Simple Theory of Stress–Strain Properties of Filled Polymers

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Synopsis

By the use of simple models of filled plastics, approximate equations are derived for the elongation to break in the case of perfect adhesion between the phases and for the tensile strength in the case of no adhesion between the polymer and filler phases. By combining these equations with equations for the modulus (assuming Hookean behavior) all the stress–strain properties can be derived, including rough estimates of the impact strength, as a function of filler concentration. Among other things, the theory predicts a very rapid decrease in elongation to break as filler concentration increases, especially for the case of good adhesion. It is also predicted for the case of good adhesion that the tensile strength of a filled polymer can be greater than that of an unfilled polymer.

Introduction

Except for a number of theories of the elastic modulus of filled polymers, very little can be found in the literature to explain the mechanical properties of polymers filled with small rigid particles. By using very simple models for such systems, it is possible to predict qualitatively and possibly semiquantitatively the stress–strain properties as a function of filler concentration for the two cases of perfect adhesion and no adhesion between the filler and polymer phases.

Case of Perfect Adhesion Between Filler and Polymer

The simplest model is shown in Figure 1A, in which the filler particles are attached to the polymer in a series arrangement. Perfect adhesion is assumed between the two phases. Shear effects around the filler particles, triaxial stresses in the polymer, and effects due to Poisson's ratio are all neglected at this point in the analysis. Several other more complex models have been casually investigated and appear as a first approximation to give roughly the same results as this simple model. Figure 1A shows that, for a given elongation of the model, the actual elongation experienced by the polymer must be greater. By carrying out a calculation similar to that used by Bueche[1] to explain the Mullin's effect, it is found that the actual microscopic elongation (strain) of the plastic relative to the observed elongation of the filled system is:
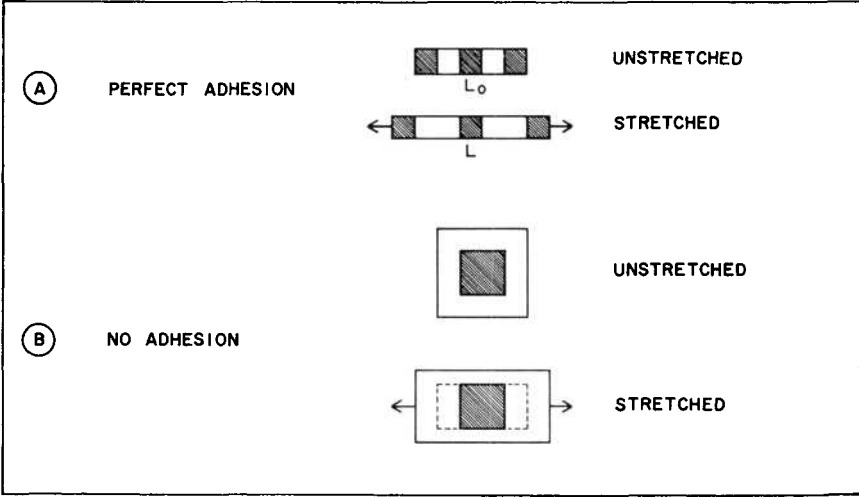
Fig. 1. Models for filled polymers.

$$\epsilon'/\epsilon \doteq 1/(1 - \phi_{\mathrm{F}}^{1/3}) \tag{1}$$

where ϵ' is the actual elongation of the plastic, ϵ is the overall elongation of the filled system defined as $(L - L_0)/L_0$, and ϕ_{F} is the volume fraction of the filler.

If one assumes that the polymer breaks at the same elongation in the filled system as the bulk unfilled polymer does, then the elongation to break of the filled system relative to the unfilled polymer is:

$$\epsilon_{\mathrm{B}} \text{ (filled)}/\epsilon_{\mathrm{B}} \text{ (unfilled)} \doteq 1 - \phi_{\mathrm{F}}^{1/3} \tag{2}$$
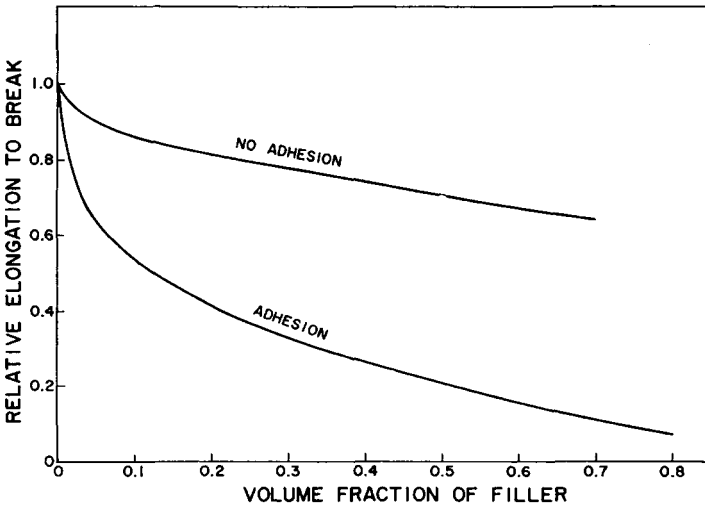

Fig. 2. Theoretical curves for the elongation to break for the cases of perfect adhesion and no adhesion between the filler and polymer phases.
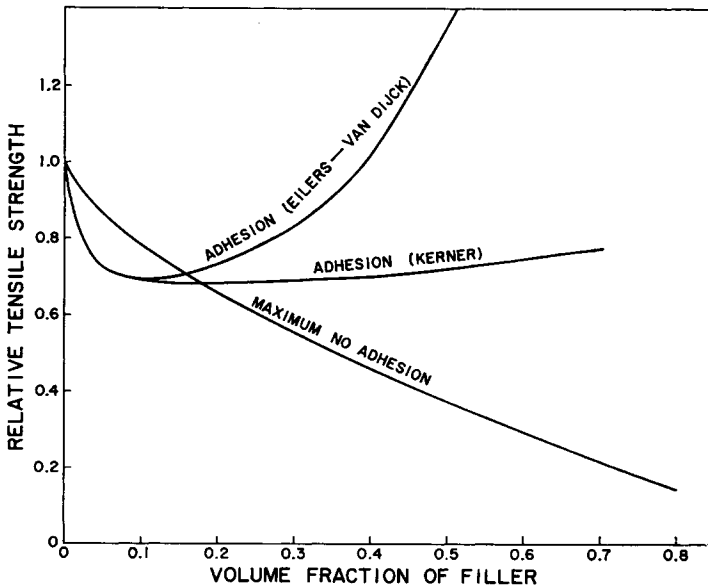
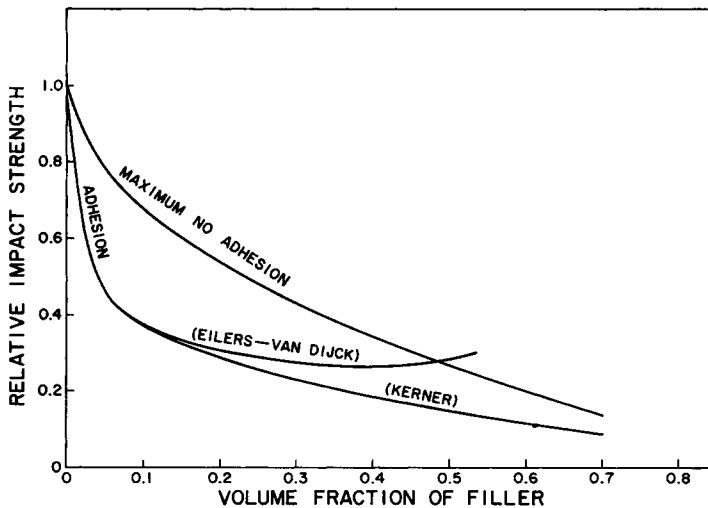Fig. 3. Theoretical curves for the tensile strength of filled polymers.

Fig. 4. Theoretical curves for the impact strength (energy under the stress–strain curve) of filled polymers.

ϵ_B (filled) is the elongation $(\Delta L/L_0)$ to break as measured in a tensile stress–strain test of the filled system. This relation is plotted as the lower curve in Figure 2. A polymer containing 40 vol.-% filler should break at an elongation of roughly $1/4$ that of the unfilled polymer. The curve indicates that small amounts of filler are relatively more detrimental than large amounts as long as aggregation does not occur and perfect adhesion

is maintained.   The size of the filler particle does not enter into the equation; this is analogous to the theories of the modulus.

We now wish to calculate other stress–strain properties, such as tensile strength and impact strength, i.e., the area under the stress–strain curve. At this point our simple model in Figure 1A breaks down and will be abandoned, since it does not allow for the filler particles to carry part of the load.   In the theories for the elastic moduli of materials, however, stresses are applied to the filler particles, so the results of these theories will now be combined with our result for the elongation to break.   By combining eq. (2) with the theoretical equations for the modulus of filled systems containing spherical particles, estimates can be made of the tensile strength and impact strength of rigid polymers which have linear (Hookean) stress–strain curves.   It is assumed that tensile strength σ_B is given by

$$\sigma_B = E\epsilon_B \qquad (3)$$

where E is Young's modulus of the filled polymer.   The impact strength (area under stress–strain curve) is assumed to be

$$\text{Impact strength} = \sigma_B\epsilon_B/2 = E\epsilon_B^2/2 \qquad (4)$$

The predicted results are illustrated in Figures 3 and 4 on the basis of the theories of Kerner[2] and Eilers and Van Dijck[3] for the modulus.   The equations for the moduli are given in the Appendix.

Both the Kerner and the Eilers–Van Dijck equations give similar results for the impact strength but differ greatly on the tensile strength at high filler contents.   Both the tensile strength and the impact strength decrease drastically with only small amounts of filler.   The impact strength continues to decrease to low values as the filler concentration increases.   However, the tensile strength increases with added filler above a volume concentration of about ten per cent.   The Eilers–Van Dijck curve even predicts a value of tensile strength greater than that of the unfilled polymer at high concentrations.   Since Kerner's equation generally predicts a modulus that is too low while the Eilers–Van Dijck equation gives values more in line with experiment, the experimental values for the tensile strength might be expected to fall near the Eilers–Van Dijck curve.   In any case, both theories predict a beneficial increase in tensile strength at high filler loadings, if good adhesion between filler and polymer can be achieved and if the filler particles can be well dispersed without weak aggregates being formed.

Case of No Adhesion Between Filler and Polymer

In the case of no adhesion, the filler particles can not carry any of the load, so all the load must be carried by the polymer.   In any given cross section the fraction occupied by polymer is equal to the volume fraction of polymer, so it might be expected that the tensile strength would be equal to the product of the tensile strength of the unfilled polymer and the volume fraction of the polymer.   However, the filler particles distort the stress

fields, so that, when the material breaks, the fracture travels from one filler particle or void space to another. Therefore, a model similar to that shown in Figure 1B might be more realistic. This model accounts for the decrease in cross-sectional area of the polymer phase as filler is added, but it does not enable one to calculate the additional factor of stress concentration around the particles. Thus, the values of tensile strength calculated by this model may be considered as maximum values; stress concentrators will lower these values by an undetermined amount. The predicted relative tensile strength is given by:

$$\sigma_B \text{ (filled)}/\sigma_B \text{ (unfilled)} \simeq (1 - \phi_F^{2/3})S \qquad (5)$$

where S is the stress concentration function, which can have a maximum value of 1.0 when there is no concentration. Generally S is expected to have a value of the order of one-half. Equation (5) is plotted in Figure 3 for the case where $S = 1$. The curve shows that the tensile strength decreases rapidly as filler content increases. Surprisingly enough, however, at volume fractions below about 15% the no-adhesion curve is higher than the curves for perfect adhesion; undoubtedly this is due in part to neglecting the effect of stress concentrators. Possibly if the effect of stress concentrators could be evaluated, the curve for the case of no adhesion would be shifted to below the curves for perfect adhesion.

If one incorporates eq. (5) into the theory of Sato and Furukawa[4] for the modulus of filled systems with no adhesion, the elongation to break and the impact strength can be estimated for the case of no adhesion. (The equation of Sato and Furukawa is given in the Appendix.) The calculated elongation to break is shown in Figure 2. Again neglecting stress concentration factors, the elongation remains high even at high filler loadings. The maximum impact strength is shown in Figure 4. The impact strength drops off rapidly and continues to decrease, even at high filler contents, in contrast to the leveling off for the case of good adhesion. Over most of the range, the curve for no adhesion is higher than for the case of perfect adhesion. Again, if the stress concentration factor could be computed, the no-adhesion curve would probably be shifted to below the other curves but would retain the same general shape.

Summary

As crude as these simple models are, it appears that they predict the same trends and roughly the same values as actually observed experimentally. These approximate theories clearly show the effects to be expected by changes in the strength of the adhesive bond between the polymer and filler phases.

In order to calculate all the stress–strain properties, rigid polymers obeying Hooke's law were assumed. However, no such restriction is required to use the theory to calculate only the elongation to break for the case of perfect adhesion. Likewise, no such restriction on the shape of the

stress–strain curve is required to calculate the maximum tensile strength for the case of no adhesion.

Although only polymers were discussed, the theory should be equally applicable to any type of material as the matrix.

APPENDIX

Kerner's equation is:

$$\frac{E \text{ (filled)}}{E \text{ (unfilled)}} = \frac{G_F\phi_F/[(7\text{-}5\ \nu)G_P + (8\text{-}10\ \nu)G_F] + \phi_P/[15(1\text{-}\nu)]}{G_P\phi_F/[(7\text{-}5\ \nu)G_P + (8\text{-}10\ \nu)G_F] + \phi_P/[15(1\text{-}\nu)]}$$

where G_P and G_F are the shear moduli of the plastic and filler, respectively, ν is Poisson's ratio of the plastic, and ϕ_P is the volume fraction of the plastic. E (filled) and E (unfilled) are the Young's moduli of the filled and unfilled systems.

The modified Eilers-Van Dijck equation is:

$$E \text{ (filled)}/E \text{ (unfilled)} = \left\{1 + [1.25\phi_F/(1 - V\phi_F)]\right\}^2$$

where V = sedimentation volume of filler/true volume of filler.; in the calculations in this paper, $V = 1.2$.

The equation of Sato and Furukawa is:

$$E \text{ (filled)}/E \text{ (unfilled)} \doteq \left\{1 + [y^2/2(1 - y)]\right\} (1 - \psi\zeta)$$
$$- [y^2\psi\zeta/(1 - y)\ y^3]$$

where $\phi_F = y^3$
and

$$\psi = (y^3/3)\ (1 + y - y^2)/(1 - y + y^2)$$

and ζ is the adhesion parameter; $\zeta = 0$ for perfect adhesion, and $\zeta = 1$ for no adhesion.

The surface effect in the theory of Sato and Furukawa has been omitted from the above equation for moduli.

References

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2. Kerner, E. H., *Proc. Phys. Soc. (London)*, **69B**, 808 (1956).
3. Eilers, H., *Kolloid-Z.*, **97**, 313 (1941).
4. Sato, Y., and J. Furukawa, *J. Fac. Textile Sci. Tech. Shinshu Univ. (Japan)*, **35F**, 1 (1962); *Rubber Chem. Technol.*, **36**, 1081 (1963).

Résumé

En utilisant des modèles simples pour des plastiques chargés, on peut dériver des equations approchées pour des elongations à la cassure dans le cas d'une adhésion parfait entre les phases, et pour la force à la tension dans le cas de non-adhésion entre les polymeres et les charges. En combinant ces équations avec les équations pour le module (en admettant un comportement de Hook) toutes les propriétes de tension-elongation peuvent etre derivées y compris des estimations grossières de la force à l'impact en fonc-

tion de la concentration de la charge. Entr'autres choses la theorie prédit une diminution très rapide de l'élongation à la rupture, quand la concentration en charge croît. Dans le cas d'une bonne adhésion, la force à la tension d'un polymère chargé peut etre plus elevee que celle d'un polymère non chargé.

Zusammenfassung

Mit einem einfachen Modell für gefüllte Kunststoffe werden Näherungsgleichungen für die Bruchdehnung in Falle einer vollkommenen Adhäsion zwischen den Phasen und für die Zugfestigkeit im Falle fehlender Adhäsion zwischen der Polymer- und der Füllstoffphase abgeleitet. Durch Kombination dieser Gleichungen mit Gleichungen für den Modul (unter Annahme eines Hookeschen Verhaltens) können alle Spannungs-Dehnungseigenschaften als Funktion der Füllstoffkonzentration abgeleitet werden und eine rohe Schätzung der Stossfestigkeit gegeben werden. Unter anderem sagt die Theorie, besonders für den Fall einer guten Adhäsion, eine sehr rasche Abnahme der Bruchdehnung mit steigender Füllstoffkonzentration voraus. Weiters wird für den Fall guter Adhäsion vorausgesagt, dass die Zugfestigkeit eines gefüllten Polymeren grösser als diejenige eines ungefüllten Polymeren sein kann.