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Ageing of Filled Polymers

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Abstract: It is tried to examine briefly all the aspects of filler interactions with polymer ageing, including direct chemical (catalysis of degradation, stabilising effects) and physical (screen and thermooptical effects, modification of transport properties) interactions as well as indirect ones such as stabiliser trapping, influence on the rate of mechanical properties change or interfacial phenomena.

Key words : POLYMER, FILLER, AGEING

INTRODUCTION

There is an extensive literature on mineral fillers effects on polymer ageing, showing that there is no general trend of influence. Certain fillers, such as carbon black can be efficient stabilisers in the context of oxidative ageing but can appear as ageing « activators » in other contexts, for instance plasticizer loss under exposure to filtered or unfiltered solar radiation. Other fillers such as certain titanium dioxide grades, exert a stabilising effect through a strong screen effect but accelerate the photooxidation in superficial layers as a result of their well known photocatalytic action. This latter, however, can be positive in certain cases (PVC) where oxidation can contribute to the destruction of chromophoric species (polyenes) responsible for discoloration.

It appears thus that fillers can influence ageing through many, sometimes contradictory, ways. It seemed to us interesting to review briefly the main filler-ageing interaction basic mechanisms, emphasis being put on oxidative ageing. The following mechanisms were distinguished. Direct chemical and physical interactions of filler with the ageing process ; interactions between fillers and stabilisers (synergism, antagonism) ; indirect interactions through filler effect on morphology or mechanical behaviour, and interfacial processes.

1 DIRECT CHEMICAL INTERACTION

1-1 INTRODUCTION

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Direct chemical interactions between fillers and polymer ageing have been essentially observed in the case of low to moderate temperature oxidation as well thermally as photochemically initiated. The kinetic models are generally derived from the following standard mechanistic scheme (1).

$\lambda POOH$	$\rightarrow 2P^\circ$	(initiation)	(k_1)	$(\lambda = 1 \text{ or } 2)$
$P^\circ + O_2$	$\rightarrow PO_2^\circ$	propagation I	(k_2)	
$PO_2^\circ + PH$	$\rightarrow PO_2H + P^\circ$	propagation II	(k_3)	
$P^\circ + P^\circ$	→ inactive. prod.	termination	(k_4)	
$P^\circ + PO_2^\circ$	→ inact. prod	termination	(k_5)	
$PO_2^\circ + PO_2^\circ$	→ inact. prod + O_2	termination	(k_6)	

Fillers can interact with this process at three levels :

→ Oxygen transport (decrease of O_2 diffusivity and thus shift of the boundary between diffusion controlled and non diffusion controlled kinetic regime : see chap 2).

→ Initiation, essentially by redox catalysis or by photocatalysis. The reaction displays usually an induction period and a pseudo steady state. An acceleration of the hydroperoxide decomposition process leads to a shortening of the induction period without a change of the steady state regime as illustrated by the results of Gisjman and al (2) in the case of PP thermal oxidation, and theoretically predicted by the kinetic analysis in the case of O_2 excess (3).

→ Termination, essentially by radical capture

$P^\circ + Q$ (filler) → inactive prod. (k_7)

$PO_2^\circ + Q$ → inactive prod. (k_8)

Indeed, increase of the termination rate by such unimolecular processes, would decrease the overall oxidation rate especially in steady state regime in which the oxidation rate (in the case of oxygen excess) is proportional to $k_3^2\,(PH)^2/k_6$

As it will be seen below, both accelerating and retardating effects can be observed in the oxidation of industrial filled polymer systems.

1-2 ACCELERATING EFFECT OF FILLERS ON OXIDATION

<u>Redox catalysis of POOH decomposition</u> is probably the most usual mechanism of filler accelerating effect on polymer oxidation. This mechanism has been elucidated more than forty years ago ; it can be ascribed as follows :

$POOH + M^{i+} \rightarrow PO° + OH^{-} + M^{(i+1)+}$
$POOH + M^{(i+1)+} \rightarrow POO° + H^{+} + M^{i+}$

Most of the transition metal ions, especially Cu, Fe, Co, Cr, Ti...display a strong catalytic effect as illustrated for instance by the study of the effect of $Ti\ Cl_3$ traces in PP thermal oxidation (2). Copper effect has been extensively studied owing to the great importance of polymer-copper contact in electrical applications, but in the domain of industrial fillers, iron is probably the most important element because it is an usual impurity of natural fillers such as calcium carbonate, or mica or even silica. Its concentration can vary strongly with the extraction site, which explains the existence of contradictory sentences, about the filler effect on durability, in the literature. To our knowledge, pure calcium carbonate, iron free mica or pure silica have no direct effect on the oxidation rate.

To well put in evidence a such catalytic effect on oxidation kinetics, it is interesting to start from a kinetic model. For instance in the case of the non diffusion controlled oxidation initiated by the unimolecular hydroperoxide decomposition, one can suppose that initiation results from two reactions :

Non catalysed : POOH decomposition : $POOH \rightarrow \alpha' P°$ (k'_1) ; Activation energy : H'_1

Catalysed POOH decomposition : $POOH + M^{i+} \rightarrow \alpha'' P°$ (k''_1) Activation energy : H''_1

One can write : $\frac{d[POOH]}{dt} = -k'_1[POOH] - k''_1[M^{i+}][POOH]$

so that $\frac{d[POOH]}{dt} = -k_1[POOH]$ where $k_1 = k'_1 + k''_1\,[M^{i+}]$

In a such process, the induction time t_i is of the order of : (3)

$$t_i = \frac{3}{k_1}$$

Since $H''_1 < H_1$, one expects that the Arrhenuis plot of t_i will have the shape of Fig. 1.

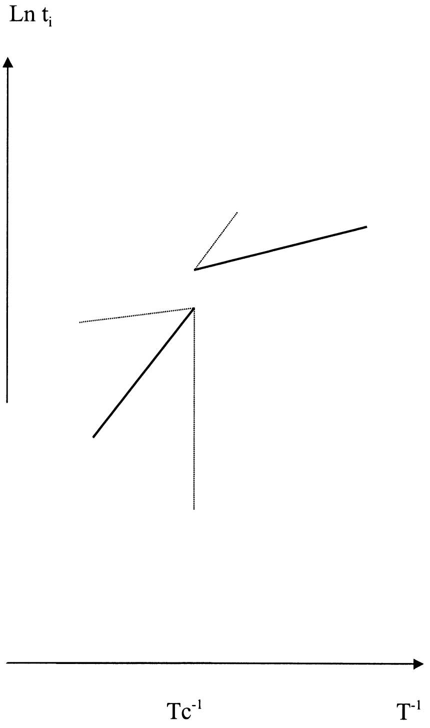

Fig.. 1 : Shape of the plot of oxidation induction time in the case of catalytic effect of filler impurities.

It is very easy to show that :

i) The catalytic effect is more apparent in « soft » conditions (low temperature) than in « hard » conditions (high temperature).

ii) Due to the coexistence of catalysed and non catalysed reactions, the temperature variation of t_i is non arrhenian, it displays a transition at a temperature T_c such as :

$$k'_{10}\ \exp - \frac{H_1'}{RT_c} = k''_{10}\left[M^{i+}\right]\exp - \frac{H_1''}{RT_c}$$

so that $T_c = \dfrac{H'_1 - H''_1}{R\,\mathrm{Ln}\dfrac{k'_{10}}{k''_{10}\left[M^{i+}\right]}}$

iii) An interesting characteristic of a such catalytic effect is that it does not influences the steady state oxidation rate as well illustrated by Gisjman's results (3).

The best ageing quantity to characterise a catalytic effect of fillers is thus the induction time which can be routinely determined by DSC. manometric oxygen absorption, chemiluminescence etc....

Photocatalytic effect of fillers or pigments, especially TiO_2 and ZnO, is relatively well known because photocatalysis can be industrially used in organic synthesis. Several mechanisms of « photosensitization » have been proposed (4)', they can involve the formation of O_2^- radical anion, singlet oxygen, hydrogen peroxide or OH° radicals from the Ti O_2 or ZnO excited state. In the case of TiO_2, the anatase form is well known to be more active than the rutile one. The photoactivity can be decreased by appropriate surface treatments (aluminosilicates, zirconates, phosphates....). Microwave absorption spectrum seems to be a good analytical tool to distinguish between the various TiO_2 forms (5).

There is one case : rigid PVC, where a slight prooxidant effect could be favourable because yellowing results from conjugated polyene build up. Oxidation destroys, in this case, the formed polyenes. It is however difficult to distinguish, here, between this effect and the screen effect (see below).

From the kinetic viewpoint : the photocatalytic effect can be in principle treated as the precedingly seen redox catalysis : it increases selectively the initiation rate constant.

1-3 STABILISING EFFECT OF FILLERS (CHEMICAL MECHANISMS)

Many industrial fillers or pigments display a small but significant stabilising effect in photochemical ageing but it is due mostly to their screen effect (see below). The only case where a chemical interaction is clearly established is the case of carbon black which works as a primary antioxidant, probably by radical capture (6) :

$P^\circ + [C^\circ] \rightarrow P\text{-}C$

(P° is a polymer radical, C° is a radical site on carbon black)

or by chain breaking classical stabilising reaction :

$P\text{-}O\text{-}O^\circ + [C]\,OH \rightarrow POOH + [C]\,O^\circ$

$[C]\,O^\circ \rightarrow$ stable species

([C] OH is a phenolic group present at the surface of carbon particles) (7)

Photophysical quenching effects have been also suggested.

In practice, concentrations of 2 to 5 % w/w of channel black constitute an efficient stabilisation way, except in cases where thermal ageing mechanisms other than oxidation (see below) can occur. Indeed, the quality of the dispersion determines the stabilising efficiency. From the kinetic point of view, chain breaking or radical trapping effects can be treated as unimolecular terminations, for instance :

polymer $\rightarrow P^\circ$ (radicals) (r_i)

$P^\circ + O_2 \rightarrow PO_2^\circ$ (k_2)

$PO_2^\circ + PH \rightarrow PO_2H + P^\circ$ (k_3)

$PO_2^\circ + S \rightarrow$ inact prod (S=stabiliser) (k_t)

One sees that in stationary state, and for a large stabiliser excess, one can write :

$$r_{ox} = r_i\left[\frac{k_3(PH)}{k_t(S)} + 1\right]$$

If the stabiliser is very efficient, k_t (S)>>k_3 (PH) and r_{ox} =r_i, the oxidation rate is reduced to the initiation rate, the stabiliser prevents the « amplifying » effect of the chain propagation.

A such process is a heterogeneous reaction, it can be efficient only if any polymer volume element undergoing oxidation is sufficiently close to the filler particle. The avearge interparticular distance is thus :

$$\bar{d} = \left(\frac{4\pi}{3\varphi}\right)^{1/3} r$$

where r is the particle radius and φ the filler volume fraction :

$$j = \frac{1}{1 + \frac{1 - W\rho_F}{W\ \ \rho_F}}$$

where W is the filler weight fraction, ρ_F and ρ_F being the respective densities of the filler and the polymer. The maximum distance from a given matrix volume element and the closest particle surface would be thus : $\bar{d}_m = \frac{\sqrt{2}}{2}\left[\bar{d} - r\right]$, which corresponds to about 4.5 r for w = 2% and 3r for W= 5 % taking $\rho_F / \rho_P = 2$.

One sees from this simple model that be the best stabilising efficiency is obtained with the smallest particle size. In the case of carbon black, particle sizes of the order of 10-100 nm give generally the best results. The smaller the particle diameter is, the higher the particle surface for a given mass fraction and the higher the carbon reactivity towards radical species, i. e the higher its stabilising efficiency. Indeed, the problem of filler dispersion becomes, here, critical.

2 DIRECT PHYSICAL INTERACTIONS OF FILLERS WITH POLYMER AGEING

2-1 OPTICAL AND THERMO-OPTICAL PROPERTIES

Pigments or fillers display a more or less marked screen effect in polymer matrices : If one defines the thickness of light penetration (TLP) as the thickness in which an arbitrary fraction, for instance 90 % of the incident light is absorbed, it appears very generally that TLP is decreased in the presence of pigments fillers. Both absorption and diffusion phenomena can contribute to this screen effect, the most efficient screens, for instance carbon black (whole UV-visible range) ; TiO_2 (UV at $\lambda < 390$ nm and Zn 0 (UV at $\lambda < 360$ nm) being characterised by a strong absorption in the UV range. The stabilisation efficiency can depend on the property under consideration. If the main ageing problem is discoloration (white fillers), the screen effect can be useful in the case where discoloration predominates in a subcutaneous layer, as in the case of PVC (8). As a matter of fact, polyene build-up, responsible for yellowing/darkening in PVC, can occur only at a certain distance L of the surface where the oxygen concentration is low owing to the diffusion controlled character of photooxidation kinetics.

If the main ageing problem is embrittlement, then the screen effect can be efficient if it reduces the thickness of degraded layer to a value lower than a critical dimension hc linked to the material's toughness. According to Griffith, this value would be : $h_c = \frac{2\,Ee}{\sigma^2{}_y}$

where σ_y would be the initial yield stress, E the modulus and e the surface energy. $2E/\sigma^2$ is of the order of 1-10 $m^3.MJ^{-1}$ for most of the industrial polymers. e can be considered as the sum of two components :

$$e = e_E + e_p$$

where e_E (elastic component) is essentially linked to the cohesion and e_p (plastic component) is linked to the plastic deformation (chain streching). NB : In fact, the Griffith relationship is not exactly valid for ductile materials but the reasoning remains valid.

One sees thus that relatively low screen effects can in principle protect ductile polymers ($e_p >> e_E$) whereas brittle polymers need highly absorbing systems. One must however recall that fillers reduce generally the ductility.

Thermooptical properties (overall absorptivity/emissivity) can be important in outdoor ageing because they determine the equilibrium temperature under irradiation, which can be more than 20°C higher for a black than for a white specimen (Fig. 2).

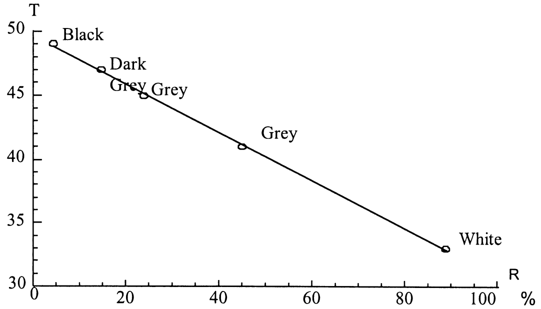

Fig.. 2 : Surface temperature under irradiation in weather 0 meter for various sample refectances (ambient temperature 27°C).

This can be important in the case where ageing results from a thermal process, for instance plasticizer loss by evaporation : white samples will appear more stable than black ones, all the other compositions parameters being equal.

Let us recall that, according to Arrhenius law, a temperature increase of 20°C leads to a rate increase by a factor of 4 to 13 for activation energy values ranging between 50 and 100 $kJ.mol^{-1}$.

2-2 TRANSPORT PROPERTIES

Inorganic fillers are generally totally impermeable to gases and vapors so that they tend to lower the transport rate of reactive gases (oxygen, water...) and then to decrease the ageing rate in diffusion controlled conditions.

The effect of filler in diffusivity D could be tentatively represented by the following relationship.

$$D = D_o \psi \ (1-\varphi)$$

where φ is the filler volume fraction and ψ is a tortuosity coefficient which can vary suddenly in the vicinity of a percolation threshold, and can be especially low when the filler (of lamellar shape) is oriented parallel to the sample surface. This is often spontaneously realised in the case of injection molding, for instance in mica reinforced thermoplastics, as a result of shear flow during mold filling (9).

3 INTERACTIONS OF FILLERS WITH STABILISING ADDITIVES

Cases of synergism and antagonism have been reported in filler-stabiliser combinations.

Synergism is often linked to the fact that the filler displays contradictory stabilising (for instance through screen effect) and destabilising (for instance through catalytic effects) properties. In such cases, organic stabilisers capable to inhibit the destabilising process (for instance by complexing active metallic ions), or to destroy rapidly the hydroperoxides resulting of the catalysed oxidation in the polymer superficial layers, can display interesting synergisms with the filler. This is for instance the case of natural ageing of zinc oxide filled PE : the lifetime is about 3.5 times longer for ZnO - sulphide or ZnO - phosphite combinations than for pure Zn O for IdPE and about 30-40 times for hd PE (10).

Antagonism results generally from the fact that the filler absorbs the organic additives and behaves as a stabiliser trap. This is observed for instance in the case of silica-irganox 1010 or Silica-Tinuwin (2) systems where lifetime to embrittlement of PP films is reduced by a factor of 5 to 7 in the presence of silica (11). Entrapment of certain stabilisers by fillers such silica can be however favourable to stability in certain cases where stabiliser desorption by the filler allows to control the stabiliser release (12).

4 INDIRECT PHYSICAL INTERACTIONS WITH POLYMER AGEING

4-1 Through morphological changes

Certain fillers such as for instance talc in polypropylene (13), play a nucleating role on polymer cristallisation. On the other hand, crystalline morphology (14) can influence, in a complex way, the course of oxidative or hydrolytic ageing. No clear tendency can be however observed in this field.

4-2 Through mechanical effects

Fillers induce often brittleness due to stress concentration effects. On the other hand, ageing affects considerably less brittle polymers than ductile ones (15) As a matter of fact, the transition from ductile to brittle behaviour needs only a small number of chain scissions, typically :

$$n = \frac{1}{M_c} - \frac{1}{M_{no}}$$

where n is the number of chain scissions at the embrittlement point, M_c the critical molar mass (at the entanglement threshold) and M_{no} the initial molar mass.

In contrast, the ultimate properties in brittle regime depend practically only of cohesion (which does not change or even increases during ageing) and flaw size. One cannot expect thus fast changes of the ultimate properties of brittle materials during ageing (Fig. 3).

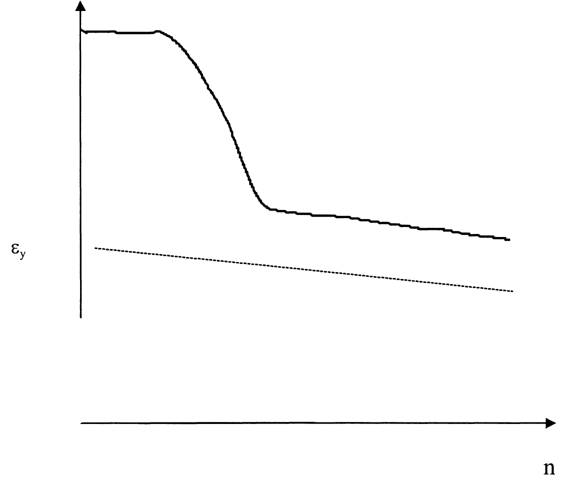

Fig. 3 : Shape of the variation of ultimate elongation with the number of chain scissions for an initially ductile polymer (full line, yield elongation ε_y) and for an initially brittle polymer (dashed line).

Thus, as far as ageing is judged from a relative change of properties, fillers will appear as stabilisers. However, if endlife criteria are absolute values of a given ultimate property, it becomes absurd to compare an initially ductile polymer and its filled counterpart.

5 ROLE OF POLYMER-FILLER INTERFACE

The role of polymer-reinforcing agent interface has been extensively studied in the case of fibre reinforced composite materials, in contrast particulate filled polymers have received little attention and this research field remains largely open. Many cases have to be considered.

a) In the case of weak or non existent bonding, the interfacial zone is a privileged way for migration of small molecules. The diffusivity appears as an increasing function of the filler content and it can eventually increase abruptly in the vicinity of a percolation threshold, as found for instance in the case of water transport in PMMA based orthopaedic cements (16).
In such cases, the filler favours the penetration of reactive agents into the material's thickness which has a defavorable influence on durability.
b) In the case of strong bonding, the interfacial zone can play a positive role on humid ageing as in the case of organic matrix-fiber composites. When coupling agents such as for instance trialkoxy silanes are present, they form a network layer of which the resistance to water attack can depend sharply on the structure, and especially polarity of the organic group meant for bonding to the matrix. (17).

6 CONCLUSIONS

Fillers can influence ageing by various, sometimes contradictory ways : For instance TiO_2 can exert at the same time a strong screen effect and a photocatalytic effect in the superficial layer of UV exposed materials. They can act at various levels of the ageing causal sequence, for instance by changing :

- The oxygen diffusivity (and thus the distribution of oxidation events in the sample thickness)
- The oxidation rate through, for instance, a catalytic effect in hydroperoxide decomposition
- The change of mechanical properties for a given conversion ratio of the oxidation process.

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