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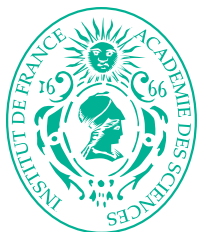
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Contributions in mechanics of materials

Physico-chemical approach of polymer chemical ageing: a short review

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Abstract. Polymers are known to degrade in their use conditions, with the risk that their properties reach unacceptable level. This paper reviews the modeling of modifications occurring at molecular and architectural changes occurring during their chemical ageing, with the aim of predicting the physical (mechanical) properties, all values being linked by structure properties relationships.

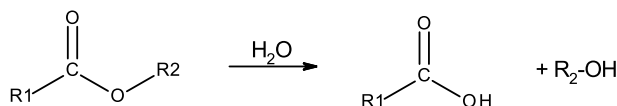
Keywords. Polymers, Ageing, Modeling, Oxidation, Hydrolysis, Kinetics.

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1. Introduction

Polymers and composites become increasingly used because weight and costs saving but also improved specific mechanical properties such as ratio of stiffness or failure stress over density or fatigue resistance. For many industrial applications, long lasting properties are needed which arises the issue of interaction between polymer and its environment. One can usually distinguish

- physical ageing where the polymer skeleton remains unchanged but the distance between polymer chains is modified for example in case of water diffusion in an epoxy-diamine thermoset networks [1, 2], or physical ageing by structural relaxation for glassy polymers aged under their glass transition temperature [3]. Diffusion of penetrants generally induces a decrease in glass transition and stiffness [1, 4, 5], contrarily to structural relaxation inducing an increase in yield stress for example [6, 7]. Physical ageing is in principle reversible [8]. In the case of water ageing, the amount of desorbed water after complete drying must correspond to amount of absorbed one during immersion (apart if penetrant reacts which is a case of chemical ageing described here below [9]).
- chemical aging where polymer slowly reacts with chemicals (water, oxygen...) under the action of UV light, temperature, or gamma rays [10–12]. Chemical changes are usually irreversible.



Scheme 1. Hydrolysis of an ester group.

In many cases, designers try to address the lifetime prediction issues by using very simple laws (one the best examples is the use of Arrhenius law for lifetime value [13]) but those later however fail because of the complexity of physico-chemical phenomena [14]. That is the reason why non empirical approach is needed and involves a multiscale modeling of degradation phenomena [15], the aim of which is:

- to predict the rate of degradation at molecular scale giving the rate of structural changes
- to use structure properties relationships for predicting the consequences of any given change at molecular scale.

The combination of both approaches allows predicting the time at which engineering properties are out of the range of required properties, in other words the lifetime of polymer.

2. Ageing study at molecular scale

Water permeation can induce a decrease in thermomechanical properties (glass transition, elastic modulus...) due to plasticization. However, the main damage induced by water is observed in case where water slowly reacts with specific groups in polymer (esters, amides...) generating chain scissions (Scheme 1) as observed for example in polyesters (PLA, PET) [16] or polyamides [17, 18].

For this last mechanism, a simple equation can be implemented for describing the changes of ester groups (in concentration $[e]$) belonging to polymer chain and the appearance of chain scissions:

$$\frac{d[e]}{dt} = -k_u[w][e]. \quad (1)$$

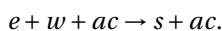
This means that there case where water is poorly soluble in polymer but reacts by hydrolysis (as for example PBT where the maximal water uptake is about 1%) but the damage is higher than in some case where water is more soluble but does not react with polymer (as for example the DGEBA-DDS epoxy thermoset).

The general mechanism for hydrolysis is the following but several subcases can be distinguished

- reversible hydrolysis, for example in PA11 [17]
- water diffusion controlled hydrolysis [19]
- auto-accelerated hydrolysis, either because hydrolysis induced groups induce an increase in hydrophily [18, 20]

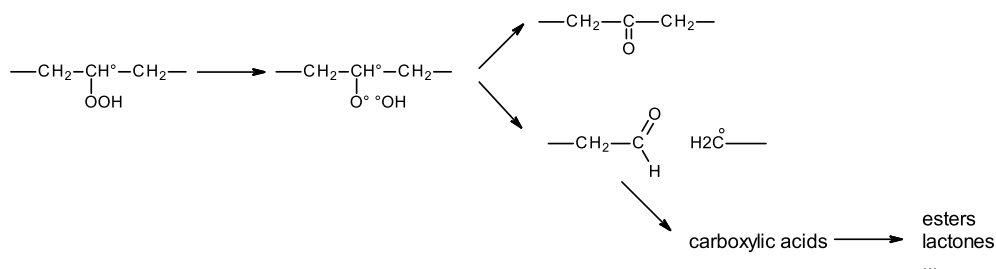
$$[w] = [w]_0 + \text{a.s.} \quad (2)$$

Or because carboxylic acids usually catalyze further hydrolysis reactions. In this case, a secondary equation must be added [21]:



The rate expression becomes:

$$\frac{d[e]}{dt} = -k_u[w][e] - k_c[w][e][ac] \quad (3)$$



Scheme 2. Radical oxidation of polyethylene.

i.e., since each ester is transformed into an acid by hydrolysis:

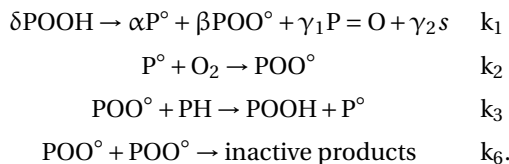
$$\frac{d[e]}{dt} = -k_u[w][e] - k_c[w][e]([e]_0 - [e]) \quad (4)$$

and the following expression of the ester concentration is obtained:

$$[e] = [e]_0 \frac{(1 + A) \exp -Kt}{1 + A \exp -Kt} \quad \text{with } K = k_c[e]_f[w] \quad \text{and: } A = \frac{k_c[e]_0}{k_u}. \quad (5)$$

In the case of thermal oxidation, there are other mechanisms responsible for chemical changes, as illustrated in Scheme 2 for the radical oxidation of polyethylene [22].

Basing on the Autooxidation Scheme established by Bolland and Gee [23], the study of the oxidation of aliphatic substrates lead to the following mechanistic scheme [24, 25]:



In the frame of radical kinetics, this mechanistic scheme leads to a differential system. This latter can be analytically solved in some simple case (using some simplifying hypothesis) or numerically solved. The outputs of the model are the concentration in reactive species ($[\text{P}^\bullet]$, $[\text{POO}^\bullet]$, $[\text{POOH}]$) and of stable products (carbonyls, chain scissions...):

$$\frac{d[\text{P}=\text{O}]}{dt} = \gamma_1 k_1 [\text{POOH}]^\delta \quad (6)$$

$$\frac{ds}{dt} = \gamma_2 k_1 [\text{POOH}]^\delta. \quad (7)$$

In most cases, the derived kinetic models are more complex (in order to take into account the occurrence of other termination processes [26], reaction of double bonds [27, 28], presence of stabilizers [29], reaction-diffusion coupling of oxygen [30]...). The finality remains the same: predict the concentration in trackers of chemical ageing (and chemical changes) versus time. Rate constants are usually determined in accelerated conditions (i.e. at enhanced temperatures) and later extrapolated to temperatures corresponding to use conditions using the well-known Arrhenius equation:

$$k_i(T) = k_{i0} \cdot \exp\left(-\frac{E_i}{RT}\right). \quad (8)$$

The validation of such kinetic models by comparing outputs with for example experimental observations by FTIR remains quite tricky for example:

- in a case of hydrolysis, esters are consumed to give carboxylic acids but the signal of both group overlap.

- in the case of radical oxidation of hydrocarbon polymers, a broad band appears with several maximal or shoulders (for example 1713 cm^{-1} for carboxylic acids, 1720 cm^{-1} for ketones, 1735 cm^{-1} for esters, 1780 cm^{-1} for lactones in polyethylene [31]). At first, it is not trivial to find out the mechanism of formation for some of those species (for example lactones, or esters). Moreover, some species are accompanied by a chain scission (carboxylic acid) and some other not (ketones) so that the assessment of the macromolecular damage from FTIR spectra requires to perform a reliable deconvolution and the knowledge of the molar absorptivity of each species.

In other words, approach can be flawed due to the complexity of the polymer. It is thus needed to study the effect of degradation on polymer architecture so as to predict its effect on mechanical properties.

3. Study of degradation at macromolecular scale

In a second step, the damage of polymer must be studied at macromolecular scale in order to implement structure properties involved in polymer ageing. For that purpose, experimental approaches are needed to assess the concentration in structural changes, i.e. chain scissions and/or crosslinks.

In thermoplastic polymers, the predominance of chain scissions or crosslink can be quite easily estimated from the changes in molar mass. Those latter can be measured:

- from rheometric measurements at molten state, where the Newtonian viscosity is linked to molar mass by the formula [32]:

$$\eta = k \cdot M_w^{3.4}. \quad (9)$$

There are several papers illustrating the predominance of chain scissions for example in linear polymers such as polyolefins [33], and the predominance of crosslinking in unsaturated (uncured) elastomers such as Ethylene Propylene Diene Monomer (in link with the presence of carbon carbon double bonds) [34].

- from liquid chromatography, this latter allowing to estimate both number and weight average molar mass. Using some statistical analysis proposed by Saito, the concentration in chain scission and in crosslink can be simultaneously estimated by [35]:

$$\frac{1}{M_N} - \frac{1}{M_{N0}} = s - x \quad (10)$$

$$\frac{1}{M_W} - \frac{1}{M_{W0}} = \frac{s}{2} - 2x \quad (11)$$

where s and x are respectively the concentration in chain scissions and in crosslinking.

Elastomers and thermoset networks are in essence insoluble and cannot be molten, which prevents the use of the here above experimental techniques. The “key” parameter is the concentration elastically active chains (linked to 2 crosslink nodes), which must increase in case of predominant crosslinking. Experimentally, the concentration in chain scission can be assessed

- from the residual soluble fraction (sol) using the Charlesby approach [36,37]:

$$\frac{\nu}{\nu_0} = \left(\frac{1 - \text{sol}^{1/2}}{1 - \text{sol}_0^{1/2}} \right)^2 \quad (12)$$

- or the glass transition value (T_g) [38]:

$$T_g = \frac{T_{gl}}{1 - K_{DM} \cdot F \cdot x}. \quad (13)$$

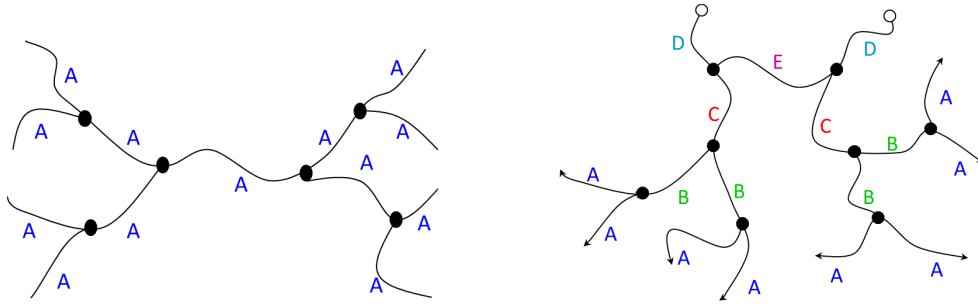


Figure 1. Schematization of an undegraded ideal networks (all chains are elastically active and denoted by A) and of an degraded networks. NB: arrows indicate that chain are linked to other chains belong to network whereas open circle correspond to the end of a dangling chain.

The concentration in chain scissions can thus be estimated from the decrease in elastically active chains. In a simplified approach, one can assume that for a tridimensional network [39]:

$$n = n_0 - 3s + 2x \text{ (if chain scission and crosslinking coexist)} \quad (14)$$

$$\text{or } n = n_0 - 3s \text{ (if they are only chain scissions).} \quad (15)$$

In this last case, some simplified relationships can be derived [36]

$$s = \frac{v_0}{3} \left(1 - \left(\frac{1 - \text{sol}^{1/2}}{1 - \text{sol}_0^{1/2}} \right)^2 \right) \quad (16)$$

$$s = \frac{T_{gl}}{2K_{DMF}} \cdot \left(\frac{1}{T_g} - \frac{1}{T_{g0}} \right). \quad (17)$$

However, Equations (14)–(15) are a simple approximation which is valid only at low conversion degree. For summarizing, it is clear that one chain scission induces the loss of three elastically active chains (denoted by A in Figure 1) in an unaged network. Reversely, at higher conversion degree of the chain scission process, networks look like depicted in Figure 1b. One can thus imagine that a chain scission can occur on a chain denoted by B, C or E (dangling chain with a limited consequence on elastic properties), or on a dangling chain (denoted by D) which is linked by one single node to the rest of network, and becomes soluble.

A most refined approach was proposed by Gilormini *et al.* [21]. Network is here composed of a (elastically active chains connected to two nodes connected themselves with elastically active chains), b (elastically active chains connected to one node connected with elastically active chains and another node connected with dangling chains).

In this approach, the concentration of reactive groups held by “a chains” and “b chains” changes with the concentration of chain scissions occurring on each kind of chain (s_A , s_B) as follows:

$$\frac{d[a]}{dt} = -5L \frac{ds_A}{dt} - 4L \frac{ds_B}{dt} \quad (18)$$

$$\frac{d[b]}{dt} = 4L \frac{ds_A}{dt} + 2L \frac{ds_B}{dt}. \quad (19)$$

The concentration in chain scissions can be predicted as follows

$$s = s_A + s_B \quad (20)$$

$$\frac{ds_A}{dt} = \frac{[a]}{[e]} \frac{ds}{dt} \quad \text{and} \quad \frac{ds_B}{dt} = \frac{[b]}{[e]} \frac{ds}{dt} \quad (21)$$

and

$$\frac{1}{[e]} \frac{ds}{dt} = \frac{K}{1 + A \exp(-Kt)}. \quad (22)$$

The solution of the differential system gives:

$$\frac{[a]}{[e]_0} = \left[\cos\left(\frac{\sqrt{15} \cdot KLu}{2}\right) - \frac{7}{\sqrt{15}} \sin\left(\frac{\sqrt{15} \cdot KLu}{2}\right) \right] \cdot \exp\left(-\frac{3}{2} \cdot KLu\right) \quad (23)$$

$$\frac{[b]}{[e]_0} = \frac{8}{\sqrt{15}} \sin\left(\frac{\sqrt{15} \cdot KLu}{2}\right) \cdot \exp\left(-\frac{3}{2} \cdot KLu\right) \quad (24)$$

with

$$u = -\frac{1}{K} \ln(1 - x). \quad (25)$$

Those equation lead to a fair prediction of decrease in elastically active chain concentrations which is sufficient for several industrial applications (Figure 2).

It remains interesting to focus on the prediction of degel, i.e. the critical stage at which chain scissions have cleared out all the elastically active chains and the network reverts back to a soluble material (with the possibility to regenerate chemicals and repolymerize them later). An original approach for predicting the degelation was developed by Gilormini *et al.* [40]: in the simplest version of this approach, a chain contains L reactive groups likely to undergo a chain scission process.

The probability of any chain to be uncut is given by:

$$u(x) = (1 - x)^L. \quad (26)$$

Let us focus now on the possibility for a node to belong to the gel or to belong to the soluble fraction of network (i.e. to be a free chain). The Figure 3 summarizes three possibilities:

- either the node is attached to 2 soluble chains, or at least 1 or 2 chains are attached to the network (with a probability $g(x)$). It gives the probability of the node to belong to the soluble fraction:

$$P(x) = [1 - g(x)]^2. \quad (27)$$

So that the probability for node#2 to belong to the gel:

$$P(x) = 1 - [1 - g(x)]^2 \quad \text{if } f = 3 \quad (28)$$

or:

$$P(x) = 1 - [1 - g(x)]^{f-1} \quad \text{for any } f. \quad (29)$$

It gives the probability for a chain to be uncut and belong to the gel:

$$g(x) = u(x) \cdot [1 - (1 - g(x))^{f-1}] \quad (30)$$

so that, at degel:

$$x_d = 1 - \frac{1}{(f-1)^{1/L}}. \quad (31)$$

This approach was for example successfully validated in the case of methyl methacrylate-ethylene glycol di methacrylate radiolysis [41]. It is clear that it will be helpful in a close future given the increasing need to recycle by mechanical or chemical processes thermosets and rubbery networks.

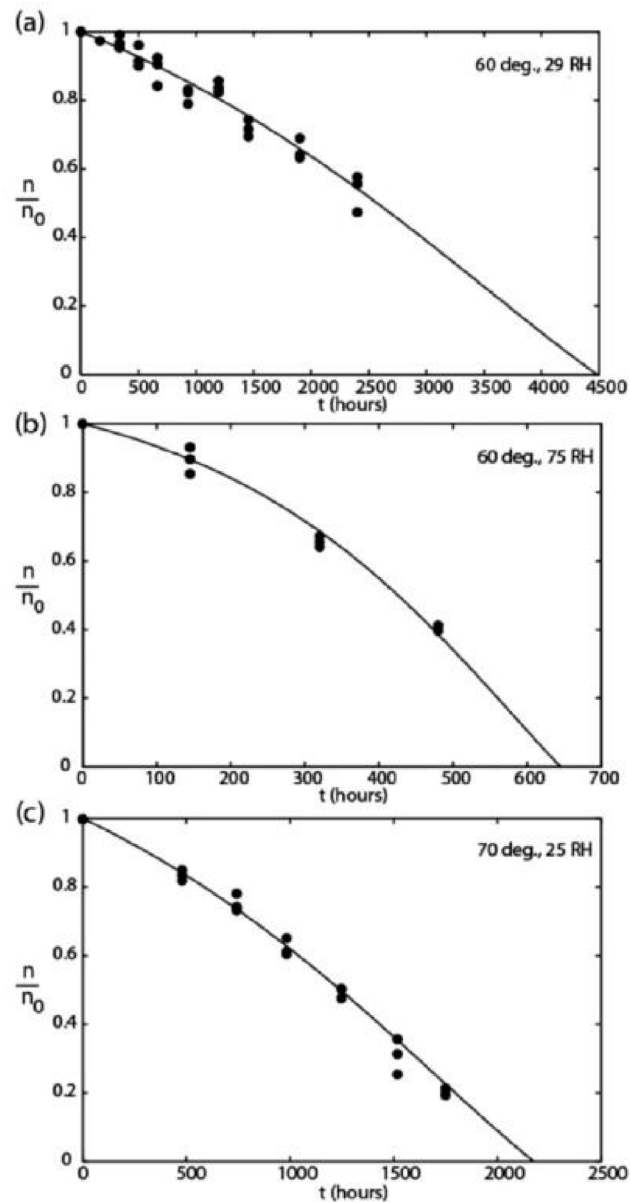


Figure 2. Decrease in elastically active chains concentration of a polyester urethane rubbery network for several ageing conditions.

4. Structure-properties involved in the prediction of ageing induced failure

According to previous parts, it seems possible to predict the appearance of chain scissions or crosslink nodes in either thermoplastics or networks, and subsequently the changes in average molar mass (for thermoplastics) or crosslink density (for networks). It remains to establish the effect of such changes on the mechanical properties of polymers.

In the field of thermoplastic polymers undergoing mainly chain scissions, the main effect is the plasticity loss. A first end of life criteria was established basing on the observation that plastic

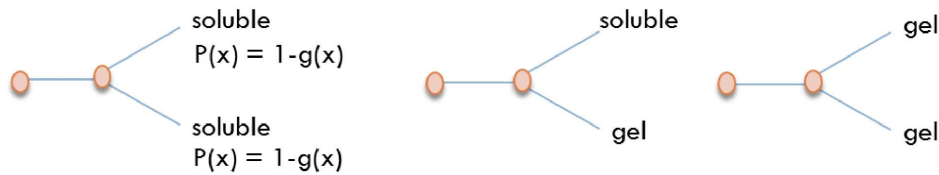


Figure 3. Schematization of network degradation.

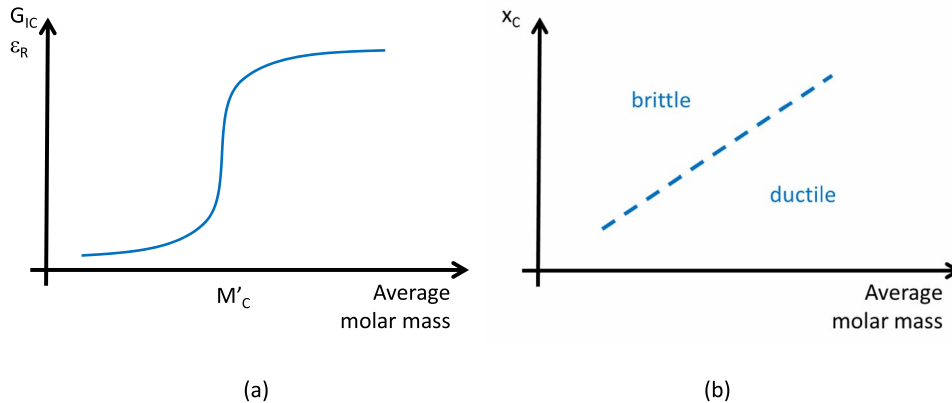


Figure 4. Schematization of embrittlement criterion for thermoplastic polymers.

deformation was possible only when residual average molar mass was higher than a “critical value” (denoted by M'_C) as depicted in Figure 4a. This latter was carefully discussed [42] in the past and it was observed that:

- in amorphous thermoplastics (PMMA, PC, PS...), its value was slightly higher than the molar mass between entanglements, indicating that failure occurs when the polymer is severely damaged.
- in semi-crystalline polymers (in particular with amorphous phase in rubbery state), the ratio of “critical” molar mass to the molar mass between entanglement clearly exceeds 1, meaning that only a few chain scissions strongly reduce the plasticity. This pointed out the “morphological” origin of embrittlement. The following scenario was evidenced: chain scissions liberate “small” segments in amorphous phase and those latter join the crystalline phase which is, in essence, less deformable. This led to a “mixed” end of life criterion expressed in an “average molar mass–crystalline ratio” window (Figure 4b): polymers made with longer chains and poorly crystalline are ductile whereas polymers made of short chains with a high crystalline ratio are brittle.

In rubbery networks, one of the key properties is the changes in elastic modulus. Based on the fact that elasticity has an entropic origin in rubbery networks, it is established for years that elastic modulus depends on the concentration in elastically active chains i.e. [43]:

$$G = n_A \cdot RT \quad (32)$$

with

$$E = 3 \cdot G. \quad (33)$$

The failure of networks can be described by the critical strain energy release rate in mode I (G_{IC}). This later is shown to vary as follows in network:

- at first, G_{IC} can increase with the crosslinking concentration because crosslinking positively influences the elastic modulus,
- in the same time, crosslinking decreases the maximal chain extensibility.

It results in curves displaying a maximum as depicted in [44].

In thermosets, there are also data highlighting the relationship between crosslink density and toughness [45]. However, it was recently proposed that for networks with a sub-glassy relaxation such as epoxies, the end of life is governed by the depletion of groups responsible for this low temperature mobility [46].

5. Conclusions

This short paper summarizes the mathematical description of multiscale changes induced by the “chemical” ageing, i.e. the effect of the reactions of chemicals (oxygen, water) with polymer. Kinetic approaches can allow a fine prediction of the rate of chemical changes at “molecular scale”. The use of statistical theories allows thus to address the changes at macromolecular scale, even up to advanced degradation levels (such as the degelation). Last, the use of well-known structure properties relationships established for virgin polymers, together with the prediction of changes in macromolecular architecture with chains scissions or crosslinking allow predicting the changes in some physical properties and later offer to engineers a complete physico-chemical toolbox for addressing polymer lifetime issues by a non-empirical approach.

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