

Energy Dissipation in Stretching Filled Rubbers

A. N. GENT, *Institute of Polymer Science, The University of Akron,
Akron, Ohio 44325*

Synopsis

Energy expended irreversibly in stretching filled rubbers is calculated for a simple two-phase series model: a soft phase resembling the corresponding unfilled rubber and a hard phase in series with the soft phase. It is assumed that the rubber is initially wholly in the hard state and that it changes progressively into the softened state on stretching, as proposed by Mullins and Tobin. For a wide range of model parameters, the dissipation of mechanical energy is predicted to rise to about 40% of the input energy at large strains. This predicted behavior is in reasonably good agreement with observations of extra energy dissipation in carbon black-filled rubbers, in comparison with corresponding unfilled rubbers, suggesting that the proposed mechanism of hysteresis by phase transformation is valid. A method of combining energy losses from two simultaneous dissipative processes is also proposed.

INTRODUCTION

Filled rubbers show a characteristic softening after straining, shown schematically in Figures 1 and 2. After a previous extension e_1 , the material is softer for subsequent extensions less than e_1 but unaffected for extensions greater than e_1 . Moreover, almost all of the softening is achieved in the first extension, little further softening taking place during subsequent strain cycles up to e_1 .

Two principal methods of characterizing the degree of softening have been proposed. The first, due to Mullins and Tobin,¹ is based on similarity between the second extension relation and that exhibited by the corresponding unfilled rubber. A two-phase series model is therefore proposed: an original hard phase and a softer phase, resembling the unfilled material, formed from the hard phase by a stress-induced transformation (Fig. 3).

The fractional amount α of material transformed into the soft phase is assumed to increase continuously with imposed stress. After a given stress level has been attained, however, the fraction α remains unaltered for subsequent deformations at stresses which do not exceed this level. This two-phase model accounts satisfactorily for the initial stress-softening process and for the stress-strain behavior of softened material, in terms of a simple physical representation of filled rubber. It is necessary to know only the stress-strain behavior of the corresponding unfilled rubber and the relation between α and prior stress (or prior strain). A more detailed account of the model is given in the following section.

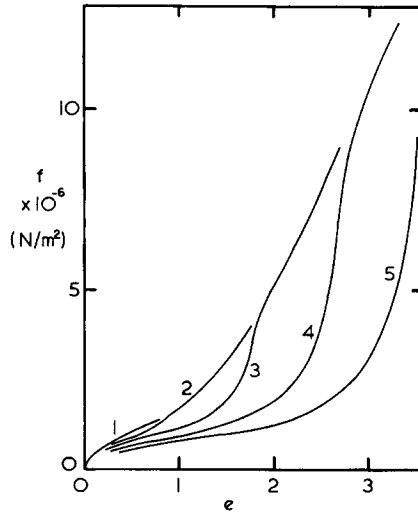


Fig. 1. Tensile stress-strain relations for a carbon black-filled SBR material, subjected to successive extensions of increasing amount.

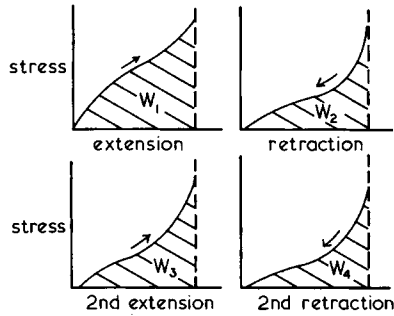


Fig. 2. Schematic diagram showing input energies W_1 and W_3 , and energies W_2 and W_4 returned on retraction.

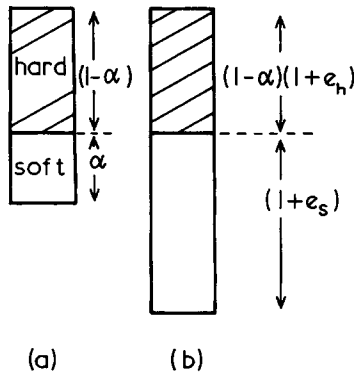


Fig. 3. Two-phase model of filled rubber: (a) partially softened; (b) stretched.

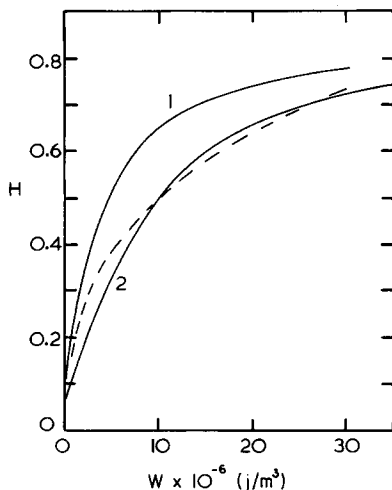


Fig. 4. Experimental relations between energy dissipation ratio H and input energy W_1 . Curve 1 from Harwood et al.⁴ and Charrier and Gent.⁵ Curve 2 from Dannenberg.² Broken curve: theoretical relation (H') calculated as described in text.

A second way of characterizing the amount of softening is by means of the energy loss ratio $H = (W_1 - W_2)/W_1$, where W_1 denotes energy input on stretching and W_2 denotes energy returned on retraction (Fig. 2). The dissipation ratio H_2 for a second strain cycle, given by $(W_3 - W_4)/W_3$, is found to be appreciably smaller than H , and all subsequent strain cycles yield similar values. To the degree that H exceeds H_2 , therefore, the material undergoes a unique softening process during its first straining.

A general relationship has been proposed to exist between H and the input energy W_1 , for filled rubbers.²⁻⁴ It is shown in Figure 4. Unfilled rubbers show a similar dependence of energy dissipation upon input energy, although the values obtained for H are somewhat lower in this case, about three fourths as large (Fig. 5). (Values similar to those for filled rubbers have been reported for a strain-crystallizing rubber under high-strain conditions⁴, when extensive crystallization occurs. Unfilled non-crystallizing rubbers, although difficult to examine at high strains because of their lower strength and extensibility, appear to give generally lower values for H .)

We now turn to the relationship between these two different representations of stress softening. In the following section, the energy loss ratio H is calculated as a function of input energy W_1 for the two-phase series model proposed by Mullins and Tobin, assuming that both the hard and soft phases are themselves perfectly elastic, nondissipative materials, but that energy is inevitably dissipated in the transformation step. The combined effect of this energy dissipation due to phase transformation and energy losses within the softened phase (assumed to behave like the corresponding unfilled material) is then calculated and compared with experimental measurements on filled rubbers.

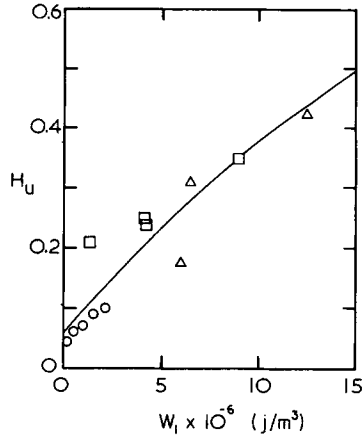


Fig. 5. Energy dissipation ratio H_u vs. input energy W_1 for unfilled rubbers. Results from: (Δ) Harwood et al.⁴; (\circ) Charrier and Gent.⁶ (\square) Henry.⁸

STRESS-SOFTENING EFFECTS AND ENERGY DISSIPATION IN A TWO-PHASE SERIES MODEL

The Mullins-Tobin model for a partially stress-softened material is shown schematically in Figure 3. We consider first how the softened fraction α increases (presumably from zero) as the material undergoes its first extension. The simplest possible relation between α and the imposed extension is a linear one, e.g.,

$$\alpha = ke \quad (1)$$

where e is the overall extension. This form is also suggested by stress-strain relations for previously stretched test pieces. They may be superimposed by scaling the strain axis appropriately in each case, using a multiplying factor α^{-1} which depends upon the previous strain in accordance with eq. (1). Experimental values for k obtained in this way range from 0.06 to 0.16, increasing as the amount of filler or its reinforcing power decreases.¹ Indeed, the parameter k may be regarded as an inverse measure of the strength of the hard phase.

If the hard phase is completely inextensible, then the actual extension e_s of the softened phase is given by e/α ($= k^{-1}$). Thus, on this hypothesis, the softened phase undergoes a constant extension (k^{-1}). The softening transformation will therefore occur at constant stress, whatever form of stress-strain relationship is obeyed by the softened phase. This is contrary to general experience: the first deformation is not usually found to take place at constant stress (although stress-strain relationships of this form are observed in some circumstances; for example, when large amounts of filler are employed⁵).

We now suppose that the hard phase is not completely inextensible but is merely a stiffer version of the soft phase, so that for any applied stress the strain e_h of the hard phase is a constant fraction β of the strain e_s in the

soft phase. In this case the overall strain e , relative to the strain e_s in the soft phase, is given by

$$\alpha' (= e/e_s) = \alpha (1 - \beta) + \beta \quad (2)$$

where α is the fractional amount of soft phase present. The value of α now depends in an unknown way upon the prior extension e_1 . In practice it appears to be approximately linearly dependent,¹ as in eq. (1), and the value of β is found to be approximately 0.1.^{1,6}

In order to calculate the energy input W_1 and energy regained W_2 to determine the loss ratio H , we need to know stress-strain relationships for the hard and soft phases. The energy input W_1 is then given by

$$W_1 = \int_0^{e_1} f de \quad (3)$$

where f denotes the applied stress (force per unit of unstrained cross-sectional area) at an overall extension e during the first extension. The energy W_2 returned is given by

$$\begin{aligned} W_2 &= \alpha W_{s,e_1} + (1 - \alpha)W_{h,e_1} \\ &= \alpha' W_{s,e_1} \text{ from eq. (2)} \end{aligned} \quad (4)$$

where W_s and W_h denote strain energy densities in the soft and hard phases, respectively.

For illustrative purposes, two particularly simple forms for f and W_s are employed here: those for a linearly elastic material, obeying Hooke's law, i.e.,

$$f = E_s e_s \quad (5)$$

and

$$W_s = 1/2 E_s e_s^2 \quad (6)$$

where E_s is Young's modulus for the soft phase; and those for a neo-Hookean material obeying the kinetic theory of rubber-like elasticity,⁷ i.e.,

$$f = 1/3 E_s (\lambda_s - \lambda_s^{-2}) \quad (7)$$

and

$$W_s = 1/6 E_s (\lambda_s^2 + 2\lambda_s^{-1} - 3) \quad (8)$$

where $\lambda_s = 1 + e_s$.

For a linearly elastic material, the maximum value of the energy dissipation ratio H is obviously 0.5 (Fig. 6) when the hard phase is completely inextensible ($\beta = 0$). The corresponding result for neo-Hookean materials when the hard phase is inextensible is similar, but it now depends slightly upon the value chosen for k ; as k increases from 0.05 to 0.2, the value obtained for H decreases from 0.478 to 0.442. Thus, for a wide range of elastic behavior and stress-softening criteria, the maximum value obtained for H lies between 0.44 and 0.5. Under the worst conditions, therefore, nearly

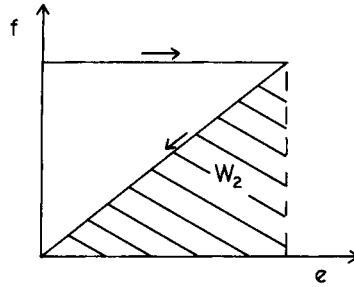


Fig. 6. Stress-strain relation for a two-phase series model with transformation taking place from an inextensible hard phase to a linearly elastic soft phase at constant stress.

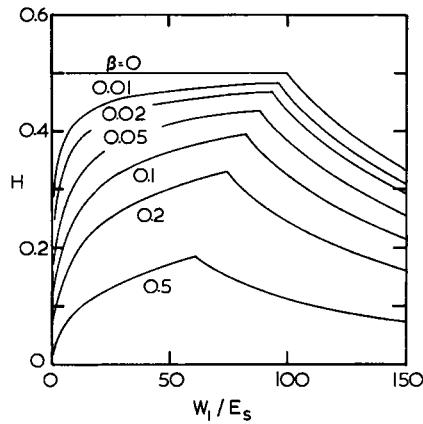


Fig. 7. Theoretical relations between the energy dissipation ratio H and input energy W_1 for a two-phase linearly elastic model; β denotes the stiffness ratio of the two phases. The softening parameter k , defined by eq. (1), is given the value 0.1.

one half of the input energy is dissipated. This result is rather independent of details of the model employed.

Finite values of β are now considered, corresponding to various levels of hardness of the hard phase. Values of the energy dissipation ratio H may be calculated from eqs. (3) and (4), using either eqs. (5) and (6) or eqs. (7) and (8) for f and W_s , and integrating eq. (3) using relations between e and e_s obtained from eqs. (1) and (2). Some results for linearly elastic materials are shown in Figure 7 for a wide range of values of β , using a representative value of k (0.1), and in Figure 8 for a wide range of values of k , using a representative value of β (0.1).

One special feature of these calculations should be noted. At a particular level of deformation e and energy input W_1 , determined by the parameter k in eq. (1), the fraction α of material in the soft phase becomes equal to unity. At this point, all of the material has been transformed into the softened state. For larger deformations, therefore, the extra deformation energy supplied is wholly regained on release because it is devoted solely

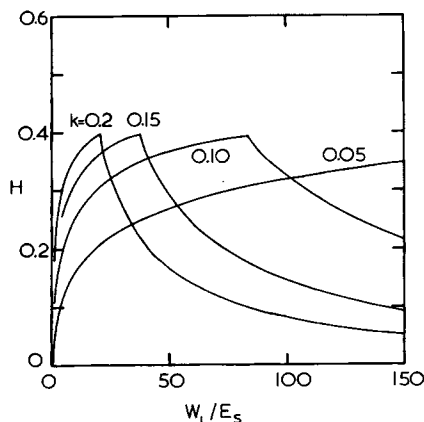


Fig. 8. Theoretical relations between the energy dissipation ratio H and input energy W_1 for a two-phase linearly elastic model, with various values for the softening parameter k . The stiffness ratio β is given the value 0.1.

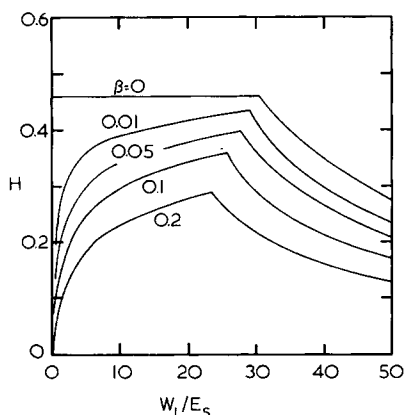


Fig. 9. Theoretical relations between the energy dissipation ratio H and input energy W_1 for a two-phase neo-Hookean model, with various values of the stiffness ratio β . The softening parameter k is given the representative experimental value 0.11.^{1,6}

to stretching softened material, assumed here to be perfectly elastic. The energy dissipation ratio H will thus decrease continuously after that deformation at which $\alpha = 1$ is passed, because an increasing proportion of the total energy input is then returned without loss. This feature is clear in Figures 7 and 8.

In Figure 9, results are given for a two-phase series model using neo-Hookean materials, eqs. (7) and (8), with a wide range of values for the stiffness ratio β and a particular value of k , 0.11, found to apply to a representative carbon black-filled material^{1,6} (50 parts by weight of HAF N330 carbon black per 100 parts by weight of styrene-butadiene copolymer SBR 1502, plus the usual vulcanization additives). Again, the choice of a different

strain energy function and stress-strain relation has not materially altered the results.

The relations shown in Figure 9 are closely similar to those shown in Figure 7, the principal difference being in the scales employed for W_1 . Neo-Hookean materials show pronounced nonlinearity in their tensile stress-strain behavior, eq. (7); in consequence, the input energy at relatively large strains is smaller relative to Young's modulus E than it is for linearly elastic materials. This difference is reflected in the W_1/E_s scales in Figures 7 and 9. For neo-Hookean materials (Fig. 9), similar values of H are obtained when the values of W_1/E_s are only about one third of those for the linearly elastic materials, Figure 7. In all other respects, however, the loss ratios in neo-Hookean systems are calculated to be quite similar to those in linearly elastic systems. Indeed, other calculations yielded similar values for H when stress-strain relations incorporating finite extensibility effects (turning sharply upward as a maximum extension is approached) were employed in place of those discussed here. We conclude that the results for H are not particularly sensitive to the form chosen for the stress-strain relationship of the soft phase. In the following section, the results for neo-Hookean materials (Fig. 9) are employed for comparison with experimental results for filled rubbers.

Combined Effects of Stress Softening and Energy Dissipation in the Soft Phase

Energy is dissipated in stretching the softened phase, presumably by the same mechanisms and to the same degree as in stretching the corresponding unfilled material. The energy W_2' available on release will therefore be less than the amount W_2 calculated from eq. (4), i.e., the energy required to stretch the soft and hard phases to their strain conditions at an overall extension e_1 . Neglecting the relatively small proportion of strain energy stored in the hard phase, we assume that a fraction $H_u W_2$ of the energy W_2 is dissipated in processes which take place in the soft phase, where H_u is the energy loss ratio for unfilled rubber at an energy input of W_2 . Thus, the overall dissipation ratio H' , defined by $(W_1 - W_2')/W_1$, will be given by

$$H' = H + H_u - HH_u \quad (9)$$

where H is obtained from eqs. (3) and (4).

Values of the overall dissipation ratio H' can now be calculated by means of eq. (9), provided that values of H_u are available. The procedure adopted here is as follows. First, values of the energy dissipation ratio H are calculated on the assumption that no energy is dissipated in the soft phase by means of eqs. (3) and (4), for a wide range of values of W_1 and using appropriate values for the stiffness ratio β , softening parameter k , and Young's modulus E_s of the soft phase. Typical results are given in Figure 9 for neo-Hookean materials. Then, using corresponding values of W_2 , values of H_u are read from the experimentally determined relation between H_u and W_1 given in Figure 5. Finally, values of H' are calculated from

eq. (9). Typical relations between H' and input energy W_1 obtained in this way are represented in Figure 4 by a broken curve. They were calculated using values for E_s of 1–2 MN/m² (10–20 kg/cm²), for β of 0.05–0.1, and for k of 0.11. As the resulting relations are all rather similar, only an average result is shown in Figure 4.

Reasonably satisfactory agreement is seen to be obtained between calculated overall dissipation ratios H' and experimentally determined values. At large deformations, the predicted results seem slightly lower than the measured values, but in this region the calculations involve values of H_u at large deformations, where they are difficult to determine and somewhat uncertain (Fig. 5). On the whole, the general magnitude of energy dissipation in filled rubbers and its dependence upon strain seem fully accounted for by the combined effects of phase transformation and hysteresis in the soft phase resembling that in unfilled rubbers.

DISCUSSION AND CONCLUSIONS

Several features of this comparison between calculated energy dissipation and measured values call for comment:

(i) Values of H and H_u , the loss ratios for phase transformation alone and for soft-phase hysteresis alone, are generally rather similar in magnitude, the former being larger at low deformations and the latter, at high ones. Thus, the two contributions are of roughly equal importance. This point has not been recognized in the past,^{3,4} probably because the two quantities are not simply added together to yield the overall dissipation ratio but are combined in a more complicated way, eq. (9). For example, if H is 0.5 and H_u is 0.6, the overall dissipation ratio H' is 0.8. In these circumstances, if H_u alone is compared with H' , it might well be concluded that hysteresis of the unfilled material accounts for the major part (³/₄) of the observed energy loss, whereas its contribution in this example is quite similar to that from phase transformation.

(ii) The proposed relationship for two dissipative processes occurring simultaneously, eq. (9), may have general applicability. It is clearly correct when either H or H_u is zero and also when either H or H_u is unity, and thus is probably valid over the entire range.

(iii) Calculated values of the energy loss ratio H are surprisingly independent of details of the two-phase model employed, within the range appropriate to normal filled rubbers. However, some general trends are evident. Energy losses are higher when the relative hardness of the hard phase is increased (Figs. 7 and 9), and higher energy losses are observed at lower deformations when the transformation takes place more rapidly with deformation (Fig. 8).

(iv) The maximum energy input employed for carbon black-filled rubbers, about 3×10^7 J/m³, is almost but not quite enough to bring the material completely to the softened state, $\alpha = 1$. It was not found necessary to continue calculations past the deformation at which $\alpha = 1$ in order to ac-

count for the observed energy losses (Fig. 4), using reasonable values for E , β , and k . However, other less strongly reinforced materials might continue to deform after the whole sample is softened. They should then exhibit smaller loss ratios at high strains than at intermediate strains.

It is noteworthy in this connection that filled rubbers show a rather pronounced maximum in loss ratio at small deformations, under repeated (dynamic) straining conditions.^{9,10} A small-strain softening process, associated with the disruption of carbon particle associations, is known to take place under these circumstances. If it can also be successfully represented by a two-phase series model; i.e., if the present hard phase can be regarded as a two-phase material, transforming from a harder to a less hard state at quite low strains, then the analysis outlined here should also apply. However, it is necessary to assume that recovery from stress-induced softening occurs between one deformation and the next if the present model is employed to predict energy losses under repeated deformations. Small-strain dynamic softening seems to be in part recovered and in part relatively permanent,⁹⁻¹² although full information on this aspect is lacking.

This work was supported by a research grant from the Engineering Division of the National Science Foundation. A brief preliminary account of it was included in a paper⁶ presented at the International Symposium on Elastomer Reinforcement, Obernai, France, September 24-26, 1973. Computational assistance by Mr. L. K. Djiauw and helpful discussions with Dr. J. M. Charrier are also gratefully acknowledged.

References

1. L. Mullins and N. R. Tobin, Proc. 3rd Rubber Technol. Conf. 1954, W. Heffer and Sons Ltd., London, 1956, p. 397; *Rubber Chem. Technol.*, **30**, 555 (1957).
2. E. M. Dannenberg, *Trans. Inst. Rubber Ind.*, **42**, T26 (1966).
3. J. A. C. Harwood and A. R. Payne, *Trans. Inst. Rubber Ind.*, **42**, T14 (1966).
4. J. A. C. Harwood, L. Mullins, and A. R. Payne, *J. Inst. Rubber Ind.*, **1**, 17 (1967).
5. K. C. Bryant and D. C. Bisset, Proc. 3rd Rubber Technol. Conf. 1954, W. Heffer and Sons Ltd., London, 1956, p. 655; *Rubber Chem. Technol.*, **30**, 610 (1957).
6. J. M. Charrier and A. N. Gent, Proc. Int. Symposium on Elastomer Reinforcement, Obernai, France, Sept. 24-26, 1973.
7. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Oxford University Press, London, 1958.
8. A. W. Henry, Ph.D. Thesis, The University of Akron, 1967.
9. W. P. Fletcher and A. N. Gent, *Trans. Inst. Rubber Ind.*, **29**, 266 (1953).
10. A. B. Davey and A. R. Payne, *Rubber in Engineering Practice*, Palmerton, New York, 1964, Chap. 2.
11. W. P. Fletcher and A. N. Gent, *Trans. Inst. Rubber Ind.*, **26**, 45 (1950).
12. K. E. Gui, C. S. Wilkinson, and S. D. Gehman, *Ind. Eng. Chem.*, **44**, 720 (1952).

Received September 23, 1973