

Classification of Properties of Elastomers Using the "Optimum Property Concept." I. Introduction

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Synopsis

An attempt is made to distinguish properties of elastomers by types. "Basic properties of materials" or "network properties" in elastomers are properties which either increase or decrease from the liquid to the solid state of materials or over the range of the "elastomeric plateau" of elastomers. From these are distinguished properties that exhibit characteristic maxima and are therefore "maximum properties" or bivalued properties. Mechanical failure properties show the characteristics of "maximum properties." The maxima in "maximum properties" generally do not coincide. This noncoincidence of the maxima with a change in a "basic property of a material" has major theoretical and practical implications, for example, it is the cause of the crossovers in the relative performance rating of materials under different test conditions. The implications of this noncoincidence of the failure property maxima on the relevance of correlations between these properties are discussed. A change in the testing conditions is reflected in a shift of the optimum value in a "basic property of a material" with respect to a specific "maximum property." Data and certain conclusions in the literature are interpreted on the basis of this concept. Examples of the limitations of the validity of mathematical relationships are presented. Also, a definition of the term "state of cure" is proposed and a suggestion for the rating of severities of test equipment and applications of elastomeric materials recommended. The effect of increased degrees of crosslinking for a series of polymers and crosslinking agents is assessed. It is suggested that the "mechanisms" of failure properties will remain elusive if their rationalization is attempted on the basis of other failure properties, e.g., the mechanism of abrasion on that of tear strength or cut growth. The main purpose of this proposal is to provide support for a drastic reduction in laboratory testing by identifying those properties which can lead to different relative ratings in routine evaluations and actual applications. A more empirical approach to materials evaluations is recommended based on the calibration of laboratory instrumentation with respect to specific applications. A de-emphasis of routine evaluations of materials on the basis of their "maximum properties" seems to be justified.

INTRODUCTION

In the past, several classifications of polymer properties have been attempted, but the criteria have been chosen somewhat arbitrarily. For example, a distinction of three categories has been proposed¹: strength properties connected with high stress levels and short periods; strength properties connected with low stress levels and long periods; and properties such as hardness, scratch resistance, friction, and heat distortion. A distinction has also been made¹ between adhesion, ultimate or failure properties, and use-related properties.^{2,3}

An attempt to introduce a new classification can be justified if it can lead to the rationalization of generally observed phenomena, to an understanding of apparent contradictions, and to a greater efficiency in future evaluations of materials. The purpose of scientific classification is to identify related types or objects and increase the knowledge of a less well-known object on the basis of the understanding of a well-known object of the same type. In the case of

elastomer properties, one can anticipate the responses of a given property on the basis of the observed responses of others, provided a proper classification is made. Scientific classification can seldom be achieved with absolute certainty and can be, to a large extent, pragmatic. Therefore, the value of a classification will largely depend on the insight it provides and the technological implications which result from it.

ELASTOMER PROPERTY CLASSIFICATION

The following proposal distinguishes elastomer properties in terms of their response to temperature, strain rate, and basic materials parameters such as crosslink density and crystallinity. Because of their generally different response, "basic properties of materials," such as hardness, are distinguished from those properties for which an optimum in these properties can be demonstrated.

"Maximum Properties" and "Basic Properties of Materials"

It is suggested that all elastomer properties which develop a maximum in the range of the elastomer plateau of the modulus-temperature curve of amorphous polymers, and thus exhibit an optimum temperature (T_{opt}) and an optimum modulus (Fig. 1), could be defined as "properties which exhibit a maximum," or "maximum properties." Such a maximum must not be due to a structural disintegration at high temperature and is generally not as symmetrical as shown in Figure 1. For a stricter classification, "maximum properties" must also show a maximum when the hardness or density of the material is increased and when the strain rate or the severity of a test is varied. Such complete supporting evidence is not yet available for all the proposed "maximum properties."

Properties which do not develop a maximum are defined as "basic properties of materials" (Table I). These are characterized by an overall increase or decrease as the material changes from the liquid to the solid state, although it shows prominent steps at phase transition points. Such a property will also increase or decrease as a monomer is converted into a polymeric material. The change

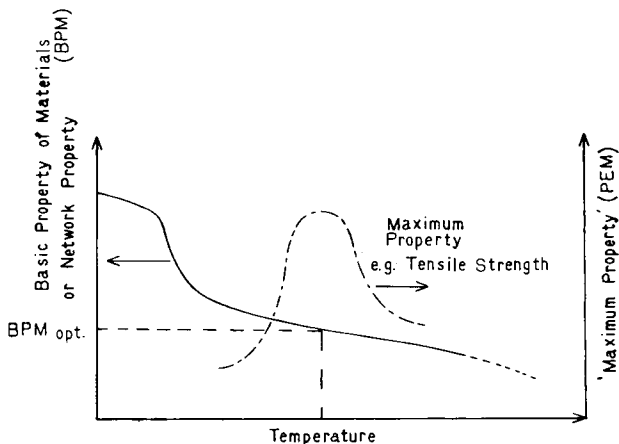


Fig. 1. Development of a "maximum property" in the modulus/temperature curve of elastomers.

TABLE I
Suggested Classification of Elastomer Properties

"Properties which exhibit a maximum" or "maximum properties" ^{a,b}	"Basic properties of materials" or "network properties"
Elongation at break ^{4,c}	Storage modulus E'
Tensile strength ^{5,c}	Shear modulus or rigidity
Tear strength ⁶	Hardness
Cut growth (Fig. 3)	Tensile stress or modulus (at a given strain)
Resilience (Figs. 4 and 5) ⁸	Crosslink density
Adhesive tack ⁹	
Adhesion ^{10,c}	
tan δ' or hysteresis ¹¹	
Friction ^{12,13}	
Loss modulus E'' ¹⁴	
Flex fatigue ¹⁵	
Abrasion resistance ¹² or wear resistance ^{16,17}	
Impact strength ¹⁸	
Sound absorption or damping ^{24,25}	

^a References indicate evidence for maxima versus temperature.

^b Nonmechanical properties are insufficiently studied to be discussed in this context. Maxima versus temperature have been observed for the dielectric constant and the dissipation factor,¹⁹ the dielectric loss factor,²⁰ thermal conductivity,^{21,22} and radio thermoluminescence.²³

^c Evidence for maxima versus strain rate is available for elongation,^{4a} tensile strength,^{5a} and adhesion.^{10a}

will be largest when the conversion leads to a crystalline material. For elastomer products, "basic properties of materials" may also be called "network properties," and both terms will be used interchangeably, although the latter term is preferred for vulcanized elastomers. It follows from the definition of "maximum properties" and "basic properties of materials" that the former will show a maximum when plotted against a "network property."

Since a maximum versus temperature is an indication of at least two temperature-dependent processes, "maximum properties" can also be termed "double- or multiple-valued properties." "Network properties" would then be "single-valued properties." A maximum for a property versus temperature represents an optimum in the sum of all molecular processes which contribute to the viscoelastic response. This optimum will depend on chain stiffness and chain interaction, including chain entanglement, on the flexibility of the crosslink and the rate at which the external mechanical stimulus or strain is applied. In order to assess the optimum in the network property or the maximum in the maximum property, a quantitative evaluation of all the contributing factors would be required. Such assessments are currently not available and cannot be expected. This severely limits the practical value of theoretical studies on failure properties.

A conceptually similar situation of a bulk response is demonstrated in the crystalline growth rate of polystyrene versus temperature.²⁷ The maximum in spherulite growth rate and therefore the ability of the system to respond to a change in external conditions depends strictly on the presence of small amounts of a plasticizer. Variations in the plasticizer level lead to displacements in the growth rate maxima similar to the effect of plasticizers on elastomer properties. Therefore, the presence of a property maximum corresponds to an optimum

temperature of intra- and intermolecular conditions with respect to an external stimulus.

It follows from the superposition principle of temperature and frequency that maximum properties will also show a maximum when plotted against test frequency. From this it further follows that maximum properties will show a maximum versus certain materials properties such as the elastic shear modulus, tensile modulus, and hardness and also versus crosslink density or molecular weight, since a variation in these parameters leads qualitatively to similar materials property changes. As mentioned above, a maximum against these properties is a second essential criterion for the assignment of a property as a "maximum property." Examples of properties that exhibit a maximum with an increase in a "network property" are adhesion,²⁸ elongation at break,²⁹ tensile strength,⁵ tear strength,³⁰ cut growth resistance,³¹ flex fatigue,^{31,32} wear resistance,³³ and impact strength,¹⁸ which are typical failure properties.

Effect of Materials Variation on Shift in Optimum and Maximum Values

Of practical interest are the shifts in the maximum property curves that arise with a variation in a basic materials parameter. Typically, such variations in a network property are obtained by changes in the molecular weight, in the amounts of additives such as particulate fillers, crosslinking agents, plasticizers, etc., and in the composition of polymer blends.

When the network property of a material is changed, the maximum of the maximum property will be at a different temperature, or there will be a shift in the optimum temperature (T_{opt}) (Fig. 2). Such shifts lead to a set of displaced maxima in which the maximum for the vulcanizate of the lowest network property will be at the lowest temperature. Such shifts can be associated with a shift in the glass transition temperature, as reviewed.^{34,35} The pattern of displaced peaks in Figure 2 can be expected for properties to which the Williams-Landel-Ferry relationship³ is applicable. For example, in addition to the well-established examples in Table I, the intrinsic strength W_t and the energy density can be expected to show the response of typical maximum properties since the applicability of that relationship has been established.³⁶ A similar pattern must be expected for all maximum properties when changes in the test condition, e.g., frequency or strain rate, are applied, even if the validity of the Williams-Landel-Ferry relationship has not yet been demonstrated. The important aspect of Figure 7 is that there can be crossovers in the relative rating of similar materials over a narrow temperature, frequency, or strain rate range.

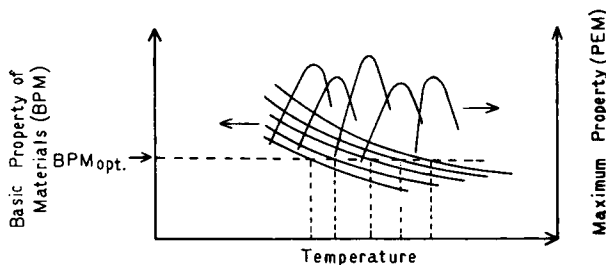


Fig. 2. Shift of the "basic properties of materials" or "network property" and "maximum property" curves vs temperature. Displacements by gradual compositional variation.

The phenomenon of displaced maxima as schematically presented in Figure 2 is frequently observed and represents technologically relevant situations. Typical examples are the effect of increasing levels of tackifiers on adhesive tack,⁹ of plasticizers on $\tan \delta$,^{20,37,38} of changes in polymer compositions on bond strength,³⁹ of the molecular weight of the "soft" segment on $\tan \delta$,⁴¹ of increasing degree of crosslinking by a change in the chemical composition in epoxy resins on $\tan \delta$,⁴² of changes in the polymer composition on impact strength,⁴³ and of the effect of cooling rate or solvent casting of polyethylene films on $\tan \delta$.⁴⁴ The displacement of the maxima is not always evident, as for example in the analysis of the effect of increasing carbon black levels on $\tan \delta$,⁴⁵ but the characteristic crossovers of the relative values with a change in temperature is nevertheless observed. In a more recent study, the displacement of both the $\tan \delta$ and tensile strength maxima for vulcanizates of different carbon black content is clearly demonstrated.³⁵ Technologically significant is the displacement of the wear resistance maxima for various compositions.¹⁷ An example of an apparently irregular displacement is the effect of filler surface treatment on the loss modulus and T_g .⁴⁶

The optimum in the "basic property of materials" is not necessarily constant, as suggested in Figure 2. The assumption of a decrease in a basic property of materials with temperature in Figures 1 and 2 is supported by the observed trends for vulcanizates containing particulate additives.⁴⁷ In contrast, the kinetic theory of rubber elasticity predicts an increase in modulus with temperature for crosslinked polymers.¹ The direction of this trend is not critical for the development of the optimum property concept. In materials of a relatively high basic property of materials, such as elastomers of high "green strength" and elastomers containing particulate additives, further increases in basic property of materials often lead only to decreases in a maximum property, and certain maxima may then not be observed. Therefore, a maximum may not be evident in a specific material tested under certain conditions, particularly when only a limited basic materials property range or temperature range is studied. In such situations only the ascending or descending part of a curve is observed. It is then important to recognize that such maximum property curves should not be linear and that equations which describe such curves apply only to specific systems when tested under specific conditions.

For two properties, cut growth resistance and resilience, the experimental support for their classification is shown in Figures 3 and 4, since the literature does not provide unambiguous examples. In addition to the examples in Table I, extensive investigations demonstrate a maximum versus temperature for several failure properties.⁴⁷

Interchangeability of Factors that Contribute to a "Basic Property of Materials"

An increase in molecular weight, even at constant crosslink density, can cause the vulcanizate to pass beyond the optimum in a "basic property" as exemplified for butyl rubber.²⁶ The optimum property concept suggests that the maximum in a property will be reached at a lower molecular weight in the presence of particulate additives, which is confirmed by trends in butyl rubber.²⁶ This indicates that there can be an interchangeability of factors that contribute to an optimum

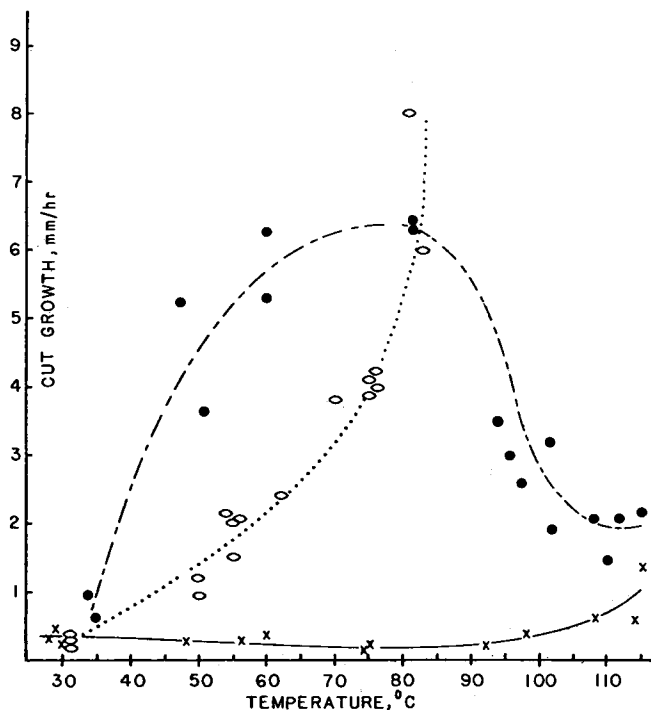


Fig. 3. Trends in cut growth of elastomers vs temperature SBR = Poly-76.5:23.5 (butadiene-*co*-styrene); NR = polyisoprene-*cis*; IIR = poly(isobutylene-*co*-isoprene) (1.6 mole-% unsaturation). (· · · ○ · · ·) SBR-1500; (—X—) NR; (- - ● - -) IIR.

value in a basic property and that there can be a mutual dependence of these contributing factors. Therefore, it will depend on the type of polymer, the degree of crosslinking, the molecular weight, the type and level of particulate additive, the test temperature, the strain rate, etc., whether a further increase in a basic property will increase or decrease a given maximum property. The full extent of this interchangeability has not yet been established but is reflected in the observation that the optimum level of carbon black for maximum friction depends on the glass transition temperature of the polymer.⁴⁷

Resilience as a "Maximum Property"

Although resilience is a mathematically derived property,⁸ it can be included as a "maximum property" since it is phenomenologically related to these properties. For example, the trend in resilience with a variation in temperature or tensile modulus is similar to other, more typical maximum properties. A maximum at a relatively high temperature has been reported⁸ and can also be observed near ambient temperature (Fig. 4). The trend in resilience in Figures 4 and 5 can be rationalized on the basis of Figure 2, which demonstrates that the maximum is expected at the lowest temperature for a sample of the lowest "basic property." This is a consequence of the optimum basic property phenomenon but is only valid for a set of samples in which the variation in the basic property is the only variable. Although a maximum in resilience at high temperatures may be due to permanent changes that take place within an elastomeric com-

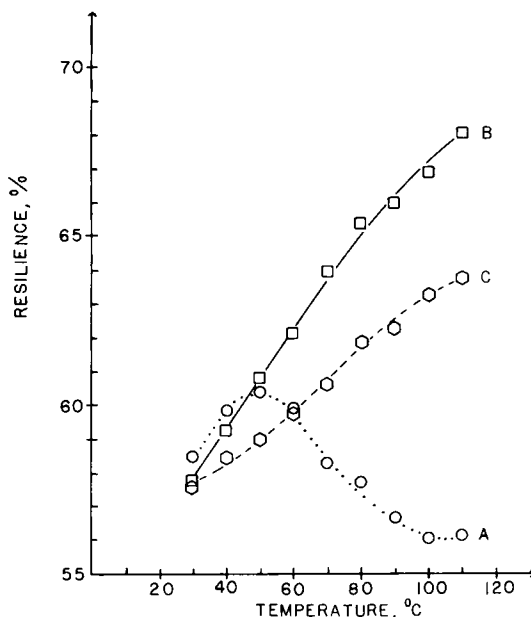


Fig. 4. Trends in resilience vs temperature for natural rubber vulcanizates containing mineral filler (HiSil 233). The vulcanizates are sulfur cured. In addition to the basic curing formulation used in A, a reaction product of polyethyleneimine and propylene sulfide was used in B, and trimethoxy-*n*-propylmercaptosilane in C. (O) 50 phr HiSil; (◻) 50 phr HiSil + 6.0 phr PPS/PEI; (○) 50 phr HiSil + 2.0 phr silane.

pound, e.g., rearrangement of crosslinks or chain scission,⁸ other viscoelastic factors may be contributing to this phenomenon. The maximum in Figure 4 is at a relatively low temperature. If the trends in Figure 5 can indeed be rationalized as representing displaced maxima, then the maximum for the vulcanizate of the lowest basic property (= tensile modulus) in the relatively stable ethylene-propylene terpolymer (EPDM) of Figure 5 would even be at a lower temperature. In general, resilience shows an asymptotic increase over a wide temperature range⁸ and is better characterized by a minimum versus temperature,⁴⁹ corresponding to a maximum loss. Therefore, resilience is not typical of maximum properties in the sense of their definition. However, the observation of a resilience maximum at a very high degree of crosslinking supports the inclusion of resilience into this group of properties.

Properties which Pass through a Minimum Versus Temperature

The presence of a minimum versus temperature is an unsatisfactory criterion for a property classification. In several instances, this minimum responds to test conditions or polymer modifications in a similar way as a property maximum. Since a resilience minimum corresponds to a maximum in lossiness, minima for different polymers⁴⁹ are symmetrically displaced. This leads to changes in the relative ratings at different test temperatures, as is typical of "maximum properties."

A technologically important example is the stress relaxation time after com-

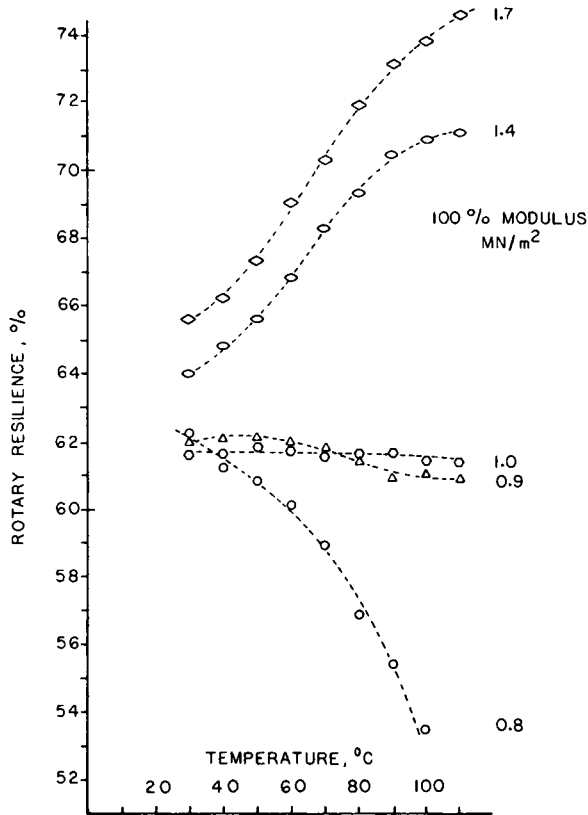


Fig. 5. Trends in resilience vs temperature for EPDM vulcanizates of increasing degree of cross-linking. EPDM = Poly(ethylene-co-propylene-co-ethylidene norbornene).

pression,⁵⁰ which shows clearly defined minima over a temperature range of 20 to 100°C for styrene-butadiene rubber. As a consequence, crossovers in the relaxation time for different materials become evident over a temperature range. Similar crossovers over a range of shear strains must then be expected.

A displacement of the minimum in the conductivity of styrene-butadiene rubber toward lower temperature with successively higher poly(vinyl chloride) levels⁵¹ leads to crossovers in the relative rating in conductivity. This indicates that conductivity is controlled by viscoelastic phenomena. It may be assumed that the position of this minimum will depend on the type of polymer or on the amount and type of filler, in addition to its dependence on the amount of plasticizer, as already demonstrated.⁵¹ It is not surprising then that a change in the order of the electrical conductivity over a temperature range is observed for samples that are thermally aged for different periods.⁵²

Implications Arising from the Reality of Property Maxima

The typical response of "maximum properties" to variations in "basic properties of materials" and in test conditions leads to conclusions and implications of practical relevance.

Shift in Optimum "Basic Property of Materials" Value

By definition, each maximum in a property is associated with an appropriate optimum in a "basic property." In general, the optimum would not be the same value for several "maximum properties." This leads to a procession of curves for a series of properties as shown in Figure 6. It is understood that the position of a given maximum will shift if the test conditions are varied, as for example by a change in the strain rate or in the test temperature. Several maximum properties are not included in the schematic presentation in Figure 6, since severity conditions under which these are measured vary widely. For example, friction or traction can be highest at a very low basic property value, yet under experimentally different conditions the optimum in the basic property can be relatively high. Wear resistance shows a similar response; when measured on laboratory equipment it generally shows its maximum near the tear strength maximum at moderate test speeds. This will be shown in a later publication. Such shifts, as indicated by an arrow on the "fatigue peak" in Figure 6, are associated with a change in the magnitude of the maximum property. From this follows that the curves for two nominally comparable tests, such as two fatigue, abrasion, friction, or adhesion tests, will also be displaced on the "network property" or temperature axis, as shown schematically in Figure 7. Each of two such tests may measure a quite different phenomenon. Although one test may measure "true" adhesion between interfaces, another may measure cohesive strength if more than a monomolecular layer of the polymer remains on the substrate. Therefore, over a range of compositional changes of a material, the trend in two nominally identical properties will not necessarily coincide, and a correlation between two such tests would not be expected. The resulting displacement of the curves for two nominally identical properties will lead to a relationship between both that is comparable with the relationship between two obviously unrelated maximum properties. A typical example is the displacement of the adhesion peak with a change in peel rate.^{52a}

The lack of the coincidence of the curves of maximum properties in actual applications and in arbitrarily chosen, nominally comparable laboratory tests reflects differences in the mechanisms involved and is the reason for the lack of correlations. Therefore, trends established for maximum properties as the result

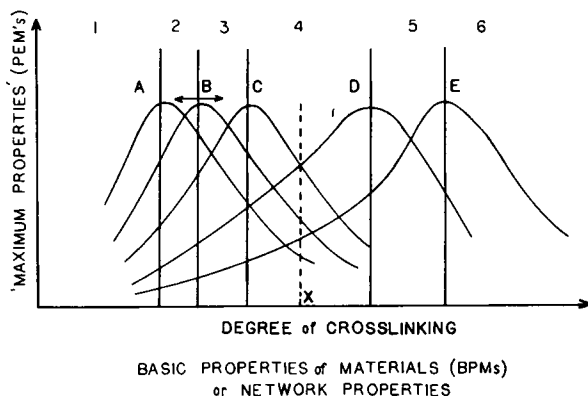


Fig. 6. Effect of increasing crosslinking on the development of "maximum properties": A = elongation; B = rototlex fatigue (in natural rubber); C = tear strength; D = tensile strength; E = resilience. The position of these peaks depends on test temperature and strain rate.

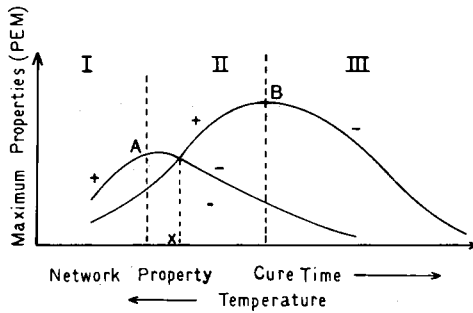


Fig. 7. General trend in two "maximum properties" A and B vs variations in "basic properties of materials" or "network properties," test temperature, test severity, and cure time (in vulcanizable polymers). Notation of + or - does not apply to "severity" since changes in "severity" may involve increased temperature or increased strain rates, or both.

of changes in the composition of materials, as for example a variation in the filler loading or in the degree of crosslinking, are not necessarily relevant to specific applications. Yet such trends which are established on arbitrarily chosen instruments are a large part of the technical literature. Such trends will only be relevant if the severity of the application is exactly matched by the tests. If the severity of the test conditions and the application are identical, then the maximum in a property for a series of test samples should coincide. A coincidence of maxima is exceptionally rare because of the complexity of the factors that contribute to the optimum value of a basic property.

In Figure 7 the ascending part of the curve toward a higher "basic property" or lower temperature—if these trends coincide—is arbitrarily defined as the positive (+) side and the descending part, as the negative (—) side. Since "maximum properties" are bivalued properties, such a definition seems essential. Ultimately, the description or definition of a maximum property value will only be complete when its location on the basic property axis, on the temperature axis, and on the strain rate axis is defined. Since this is practically impossible, the comparison of a maximum property of two materials, even under a defined set of test conditions, is of very limited value. Identical values in two materials do not guarantee that this similarity is maintained under different test conditions. Identical values of opposite denotations are nonidentical with respect to their response to a change in test severity or temperature and will change in opposite directions as a basic property is varied. If A and B correspond to one maximum property in two different materials, e.g., friction in two different polymers, an apparently identical value would be obtained at the basic property value x in Figure 7. However, the response to a change in test conditions would be quite different at such a point since it is located on opposite sides of the maximum property curve.

Crossovers in Relative Performance Ratings

The following conditions give rise to the schematic relationship in Figure 7, if curves A and B represent the trend in *one* "maximum property" for (a) two levels of one crosslinking agent versus temperature^{53,54}; (b) two levels of a particulate additive versus temperature^{47,55}; (c) two polymers versus tempera-

ture^{40,56}; (d) two types of additives versus temperature⁵⁷; (e) increasing levels of two types of curatives versus a "network property"⁵⁸; (f) increasing levels of two types of particulate additives (fillers) versus a "network property"⁵⁹; (g) two types of crosslinking systems versus temperature⁶⁰; (h) two types of polymers with increasing degree of crosslinking versus a "network property"⁶¹; (i) two levels of crosslinking agents or particulate additives versus conditions of increasing test severity, e.g., several fatigue instruments or road surfaces^{62,64}; (j) two types of polymers versus conditions of increasing test severity, e.g., a variation in the road surfaces⁶⁵ or driving speed, or at different strain levels^{66,67}; (k) two types of severities (e.g., test instruments or road surfaces in rubber tire testing) versus increasing curative levels of filler levels^{33,68}; (l) two test temperatures for peel adhesion versus peeling rate^{10a}; (m) two different peel rates versus temperature.^{52a}

Figure 7 demonstrates that crossovers in the relative performance must be expected for all maximum properties and that there will be conditions which favor a given composition over any other. A symmetrical pattern such as in Figure 7 should not always be expected, particularly when a change in the test conditions causes changes in more than one basic variable, e.g., in frequency, temperature, and strain rate. Large asymmetries are observed on fatigue curves toward low network property values when, under a given set of test conditions, the critical tearing energy is not reached. In such cases the maximum property curve rises sharply before it returns to zero. This problem will be discussed in later publications dealing with fatigue.

Most opposing trends reported in the literature, as for example the relationship between friction and wear resistance, are represented in region II of Figure 7, whereas apparent correlations would exist in regions I and III.

Relative Order of Property Maxima: Effect of Increasing Degrees of Crosslinking

Typically, a "basic property" of a crosslinkable material can be increased by increasing the degree of crosslinking. This can be achieved by increasing the crosslinking reaction time or the amount of the crosslinking agent. In each case, a "maximum property" may develop its maximum. Since the reaction time after which the optimum values in the "network property" are reached will depend on the rate of crosslinking, the maxima will be found after different cure times for different crosslinking systems. A typical example is the trend in adhesion of sulfur-vulcanized natural rubber for different accelerators (Fig. 8).⁶⁹ If the degree of crosslinking is increased by varying the cure time at different temperatures, similar displacements of the maxima are observed even for the same material.⁷³ If the degree of crosslinking is increased by varying only one component in the curative composition, again, a similar displacement of the curves is observed (Fig. 9).⁶³

If more than one maximum property is considered, a certain order is observed in which the maxima are introduced with increasing crosslinking. It is conceivable that this order is similar for different polymers. Yet such an order can only be expected for tests that are performed under identical conditions of temperature and strain rate, such as the measurement of elongation, tensile strength, and tear strength at relatively low strain rates, and resilience.

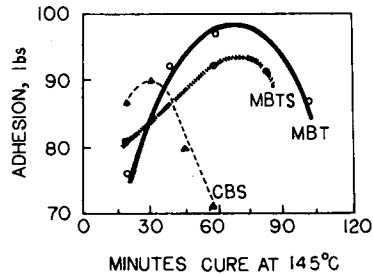


Fig. 8. Trend in adhesion vs vulcanization time. Accelerator variation.⁶⁹ MBTS = 2,2'-dibenzothiazyl disulfide; CBS = N-cyclohexyl-2-benzothiazyl sulfenamide; MBT = 2-mercaptobenzothiazole.

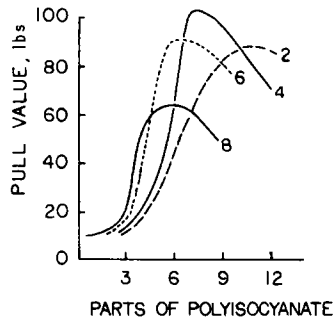


Fig. 9. Effect of increasing isocyanate levels on the pull value of a natural rubber vulcanizate containing 2.0 to 8.0 phr of an adduct of *p*-nitrosophenol and diisocyanate as crosslinking agent.

The examples in Figures 10 to 15 show the order in which the various maxima occur with an increase in a basic property, either by increasing the degree of crosslinking in several elastomers or by increasing the crystallinity in polyethylene. Figure 13 indicates that large changes in a maximum property may occur for a relatively small change in a basic property. The maxima may be wide and largely overlapping, or narrow. As a consequence, the balance of properties may undergo small or large changes as the degree of crosslinking is varied.⁷⁰ A more detailed account of the effect of increasing crosslinking on the rise and fall of maximum properties will be published separately.⁸⁴ The trends in the various properties as measured at standard laboratory test rates and temperatures can be summarized as follows:

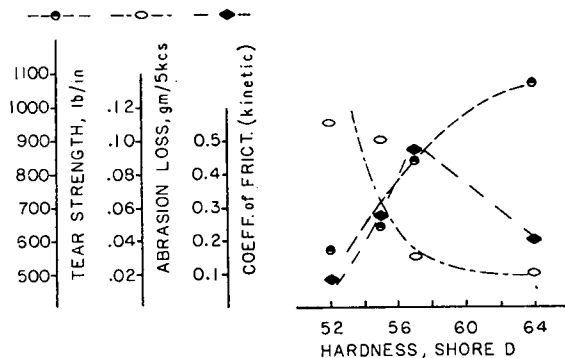


Fig. 10. Relationship between hardness and selected "maximum properties" in polyethylene (based on Ref. 77).

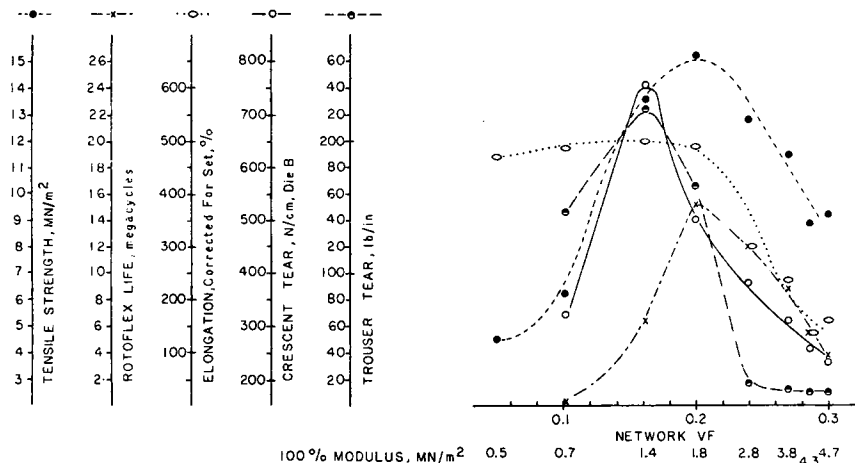


Fig. 11. Effect of increasing levels of sulfur and accelerator crosslinking agents on BR vulcanizates. BR = Polybutadiene-*cis*, network VF = volume fraction of crosslinked polymer in swollen gel.

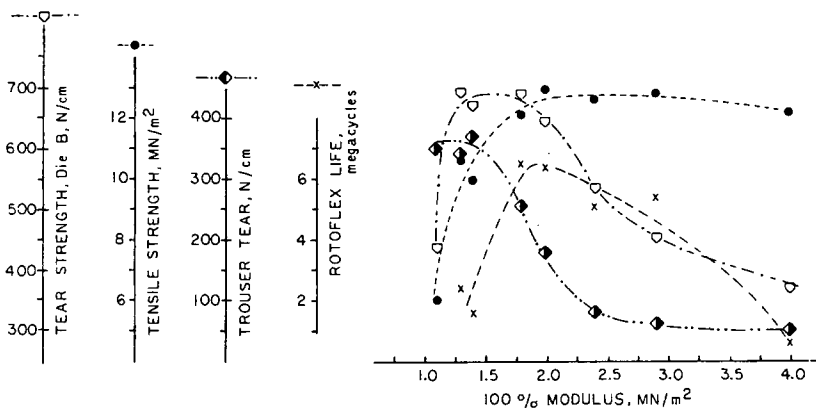
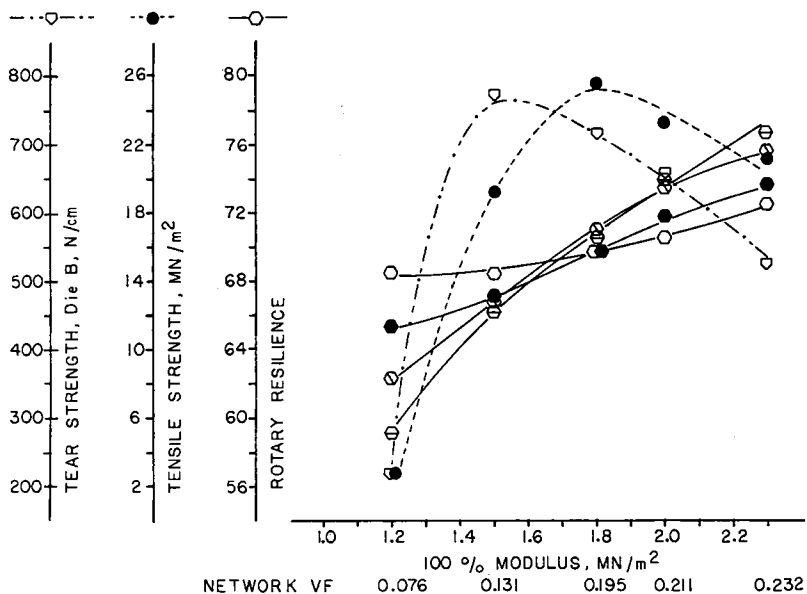
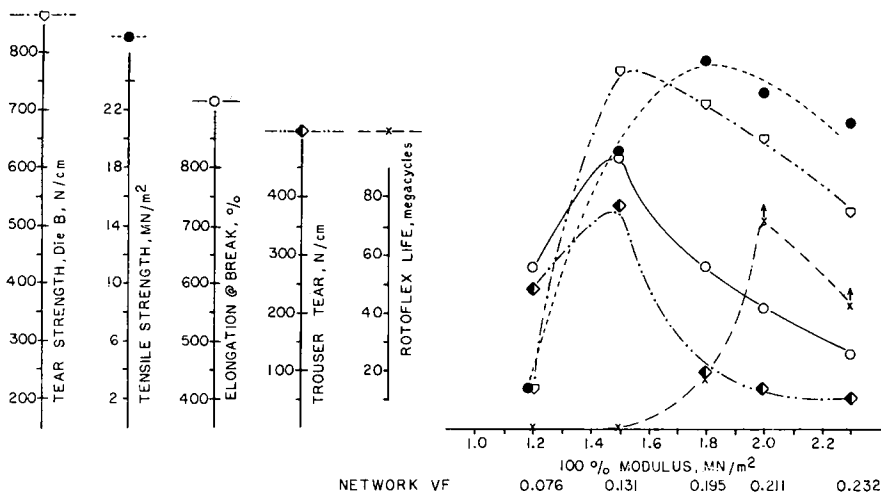


Fig. 12. Effect of increasing levels of sulfur donor (tetramethylthiuram disulfide) and sulfur as crosslinking agents in NBR vulcanizates. Cold NBR = poly-66:34butadiene-*co*-acrylonitrile.

Friction. The coefficient of friction for polyethylene (Fig. 10) shows a maximum in the range where other "maximum properties," including abrasion resistance, still increase and thus shows the lowest "basic property" value of the properties investigated. This trend is supported by previously published results^{109,110} from which it was concluded that the degree of crosslinking should be the "lowest defensible limit" in order to achieve the highest possible friction.¹¹⁰

Elongation. Similar to friction, elongation shows its highest value at a low "basic property" or "network property." A maximum is indicated in Figures 11 and 13.

Tear Strength. In contrast to elongation and friction, the maximum in tear strength is normally in the range over which the effect of the degree of crosslinking is studied.⁸⁴ The tear strength maximum is normally at a relatively low degree of crosslinking. Only in one instance is the optimum "network property" for tear strength higher than for tensile strength.⁸⁴ Two types of tear tests may lead to trends that coincide or are closely comparable (Figs. 11 to 13).



(a)

Fig. 13. Effect of increasing sulfur levels in EPDM vulcanizates. EPDM = Polyethylene-co-propylene-co-ethylidene norbornene); network VF = volume fraction of crosslinked polymer in swollen gel. (a). Effect of increasing sulfur levels in EPDM vulcanizates. EPDM = Poly(ethylene-co-propylene-co-ethylidene norbornene); network VF = volume fraction of crosslinked polymer in swollen gel. (○) 40°C; (●) 60°C; (◐) 80°C; (⊖) 100°C.

Fatigue. Rotoflex fatigue under the conditions reported⁸⁵ (a) follows the trend in elongation in natural rubber and in an SBR/BR blend,⁸⁴ (b) follows the trend in tensile strength in SBR,⁸⁴ in BR (Fig. 11), and in NBR (Fig. 12), and (c) increases over a range where tensile strength still increases in EPDM (Fig. 13) and in IIR.⁸⁴ DeMattia flex life can follow the trend in elongation in the case of an NR/SBR blend.⁸⁴ The trend in cut growth does not coincide with the trend in flex fatigue (Figs. 18 to 20) but can coincide with elongation (Fig. 17).

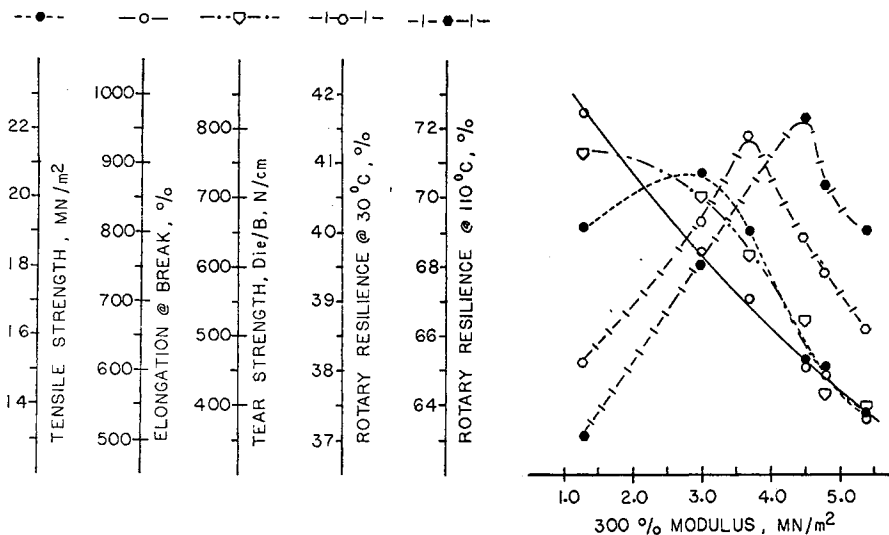


Fig. 14. Effect of increasing levels of curatives in IIR vulcanizates. IIR = Poly(isobutylene-co-isoprene) (1.6 mol % unsaturation).

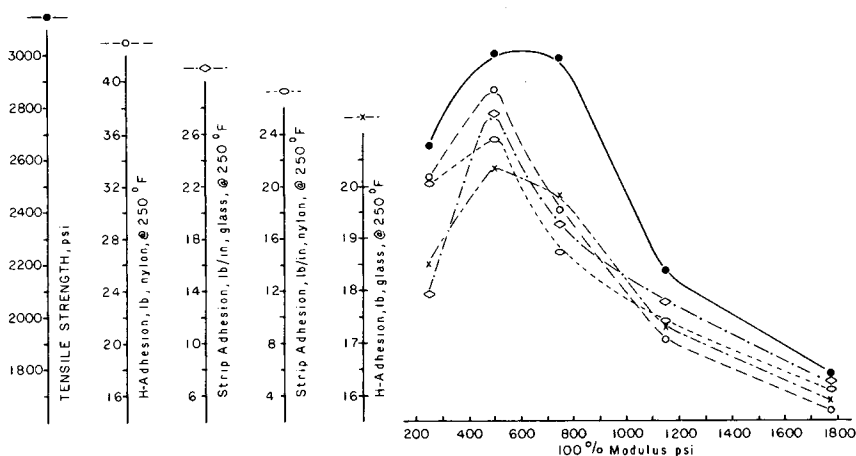


Fig. 15. Effect of increasing levels of sulfur and accelerator as curatives in an NR/SBR blend on different types of adhesion.²⁸

Tensile Strength. The maximum in tensile strength is at a high level of crosslinking (Figs. 11 to 14).

Resilience. The maximum in resilience⁸ develops at a level which is outside the range of most practical elastomer formulations (Fig. 14). The curves for resilience⁸ at different temperatures are systematically displaced (Figs. 13(a) and 14).

Wear Resistance. Wear resistance does not develop a clear maximum with an increase in the degree of crosslinking, although it is indicated in several instances.⁸⁴ A drastic decrease in wear resistance with increasing crosslink density was reported.¹¹¹ There is also evidence for a decrease in abrasion resistance with increasing hardness.¹¹² Both examples suggest that hardness, per se, is not the cause of increased abrasion resistance. The maximum in abrasion resistance

is more clearly established when the "basic property" is varied by increasing the filler loading.⁸⁴

Adhesion. It is evident from published data²⁸ that there can be a decrease in adhesion in one test but not in others as a "network property" is varied. A comparison of "strip adhesion" and H-type adhesion for nylon and glass fibers (Fig. 15) reveals that the optimum network property value can be identical. This suggests a similar adhesive failure mode.

State of Cure of a Vulcanizate

The order in the rise and fall of "maximum properties" as the degree of crosslinking is increased, provides a basis for a definition of the state of cure of a vulcanizate. The state of cure can be defined according to the position of the vulcanizate with respect to the maxima in selected properties as measured under standard conditions. The relative direction of the changes in properties will be different in each of the six sections of Figure 6. In section 1, corresponding to a state of cure 1, all properties in Figure 6 will increase. In section 5, all will decrease. Very few vulcanizates which also contain particulate additives are in state 1. A typical example is a styrene-butadiene rubber (SBR) vulcanizate,²⁹ which shows a distinct maximum in elongation as the level of crosslinking agent is increased.

Property "Improvements"

As is evident from Figure 6, it will depend on the position of a vulcanizate on the "network property" axis whether a change in such a property will cause an increase in a "maximum property." Furthermore, the commonly used term "property improvement" requires some definition since it will always be associated with a change in the balance of properties. Three different types of improvements can be considered.

1. "Apparent improvements" are obtained simply as a result of a change in a basic property, for example as a consequence of a change in the degree of crosslinking. The new balance of properties corresponds to a shift along the basic property axis in Figure 6.

2. "Selected improvements" lead to an increase in predominantly one "maximum property" at an *equal* "network property" value.

3. "Principal improvements" result from increases in all "maximum properties" with or without a change in a "network property." Such a situation arises in the first section of Figure 6, for example when the properties are introduced by the formation of elastomers from liquid polymers; the zero value would be obtained with the liquid polymer.

An improvement, even at a constant network property value, does not signify that it will be maintained under different test conditions. In fact, a change in the test conditions may change the relative rating of two polymers or vulcanizates because of the crossovers which are generally observed for test conditions of different severity (Fig. 7). As an example, a claim of improved fatigue is only meaningful if a strict definition of the conditions is included and if the relevance of these conditions to a specific application is established.

Concept of the "Severity" of Test Equipment and Applications

Figure 7 can be the basis for the relative rating or calibration of the "severity" of test instruments or actual applications. Because of the phenomenon of the displaced property maxima, the order in performance for different materials will change over a range in test severity. Such an approach is different from traditional severity ratings, e.g., weight loss of material per distance in the case of abrasion. Examples of the relative rating of road surfaces based on this principle will be published separately.^{84a}

Calculation of Property Optimum and Maximum

A scientifically important aspect of "maximum properties" is that these properties cannot be estimated from additive quantities, in contrast to molar heat capacity, molecular weight, molar refraction, etc.¹ Also, the position and the value of the maxima cannot be predicted on the basis of these parameters. It is also evident that maxima generally do not coincide. Therefore, attempts to calculate the optimum filler loading for only one property, e.g., elongation,⁷¹ would only be meaningful if such an optimum represented the optimum of one or all critical end-use properties. Such a situation is improbable.

Apparent Correlations Between "Maximum Properties"

The optimum property concept suggests that true correlations⁷² should not be anticipated between two "maximum properties" since both are individually depending variables to a change in a "network property," e.g., crosslink density. This problem is schematically illustrated in Figure 16. An increase in crosslink density is shown which causes the properties A, B, and C to pass through their maximum. Attempts to correlate property A with properties B and C would lead to the curves shown in Figures 16(a) and 16(b). It becomes obvious that the curves describing such correlations are actually envelopes and that they do not extend beyond a limited value of either maximum property. Figures 16(a) and 16(b) also indicate that the slope of such apparent correlations will depend on the range of A and B under consideration. It follows from Figures 16, 16(a), and 16(b) that correlations between laboratory test data and actual applications are represented by envelopes and that linear relationships are at best only approximations, valid only over a limited range.

It is therefore not surprising that correlations between adhesion and tensile strength,²⁸ wear and traction,³³ tire cutting or chipping, and tear strength⁷⁴ are poor and that a correlation between tire side-wall performance and fatigue has not been observed.²⁸

Limited Validity of Quantitative Relationships Between "Maximum Properties"

The limited validity of mathematical approaches and of attempts to correlate "maximum properties" can be shown in one particular example. Based on an almost linear log-log plot, a relationship between cut growth resistance—expressed in kilocycles per inch cut growth—and breaking elongation E_b was proposed⁵⁹ to be of the general form

$$\log (KC/in) = (3.65 \log E_b) - 8.31 \quad (1)$$

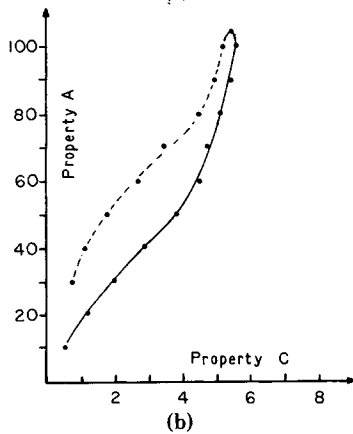
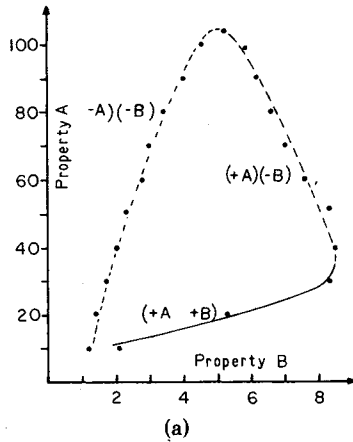
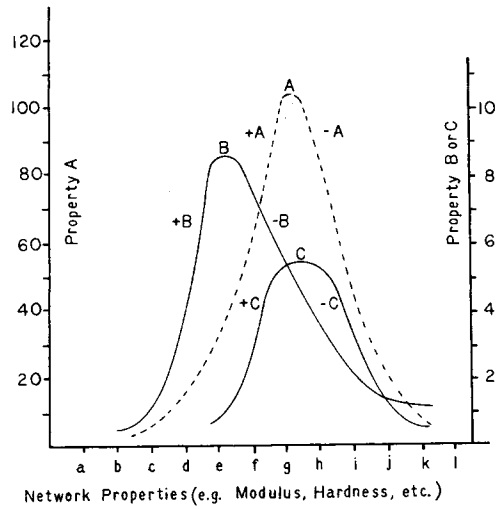


Fig. 16. Schematic presentation of the relationship between one "maximum property" (A) and two others (B and C). See also Figures 16(a) and 16(b). (a). Relationship between two "maximum properties" A and B (based on Fig. 16). (b). Relationship between two "maximum properties" A and C (based on Fig. 16).

However, when the reported data are plotted, the apparent correlation reveals itself to be a narrow loop (Fig. 17), with maximum cut growth resistance and elongation coinciding at ~ 40 phr. The equation does not indicate that the effect of increasing carbon black (Fig. 17) may cause either an increase or decrease in both properties, depending on the level of black. Not only are equations such as (1) restricted in their range of applicability, but they also require a strict definition of the test conditions. From this follows that such equations cannot be useful for end-use applications. The authors' suggestion⁵⁹ that testing under different conditions might give experimental data which more closely approximates a linear relation on the log-log plot would not then necessarily follow. Figure 17 represents an exceptional case where the performance peaks for cut growth resistance and elongation with increasing filler loading coincide.

The shift in the property maxima and the noncoincidence of two maxima have practical and theoretical implications on the so-called failure mechanism of properties such as wear or abrasion. It follows from the change in the property curves with test conditions that generalization with respect to a correlation between two properties have no general validity and that such correlation can only be valid for specific test conditions or polymer systems. This is undoubtedly the reason for conflicting statements in the literature. For example, it has been suggested that abrasion loss is inversely proportional to tensile strength⁷⁶ but also that it is related to tensile strength⁷⁷ or cut growth.⁷⁸ However, a coincidence of the abrasion resistance maximum with any other property maximum has not yet been demonstrated. The suggestion⁷⁹ that one can examine the mechanism of abrasion and draw theoretical conclusions from physical properties which affect abrasion is therefore semantically and philosophically unjustified. The understanding of the "mechanism" of wear will remain elusive not only because the term wear refers to a variety of experimental conditions but also because the implications attributed to the term "mechanism" are unspecified. For example, it has been suggested that abrasion resistance on sharp abrasives is related to tensile fatigue and abrasion resistance on dull abrasives to a fatigue-type failure.⁸⁰ As anticipated on the basis of the optimum property concept, a relationship between fatigue and abrasion could not actually be confirmed.⁸¹

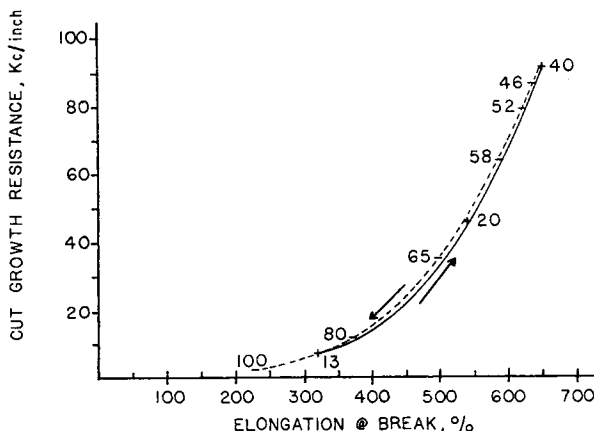


Fig. 17. Apparent correlation between cut growth resistance and elongation (based on Ref. 59). Variation in carbon black loading as shown from 13 to 100 parts per 100 parts polymer.

The only consistent effect of various experimental abrasion conditions is on the surface of the abraded polymer. The chemical functional groups introduced during conditions of abrasive or fatigue wear are essentially identical.⁸²

On the basis of the proposed concept, the relationship between tensile strength or tensile failure and abrasion⁸³ or between tensile strength and hardness or stiffness must be of similar limited validity. It is also not surprising that a correlation between tear strength and peeling force was not found.²⁸

Fatigue life and cut growth resistance or cut growth are technologically important properties. Their relationship is therefore of theoretical interest. Since these failure properties are maximum properties, a correlation between fatigue life and cut growth or cut growth resistance should not be expected. Studies of two series of materials of identical composition in which one contains the normal materials flaws and the other, a purposely introduced defined flaw are not available. According to the optimum property concept, two sets of materials are expected to show different fatigue versus network property curves. If these sets are based on vulcanizates in which the degree of crosslinking is the only variable, and if the experiment is carried out at equal strain, the more highly crosslinked samples will be subjected to higher strain energies. Since the presence of large flaws causes failures at lower strain energy, the maximum in cut growth resistance is then expected to be at a lower degree of crosslinking than that for fatigue. Figures 18 to 20 show a comparison of Rotoflex fatigue⁸⁵ between a set of samples containing a 2-mm-long cut and a set of uncut samples. In Figure 18, fatigue life shows a maximum over a range which corresponds to an increase in crosslink density and strain energy. In contrast, the life of the flawed samples is reduced over the same range. The maximum in the fatigue life is at a higher strain energy level than the maximum of the flawed sample.

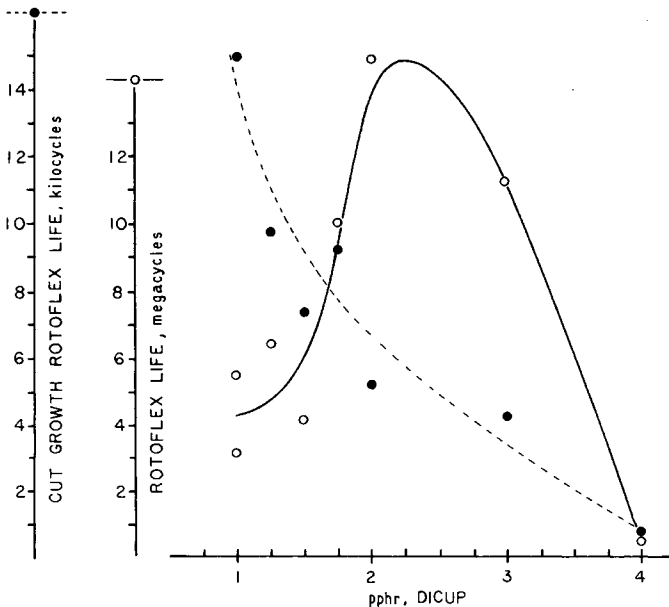


Fig. 18. Comparison of a purposely flawed (cut) Rotoflex⁸⁵ fatigue sample with an uncut sample. The effect of increasing degrees of crosslinking (SBR vulcanizate). Curing agent = dicumyl peroxide.

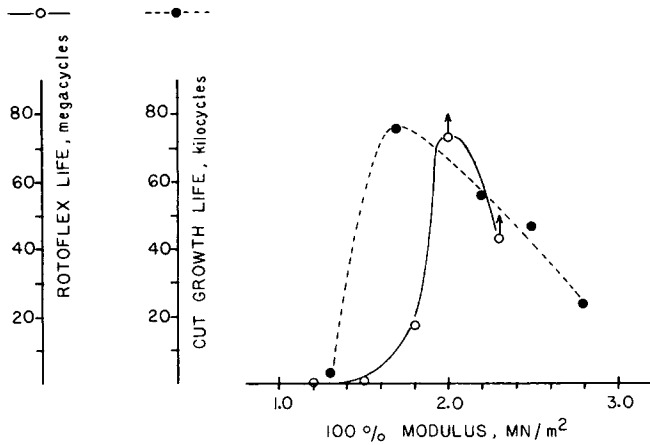


Fig. 19. Comparison of a purposely flawed (cut) Rotoflex⁸⁵ fatigue sample with an uncut sample. The effect of increasing degrees of crosslinking (EPDM vulcanizate). Arrows indicate that the tests were discontinued before all specimens had failed.

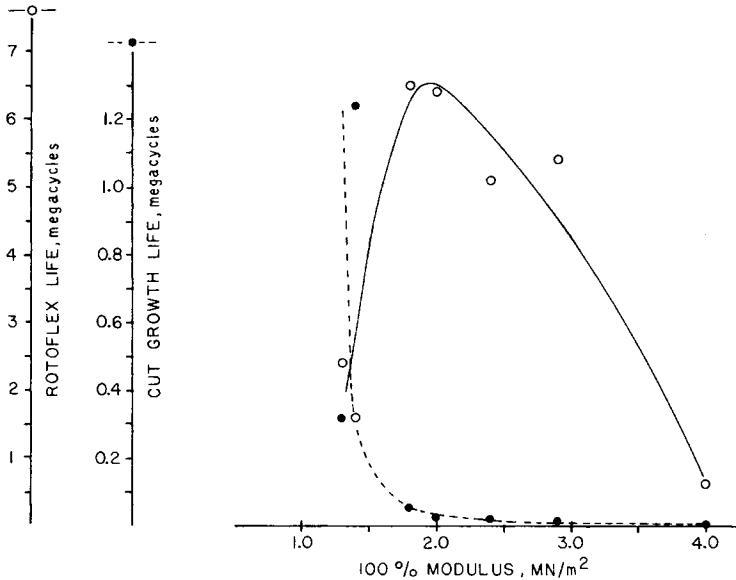


Fig. 20. Comparison of a purposely flawed (cut) Rotoflex⁸⁵ fatigue sample with an uncut sample. The effect of increasing degrees of crosslinking (NBR vulcanizate).

It is evident that fatigue life may in fact increase with increasing strain energy in an application where the sample operates at constant strain. It is also evident from Figures 18 to 20 that the trend in a maximum property as the result of an increase in a network property will depend on the initial value in that network property as expected from the optimum property concept. Thus, the optimum property concept rationalizes the suggestion⁸⁶ that the ranking of a group of compounds for crack initiation is often quite different from the ranking for crack growth. This had led to the suggestion that separate evaluations are needed. Even so, no correlation of either test with a specific application can be expected unless the severity of these tests is matched with that of a specific application.

The optimum property concept suggests, and the experimental data in Figures 18 to 20 confirm, the limited value of the suggestion that fatigue life can be seen to be a particular manifestation of cut growth.⁸⁷

Implication of Optimum Property Concept on Interpretation of Selected Published Property Trends

The optimum property concept demonstrates the limitations of linear relationships; these misrepresent the property relationships and are ultimately misleading. Linear relationships can disguise the possibility that there is an optimum for many parameters with respect to critical properties. For example, a linear relationship between tensile strength and $10^6/(M + M_c)$ was proposed (Fig. 21),^{26,58} although a curved line could not be ruled out since "the accuracy of the data left much to be desired."²⁶ The optimum property concept suggests that the nonlinear relationship in Figure 21 could be a more realistic representation of the experimental data. The proposed curve agrees with the general trend in tensile strength with an increase in crosslink density or a decrease in M_c .

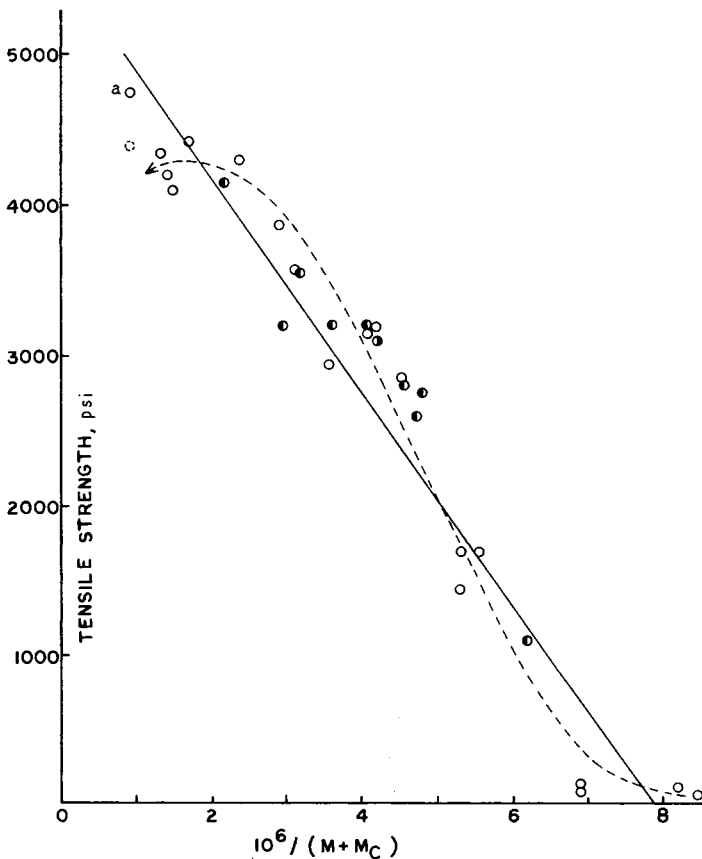


Fig. 21. Tensile strength of butyl rubber (IIR) plotted against $1/(M + M_c)$ for homogenous fractions or $1/(M_n + M_c)$ for mixtures.²⁶ (a) Cure time 60 min; (○) fractions; (●) mixtures; (◐) unfractionated polymer; (■) cure time 60 min.

The effect of the molecular weight of polymers on failure properties has become a controversial issue. It has been proposed⁸⁸ that increasing the molecular weight will lead to a plateau in such properties as tensile strength and tear strength. The initial increase in these and other properties was attributed to increasingly effective intermolecular interactions, to the stiffness of chain segments, and to the degree of crystallization. These are contributing factors to "basic properties" such as hardness and tensile modulus in the optimum property concept. Therefore, the assumption of a plateau in tensile strength and tear strength with increasing molecular weight is not expected to be valid, and decreases in "maximum properties" with an increase in molecular weight are to be expected. Later experimental evidence⁸⁹ indeed indicated reversals in the magnitude of properties toward high molecular weight. For example, with increasing molecular weight (\bar{M}_n) a decrease in De Mattia flex life is observed. Also Pico abrasion resistance decreases over an \bar{M}_n range for which Taber abrasion resistance increases.

These results support the implications of the optimum property concept, that there is an optimum molecular weight with respect to certain properties as measured under specific test conditions. Furthermore, the crossover in the abrasion resistance resembles the crossover in the abrasion resistance rating with increasing filler levels in vulcanizates.⁶⁸ The obvious conclusion is that the optimum network property value for two abrasion tests does not coincide, whether this property is increased by increasing the molecular weight or the filler level.

The optimum property concept suggests that even minor modifications of a material may lead to a shift in the optimum value. Therefore, a change in the type of the crosslink in a vulcanized polymer is expected to cause a shift in a maximum property curve. Such shifts are even evident when only the amount of the accelerator in a sulfur-vulcanized network is varied (Fig. 22).⁹⁰ For example, it had been proposed on the basis of the solid curve in Figure 22 that with respect to abrasion "the modulus level is the deciding factor, regardless of the rate of modulus development (rate of cure)."⁹⁰ We suggest that the data in Figure 22 are more appropriately represented by the proposed dotted lines. The new curves suggest that the abrasion resistance maximum shifts to a higher basic property value as the accelerator level is increased. This interpretation supports the earlier suggestion, also based on the data in Figure 22, that a good comparison could not be made by selecting abrasion curves at equal modulus when the cure rate differed considerably.^{90a}

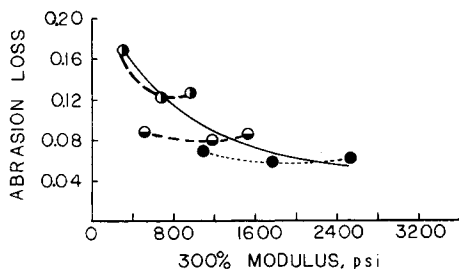


Fig. 22. Relationship between tensile modulus and abrasion loss (sulfur vulcanizates with three different accelerator levels). Based on Ref. 90. (●) 1.50 MBTS; (◐) 0.15 TMTS; (○) 0.20 TMTS.

A nonlinear relationship between a basic property and strength properties resolves the controversy whether a linear equation, eq. (2),^{91,92} or a nonlinear³⁷ equation, eq. (3), describes the relationship between the relative strength,

$$\sigma_v = a - bv_f \quad (2)$$

$$\sigma_v = \sigma_0 - bv_f^n \quad (3)$$

as a function of filler volume fraction v_f . Experimental data over a sufficiently wide range³⁷ agree with the nonlinearity proposed by the optimum property concept.

Furthermore, the optimum property concept predicts that the generally assumed inverse relationship between wear resistance and road hold or friction is a simplification and is better represented by an envelope. As a consequence, this inverse relationship can only be valid over a limited range of basic properties or test severities.

The optimum property concept also provides the explanation for the remarkable ("merkwürdig"⁹³) trend in elongation at break with increasing ethylene segments in a synthetic polyethylene-polypropylene terpolymer. The data indicate that there is an optimum level of polyethylene with respect to elongation, as determined under the specific conditions of that test.

Furthermore, the correlation proposed for abrasion and crack growth⁷⁸ must be limited to the special abrasion conditions chosen and is not necessarily valid if the composition of the polymer changes, e.g., after the incorporation of reinforcing fillers.

Because of the shape of the maximum property curves and their shift with a change in the test conditions, a mathematical correlation between tensile strength and adhesion,²⁸ as for example introduced by curative variations, will only be valid over a limited range of either. Furthermore, such correlations will lose their validity if the test conditions are varied, as for example for different types of adhesion, for different strain rates, or for different test temperatures. Such equations will be quite different for different polymers.

Because of the crossovers of the trends in adhesion for a set of vulcanizates over a range of cure times (Fig. 8),⁶⁹ and even for a single vulcanizate when the thickness and composition of the substrate is varied,⁹⁴ theoretical or mathematical approaches to the problems of adhesion show little promise. It is therefore not surprising that rubber-to-rubber adhesion is not understood⁹⁵ and that theories are not of much predictive value.⁹⁵ This conclusion is relevant to all other maximum properties because of their basically similar response.

Reported conflicting trends in cut growth or flex cracking can best be rationalized on the basis of displaced maxima. Flex cracking of natural rubber vulcanizates is reported to be reduced^{96,97} or increased^{98,99} with increasing temperature. These opposing trends may be caused by differences in the test severity or in the vulcanizate composition, or simply in the state of cure.

The concept of the displacement of performance peaks with a change in test conditions or the type of polymer also rationalizes the opposing trends in the effect of fillers in different polymers on crack growth in tires. For example, the effect of carbon black structure on crack growth has an opposite effect in natural rubber and in SBR.¹⁰⁰

The increase in elongation with crosslinking in certain polymers demonstrates the limited value of the proposed equation⁵

$$\text{Elong} \propto N^{-1/2} \quad (4)$$

which relates elongation with N_1 , the total number of chains per volume ($N = 1/M + 1/M_c$, where M = number-average molecular weight of the uncrosslinked polymer and M_c = molecular weight of the vulcanizate per crosslink unit). It is not surprising that the exponent may actually vary from -1 to -4 even for the same polymer.¹⁰¹ It follows from a shift of the maximum property curves that the exponent will vary with the type of polymer, the filler level in the polymer, the test temperature, and the strain rate. This underscores the very limited relevance of the mathematical treatment of maximum properties.

It is sometimes suggested that elongation is important to fatigue resistance.^{101,103} According to the optimum property concept, the curves for two maximum properties will not coincide, although both may have a similar trend over a limited range, and will shift as the test conditions are varied. Therefore, a correlation between two maximum properties should not have general validity. As Figures 11 to 13 indicate, fatigue follows more closely the trend in tensile strength in BR, EPDM, and IIR, even though the trend in elongation was followed in NR using the same fatigue instrument.⁸⁴ It is also not expected that the trends for two different fatigue tests are similar because of the differences in the strain rate and in the test temperature.

It has also been suggested that elongation may be considered as a network property similar to dynamic modulus.¹⁰¹ Dynamic modulus has been defined as a network property since a change in crosslink density, while holding all other properties constant, gives a predictable linear change in dynamic modulus. However, the assumption that elongation will always decrease with increasing crosslinking is not valid for all polymers, as shown by the examples of BR and EPDM (Figs. 11 and 13). This observation establishes elongation as a failure property rather than a network property.¹⁰¹ These examples demonstrate the validity of the concept of the interchangeability of factors which contribute to a basic property. For gum vulcanizates of low molecular weight or green strength, the increase in a basic property by crosslinking may be advantageous for the development of maximum elongation. In other polymers or highly filled systems, further increases in a network property are likely to cause reductions in those maximum properties whose maxima are at relatively low value.

Validity of Optimum Property Concept for Plastic Materials

The validity of the proposed concept for plastic materials has not been fully assessed but can be expected since polymers below their T_g show a viscoelastic response. Several properties of plastic materials show maxima versus temperature or a basic property of materials. Impact resistance of polycarbonates shows a well-defined maximum versus temperature,¹⁸ and complete crossovers in the relative rating of three materials over a temperature range of only 30°C have been reported.⁴³ A displacement of the impact resistance maxima with a change in impact conditions or for different polymers can therefore be expected. As a consequence, the relative rating in the impact strength of materials will depend on the type of test instrument, the test temperature, and impact rate or type, as is characteristic of all maximum properties.

The relatively low optimum basic materials property value for friction compared with other maximum properties is evident in polyethylene when density and therefore hardness is varied⁷⁷ (Fig. 10). The optimum property concept

suggests that for polyethylene, the proposed direct relationship⁷⁷ between molecular weight and ultimate elongation, tear strength, or abrasion resistance or between crystallinity and ultimate tensile strength, tear strength, or abrasion resistance will only be valid over a limited range.

Also, the linear relationships between impact strength and structural parameters for polyamides as well as between flexural modulus and tensile strength¹⁰⁵ can be valid only over a limited range. The established order for the effect of the various crosslinks of the polyamides on impact strength must then be assumed to change with a change in the test conditions, e.g., the impact temperature or impact severity. There is indeed evidence that impact strength passes through a maximum even when tensile modulus changes monotonically.¹⁰⁶

The displacement of a maximum is well demonstrated by the effect of plasticizers on poly(vinyl chloride)^{20,28,107} and other examples.^{42,44,77} Well-pronounced lap-shear bond strength maxima have been reported for various compositions of thermoplastic-thermosetting hybrid polymers.

These examples support the assumption that the basic observations on the two types of properties and their mutual relationships are applicable to polymeric materials below their transition temperature T_g .

CONCLUSIONS

1. The optimum property concept suggests that "properties which exhibit a maximum" and "basic properties of materials" or "network properties" are basically different properties. Such a classification appears justified since the response of all "maximum properties" to a change in test conditions is basically identical. The understanding of the response of one maximum property to test conditions or compositional changes can then be applied to others. Thus, a better understanding of basic elastomer properties, particularly failure properties, becomes possible.

2. The optimum property concept suggests that there is an optimum in basic materials properties for performance under specific test conditions such as temperature, strain rate, or strain amplitude at which maximum properties develop their maximum. Such a maximum is not observed when the basic materials property range is below or above the optimum with respect to that property. For example, the maximum in elongation at break is rarely observed.

3. Various maximum properties as measured under specific conditions pass through their maximum with an increase in a "basic materials property," but these maxima generally do not coincide. Examples are provided which demonstrate the various property trends introduced by a change in the degree of crosslinking. Definitions of the different types of property improvements are recommended, based on the change in the balance of properties with an increase in network property or basic property of materials.

4. A change in the test conditions or in the composition of a material causes a shift in the position of the optimum in basic properties of materials and therefore also of the maximum in a property. Such a shift will be multidimensional since a maximum can be expected (a) with a variation in the strain rate, (b) with a variation in the strain amplitude, (c) with a change in test temperature, and (d) with an increase in a basic materials property during the product's life.

5. The shift in the optimum value in a network property or basic property of materials with a change in test conditions causes crossovers in the relative rating of a set of samples. This leads to different ratings of materials when evaluated by laboratory instruments or in actual applications. An attempt is made to review those properties for which the relative rating established on a laboratory test instrument can be misleading with respect to specific applications. Most of these properties are failure properties.

6. The performance rating of a set of materials can be chosen to rate the severity of a specific application. Instrumentation which matches this rating will then match the severity of the application.

7. The limitations of laboratory testing are equally relevant to all maximum properties. For example, the technical relevance of a standard tear strength or elongation test is not higher than that of a standard abrasion or friction test.

8. Correlations between maximum properties are represented by envelopes and are therefore nonlinear. Several previously reported examples in the literature are reinterpreted and conflicting statements rationalized.

9. A qualitative analysis of the relationship between two maximum properties demonstrates that the type of correlation will change over a range of a network property. A positive correlation may change to a negative correlation over a sufficiently wide range in the degree of crosslinking. Since a maximum will also shift with a change in test conditions, mechanistic studies which attempt to establish correlations between maximum properties, as for example between abrasion and other failure properties, have no general validity. The results will only reflect specific test conditions. As the test conditions change, the balance of the various mechanisms which contribute to a failure property will also change.

10. For bivalued properties, a given value requires further identification for a stricter definition. The effect of changes in the test conditions or in a network property or basic property of materials will be different for numerically identical values in maximum properties if these are on opposite sides of a maximum.

11. Critical failure properties may decrease as the molecular weight of high polymers increases.

12. It is suggested that the principles and implications of the optimum property concept are applicable not only to rubber elastic materials but also to plastic materials.

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