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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Verdu, Jacques(1994) 'Effect of Aging on the Mechanical Properties of Polymeric Materials', Journal of Macromolecular Science, Part A, 31: 10, 1383 — 1398
To link to this Article: DOI: 10.1080/10601329409350099
URL: http://dx.doi.org/10.1080/10601329409350099

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J.M.S.—PURE APPL. CHEM., A31(10), pp. 1383–1398 (1994)

EFFECT OF AGING ON THE MECHANICAL PROPERTIES OF POLYMERIC MATERIALS

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ABSTRACT

Aging can modify polymer structure at the molecular, macromolecular, and/or the morphological level and thus induce changes in the mechanical properties. Stiffness is generally not modified for nonrubbery materials, except for mass transfer (solvent plasticization or plasticizer loss) in amorphous polymers or phase transfer (crystallization or crystal destruction) in semicrystalline polymers. The most significant modulus changes occur in the radiochemical aging of semicrystalline polymers whose amorphous phase is in the rubbery state. Yield properties generally vary in the same way as stiffness. Physical aging at $T < T_g$ can lead to a significant increase in the yield stress. Very general features can be observed for rupture properties, for instance: 1) Only ultimate elongation ϵ is a pertinent variable in kinetic studies of aging involving tensile testing and related methods, 2) the amplitude of ϵ variation for a given degradation conversion is considerably higher for initially ductile materials than for brittle ones, and 3) the rupture envelope $\sigma = f(\epsilon)$, i.e., the ultimate stress, is often very close to the initial tensile curve except for rubbery materials undergoing predominant crosslinking. The mechanisms of ultimate property changes are reviewed. A kinetic approach is proposed for the very important case of heterogeneous, diffusion-controlled aging.

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INTRODUCTION

Parts, extrudates, coatings, etc. made of polymeric materials have a more or less limited lifetime in use. Among the reasons why they fail, mechanical property changes play a very important role. Stiffness changes (for instance, hardening of initially rubbery materials, embrittlement of impact-resistant materials, and visual aspect changes due to superficial cracking) are often observed and justify the existence of an extensive literature on degradation mechanisms. Most of this literature, however, is devoted to chemical aspects, the consequences of structural changes on mechanical properties generally being considered at a purely empirical level when not ignored. The aim of this paper is essentially to show that there are still interesting research problems in this field, relevant to material science rather than to just macromolecular chemistry. A methodology for the prediction of mechanical properties of aged materials in certain cases will be proposed.

Since the pioneering work of Tobolsky [1], use of the theory of rubber elasticity in the study of rubber aging has been generalized from the field of thermal oxidation [1] to photochemical aging [2]. This approach can be now considered classical and will not be presented here. Thus, most of the examples will be taken from the field of thermoplastics and thermosets although aging-induced changes of the ultimate properties of rubbers will also be examined.

This paper will be divided into four sections. In the first one, some basic structure–property relationships will be discussed. The other sections are devoted to the main use of mechanical properties (e.g., stiffness), yield (elastic limit), and ultimate properties (ductility, toughness, fracture, rupture, etc.).

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1. POLYMER STRUCTURE–PROPERTY RELATIONSHIPS: A BRIEF REVIEW

1.1. Structural Scales

Three very important structural scales are used for polymers. Some of their characteristics are presented in Table 1.

1.2. Time–Temperature Maps

Any description of a polymer mechanical property must be referred to a temperature and time scale. In a temperature (T)–time (t) plot it is possible to define at least two boundaries, B and G, separating three distinct domains (Fig. 1). For linear polymers, an additional boundary, L, corresponds to the so-called liquid–liquid transition, e.g., to the end of the rubbery plateau. For semicrystalline polymers, another (vertical) boundary, F, corresponds to the melting point. Boundary B corresponds to the first secondary transition (generally T_β), defined as the temperature at which local skeletal motion begin to occur. In Domain 1, below B, the polymer behaves as a glass (Young's modulus generally larger than 4 GPa), displaying a brittle behavior. Its mechanical properties, such as stiffness, ultimate stress, and toughness, are essentially linked to the cohesive energy density, e.g., the molecular scale structure. Indeed, heterogeneities can affect the fracture properties if their size is above a critical value predictable by linear elastic fracture mechanics.

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TABLE 1. The Three Main Structural Scales in Polymers

Scale	Typical species	Basic physical properties	Typical size	Typical analytical tools
Molecular	Monomer unit	Cohesion chain stiffness	0.1–1 nm	Spectrometry, solvent interactions
Macromolecular	Chain, network cell	Entropy crosslinking entanglement	10–100 nm	Molar mass measure, rubber elasticity
Morphological	Crystal, nodule	Heterogeneity interfaces	10–10^6 nm	Microscopy, thermal analysis

In Domain 2 the polymer also behaves as a glass (modulus higher than 0.1 GPa) but it is considerably more ductile and tough than in Domain 1. For many commodity (PVC) and engineering (polycarbonate) plastics, Boundary B is in the −100 to −30°C range for the usual time scale of quasi-static mechanical loading (for instance, $t > 0.1$ seconds).

Boundary G corresponds to the alpha transition of amorphous polymers, i.e., to the glass transition. It is above 70°C for the precited polymers in the precited conditions. These plastics can thus be used as impact resistant, rigid mechanical parts for most applications at ambient temperature T_a. For other materials (e.g., polystyrene, polymethyl methacrylate, unsaturated polyesters) Boundaries B and G

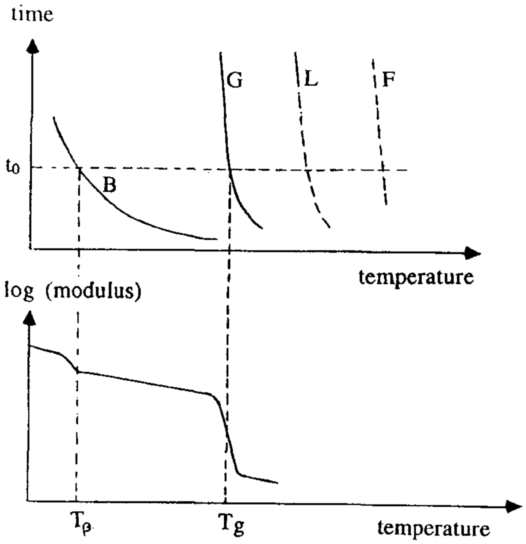

FIG. 1. Top: B and G boundaries in a (T, t) plot. The slope of G is almost vertical. The slope of B is lower. Both curves tend to be tangent at very short times and have a positive concavity. Bottom: Log (modulus) determined at constant time t_0-temperature.

are very close, so these polymer are brittle in the usual temperature region for application (Fig. 2).

It is well known that T_g is an increasing function of cohesive energy density and a decreasing function of chain flexibility. Cohesion appears as the main influence in the case of aliphatic backbone polymers having typically T_g values lower than 100°C. Chain stiffness (sharply linked to the aromatic content) is the dominant influence for high T_g polymers. Empirical or semiempirical T_g predictions are possible [3].

The first secondary transition, T_β, is not directly correlated with T_g. According to Wu [4], the ratio T_β/T_g is a linear decreasing function of the chain static flexibility (linked, for instance, to the persistence length).

1.3. Chain Entanglement and Ductility/Toughness

In the above-defined Domain 2, ductility and toughness are associated with large plastic deformations. As initially proposed for metals [5], the classical Griffith criterion can be written as

$$\sigma = (2(e_s + e_p)E/\pi h)^{1/2}$$

where σ is the stress of crack propagation, E is Young's modulus, h is the half crack length, e_s is the surface energy, and e_p is the work of plastic deformation. For plastics, e_p is usually 10^2 to 10^4 times larger than e_s [6].

Large plastic deformations involve chain uncoiling, which is only possible if the chains participate to a network structure. In linear polymers, physical crosslinks can exist only if the chain length is higher than a critical value whose order of magnitude is always 10 kg/mol^{-1}. In the case of amorphous polymers, physical crosslinking is due only to entanglements. In the case of semicrystalline polymers, plastic yielding requires the presence of tie molecules [7] which can exist only above a certain chain length. In any event, lamellae interconnection seems to be essentially

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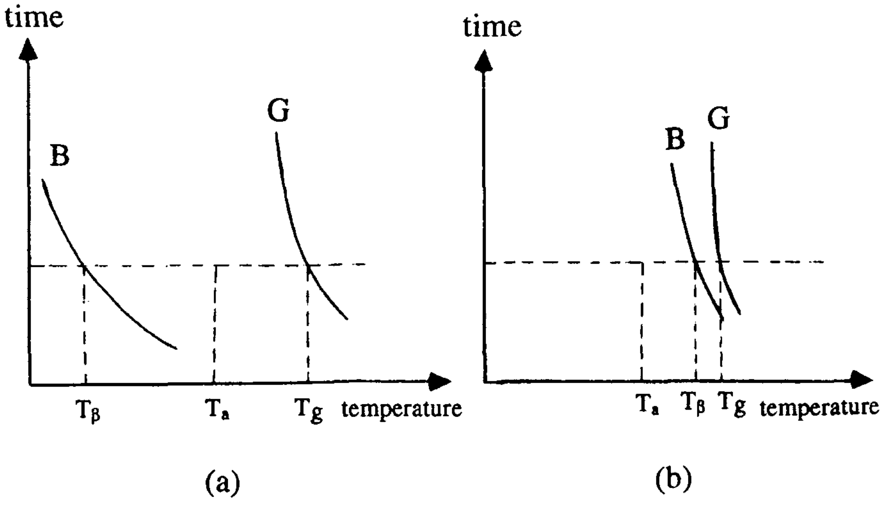

FIG. 2. Time-temperature maps for a ductile (a) and a brittle (b) polymer.

due to chain entanglement in the amorphous phase, as illustrated by the well-known example of the long-term brittle fracture of polyethylene [8]. It thus appears that despite the fact that plastic deformation mechanisms of amorphous and semicrystalline polymers are very different, the structural conditions (at the macromolecular scale) for ductile behavior are practically the same. The effect of entanglements is well illustrated by the variation of the crack propagation energy G_{IC} with the molar mass for glassy polymers [9], Fig. 3.

2. STIFFNESS CHANGES

2.1. Glassy Polymers

Only very small modulus changes are expected to result from aging of glassy polymers. As seen in the preceding section, stiffness is essentially linked to cohesion, and cohesion can undergo significant changes only at high conversions of the degradation process, whatever its mechanism. Generally, rupture properties are so decreased that samples must be handled with caution long before modulus changes are observable. A good example is the case of PMMA radiolysis, where the tensile modulus remains almost constant, or even increases slightly, whereas the molar mass has been divided by more than 10 and the material behaves like an eggshell [10].

Small stiffness changes can be observed if the secondary transitions are affected by degradation, as in the precited example of PMMA radiolysis, where some antiplasticization effect, presumably linked to the split-off of lateral ester groups, has been observed [11].

Indeed, plasticization by solvents or plasticizer loss [12] can modify the elastic behavior, especially in the vicinity of the glass transition. In the case of glassy polymers used in the glassy state far from T_g, these effects are generally low and failure occurs from crazing or cracking [13, 14].

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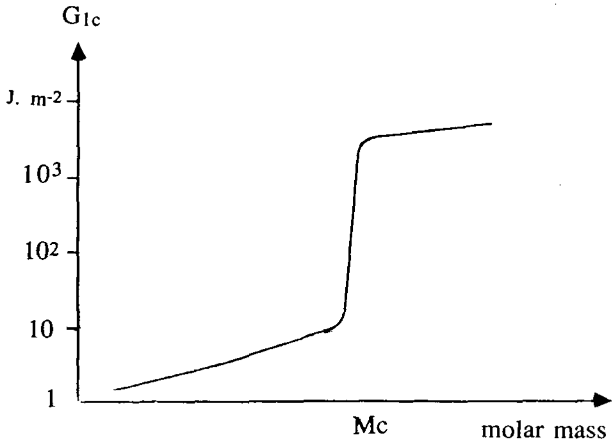

FIG. 3. Shape of crack propagation energy variation with molar mass for linear polymers.

2.2 Semicrystalline Polymers

Only melting, plastic deformation, or radiochemical processes are capable of destroying the crystalline phase of polymers. In this case a simple mixture rule can be written:

$$\begin{aligned} E &= vE_c + (1 - v)E_a \\ &= E_a(1 + v\,\Delta E/E_a) \end{aligned}$$

where $\Delta E = E_c - E_a$. E_c and E_a are the respective moduli of the crystalline and amorphous phases, E is the material's modulus, and v is the volume fraction of the crystalline phase.

Two cases are to be distinguished:

1. The amorphous phase is in the glassy state (for instance, in the case of PET, $T_g = 80°C$, aged at ambient temperature). For most polymers:

$$\Delta E/E_a \approx 1$$

so that the modulus appears to be sensitive only to relatively large changes of the crystallinity ratio.

2. The amorphous phase is in the rubbery state (for instance, in the case of polyethylene, $T_g = -80°C$, aged at ambient temperature). In this case

$$\Delta E/E_a \gg 10$$

so that, practically,

$$E \approx vE_c$$

In polyethylene, for instance,

$$\Delta E/\Delta v \approx 1.8\ \text{GPa}\ [15]$$

For Case 2, small variations of the crystallinity ratio can induce significant modulus changes.

A good example of aging-induced modulus changes is given by polyethylene radiochemical degradation as studied by Charlesby [16]. A plot of polyethylene behavior is presented in Fig. 4. In the early period of exposure, crystal destruction effects predominate and the modulus decreases. After a certain exposure time, however, the polymer is almost completely amorphous and its behavior is governed by radiochemical crosslinking of the polymer, which leads to a modulus increase as predicted by the theory of rubber elasticity.

In the majority of practical cases, however, there are only small modulus changes of generally insignificant consequences for the use properties.

3. YIELD PROPERTY CHANGES

Plastic yielding characteristics obey generally two rules.

1. The yield stress is almost proportional to the modulus. For instance, at ambient temperature, for a wide variety of cases where the samples differ in their monomer structure, their crystallinity ratio, or their orientation, it can be written [17]:

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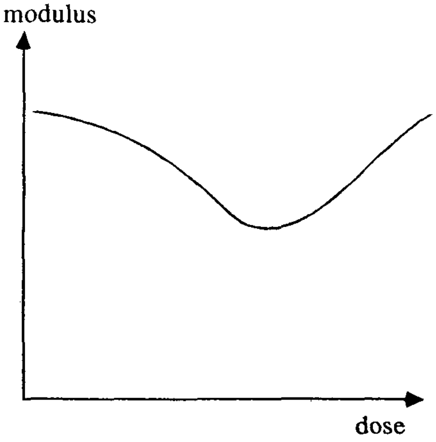

FIG. 4. Shape of modulus variations during the radiochemical degradation of polyethylene.

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$$\sigma_y/E = 0.025 \pm 0.015$$

Thus, in the case of semicrystalline polymers with a rubbery amorphous phase (e.g., polyethylene), crystallinity changes can induce strong changes of the yield stress according to the above relationship.

2. When modulus changes are low, the yield stress remains constant or vanishes when a brittle mechanism of deformation becomes competitive with plastic yielding. This process will be studied in detail in the next section. In the case of glassy polymers, physical aging in Domain 2 of Fig. 1 leads to an increase of the yield stress and a decrease of the creep compliance [18]. For polycarbonate, for instance, aging in the 100–140°C temperature range can lead to an increase of

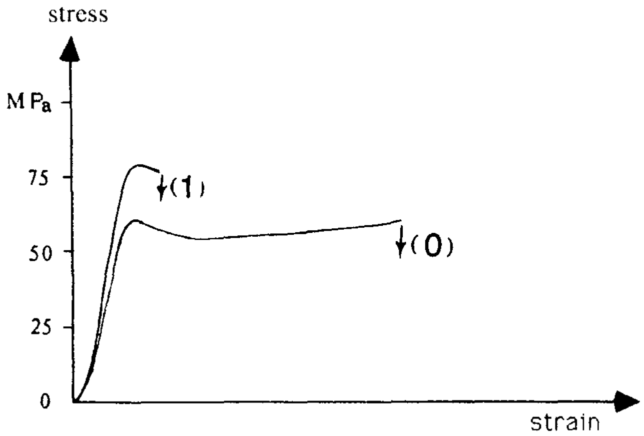

FIG. 5. Plot of the effect of physical aging on the tensile properties of polycarbonate. (0) Virgin sample. (1) Sample aged at 100–140°C.

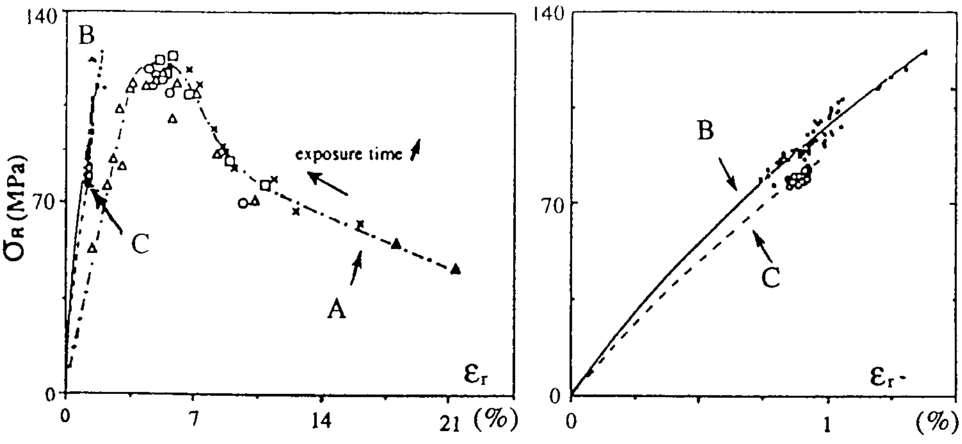

FIG. 6. Rupture envelopes of epoxy Samples A, B, and C (see text) for thermal aging in the 125–200°C temperature range. The symbols correspond to various exposure times and various temperatures.

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σ_y from about 60 MPa to more than 70 MPa whereas the ductility is decreased (Fig. 5).

4. CHANGE OF FRACTURE PROPERTIES

4.1. General Features. Rupture Envelopes

A very interesting approach to aging effects on ultimate properties involves the use of rupture envelopes as first proposed by Smith to study unaged rubbers [19]. Each mechanical measurement after time t of aging gives a data couple: (σ_r, ϵ_r). The method consists of plotting σ_r against ϵ_r. The main tendencies of aging effects on rupture properties are well illustrated by the case of thermal aging of anhydride-cured flexibilized epoxies [20]. In Fig. 6 we have plotted the rupture envelopes corresponding to the thermal aging of three samples:

A: unreinforced matrix, $T_g = 63°C$

B: A + silica floor (60% by weight)

C: A + 50% aluminum trihydrate + 10% silica floor

These results can be summarized as follows.

1. For the initially ductile Sample A, aging leads to a strong decrease of the ultimate elongation and the sample becomes brittle after a certain time which depends on the temperature.
2. For both initially brittle Sample B and C there are considerably smaller changes in the ultimate elongation. A significant decrease is observed, however, in Sample B which displays some viscoelastic behavior at stresses typically higher than 75 MPa. In contrast, for Sample C, which displays practically no viscoelastic behavior in the unaged state, no significant change of rupture properties was observed during the entire exposure time (more than 4000 hours).

3. In all cases the rupture envelope is very close to the initial stress–deformation curve.

These results can be widely generalized to all cases of nonrubbery materials in which aging does not involve important mass (plasticizer loss, solvent absorption) or phase (crystallization, crystal destruction, vitification) transfer. Examples can be cited as well for thermal aging of thermosets (see above), for hydrolysis of unsaturated polyesters [21], and for photooxidation of many semicrystalline or amorphous liner polymers [10].

4.2. Case of Initially Brittle Materials

As noted above, the tensile ultimate coordinates (σ_r, ϵ_r) decrease slowly during the aging of such initially brittle polymers as polystyrene and styrene crosslinked polyesters. It is generally observed that the secant modulus E_r at rupture ($E_r = \sigma_r/\epsilon_r$) increases slowly and tends asymptotically toward the tangent modulus E_0.

Aging leads to the formation of defects in most cases (for instance, oxidized skin, osmotic cracks [21, 22] in hydrolytically aged polymers, etc.).

For a surface defect of depth h in a sample with dimensions much greater than h, the Griffith equation [23] can be applied:

$$\sigma = (2Ee/\pi h)^{1/2}$$

where E is the modulus and e is the surface energy. A value of the critical defect size can be derived from this relationship. It is noteworthy that $\sigma^2/2E$ is of the order of magnitude of 0.1–0.5 $\mathrm{MJ \cdot m^{-3}}$ for most polymers.

A reason for the formation of "spontaneous cracks" at the surfaces of linear polymers can be found in Fig. 3. When the chain length becomes lower than the entanglement limit, the sample becomes so brittle that small differential dilations due to temperature fluctuations or density gradients due to heterogeneous degradation can be sufficient to initiate cracking.

Similar mechanisms probably also exist for networks. It is noteworthy that despite the fact that degradation (chain scission) leads to an increase in the molar mass M_c of elastically active segments, and that toughness is usually an increasing function of M_c [24], degradation always leads to a decrease of the ultimate properties.

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4.3. Case of Initially Ductile Polymers

4.3.1. Phenomenological Aspects

There is an impressive quantity of published data on the aging-induced changes of the ultimate properties of ductile polymers. Despite that, some important mechanisms have been elucidated only in recent years, and this research field still remains largely open. The rules cited in Section 4.1 are valid in most the cases, at least when aging results from random chain scission. In the case of semicrystalline polymers having a rubbery amorphous phase capable to undergo competitive chain scission and crosslinking (the case of polyethylene and radiochemical aging), the predominant process can be recognized from rupture envelopes [25], Fig. 7.

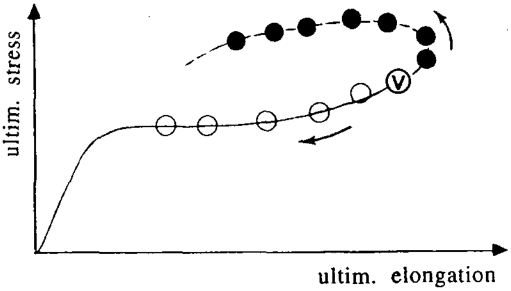

FIG. 7. Schematic of rupture envelopes for predominant chain scission (open symbols) and predominant crosslinking (closed symbols). v is the virgin sample. The full line represents the initial tensile curve.

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The case of predominant crosslinking is relatively scarce compared to chain scission which practically always predominates in oxidative or hydrolytic processes.

From the point of view of kinetics, all these processes have in common the features illustrated by Fig. 8. The ultimate elongation decreases continuously, but the slope $d\epsilon_r/dN$ decreases strongly when ϵ_r reaches the vicinity of the initial elongation at yield ϵ_y. The latter remains constant until the yield vanishes when the sample becomes brittle. Modulus E remains practically constant (except for small changes due to morphological changes or to mass transfer). This latter characteristic is somewhat surprising for those accustomed to monitor damage by modulus/compliance changes.

Because the rupture envelope corresponds to the initial tensile curve, changes of the ultimate stress depend of the initial (σ, ϵ) behavior. In the case of Fig. 6 (epoxy), the stress first increases rapidly and then decreases slowly. For the case of tensile curves displaying a final hardening process, the ultimate stress changes are as

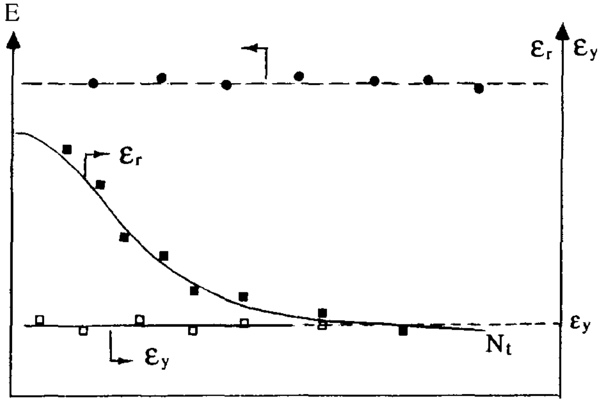

FIG. 8. Modulus (E), ultimate elongation (ϵ_r), and elongation at yield (ϵ_y) against number of chain scissions per mass unit. $N_t = (M_{nt})^{-1} - (M_{n0})^{-1}$.

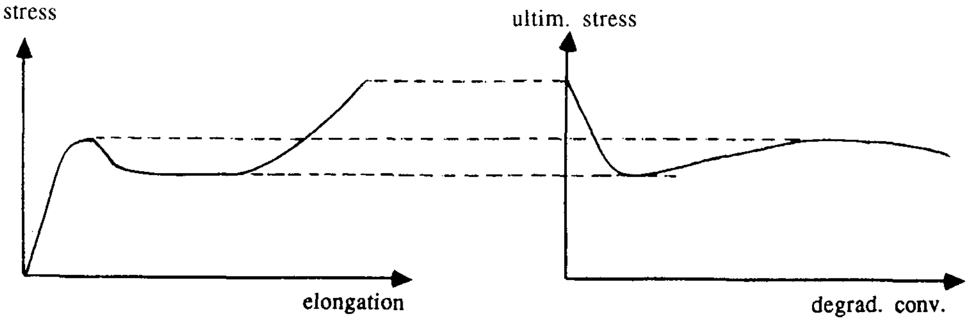

FIG. 9. Tensile curve displaying orientation hardening and corresponding ultimate stress change against degradation conversion.

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shown by Fig. 9. A good example of such behavior is given by the photooxidation of polyolefins [10] or by the thermal aging of engineering plastics [28].

The general trends of aging-induced variations of ultimate properties call for the following comments:

1. Only ultimate elongation appears as a pertinent variable for characterizing aging from classical tensile testing because it varies monotonically. Note: For obvious reasons the work at rupture, $w = \int \sigma \, d\epsilon$, could also be used.
2. If x is the conversion of the degradation process, the slope of $d\epsilon_r/dx$ is considerably higher in the plastic domain ($\epsilon_r > \epsilon_y$) than in the viscoelastic domain ($\epsilon_r < \epsilon_y$) as a consequence of structure–property relationships.
3. In both domains there are no simple relationships between x and ϵ_r, so it would be incorrect to treat ϵ_r as a chemical variable in models of lifetime prediction. In fact, the change of ϵ_r can be described as a ductile–brittle transition spread out over the aging time.
4. The most reasonable approach to lifetime prediction consists of supposing that the ductile–brittle transition occurs when a given structural variable reaches a critical value, the corresponding time being predictable in principle, from chemical kinetics (see below). Classical, arbitrarily chosen end of life criteria (for instance, the half value of the initial ultimate stress), are not useful, as demonstrated in the case of thermal aging [20–26].

It remains to establish kinetic models to predict the time at the ductile–brittle transition. Two cases have to be distinguished: The case where the degradation chemical events are homogeneously distributed into the whole sample volume, and the case where their spatial distribution displays heterogeneities above a certain critical size, e.g., capable of initiating cracks under mechanical loading.

4.3.2. The Case of Homogeneous Degradation

In principle, a degraded polymer is physically equivalent to a virgin polymer with the same molecular mass distribution, so the structure–property relationships established for nondegraded polymers are applicable to lifetime modeling. This is true in the case of polymers degraded in solution or in the molten state. In contrast, this is questionable for polymers degraded in solid state where chemical processes can affect certain nonequilibrium properties such as the conformational order [11]. In the case of semicrystalline polymers aged at temperatures above the glass transition, chemicrystallization induced by chain scission in the amorphous phase (e.g., PET hydrolysis [27]) can also complicate lifetime modeling.

For the simplest case of random chain scission, where all these secondary processes are negligible, Fig. 3 provides a good approach of lifetime modeling since it allows a critical molar mass M_c corresponding to the ductile–brittle transition to be determined.

Chemical kinetics study gives

$$N_t = (M_{nt})^{-1} - (M_{n0})^{-1} = f(t)$$

thus:

$$t = f^{-1}(N_t)$$

where f^{-1} is the reciprocal function of f. The lifetime t can then be defined by

$$t_c = f^{-1}(N_c)$$

where

$$N_c = (M_c)^{-1} - (M_{n0})^{-1}$$

In the absence of the above cited complications, N_c is independent of exposure conditions and we dispose of a nonempirical method of lifetime prediction. Polycarbonate hydrolysis [28] is a good example of the usefulness of this approach.

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4.3.3. Case of Heterogeneous Degradation

a) *Heterogeneities at the Morphological Scale.* It is well known that molecular reactants such as oxygen or water cannot penetrate the crystalline phase, so that the degradation of semicrystalline polymers is generally restricted to the amorphous phase. The crucial role of this in mechanical behavior was reported in Section 1.3. The consequences of the destruction of entanglement network segments and tie molecules on polymer embrittlement are well understood at the qualitative level, but quantitative relationships are generally lacking. The problem is often complicated by the existence of two morphological structural scales: individual lamellae and spherulites, with the corresponding (distinct) brittle failure mechanisms [29] and probably distinct chemical reactivities due to differences in molecular mobility between the intra- (interlamellar) and interspherulitic amorphous phase [30]. The determination of nonempirical structural criteria for the oxidation-induced embrittlement of polypropylene, for example, remains a challenge.

For semicrystalline polymers of the polyethylene type which display a long-term brittle fracture mechanism [8], a new boundary appears in the time–temperature map (Fig. 10). Insufficient attention has been paid to its aging-induced changes. As a matter of fact, it is expected to be highly sensitive to chain scission in the amorphous phase.

Similar observations can be made in the case of polymer alloys in which aging selectively destroys one phase. The oxidation of styrene–butadiene blends or block copolymers is a well-known example: polybutadiene is completely oxidized far be-

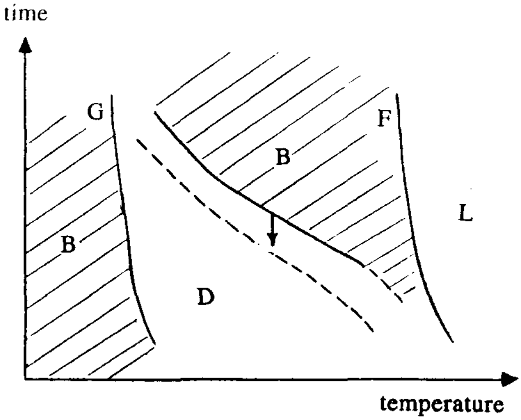

FIG. 10. Time-temperature (t, T) map for a semicrystalline polymer of the PE type. L: liquid state, B: brittle domain, D: ductile domain. Arrow: Presumed effect of aging on the B-D boundary.

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fore the thermoplastic phase has undergone significant changes. Here, impact strength is generally a convenient variable to monitor aging (Fig. 11), but kinetic modeling appears very difficult.

b) Heterogeneities at the Macroscopic Scale. The most important case of macroscopic heterogeneity is where diffusion-controlled degradation kinetics lead to a core-shell structure. This case has been recently reviewed [31] and illustrated by the thermal oxidation of crosslinked PE [32]. Some important points can be summarized as follows.

(1) The thickness of the degraded layer (TDL) can be estimated in all cases by

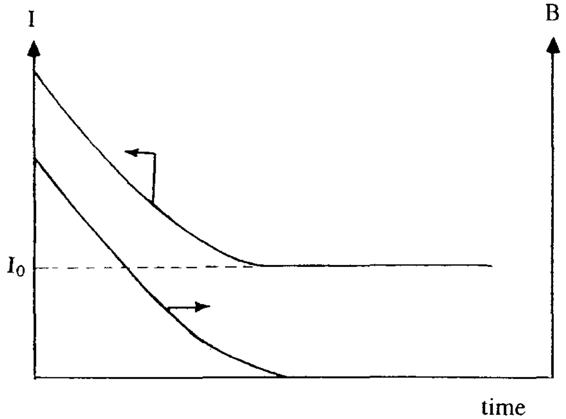

FIG. 11. Schematic of the time variations of the impact strength (I) and butadiene double bond concentration (B) during oxidative aging of a styrene-butadiene alloy. I_0 corresponds to the typical impact strength of unreinforced PS homopolymer.

$$\mathrm{TDL} = (D/k)^{1/2}$$

where D is the reactant diffusion coefficient of the polymer and k is a pseudofirst-order rate constant of reactant consumption defined by $k = r/C$ where r is the reactant consumption rate in the surface layer and C is the reactant equilibrium concentration in the polymer. Thus, schematically, if TDL $> L/2$ (where L is the sample thickness) the degradation can be considered homogeneous (not diffusion controlled). If, in contrast, TDL $< L/2$, there is a nondegraded core zone of thickness $L - 2\mathrm{TDL}$.

(2) Influence of TDL on fracture behavior. After the pioneering work of Rolland et al. [33] and Schoolenberg [34], fracture mechanics appears to be a fruitful approach to predict the failure of heterogeneously degraded polymers. Schematically, a degraded layer can "sensitize" the whole sample to fracture if its size is larger than a critical value which depends on the material toughness for the testing conditions under study. The key variable is the crack propagation rate, $(\mathrm{CPR})_i$, at the degraded-nondegraded interface. If $(\mathrm{CPR})_i$ is higher than a limit which is a property of a material, the crack continues to propagate through the sound core and sample rupture is observed. In contrast, if $(\mathrm{CPR})_i$ is lower than this limit, the crack blunts and there is no sample rupture. Indeed, $(\mathrm{CPR})_i$ depends, among other variables, on TDL since, in a classical tensile test, the crack propagation rate increases as fast as it propagates. The existence of such a threshold is easy to establish in the case of radiation aging at constant temperature. As a matter of fact, in these conditions the diffusivity D, which depends only on temperature to a first approximation, remains constant whereas the rate constant k is an increasing function of the radiation intensity I.

If, for instance, this dependence is represented by a power law:

$$k = aI^{\alpha}$$

where a and α are positive constants, then

$$\mathrm{TDL} = bI^{-\alpha/2}$$

(b = constant). TDL is thus a monotonic decreasing function of radiation intensity, as experimentally observed. If we thus define an end of life criterion, f [for instance, ultimate elongation after irradiation at constant dose (energy)], its variation with I will be as shown in Fig. 12. In this figure, f_∞ is the value characteristic of the undegraded sample. For a very large value of I (e.g., of k), the degraded layer is too thin to have a significant influence on mechanical properties. This situation is well illustrated by the case of plasma-treated samples where the superficial layer is so degraded that it is converted into a wax but all the mechanical properties remain practically unchanged. Radiation crosslinking of bulk samples is possible in air thanks to very high radiation intensities leading to very thin oxidized zones.

For very low values of I, degradation is nondiffusion controlled, e.g., homogeneous, and sample embrittlement is governed by structural changes at the morphological and macromolecular structural levels. Indeed, a transition is observed for medium values of I around I_c, the intensity for which the crack propagation rate reaches its critical value at the degraded-nondegraded interface.

(3) Consequences. These results are encouraging because they open a way to nonempirical methods of lifetime prediction. Examples of methodological advances

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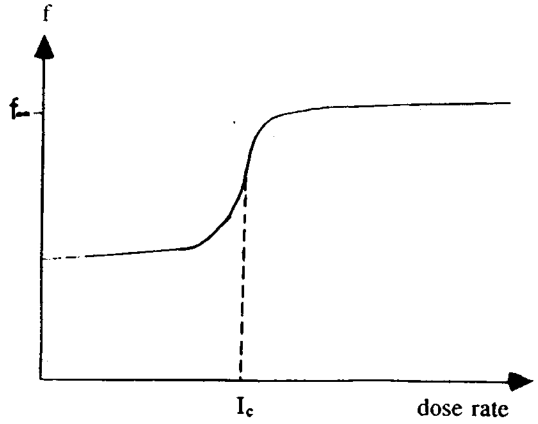

FIG. 12. Shape of the change of fracture properties at constant dose with radiation intensity.

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in this field are to be published shortly [35]. On the other hand, they reveal that in most cases of accelerated aging, as a result of the relationship

$$\mathrm{TDL} = (D/k)^{1/2}$$

it is impossible, or at least difficult, to obtain the same degraded state as in natural aging. As a matter of fact, the case where D varies in the same way as k with exposure conditions can only result by coincidence.

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