also includes the energy that is dissipated by viscous losses, strain-induced crystallization, microscopic tearing near the crack tip, and the breakdown of a filled system.

There are several ASTM test methods regularly used to report the tear strengths of elastomers. Although tear strength values obtained using the various conventional tests do not correlate, Thomas^{7,8} has shown that measurements of tear or crack propagation in elastomers, using test pieces of very different geometries, give equivalent results when expressed in terms of the tearing energy. The tearing energy is, therefore, a more fundamental measure of resistance to crack propagation or to tearing than are tear strength values obtained using the various conventional ASTM test methods, although the tearing energy does depend on the rate of tearing and on the temperature.

Data given in commercial product literature are almost always reported as values of tear strength, obtained using one of the various standard ASTM test methods. The most realistic and most severe tear test routinely used is the "Trouser or Split Tear" method ASTM D470. Fortunately, it is easy to convert tear strength values obtained using the Trouser Tear test method to values for the tearing

energy.⁶ For a Trouser Tear test specimen, if the material in the legs does not undergo large deformations during the test, the tearing energy is numerically equal to the tear strength multiplied by a factor of two ($2\times$ tear strength). The test method used in this article to report values for the tear strength of fluoroelastomers is the Trouser Tear test method ASTM D470. All tear tests were performed at 20 in./min rate of separation of the grips of the test apparatus. It is possible to compare results using other tear test methods to the tear strength values reported in this article through the concept of the tearing energy.

EXCESS TENSILE STRESS CONCENTRATED AT THE TIP OF A CUT

Consider a strip of a linearly elastic material that has an elliptical hole in the center and that is stretched, under uniaxial tension, by a tensile stress, S . It has been shown⁹ that, for a narrow ellipse or crack of length 2λ having a notch radius, ρ_n , a stress concentration is developed at the tip of the cut that is approximately given by $2S(\lambda/\rho_n)^{1/2}$. Thus, for a long narrow cut in an elastic material, the tensile stress at the tip of the cut becomes very large as the radius of curvature of the tip, ρ_n , becomes smaller. The tensile stress is concentrated at the tip of the cut and can become much larger than the stress, S , which is applied to stretch the sample.

For a "fine crack" with "perfectly sharp" ends, the radius of curvature becomes vanishingly small. Along the extension of the "crack axis" into the material region, the tensile stress close to the tip of the crack is given by¹⁰

$$\sigma_{zz} = S(\lambda/2\xi)^{1/2}[1 + O(\xi^{1/2})] \quad (1)$$

where ξ is the distance from the tip of the crack. Thus, for a perfectly sharp crack, the tensile stress has a singularity at $\xi = 0$, the crack tip.

It is this large stress concentration at the tip of a sharp crack or cut that causes the force required to tear an elastomer strip containing a cut to be much less than the force required to break an unnotched strip. Elastomers tend to adjust to these large stress gradients by the formation of an anisotropic structure (strain-induced crystallization at the tip of the cut), through stress relaxation (crack-tip blunting), or through structural breakdown of a filled system. It is this ability of an elastomer to adjust to a stress concentration that determines its tear strength. It is to be expected that any mecha-

nism that reduces the excess stress concentrated at the tip of a cut should result in a corresponding increase in tear strength.

MECHANISM TO REDUCE STRESS CONCENTRATION AT THE TIP OF A CUT

One of the most effective mechanisms for reducing the stress concentration at the tip of a cut is the plastic yielding that occurs prior to failure in ductile materials. Yielding causes a deviation in the shape of the stress-strain curve. It has been shown¹¹ that when such a deviation occurs it causes a reduction in the excess tensile stress at the tip of a cut.

The expression for the tensile stress close to the tip of a cut or crack, given in eq. (1), was derived for small deformations of a linearly elastic material, i.e., a material with a linear stress-strain curve. Generally, numerical analysis must be employed to determine the complete stress distribution around the tip of a cut for a material that has a nonlinear stress-strain curve. However, the singularity (stress concentration) dominating the behavior at the tip of a cut can be obtained in a simple analytical form for a material with a piecewise linear stress-strain curve, as shown in Figure 1. Although this is only an idealized approximation of the stress-strain curve of a yielding material, it does model certain features of plastic flow, without the need for numerical computation. For such a piecewise linear relationship, it has been shown¹¹ that the dominant singularity (excess stress) at the tip of a cut is the same as that given in eq. (1) for a linear material, but reduced by a factor of $(E_{\text{tan}}/E_i)^{1/2}$, where E_{tan} is the slope of the piecewise linear stress-strain curve at break and E_i is the initial modulus or initial slope of the stress-strain curve. For materials such as elastomers, which have a Poisson's ratio of $\nu = \frac{1}{2}$, this result is valid for both plane stress and plane strain.¹¹

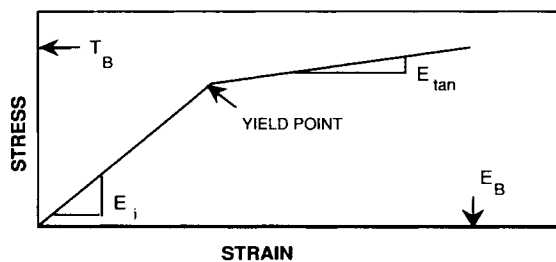


Figure 1 Nonlinear stress-strain curve where E_i = initial slope of stress-strain curve; E_{tan} = slope of stress-strain curve at break.

For a material that initially has a linear stress-strain curve, if the slope of the stress-strain curve at break, E_{tan} , can be reduced in some way, one might expect an increase in the tear strength of the material to be proportional to the quantity $(E_i/E_{\text{tan}})^{1/2}$, i.e., inversely proportional to the reduction in excess tensile stress at the tip of a cut. Therefore, if one can change the shape of the stress-strain curve of a material such as a fluoroelastomer that has a practically linear stress-strain curve to a close approximation of the piecewise linear behavior given in Figure 1, then one would expect an increase in the tear strength of the fluoroelastomer on the order of $(E_i/E_{\text{tan}})^{1/2}$. To be commercially successful, however, this must be accomplished without unacceptable changes in certain other physical properties, such as hardness and compression set.

This result, since it is derived using the theory of linear elasticity, is strictly valid only for very small deformations, where crack-tip blunting can be ignored, and for an applied stress sufficiently low that the plastic-yielding zone is very small relative to the crack length. The goal of this analysis is to develop a new mechanism for increasing the tear strength of fluoroelastomers at high temperatures. The tear strengths of fluoroelastomers at the temperatures of interest are very low, and notched samples tear with very little deformation. Frequently, notched samples cannot even be tested at high temperature since they tear completely when one attempts to position them in the grips of the testing apparatus. Thus, one would expect that an analysis based on the theory of linear elasticity should provide a useful model, at least for certain fluoroelastomer compositions at sufficiently high temperatures, which is of significant practical importance.

Control of the Shape of Stress-Strain Curves of Fluoroelastomers

The shape of the stress-strain curve can be controlled, to some extent, by changing the nature of the cross-linked structure of an elastomer. Generally, most changes, other than simply reducing the degree of cross-linking, lead to deviations from linearity in the positive sense, i.e., $E_{\text{tan}} > E_i$, rather than to low values of E_{tan} . A reduction in the degree of cross-linking does result in a lower value of E_{tan} , and it is known that this will also lead to increased tear resistance. However, this does not provide an adequate solution to the problem of low tear strength, since a lower degree of cross-linking also leads to an unacceptable increase in compression set.

Another possible method of changing the shape of the stress-strain curve of an elastomer is through the addition of filler particles. The addition of rigid or high modulus filler particles increases the slope (modulus) of the stress-strain curve of an elastomer, whereas the addition of particles softer than the elastomeric matrix decreases the slope. Thus, one possible technique for obtaining a stress-strain curve of the form shown in Figure 1 would be through the addition of rigid filler particles that exhibit plastic yielding (slope = 0) at some particular stress value. Figure 2 shows an idealized representation of the effect that the addition of such yielding plastic filler particles would have on the shape of the stress-strain curve of a typical noncrystallizing elastomer.

It is indicated in Figure 2 that to be effective the plastic particles must yield at a stress that is less than the tensile strength of the elastomer, since the particles must yield before the elastomeric matrix breaks or pulls away from the particles. Actually, whenever rigid particles are dispersed in a softer matrix and the composite is held under tension, the tensile stress within the particles is greater than the tensile stress in the matrix if the adhesion between the particles and the matrix is sufficient.¹² The excess stress within the particles depends on the shape of the particles and their modulus as well as on the modulus of the matrix. In general, to avoid the unacceptable stiffness that results when long fibers are compounded into elastomers, the yield stress of the dispersed plastic phase should be of the same order of magnitude as the tensile strength of the elastomeric matrix. This allows one to use plastic filler particles of low aspect ratio (length/diameter) but still enables the particles to yield sufficiently before the elastomeric matrix breaks. Since fluoroelastomers have very low tensile strengths at high temperatures, this restriction does limit the variety of yielding plastic filler particles that can be expected to be useful for improving the high-temperature tear strengths of these elastomers.

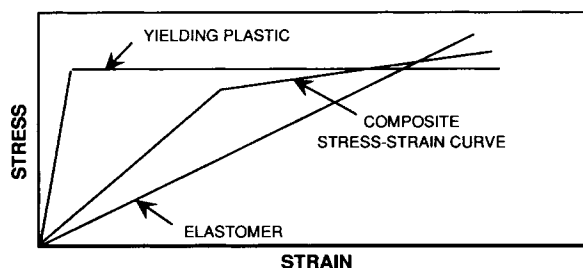


Figure 2 The effect of yielding plastic-filler particles on the stress-strain curve of a noncrystallizing elastomer.

CALCULATION OF THE EFFECTS OF YIELDING PLASTIC-FILLER PARTICLES ON TEAR STRENGTH

When small plastic particles are dispersed in an elastomeric matrix under the usual high-shear compounding conditions, they may remain as individual small particles if they are compatible with the matrix or they may agglomerate and be drawn into the form of fibers or platelets. Certain physical properties of the composite, such as the tensile modulus, tensile strength, shape of the stress-strain curve, and, consequently, the tear strength, will depend on the manner in which the plastic is dispersed in the elastomer. Through the use of well-known relationships, the tensile modulus and the stress-strain curve can be predicted for yielding plastic spheres, fibers, or platelets dispersed in an elastomeric matrix. This can then be used to predict improvements in the tear strength of the elastomer using the piecewise linear model described above.

Yielding Plastics Dispersed as Fibers

When a long, high-modulus, plastic fiber is embedded in an elastic matrix of lower modulus, and the composite is held under uniaxial tension, it can be shown¹³ that if the fiber lies in the same direction as the applied tensile stress there is a stress concentration in the matrix near the fiber ends. If perfect adhesion is assumed, stress transfer from the matrix to the fiber occurs as the result of a shear stress at the fiber-matrix interface. If the fiber is sufficiently long, stress transfer occurs only near the fiber ends and the shear stress at midfiber length is zero.

As the tensile stress is increased, one of three events will occur: If the stress in the matrix exceeds the strength of the matrix material, failure will occur in the matrix. If the shear stress at the surface of the fiber, near the fiber ends, exceeds the strength of the matrix-fiber bond, the fiber will pull out of the matrix. If the tensile stress in the fiber exceeds the yield stress of the fiber material, the fiber will yield. To some extent, it is the aspect ratio (length/diameter, l/d) of the fiber that determines the order in which these events will occur. By analogy with the analysis of reinforcement in short-fiber composites,¹⁴ a critical aspect ratio, $(l/d)_c$, can be defined as

$$(l/d)_c = \sigma_y / 2G_S \quad (2)$$

where σ_y is the yield strength of the plastic fiber and

G_S is the lesser of the shear strength of the matrix or the shear strength of the bond between the fiber and the matrix. If failure occurs in the elastomeric matrix when the strain energy of distortion reaches a certain limit characteristic of the material,¹⁵ then the ratio of the tensile strength of the elastomer to the shear strength, T_B/G_S , is equal to $3^{1/2}$. If perfect adhesion is assumed, eq. (2) can then be rewritten as

$$(l/d)_c = 3^{1/2}\sigma_y/2T_B \quad (3)$$

Therefore, for a plastic dispersed as particles with low aspect ratio ($l/d = 1$), if the adhesion to the fiber surface is sufficient, the yield strength of the plastic must be less than about $(2T_B/3^{1/2})$, where T_B is the tensile strength of the matrix elastomer. If the aspect ratio of the fiber is greater than the critical value given in eq. (3) and adhesion is sufficient, the fiber will yield before failure occurs in the matrix or at the fiber-matrix interface, and it is assumed that the fiber will be effective in increasing tear strength. If the aspect ratio is less than this critical value, failure will occur prior to yielding with no expected increase in tear strength.

The elastic coefficients of a unidirectional (orthotropic) fiber-filled composite can be calculated from equations derived by Halpin and Tsai.¹³ From these, the expected increase in tear strength that results from fiber yielding can be determined. The Halpin-Tsai equations for fibers with length/diameter ratio, (l/d) , can be written as

$$E/E_m = (1 + \delta\Theta\Phi)/(1 - \Theta\Phi) \quad (4)$$

where

$$\Theta = (E_f/E_m - 1)/(E_f/E_m + \delta) \quad (5)$$

$$\delta = 2(l/d) \quad (6)$$

and E = composite moduli, E_L or E_T ; E_m = matrix modulus; E_f = fiber modulus; E_L = longitudinal modulus; E_T = transverse modulus; and Φ = volume fraction of fibers or particles.

For a random fiber orientation, the moduli will be isotropic in the plane of the sheet; this situation is described in laminated plate theory as quasi-isotropic. The modulus of the composite, E_C , for a quasi-isotropic orientation of short fibers, can be expressed as

$$E_C = (3/8)E_L + (5/8)E_T \quad (7)$$

Equations (4)–(7) can be used to calculate the initial modulus, E_i , of a composite of an elastomer filled with plastic spheres, short fibers, or platelets, by choosing the proper value for the aspect ratio, (l/d) . For spheres, $(l/d) = 1$; for platelets, (l/d) is the ratio of the diameter of the plate to the thickness. For high-modulus fibers, one can assume that $E_f \gg E_m$.

If the plastic filler has a sufficiently low yield strength, as described in eqs. (2) and (3), then the plastic particles will yield before the composite breaks or the particles pull out of the elastomer matrix. In addition, if the aspect ratio of the particles is sufficiently high, the so-called ineffective length at the ends of the particles, over which the shear stress is transferred from the matrix to the particles, will be relatively small. The slope of the stress-strain curve of the composite at break, E_{tan} , can then be calculated from eqs. (4)–(7) by setting $E_f = 0$, where E_f is the fiber or particle modulus.

If it is assumed that the increase in tear strength is inversely proportional to the decrease in excess stress at the tip of the cut, then, as discussed above, the tear strength of the elastomer composite, Γ_c , which contains the yielding plastic-filler particles, can be calculated from the expression

$$\Gamma_c = \Gamma_m(E_i/E_{tan})^{1/2} \quad (8)$$

where Γ_m is the tear strength of the elastomer matrix prior to the addition of the yielding plastic-filler particles.

Figure 3 shows the predicted tear strength ratio, $\Gamma_r = (\Gamma_c/\Gamma_m)$, as a function of volume fraction of plastic-filler particles, Φ , calculated using eqs. (4)–(8), for yielding plastic spheres, for yielding platelets with an aspect ratio of 10, and for yielding fibers with aspect ratios of 10 and 100. It was assumed that $E_f \gg E_m$ in eq. (5).

The theory predicts that the addition of yielding plastic-filler particles can be very effective in increasing the tear strength of elastomers. To be most effective, the plastic must have a low yield strength and should be dispersed in the elastomer in the form of fibers or platelets.

The initial modulus of a composite, E_i , increases rapidly with increasing aspect ratio of the plastic filler. Such an increase could be unacceptable if it caused poor processing behavior, if it led to unacceptably high values for the hardness, or if it led to higher values for compression set. However, since it is predicted that the stress-strain curve of the composite will be nonlinear, a high value for the initial modulus of the composite might not be re-

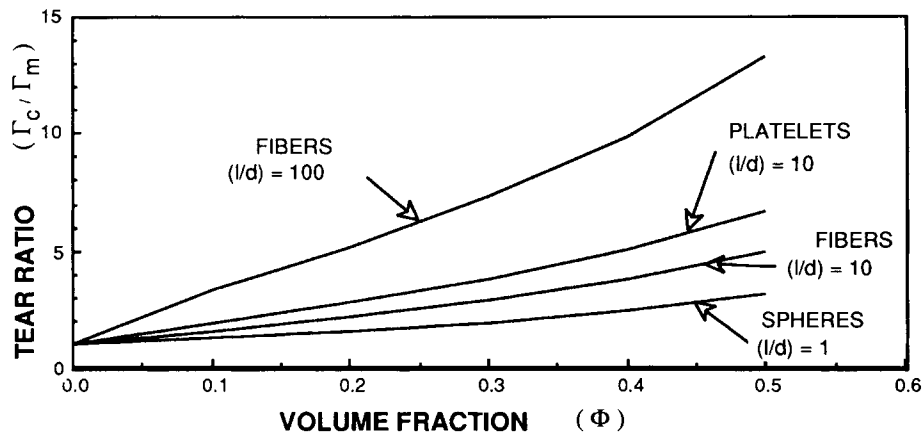


Figure 3 Tear strength ratio, Γ_c/Γ_m , for an elastomer containing yielding spheres, fibers, and platelets, where Γ_c is the tear strength of the elastomer composite that contains the yielding plastic-filler particles and Γ_m is the tear strength of the elastomer matrix prior to the addition of the yielding plastic-filler particles.

flected in values for the tensile stress at higher elongations, such as M_{100} . For carbon-black-filled elastomeric composites, the increased modulus that results from the addition of yielding plastic-filler particles with a high aspect ratio can be partially compensated by a reduction in the level of carbon black.

EXPERIMENTAL TEST OF THE EFFECTIVENESS OF YIELDING PLASTIC FILLERS IN INCREASING THE TEAR STRENGTH OF FLUOROELASTOMERS

As discussed in the section above, the addition of properly selected yielding plastic fillers to fluoroelastomers should result in a very large increase in tear strength. To be most effective, the plastic filler must have a sufficiently low yield strength and should be dispersed in the elastomer in the form of fibers or platelets. To be useful, the plastic filler should also be thermally stable, should not interfere with the curing chemistry of the fluoroelastomer, should not adversely affect heat aging, and should be able to withstand the same harsh environments as can the fluoroelastomer.

When one examines the literature to find a plastic that yields at a sufficiently low value of tensile stress, is thermally stable, and has a high melting temperature, to make it useful over a broad temperature range, one finds that there are few candidates. The most promising material seems to be high molecular weight polytetrafluoroethylene (PTFE) homopolymer. The tensile yield strength of high molecular weight PTFE at 25°C is 13 MPa [1885 psi], which

is about the same as the tensile strength of fluoroelastomers. Therefore, one would expect that the addition of PTFE to a fluoroelastomer composite would increase tear strength, at least at room temperature, even if the PTFE were dispersed in the fluoroelastomer in the form of fibers or platelets with relatively low aspect ratio. In fact, high molecular weight PTFE would seem to be the ideal reinforcing agent for increasing the high-temperature tear strength of fluoroelastomers.

Addition of Fluoroplastic to Fluoroelastomers

The addition of high molecular weight PTFE to elastomers was first studied in silicone elastomers¹⁶ in 1955 and in fluoroelastomers^{17,18} in 1968. It was observed that obvious agglomeration and fibrillation of the PTFE occurred during compounding, and white streaks of PTFE were clearly visible, aligned in the direction of mill rotation during the final sheeting out step of the compounding operation. Dissolving away the uncross-linked elastomer showed that the PTFE was dispersed as a continuous web, in the form of nodes-and-fibers, typical of PTFE articles made using a paste extrusion process. This weblike structure did greatly reinforce the elastomers, but it also resulted in unacceptably high hardness and modulus with distortion of final vulcanizates. To be useful in applications where molded parts are required, it is clear that massive agglomeration of the PTFE must be avoided and fibrillation must be controlled.

A high molecular weight micropowder based on a tetrafluoroethylene/hexafluoropropylene (TFE/HFP) fluoroplastic copolymer has recently been

developed¹⁹ that forms short fibers, ribbons, or platelets when compounded with sufficient shear into elastomers. The controlled structure developed during compounding allows high levels of incorporation of the micropowder into elastomers with uniform dispersion. Elastomer composites containing up to 80% by weight of the TFE/HFP micropowder (volume fraction $\Phi = 0.77$), in the form of small platelets, still maintain a rubbery character. This provides tough elastomeric compositions with very high tear strength and abrasion resistance. In addition, it is observed that platelet formation leads to more isotropic reinforcement than does fibrillation.

The improvement observed in the tear strength of an elastomer containing the TFE/HFP micropowder is controlled by the yielding behavior of the fluoroplastic copolymer. To be effective, the elongation at break of the TFE/HFP resin must be greater than about 100% and the ratio of the stress at yield to the stress at break must be greater than about 0.6; i.e., the shape of the stress-strain curve of the TFE/HFP copolymer must be similar to the idealized stepwise stress-strain curve depicted for the yielding plastic in Figure 2. Figure 4 shows the stress-strain curves, measured at 177°C, of vulcanizates of a vinylidene fluoride/hexafluoropropylene (VF₂/HFP) fluoroelastomer, a tetrafluoroethylene/perfluoro(methyl vinyl ether)/cure-site (TFE/PMVE/cure-site) fluoroelastomer, and an ethylene/tetrafluoroethylene/perfluoro(methyl vinyl ether)/bromotetrafluorobutane (E/TFE/PMVE/BTFB) fluoroelastomer as well as the stress-strain curve, at 177°C, of the TFE/HFP fluoroplastic copolymer.¹⁹

It can be seen that the stress-strain curves of the fluoroelastomers are practically linear at 177°C. The stress-strain curve of the TFE/HFP fluoroplastic copolymer is a close approximation of the idealized stress-strain curve of a yielding plastic filler, depicted in Figure 2. The TFE/HFP fluoroplastic copolymer in this example consisted of dispersion-process-produced, non-melt-fabricable copolymer, Teflon® MP1500 (DuPont). Since the yield strength of the TFE/HFP copolymer is greater than the tensile strengths of the fluoroelastomers, it is predicted from eq. (3) that to increase tear strength the TFE/HFP particles must be dispersed in these fluoroelastomers in the form of fibers or platelets with aspect ratio greater than about 3.

Figure 5 shows the stress-strain curves, measured at 177°C, of VF₂/HFP, TFE/PMVE/cure-site, and E/TFE/PMVE/BTFB vulcanizates containing 40 parts per 100 parts of rubber (phr) of the TFE/HFP copolymer dispersed as platelets.

The incorporation of the TFE/HFP copolymer as platelets into the fluoroelastomer formulations changes the shape of the respective stress-strain curves as expected. The initial slope of each of the stress-strain curves, E_i , is increased, while the slope of each curve at break, E_{tan} , is decreased.

Table I shows the effects on the tensile and tear properties, of adding the TFE/HFP copolymer to a typical carbon-black-filled VF₂/HFP fluoroelastomer formulation. Measurements were made in the mill direction and transverse to the mill direction and were averaged.

Abrasion resistance was measured using the Taber Abrasion Test, ASTM D1044, wheel H-22, 1000 g weight, and is reported as weight loss in grams per

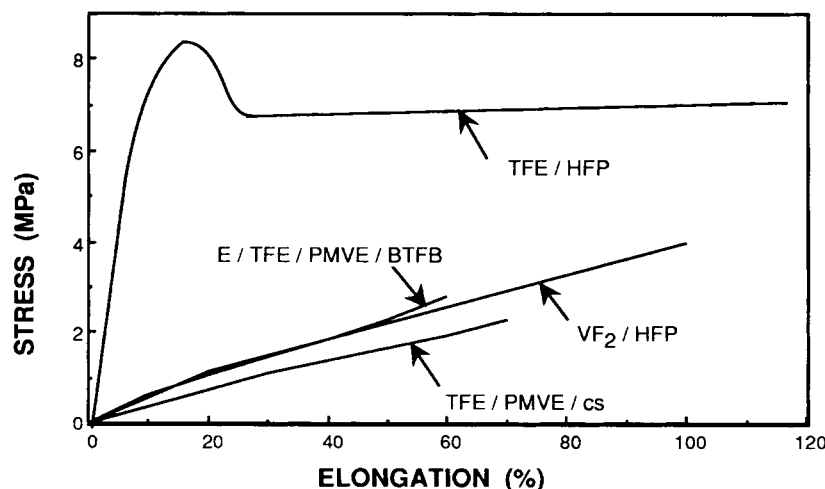


Figure 4 Stress-strain curves at 177°C of VF₂/HFP, TFE/PMVE/cure-site, and E/TFE/PMVE/BTFB fluoroelastomer vulcanizates and TFE/HFP fluoroplastic copolymer.

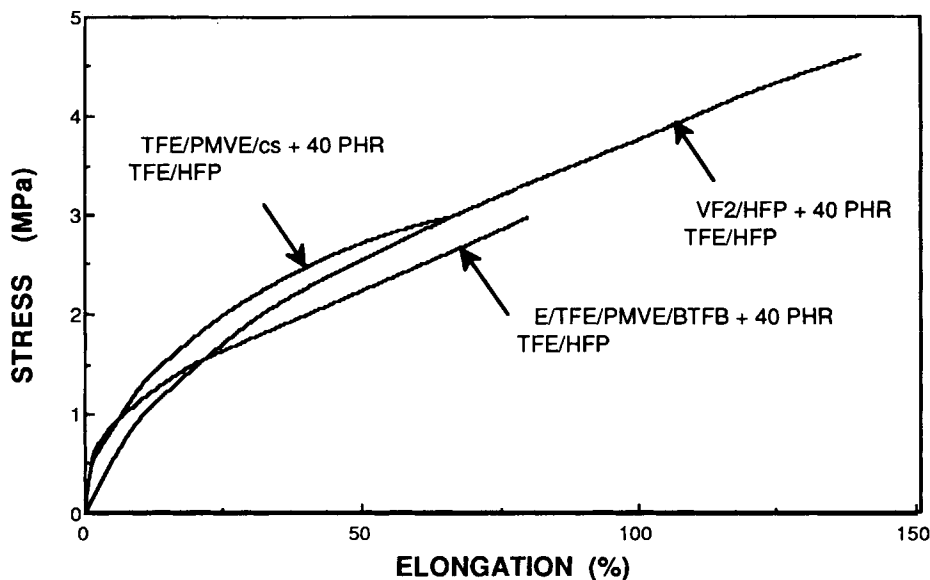


Figure 5 Stress-strain curves at 177°C of VF₂/HFP, TFE/PMVE/cure-site, and E/TFE/PMVE/BTFB vulcanizates containing 40 phr TFE/HFP copolymer dispersed as platelets.

1000 revolutions. The TFE/HFP copolymer was uniformly dispersed in all samples as platelike aggregates of 5–10 microns in diameter and 1–2 microns thick. Comparison of compound 1.D with the control, 1.A, shows that the TFE/HFP resin provides over a 4× increase in tear strength at 177°C. This increase in tear strength is in agreement with the theory that, as is shown in Figure 3, predicts a value for the tear strength ratio (Γ_c/Γ_m) of about 3.3 for yielding platelets with aspect ratio (l/d) = 10 and at a volume fraction of $\Phi = 0.25$ (40 phr). Improvements in tear strength and abrasion resistance at 25°C are also observed.

Table II shows the effects on the tensile and tear properties of adding TFE/HFP copolymer particles to a carbon-black-filled (TFE/PMVE/VF₂) fluoroelastomer formulation.

Abrasion resistance was measured as in Table I. The vulcanizates were smooth and rubbery and the TFE/HFP copolymer resin was dispersed as platelike aggregates of distinct particles. Comparison of compound 2.B with the control, 2.A, shows that the TFE/HFP resin provides almost a 5× increase in tear strength at 177°C as well as improvements, at 25°C, in tear strength and abrasion resistance.

Table III shows the effects on the tensile and tear properties of adding the TFE/HFP copolymer particles to a typical carbon-black-filled E/TFE/PMVE/BTFB formulation.

The vulcanizates were smooth and rubbery and the modified PTFE resin was dispersed as platelike

aggregates of distinct particles. Comparison of compound 3.B with the control, 3.A, shows that the TFE/HFP resin provides a 4× increase in tear strength at 177°C.

APPLICATION TO OTHER ELASTOMERS AND YIELDING PLASTICS

The analysis of the use of yielding plastic-filler particles to increase tear strength at high temperatures is not limited to fluoroelastomers. The tensile strength of most elastomers, when properly reinforced, is generally greater than the yield strength of the TFE/HFP copolymer described above, at least at room temperature. Thus, one would expect that this copolymer should be as effective in increasing the tear strengths of ordinary hydrocarbon and silicone elastomers, which do not undergo strain-induced crystallization, as they have been found to be in fluoroelastomers. In fact, it has been found¹⁹ that the addition of the TFE/HFP copolymer to a broad range of noncrystallizing elastomers does increase tear strength over a broad temperature range, improves abrasion resistance, and lowers the coefficients of friction.

In a similar manner, plastics that have a sufficiently low yield strength, other than PTFE, should be effective in increasing the tear strength of elastomers. Fluoroplastics are ideally suited as reinforcing agents in fluoroelastomers since they are

Table I The Effects of the Addition of TFE/HFP Copolymer Particles to a VF₂/HFP Fluoroelastomer

	Sample			
	1.A	1.B	1.C	1.D
	TFE/HFP Copolymer (phr)			
	None	10	25	40
	Volume Fraction TFE/HFP (Φ)			
	0	0.08	0.17	0.25
Tensile at 25°C				
M_{100} (MPa)	5	5	7	9
T_B (MPa)	14	15	15	16
E_B (%)	280	260	250	230
$T_B \times E_B$	3920	3900	3750	3680
Tear (kN/m)	4	6	7	7
Tensile at 177°C				
M_{100} (MPa)	4	4	4	4
T_B (MPa)	4	5	5	4.6
E_B (%)	100	125	125	140
$T_B \times E_B$	400	625	625	644
Tear (kN/m)	0.5	0.9	1.6	2.3
Abrasion resistance at 25°C				
wt loss (g/krev)	0.2	—	—	0.06

phr = parts per 100 parts of rubber by weight; M_{100} = stress at 100% elongation ASTM D412; T_B = tensile stress at break ASTM D412; E_B = elongation at break ASTM D412; tear = tear strength (Trouser Tear) ASTM D470. All tests run at 20 in./min. Formulation: 100 VF₂/HFP fluoroelastomer, 3 MgO, 6 Ca(OH)₂, 1.3 Viton® Curative #20, 2.8 Viton Curative #30, 30 MT carbon black, TFE/HFP copolymer as indicated. Press cure 30 min at 177°C. Postcure 24 h at 232°C. The fluoroelastomer in this example was Viton E-45 (DuPont). The TFE/HFP copolymer was Teflon MP-1500 (DuPont).

thermally stable, have the chemical resistance required for typical fluoroelastomer applications, and are reinforcing even at high temperatures. However, the cost of fluoroplastics may rule out their use in conventional, low-cost elastomer formulations.

Several nonfluoropolymer elastomer and yielding plastic combinations have been disclosed that have improved tear strength and abrasion resistance. In particular, it has been found⁴ that the tear strengths of chlorinated polyethylene and chlorosulfonated polyethylene can be increased by up to 5× by the addition of 20 phr ultrahigh molecular weight polyethylene (UHMW-PE). Tear strengths are increased even at temperatures up to 150°C, since, as

is the case with high molecular weight PTFE, UHMW-PE does not flow above its melting temperature. Nylon 6/610/612 terpolymer, which has a relatively low yield stress, has also been found to be very effective in increasing the tear strengths of chlorosulfonated polyethylene and chlorinated polyethylene.

The tear strengths of elastomers that undergo strain-induced crystallization, such as natural rubber and neoprene, are relatively high without the addition of any reinforcing additives. The addition of a yielding plastic filler to these elastomers does not increase tear strength at room temperature for, most likely, the same reason that the addition of carbon black does not increase the work-to-break. At higher temperatures, as strain-induced crystallization disappears, the tear strengths of these elastomers are substantially increased with the addition of yielding plastic fillers, including the TFE/HFP copolymer.

Table II The Effects of the Addition of TFE/HFP Copolymer Particles to TFE/PMVE/VF₂ Fluoroelastomer

	Sample	
	2.A	2.B
	TFE/HFP Copolymer (phr)	
	None	40
	Volume Fraction TFE/HFP (Φ)	
	0	0.27
Tensile at 100°C		
T_B (MPa)	4	4
E_B (%)	80	70
$T_B \times E_B$	320	280
Tear (kN/m)	1.5	3.5
Tensile at 177°C		
T_B (MPa)	2	3
E_B (%)	70	65
$T_B \times E_B$	140	195
Tear (kN/m)	0.4	1.8
Abrasion resistance at 25°C		
wt loss (g/krev)	0.1	0.07

Formulation: 100 TFE/PMVE/VF₂ fluoroelastomer, 10 SAF carbon black, 4 PbO, 3 K₂AF, 4 DCH-Crown, TFE/HFP copolymer as indicated. Press cure: 30 min at 177°C. Postcure: step cure 48 h to 288°C in N₂.

Table III The Effects of the Addition of TFE/HFP Copolymer Particles to E/TFE/PMVE/BTFB Fluoroelastomer

	Sample	
	3.A	3.B
	E/TFE/PMVE/BTFB	
	100	100
	TFE/HFP Copolymer (phr)	
	None	40
	Volume Fraction TFE/HFP (Φ)	
	0	0.25
Tensile at 25°C		
M_{100} (MPa)	9	12
T_B (MPa)	15	13
E_B (%)	150	150
$T_B \times E_B$	2250	1950
Tear (kN/m)	2.7	7.6
Tensile at 177°C		
T_B (MPa)	2.8	3.0
E_B (%)	60	80
$T_B \times E_B$	168	240
Tear (kN/m)	0.2	0.8

Formulation: 100 E/TFE/PMVE/BTFB copolymer, 30 MT carbon black, 3 PbO, 2.5 TMAIC, 5 Luperco 101-XL, 0.5 RCR-6156, TFE/HFP copolymer as indicated. Press cure 15 min at 177°C. Postcure 24 h at 232°C.

CONCLUSION

In conclusion, it is shown that the incorporation, into elastomers, of a plastic filler with the proper yield strength can substantially increase tear strength by decreasing the excess stress that develops at the tip of a sharp cut in an elastomer strip under tension. To be effective at low aspect ratio, the yield strength of the plastic must be of the same order of magnitude as the tensile strength of the elastomer to which it is added. The analysis is strictly valid only for very small deformations, where crack-tip blunting can be ignored, and for an applied stress sufficiently low that the plastic-yielding zone is very small relative to the crack length. It provides a useful model, at least, for the development of a

new mechanism for increasing the tear strength of fluoroelastomers at sufficiently high temperatures, which is of significant practical importance. A new high molecular weight TFE/HFP fluoroplastic micropowder is described, which is readily dispersed as platelets into elastomers and which has the proper yield strength to provide substantial improvements in tear strength, dynamic cut-growth resistance, and abrasion resistance of a broad range of elastomers by the mechanism of reducing the excess stress at the tip of a sharp cut. Examples of the use of this fluoroplastic micropowder to provide over a fourfold increase in tear strength of several fluoroelastomers at high temperatures are given.

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