

Filler Particle Size and Mechanical Properties of Polymers

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Synopsis

Literature data for the effect of mineral fillers on the mechanical properties of polyethylene at two temperatures, styrene-butadiene rubber, and natural rubber were examined. The data for modulus, tensile strength, elongation at yield, and ultimate elongation could be well represented by linear plots of the relative mechanical property (ratio of the values for the filled to the unfilled) as functions of the reciprocal of the filler particle size. A plot of one of these properties versus reciprocal filler size shows a family of lines, one line for each concentration of filler, and independent from the chemical nature of the filler. The dependence of the mechanical properties on reciprocal particle size may express a dependence on the surface-to-volume ratio of the filler, a balance between the effective cross-linking due to the large surface area of the filler, and the dilution of the polymer by the volume of filler present.

Introduction

The effect of particulate fillers on the mechanical properties of resins and rubbers is well documented for a wide variety of systems. Some fillers, particularly those of very small particle size, may reinforce the polymers, an effect well known for rubbers but rarely encountered with other polymers. The reinforcing effect has been associated with the chemical nature of the filler particle's surface, particularly with adsorption or adhesion effects between a filler and a rubber. (See Bateman¹ for a recent review.) Strength enhancement depends principally on the particle size of the filler, increasing with decreasing particle size; yet, there is no generally applicable graphical or analytical description of the effect of filler particle size on the mechanical properties of polymers. For example, Guth's equation for expressing rubber modulus as a function of volume concentration of filler includes a shape correction but not a size term.² A more recent and detailed molecular theory of filler reinforcement makes more allowance for particle size, but again only indirectly.³ Existing data for filled polymers were examined to see if the influence of filler particle size could be expressed quantitatively.

Treatment of Experimental Data

An examination was made of the literature of the effect of filler size on the mechanical properties of plastics and rubbers. Data for rubber-

TABLE I

Filler	Average particle radius, μ	Description
Aluminum hydrate C-741	0.05	Stearic acid-coated Al trihydrate
Cab-O-Sil	0.018	Pyrogenic silica
Hi-Sil	0.025	Precipitated hydrous silica
Silene EF	0.03	Precipitated calcium silicate
Multiflex MM	0.05	Precipitated calcium carbonate
Calcene TM	0.10	" " "
Zinc oxide	0.20	" " "

carbon black systems were purposely omitted so as not to introduce the possibility of specific chemical interaction. The data chosen for detailed analysis were for mineral fillers in polyethylene,⁴ styrene-butadiene, and natural rubbers.⁵ The suppliers' literature for the various fillers was the source for filler particle size and density.

The literature data for modulus, tensile strength, elongation at yield, and ultimate elongation were plotted as a function of filler content for each system. Tables were constructed from these plots so as to permit comparison of the various fillers at the same volume loading and as a function of particle size. The data could easily be separated into two categories, one for fillers less than 0.2μ in radius and a second for larger particles. Because the data for the larger particles showed serious inconsistencies, no further analysis was made of these data. The data for the smaller particle

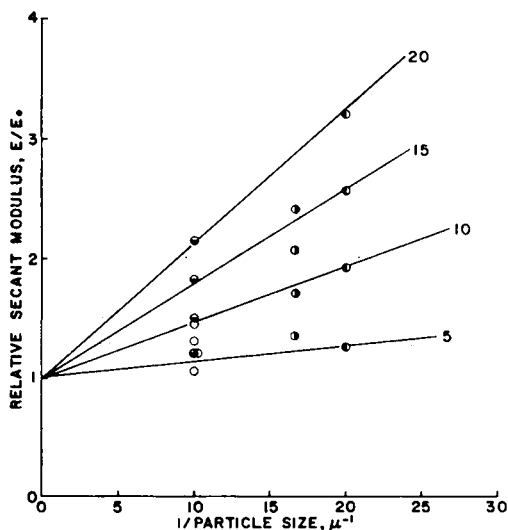


Fig. 1. Relative secant modulus (1% extension) of polyethylene at 23°C. for samples containing various fillers at the indicated volume per cent loadings as a function of reciprocal filler particle diameter: (O) aluminum hydrate C-741; (●) Multiflex MM; (●) Silene EF; (●) Hi-Sil.

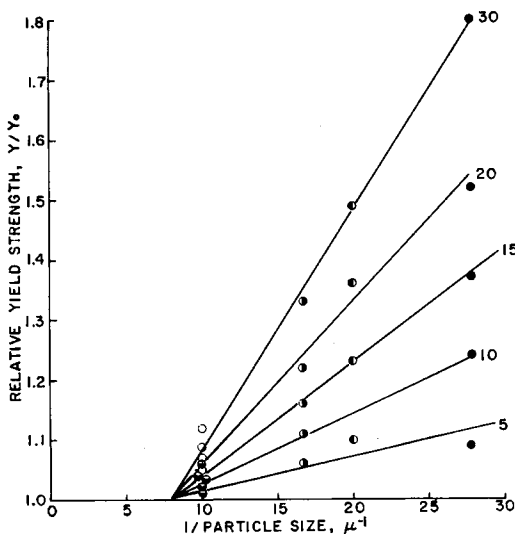


Fig. 2. Relative yield strength of polyethylene at 23°C. for samples containing various fillers at the indicated volume per cent loadings as a function of reciprocal filler particle diameter: (O) aluminum hydrate C-741; (\ominus) Multiflex MM; (\bullet) Silene EF; (\circ) Hi-Sil; (\bullet) Cab-O-Sil.

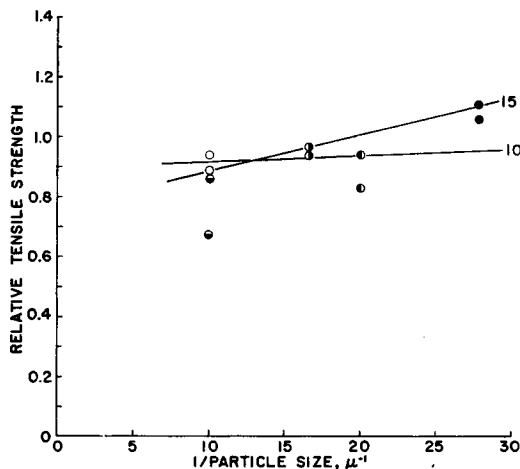


Fig. 3. Relative tensile strength of polyethylene at 23°C. for samples containing 10 and 15 vol.-% of various fillers as a function of reciprocal filler particle diameter: (O) aluminum hydrate C-741; (\ominus) Multiflex MM; (\bullet) Silene EF; (\circ) Hi-Sil; (\bullet) Cab-O-Sil.

fillers were examined in detail as outlined below, on the basis of the results for the fillers listed in Table I.

The dependence of the mechanical properties of the filled polymers on filler particle size was tested by plotting the values of the mechanical properties as various functions of the filler size. The data for polyethylene

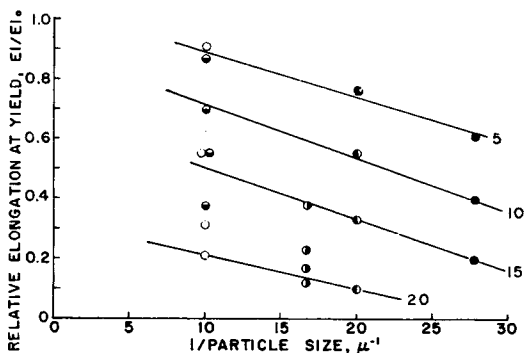


Fig. 4. Relative elongation at yield of polyethylene at 23°C. for samples containing various fillers at the indicated volume per cent loadings as a function of reciprocal filler particle diameter: (O) aluminum hydrate C-741; (◐) Multiflex MM; (◑) Silene EF; (◒) Hi-Si; (●) Cab-O-Sil.

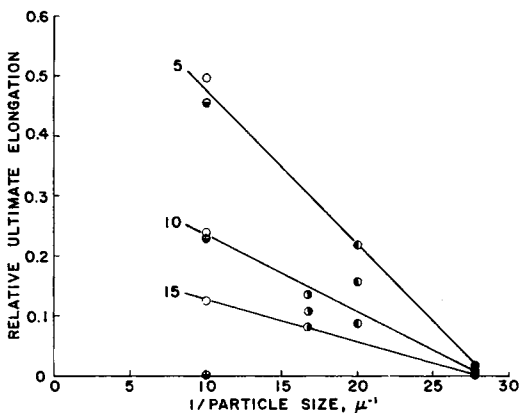


Fig. 5. Relative ultimate elongation of polyethylene at 80°C. for samples containing various fillers at the indicated volume per cent loadings as a function of reciprocal filler particle diameter: (O) aluminum hydrate C-741; (◐) Multiflex MM; (◑) Silene EF; (◒) Hi-Si; (●) Cab-O-Sil.

at 23°C., plotted as functions of reciprocal particle diameter, are shown in Figures 1-4 for the secant modulus (1% extension), tensile strength, yield strength, and elongation at yield. The relative mechanical properties (ratio of the value for the filled to the unfilled) can be represented as linear functions of the reciprocal diameter. Similar results were obtained for the same polyethylene properties measured at 80°C. Each figure shows a family of lines, one line for each volume concentration of filler, independent of the nature of the filler. Figures 1 and 2 have the interesting feature that the lines through the data points extrapolate to a common point. From the convergence of the lines in Figure 2, it can be seen that at any volume loading of filler there is no enhancement of the yield strength of polyethylene for filler particles larger than about 0.12 μ .

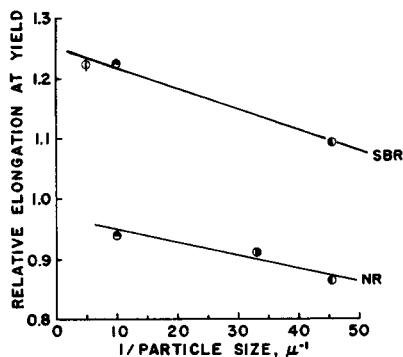


Fig. 6. Relative elongation at yield of styrene-butadiene (SBR) and natural (NR) rubbers containing 30 vol.-% of various fillers as a function of reciprocal filler particle diameter: (⊙) zinc oxide; (⊕) Calcene TM; (●) Silene EF; (⊙) Hi-Sil.

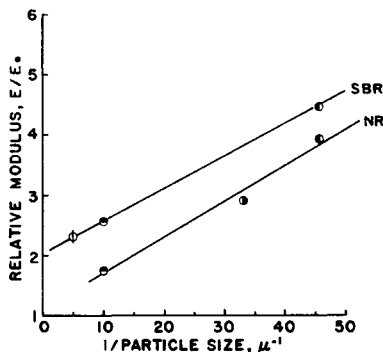


Fig. 7. Relative modulus (300%) of styrene-butadiene (SBR) and natural (NR) rubbers containing 30 vol.-% of various fillers as a function of reciprocal filler particle diameter: (⊙) zinc oxide; (⊕) Calcene TM; (●) Silene EF; (⊙) Hi-Sil.

The data for the ultimate elongation of filled polyethylene, measured at 23°C., were scattered. The data for ultimate elongation measured at 80°C. are plotted in Figure 5. This figure shows that this property, too, is a linear function of the reciprocal particle size. Figure 5 also indicates that the lines are independent of the nature of the filler, depending only on the filler size, and extrapolate to a common point.

The literature data used here for mineral fillers in natural rubber and styrene-butadiene rubber are not as complete as the data for polyethylene, and only two mechanical properties of the rubbers are considered here. Figures 6 and 7 show that at 30 vol.-% loading of various fillers, both the moduli (300%) and elongations at yield of both types of rubber are linear functions of the reciprocal particle radius.

Discussion

It has been demonstrated, by using literature data from two sources for three polymers, that the mechanical properties of filled polymers are, to a

reasonable approximation, linear functions of the reciprocal of the filler particle diameter and that they are independent of the nature of the filler. The data fit this relationship remarkably well considering the usual precision of measurement of mechanical properties.

The results for the variation of modulus with particle size are similar to the results of Guth² and Cohan.⁶ Guth's equation for the variation of the modulus of a filled rubber with filler content may be expressed:

$$E/E_0 = 1 + c_1fv + c_2f^2v^2 + \dots$$

where c_1 and c_2 are constants, v is the volume concentration of particles, and f is a shape factor for the filler particles, the ratio of their length to diameter. The family of curves in Figure 1 may be described by the equation:

$$E/E_0 = 1 + g(v)/d + \dots$$

where d is the particle diameter and $g(v)$ is the variation of the slope with volume concentration. A plot of the slope of each of the lines in Figure 1 against v is linear. The approximate function is:

$$g(v) = 0.03 + 0.8v$$

Plots of the original data for polyethylene as E/E_0 versus v are linear up to about $v = 0.2$. However, the data do not fit Guth's equation in that the families of lines, one for each filler, do not have a common intercept.

There are two possible hypotheses to explain the $1/d$ dependency. The first is that $1/d$ is a particle shape factor correction, as proposed by Guth. The second is that the $1/d$ function expresses a dependence on the surface-to-volume ratio of the filler. The filler is a diluent in the polymer, so that the modulus is inversely proportional to the filler volume, or d^3 . The polymer also adsorbs and adheres to the filler surface, forming a network or composite structural entity, increasing the modulus in proportion to the number of attachments, in proportion to the surface area, d^2 . The net effect is the dependence on $1/d$. The significant independence of the nature of filler suggests that the polymer-filler adhesion, per unit available surface, is the same for all of the fillers. This seems reasonable if the non-polar polymers wet the higher surface energy fillers.

It is a pleasure to acknowledge the assistance of Mrs. Helen Hsiao in replotting the literature data.

References

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Résumé

Les données de la littérature concernant l'effet des charges minérales sur les propriétés mécaniques du polyéthylène (à deux températures), du caoutchouc styrène-butadiène et du caoutchouc naturel, ont été examinées. Les renseignements sur le module, la force de tension, l'élongation limitée et l'élongation complète, peuvent être représentés par des constructions linéaires de la propriété mécanique relative (quotient des valeurs pour le polymère chargé et non-chargé) en fonction de l'inverse de la dimension de la particule de charge. Un graphique d'une de ces propriétés de la charge montre une famille de lignes, une ligne pour chaque concentration de la charge, et chaque ligne indépendante de la nature chimique de la charge. La dépendance des propriétés mécaniques vis-à-vis de l'inverse de la dimension de la particule peut exprimer une dépendance vis-à-vis du quotient surface—volume de la charge, un équilibre entre la réticulation effective due aux grandes surfaces de la charge et la dilution du polymère par le volume de charge présente.

Zusammenfassung

Literaturangaben bezüglich des Einflusses mineralischer Füllstoffe auf die mechanischen Eigenschaften von Polyäthylen bei zwei Temperaturen, Styrol-Butadienkauschuk und von Naturkautschuk wurden überprüft. Die Angaben für den Modul, die Zugfestigkeit, die Elastizitätsgrenze und die Bruchdehnung konnten durch lineare Auftragung der relativen mechanischen Eigenschaften (Verhältnis der Werte für die gefüllte zu den für die ungefüllte Substanz) als Funktion des Reziprokwertes der Partikelgrösse des Füllstoffes gut dargestellt werden. Die Auftragung einer dieser Eigenschaften gegen die reziproke Füllstoffgrösse liefert eine Familie von Geraden, eine Gerade für jede Füllstoffkonzentration, unabhängig von der chemischen Natur des Füllstoffes. Die Abhängigkeit der mechanischen Eigenschaften von der reziproken Teilchengrösse ist offenbar ein Ausdruck für eine Abhängigkeit vom Oberflächen- Volumsverhältnis des Füllstoffes, nämlich für das Gegeneinanderspiel der effektiven Vernetzung durch die grosse Oberfläche des Füllstoffes und der Verdünnung des Polymeren durch einen Volumsanteil des Füllstoffes.

Received July 7, 1964