Mechanical Degradation of High Polymers*

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INTRODUCTION

Mastication of rubbers and molten plastics often often gives rise to degradation of the polymer molecules.[1,2] The amount of degradation is severely dependent upon shear rate, melt viscosity, and molecular weight of the polymer, temperature, and the presence of plasticizer. Under certain conditions, usually at low temperatures, one finds that the presence of oxygen is only of minor importance. At high temperatures, at least in certain cases, shear degradation is seriously increased when oxygen is present, even though very little degradation occurs without mastication. In this latter case, oxidative scission does not appear to take place at random along the chain but seems to occur predominantly in the central portion of the chain.[1a]

The purpose of this paper is to present a molecular theory which unifies these various observations. It will be restricted to the mechanical actions involved during mastication. The effect of oxygen on mechanical degradation will also be considered.

MOLECULAR PICTURE

Consider the polymer molecule shown in Figure 1. If this molecule is immersed in a viscous matrix, polymeric or otherwise, and the matrix is subjected to a shearing action as illustrated, the viscous matrix will cause the molecule to rotate in a clockwise direction.

It can be shown[3] that the molecule will rotate with a frequency $(^1/_2)\dot{\gamma}$, where $\dot{\gamma}$ is the shear rate. The combined effect of this rotation and the flow of the pervading matrix[3] is to stretch the molecule along the line OO' and compress it along the line II'. Of course, since the molecule is rotating, a given segment will first be pulled out towards O,

then pushed in from I', pulled out towards O', and so on. In fact it can be shown that each segment oscillates back and forth in a sinusoidal type motion.

It is tempting to speculate that at very high shear rates the chain will be stretched enough along OO' so as to cause it to break. The current theories of molecular viscoelasticity enable one to compute how much the molecule is distorted by the shearing forces, and this is done in Appendix I. It turns out that the molecule is not stretched enough by this action to give rise to any sizeable amount of degradation. The reason for this is quite simple. At very high shear rates, the molecule rotates so fast that the chain does not have time to stretch very much. For example, a segment rotating past O will be pulled away from the center of the molecule, but before it moves out very far it has already rotated to I', where it is being pushed back in. The net result is that the molecular distortion increases as the shear rate increases, but at very high shear rates the molecule approaches a certain limiting amount of distortion which is far too small to cause the chain to break.

The speculations of the preceding paragraphs are valid provided the matrix in which the polymer molecule is imbedded consists of small molecules. On the other hand, if a polymer molecule is immersed in a matrix of other polymer molecules, another complication must be considered, the en-
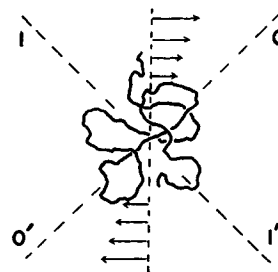

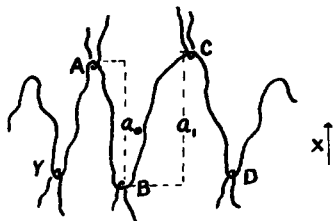Fig. 1. A typical polymer molecule in a sheared liquid.

Fig. 2. A schematic diagram showing the action of entangle-
ments.

tanglement of the molecules. It turns out, as
shown in the following, that these entanglements
give rise to very large tensions rear the central
portions of the molecules.

When a molecule entangled with other molecules
is sheared, it is necessary that the molecules dis-
entangle from each other in ordei for flow to occur.
Even though the shear rate may be small and the
molecule is not greatly distorted, the segments of
the molecule must move very swiftly if the en-
tanglements with surrounding molecules are to
be released without the development of very large
forces. This movement within a molecule, which
is necessary if the entangled chains are to be re-
leased, is known to be of major importance in de-
termining the viscosity of such systems.[4] Its
importance for shear degradation may be shown
by reference to Fig. 2.

COMPUTATION

Figure 2 is a schematic diagram showing the
action of entanglements when a molecule is sub-
jected to a tensile shear $\dot{\gamma}$ in the x direction.
Suppose the molecule consists of Z links, each link
having a molecular weight M_0. Denote the
molecular weight between entanglements by M_e.
On the average, two entanglement points such as
A and B will separate with a velocity $(1/2)\dot{\gamma}a_0$
under the action of the shearing forces.

If segment AB is taken to be the central one, it
will not move even though it is elongating. How-
ever, each link in the two adjacent segments, AY
and BC, must move with a velocity $(1/2)\dot{\gamma}a_0$. In
general, each link in the ith segment must move
with a velocity

$$(1/2)\dot{\gamma} \sum_{n=0}^{i-1} a_n \qquad (1)$$

The velocities indicated are made possible by
appropriate tensions along the molecule. A link
moving at velocity v resists movement by a viscous
force, fv, where f is a friction factor for the link.

The tension on the center link of the chain is the
sum of all the forces needed to pull either side of
the chain through its entanglements. This tension
is

$$F_0 = \sum_{i=1}^{M/2M_e} \left[(M_e/M_0)(1/2)(\dot{\gamma}f) \sum_{n=0}^{i-1} a_n \right]$$

or (see Appendix II)

$$F_0 = (1/16)\dot{\gamma}f(M_e/M_0)^{3/2}(M/M_e)^2 l \qquad (2)$$

where a, the mean x-directed end-to-end distance
of a chain of molecular weight M_e, is taken to be
$l(M_e/M_0)^{1/2}$, with l the length of a chain link.

The tension in the qth link from the center is
obtained in the same way (see Appendix II)
and is

$$F_q = F_0[1 - (4q^2/Z^2)] \qquad (3)$$

The chance that a chain bond subjected to a
tension F will break in time dt is given by[5]

$$\omega \exp \left\{ -(E - F\delta)/kT \right\} dt \qquad (4)$$

In this expression E is the energy needed to break
the bond, ω is the bond vibration frequency and δ
is a distance approximately equal to the distance
the bond will stretch before breaking.

The chance that the chain will break in time dt
is the sum of the chances for the individual bonds

$$Pdt = dt \sum_{q=0}^{Z(1/2)} \omega \exp \left\{ -(E - F_q\delta)/kT \right\}$$

$$= (Z/4)(\pi kT/F_0\delta)^{1/2} \omega \exp \left\{ -(E - F_0\delta)/kT \right\}$$

$$\times E_2[(F_0\delta/kT)^{1/2}]dt \qquad (5)$$

where $E_2[x] = \int_0^x \exp \left\{ -y^2 \right\} dy$

If P is independent of time, one has that the
number of chains N remaining unbroken after
time t out of an original number N_0 is[5]

$$N = N_0 \exp \left\{ -P\omega t \right\} \qquad (6)$$

Therefore, the rate of chain breakage is chiefly a
function of P since ω is essentially constant.

By examining the order of magnitudes in eq. (6)
one can show that if the chain is to break in any
reasonable time, then $F_0\delta/kT > 2$ and so one has to
good approximation

$$P = \omega(Z/4)(\pi kT/F_0\delta)^{1/2} \exp \left\{ -(E - F_0\delta)/kT \right\}$$

$$(7)$$

In addition, E/kT will be of the order of 10^2,
and so the exponential factor will vary much more
rapidly with the temperature and molecular vari-

ables than do the factors in front of it. We therefore write

$$P = K \exp \{ -(E - F_0\delta)/kT \} \qquad (8)$$

where K is essentially a constant.

It remains yet to express the friction factor f in terms of molecular weight and viscosity. This is easily done if all the molecules are of the same length. In that case, one has for high molecular weights[4]

$$f = (288/\rho N)(M/R^2)(M_e/M)(M_0/M)\eta \qquad (9)$$

where ρ is the polymer density, R is the root-mean-square chain-end distance, N is Avogadro's number, and η is the shear viscosity at negligible rate of shear. Even if the polymer is heterogeneous, f is still given by the above relation, provided M is replaced by M_t, an average molecular weight intermediate between the weight- and Z-average.[6] One therefore has, in place of eq. (2),

$$F_0 = (\eta\dot\gamma)(18/\rho N)(M_t/R_t^2)(M_e/M_0)^{1/2}$$
$$(M/M_t)^2 l \qquad (10)$$

The molecular weight without subscript in eq. (10) refers to the molecule which supports the force F_0 at its center.

DISCUSSION

A. Location of the Break

From eq. (3) one sees that the force along the chain reaches a maximum at the center. Therefore the most probable place for the chain to break is at its center. This fact was first discovered by Fren'kel[7] many years ago. In general, the ratio of the number of chains which break at the qth link from the center to the number which break at the center is, from eq. (4)

$$\exp \{ -(F_0\delta/kT)(4q^2/Z^2) \} \qquad (11)$$

Since $(F_0\delta/kT)$ will usually be of the order of 10 or 20, it is clear that the break will usually occur rather near to the chain center. For example, if $F_0\delta/kT = 20$, ten chains will break at the center for each chain which breaks $1/3$ of the way out from the center, i.e., where $2q/Z = 1/3$.

An interesting case to consider is the degradation of a perfectly sharp polymer fraction. Suppose the shear rate is large enough to degrade the molecular weight being considered but is still small enough so that a chain half as long does not degrade appreciably. It will be seen in a later section that this condition is not difficult to achieve. Equation (11) may be used to predict the distribution of molecular weights after all the original molecules have been broken. It turns out that in this special case

$$M_w/M_n \cong 1 + (^1/_2)kT/F_0\delta \qquad (12)$$

If $F_0\delta/kT = 10$, then $M_w/M_n = 1.05$ and so the fraction will still be extremely sharp.

B. Rate of Degradation

The rate of chain breakage may be obtained from eq. (8) and is

$$Pdt = K \exp \{ -(E - F_0\delta)/kT \} dt$$

If one restricts the discussion to a single type of molecule at a fixed density and temperature then F_0 can be written as

$$F_0 = (\text{const})\dot\gamma M^2 M_t^{1.5} \qquad (13)$$

In writing this, use has been made of the fact that $\eta = (\text{const})M_t^{3.5}$. Since M_t will vary with time as the molecules degrade, F_0 is not usually a simple function of time.

Consider first the special case where a few very high molecular weight molecules are present in a sample of much lower molecular weight. In this case the breakdown of the large molecules will not change M_t to any great extent and it can be taken as constant. Therefore, the rate of breakage of the large molecules of molecular weight M is given by eq. (6). Their number decays exponentially with a decay time τ which is given by

$$1/\tau = P\omega \qquad (14)$$

Notice that since $P \sim \exp \{ -F_0\delta/kT \}$ and since $F_0 \sim M^2$, the decay time τ is an extremely rapidly varying function of M. For example, if $F_0\delta/kT = 20$ for a given molecular weight M_0 which has a decay time τ_0, the decay time τ for a molecular weight $M = M_0/1.2$ is given by $\tau/T_0 = e^4 = 55$.

In the more general case where M_t must also be considered a function of time, the situation is much more complicated. For any given distribution one could, in principle, carry through a computation of the decay as a function of time. However, the main features of the decay process can be ascertained without doing this in detail. The initial part of the decay can be obtained from eqs. (6), (10), and (14) from data for the original polymers. The final part of the decay can be inferred in a similar fashion from the final condition of the polymer.

C. Molecular Weight Distribution

An examination of eqs. (13) and (14) shows that the rate of degradation for a particular size molecule is severely dependent upon the molecular weight of the molecule. As seen in the previous paragraphs, it is not at all unreasonable to expect that a 20% change in molecular weight would cause the rate of degradation to change by a factor of 10^2. For this reason, it is to be expected that, after a material has been masticated for a while, essentially all the molecular weights above a certain critical value M_c will no longer be present. The original molecules with M less than M_c will be augmented by the decay products of the large molecules. It should be noticed that this is true only if one starts with a low shear rate and gradually increases it to its final value.

Given the initial distribution of molecular weights and with the assumption that M_c is sharply defined, the distribution after degradation is most easily found by the following approximate procedure. All the original polymer having molecular weight $M_1 > M_c$ will appear in the final distribution as molecular weight $M_1/2^n$ where n is the smallest integer which will make $M_1/2^n < M_c$. This procedure assumes that the molecules always split exactly in the center and that τ varies extremely fast with M. Both of these assumptions are probably reasonably good.

If the original molecular weight distribution is a wide one, it is clear that mastication will narrow the distribution. As shown above, however, sharp distributions may actually be widened by mastication.

D. Effects of Temperature, Diluent, and Shear Rate

These three variables cause similar effects and are conveniently discussed together. One sees from eq. (10) that the above factors influence F_0 through the product $(\eta\dot{\gamma}/\rho)M_e^{1/2}$. Anything which increases the melt viscosity will increase F_0. If plasticizer is added, η will fall very markedly. In addition, M_e will increase with added plasticizer. This means, if one is to obtain comparable degradation in the presence of plasticizer, $\dot{\gamma}$ must be increased to compensate for the decrease in $\eta M_e^{1/2}/\rho$.

Increase in temperature will result in a large decrease in η and minor changes in ρ and M_e. Consequently, an increase in temperature must be compensated by an increase in $\dot{\gamma}$ if comparable

degradation is to occur. Since activation energies for flow in these systems are usually of the order of 15 kcal./mole, the viscosity will change by a factor of about two for a 10°C. temperature change. Therefore one would have to double the shear rate to compensate for a 10° rise in temperature. It is obvious that temperatures must be accurately maintained if reproducible mastication results are to be obtained.

E. Degradation in the Presence of Oxygen

If one considers the action of oxygen only in so far as it aids bond scission and ignores its effects upon other reactions, the effect of oxygen is nearly equivalent to reducing the energy E needed for bond rupture. Suppose that the temperature is low enough so that oxidative scission is slow in the absence of mastication. It may be that the temperature is high enough so that η, and therefore F_0, has decreased so much that chain breakage is negligible when mastication occurs in the absence of oxygen. However, if the material is masticated in the presence of oxygen, degradation may occur, since the oxygen has lowered E in eq. (8) and P may have become sizeable as a result. Since the shearing force and oxygen both act together to break a given bond, those near the center of the molecule will break most often.

Ordinarily one thinks of oxidative scission as being random. The present considerations show that oxidative scission, in a polymer which is being masticated, will occur at the most highly strained bonds. Consequently, if the temperature is not extremely high, the resultant molecular weight distributions will be those characteristic of shear degradation rather than random scission. At very high temperatures, the oxygen reaction will take place even without shear, and the distribution will change to that characteristic of random scission.

F. Relation to Experimental Results

The theoretical results found here are in accord with the limited experimental data available.[1,2] Watson and co-workers have obtained experimental results which confirm all of our results, at least in a qualitative way. Whether or not the agreement is quantitative is still unknown. Accurate measurement of degradation as a function of melt viscosity and molecular weight are needed before crucial tests can be made. It would also be of value to test the results concerning degradation of sharp fractions.

The present theory is imcomplete. It ignores the complicating features of possible chemical reactions after the chains break. These effects can be minimized by the addition of inhibitors to the polymer. However, the general case, when subsequent reactions occur, is an interesting but complex subject untouched by the present theory.

G. Recent Results

Since the time that the body of this paper was submitted, a significant paper by Bestul[9] has appeared. Although his approach is far different from that of this work, he also concludes that intermolecular interactions are of paramount importance for mechanical degradation. He does not, however, arrive at a quantitative molecular theory for their effects in terms of entanglements.

APPENDIX I

The viscoelastic behavior of a polymer molecule immersed in a viscous medium and subjected to shear can be worked out by use of a method previously outlined.[8] Knowing that the force on any link of the polymer molecule at a distance r from the mass center is given by $(1/2)\dot{\gamma}r \sin(\gamma t)$, one can substitute in the general equations previously formulated.[8] A first approximation for the motion of the links can be obtained by setting r equal to its average equilibrium value. The resultant oscillatory value found for r can then be subtracted from the assumed value to obtain a perturbation to the original average force. Assuming the system to be linear, this perturbation is used to obtain a second approximation. This process is repeated to give a convergent series for the displacement of any segment.

It is found that the amplitude of stretching of the center link of the chain is given to good approximation by

$$\Delta s = (4l/\pi Z^{1/2})\Phi[1 - (4\Phi/\pi^2)]^{-1} \quad (15)$$

with

$$\Phi = \dot{\gamma}\tau_1(1 - j\dot{\gamma}\tau_1)(1 + \dot{\gamma}^2\tau_1^2)^{-1}$$

where $j = \sqrt{-1}$. In this expression τ_1 is a characteristic relaxation time for the chain,[8] Z is the number of links in the chain and l is the length of a link. The maximum value of Δs is about $l/Z^{1/2}$. The maximum tension in this link is[7] about $(l/Z^{1/2})(3kT/l^2)$ and is much too small to cause the link to break in any reasonable time. In the same way, one can show that the chain end-to-end length is

stretched far short of its maximum possible extension.

APPENDIX II

Equation (2) in the text is obtained by evaluating the following double sum:

$$S = \sum_{i=1}^{M/2M_e} \sum_{n=0}^{i-1} a_n \quad (16)$$

Since a_n is given its average value in each case, $a_n = a = l(M_e/M_0)^{1/2}$, it is a constant and one has

$$S = a\sum_{i=1}^{M/2M_e} i$$
$$= (a/2)(M/2M_e)[(M/2M_e) + 1]$$
$$\cong (a/2)(M/2M_e)^2 \quad (17)$$

This, when substituted in the expression given in the text, yields eq. (2).

Equation (3) is obtained in the same way, except now the limits on the outer sum must be changed. One has

$$S = \sum_{i=q}^{M/2M_e} \sum_{n=0}^{i-1} a_n$$
$$\cong [(M/2M_e)^2 - q^2](a/2) \quad (18)$$

The use of this expression for the sums gives eq. (3) directly.

References

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2. Bestul, A. B., J. Chem. Phys., 24, 1196 (1956). This paper gives references to the experimental work carried out by its author on polyisobutylene and its solutions. It also contains a first approximation theory for the effects treated in this work. The treatment is quite unlike the present one.
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Synopsis

A theory for the shear degradation of high polymers is presented. It assumes the molecules to exist in the rubbery or liquid state and does not include the effects of chemical reactions which might occur subsequent to chain rupture. The computation shows that the entanglements along the chains play a major part in the rupture process. Expres-

sions for the rate of chain rupture are obtained in terms of the melt viscosity, shear rate, and molecular weight. Other factors enter also, but the sensitive variables are those listed. The variation of molecular weight distribution with shear degradation is considered. It is pointed out why oxidative scission during shear is not a random process. In general, the theoretical result agrees with the limited experimental data available.

Résumé

On présente une théorie pour la dégradation par cisaillement des hauts polymères. Elle suppose des molécules existant à l'état liquide ou élastique et n'inclut pas les effets de réactions chimiques pouvant survenir à la suite d'une rupture de chaîne. Les discussions montrent que les enchevêtrements le long des chaînes jouent le rôle le plus important dans le processus de rupture. Des expressions pour la vitesse de rupture de chaîne s'obtiennent en fonction de la viscosité à l'état fondu, de la tension de cisaillement et du poids moléculaire. D'autres facteurs interviennent mais les variables importantes sont celles citées plus haut. On considère la variation de la distribution du poids moléculaire avec la dégradation par cisaillement. On explique pourquoi la scission oxydante durant le cisaillement n'est pas un processus statistique. En général, le résultat théorique est en accord avec les résultats expérimentaux limites disponibles.

Zusammenfassung

Eine Theorie für den Abbau von Hochpolymeren durch Scherung wird vorgelegt. Sie nimmt an, dass die Moleküle sich im kautschukartigen oder flüssigen Zustand befinden und berücksichtigt nicht die Effekte chemischer Reaktionen, welche als Folge der Kettenspaltung auftreten können. Die Rechnung zeigt, dass die Verschlingungen entlang der Ketten eine Hauptrolle beim Spaltungsprozess spielen. Ausdrücke für die Geschwindigkeit der Kettenspaltung als Funktion der Schmelzviskosität, der Schergeschwindigkeit und des Molekulargewichts werden erhalten. Auch andere Faktoren treten auf, aber die ausschlaggebenden Variablen sind die angeführten. Die Abhängigkeit der Molekulargewichtsverteilung vom Abbau durch Scherung wird diskutiert. Es wird gezeigt, warum die oxydative Spaltung während der Scherung kein statistischer Prozess ist. Im allgemeinen stimmt das theoretische Ergebnis mit den vorhandenen, spärlichen Versuchsergebnissen überein.