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3. Additives

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Abstract

This chapter presents a review of the role of several additives on POM processing (lubricating agents, processing aids, nucleating agents), performances (fillers, impact modifiers) and lifetime increase (antioxidants, compounds reacting with secondary reaction products such as acids scavengers, UV stabilizers and flame retardants) and aspect properties (pigments). It is tried to review existing models permitting to describe the efficiency of these additives in POM and predict the effect of other comparable additives that are not included in this review. Last, since POM compounding can be relatively complex and additives are scarcely used alone, it was also tried to report some side effects of these additives and the possible synergistic or antagonistic effects in the case of combinations of additives.

3.1. Introduction

The development of polymers as high diffusion materials was made possible thanks to several sorts of additives that have contributed to their success. These one provide to plastics:

- Stabilization to retain the original molecular architecture of the polymer under the effect heat, light, oxygen etc... causing the chemical unstability of most polymers and subsequent changes of properties expected from material design. In other words, polymer cannot maintain their properties during processing, storage and exposure at device conditions without adding process stabilizers or light antioxidants...
- Functionalization to provide best mechanical, thermal ... properties to the polymer.

Not surprisingly, the change in consumption per year of polymers and their additives follow the same trend with a ca 5% per year growth [1]. This flourishing commercial market has aroused the interest of scientist and engineers that have published a great volume of studies aimed at illustrating the performances of additives in polymers. When browsing this rich literature, two sorts of articles can be distinguished:

- Those showing the properties of additives mixtures for seeking the optimal properties.
- Those focusing on the effect of one additive pure polymer.

This chapter is mostly aimed at reviewing the second sort of research works because they permit to better understand the first ones, and validate the existing predictive models as well. Some mechanisms of polymer degradation are recalled in the ‘chemical resistance’ chapter of this book so as to present the ‘key species’ of these mechanisms and which molecules can interact with them.

3.2. Antioxidants

3.2.1. Strategy of stabilization to inhibit thermal oxidation

There are two main ways for slowing thermal oxidation:

- Decrease the initiation rate, which is the rate of radical generation. For thermal oxidation, this rate is equal to: $r_1 = 2k_1[\text{POOH}]^\delta$ ($\delta = 1$ or 2 depending on uni- or bimolecular initiation process). For that purpose, hydroperoxides reducers (e.g. phosphites or sulfurs) are added.
- Increase termination rate, i.e. rate at which radical compounds are converted into stable products, using phenolic antioxidants, aromatic amines and Hindered Amine Stabilizers (HAS).

3.2.2. Case of hydroperoxides reducers in POM

Hydroperoxides are inherently unstable in POM (see ‘3.2.3. Thermal Oxidation’ section) and decompose essentially by an unimolecular process. From a kinetic point of view, phosphites are thus efficient hydroperoxides reducers typically if:

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$$r_D > r_{1u}$$

$$\text{i.e.:} \quad k_D[D][\text{POOH}] > k_u[\text{POOH}]$$

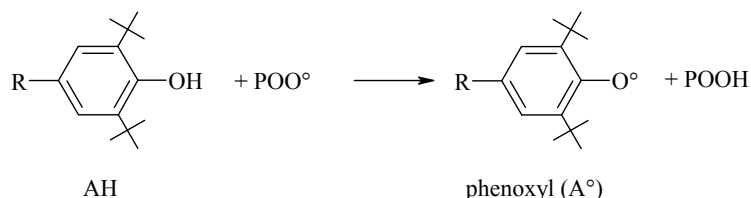
so, using: $k_u = 5.10^{-6} \text{ s}^{-1}$, $k_D = 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$:

$$[D] > 5.10^{-3} \text{ mol l}^{-1} \text{ or } [D] > 0.005 \text{ g/g}$$

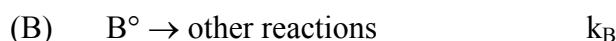
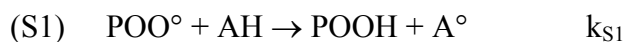
3.2.3. Case of phenolic antioxidants in POM

3.2.3.1. Mechanism of stabilization by antioxidants

Phenolic antioxidants constitute the most common stabilizer family [1]. There is a wide consensus on the nature of the first stabilization event consisting in scavenging POO° radical:

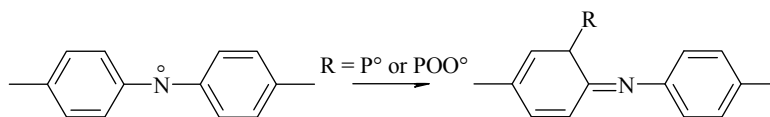


Several reactions involving A° are possible [2]. The following scheme could be ascribed:

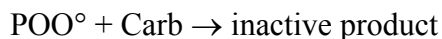
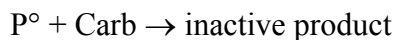


Phenols are irreversibly consumed (contrarily to hindered amine stabilizers presented in the ‘3.4. UV stabilizers’ section) and are hence called ‘sacrificial stabilizers’. Some aspects of stabilization by phenolic antioxidants will be illustrated in the next section.

Diphenylamines also belong to the family of sacrificial antioxidants and are mentioned as possible antioxidants for POM [3]. One of their drawbacks is to lead to significant darkening of polymer because of the accumulation of conjugated structures in the polymer:



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Carbon black [4] and carbon nanotubes are also expected to have some antioxidant properties, since aromatic nuclei can react with both alkyl and peroxy radicals:



Some amine stabilizers can also react with both P° and POO° radicals. They will be presented in the “3.4. UV stabilizers” section.

3.2.3.2. Effect of phenol concentration

During thermo-oxidative aging, stabilizers are continuously consumed as monitored for example by Differential Scanning Calorimetry (DSC) under oxygen [5,6]. When concentration becomes negligible, the oxidation mechanism occurs as in a pure polymer. The stabilizer efficiency can thus be quantified by its ability to delay the induction time of degradation, which is for example the time for losing 10 % of mass. Table 3.1 illustrates the changes of this characteristic time for degradation with stabilizer concentration [7]:

Table 3.1: Time to 10 % mass loss ($t_{10\%}$) in thermal ageing at 140 °C [7] for POM + phenolic antioxidants with several concentrations.

T	AO	x (%)	M (g mol ⁻¹)	f	[AH] (mol l ⁻¹)	t _{10%} (min)	SE (h l mol ⁻¹)
140°C	AO1	0.1	574	2	0.005	22	74.1
	AO1	0.3	574	2	0.015	70	78.6
	AO1	0.5	574	2	0.025	95	64.0
	AO2	0.1	638	2	0.004	18	67.4
	AO2	0.3	638	2	0.013	69	86.1
	AO2	0.5	638	2	0.022	90	67.4
	AO3	0.1	340	2	0.008	22	43.9
	AO3	0.3	340	2	0.025	66	43.9
	AO3	0.5	340	2	0.042	78	31.1

Stabilizer can be compared by their Stabilizer Efficiency (SE) factor, which could be defined as the increase in characteristic time of degradation per mole of stabilizer initially present in the polymer. Here:

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 $SE \sim t_{10} \% / [AH]_0$

As classically observed [8], SE is decreased when increasing initial stabilizer concentration because a part of stabilizer is certainly lost by evaporative process before having reacted with radicals. The relationship between phenolic stabilizer structure and physical loss will be presented in the next paragraph.

3.2.3.3. Effect of phenolic antioxidant structure

Table 3.2 illustrates the performances of several phenolic antioxidants for retarding degradation induced mass loss:

Table 3.2: Time to 2, 4 or 10 % mass loss for POM with 0.3 % antioxidants + 0.3 % ca stearate from [7,9] together with some characteristics of antioxidants (molar mass and melting temperature).

stabilizer					220°C			140°C	
	f	M (g mol ⁻¹)	T _m (°C)	[AH] (mol l ⁻¹)	t _{2%} (h)	t _{10%} (h)	SE (h l mol ⁻¹)	t _{4%} (h)	SE (h l mol ⁻¹)
AO1	2	586	75-79	0.015	0.75	1.20-1.30	82.5-89.4	3864-4000	(2.66-2.75)×10 ⁵
AO2	2	638	104-108	0.013	0.60	0.90-1.13	67.4-84.9	2520-2900	(1.89-2.17)×10 ⁵
AO3	2	636	156-162	0.013	1.08	1.75-2.08	130.6-155.5	2500-2772	(1.86-2.07)×10 ⁵
AO4	4	1176	125	0.014	0.55	0.87-1.17	59.8-80.5	2772-3000	(1.91-2.07)×10 ⁵
AO5	2	340	120-132	0.025		1	39.9	336	0.13×10 ⁵

Table 3.2 calls for the following comments:

① At low temperature: SE(AO1) > SE(AO3), SE(AO2) and SE(AO4) > SE(AO5). Solubility is the main physical parameter responsible for stabilizer efficiency at low temperature [10]. In other words, data in table 3.3 would be explained by:

solubility(AO5) < solubility(AO4) < solubility(AO2) < solubility(AO3) < solubility(AO1)

in good agreement with expected structure solubility relationships in a polyether.

② At high temperature: SE(AO3) > SE(AO1), SE(AO2) and SE(AO4) > SE(AO5). Stabilizer efficiency is possibly limited by volatile loss. The rate of evaporation was expressed as [11]:

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$$r_{\text{evap}} = \frac{V_{\text{stab}}}{[\text{stab}]_{\text{sat}}} \cdot [\text{stab}]$$

Assuming that the relative solubility of antioxidants is the same at 220 °C and 140 °C, data militate in favor of:

volatility(AO3) < volatility(AO1), volatility(AO4) and volatility(AO2)

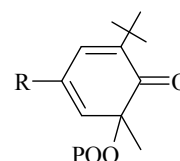
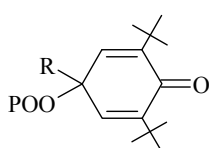
in good agreement with the link between the volatility of pure stabilizer V_0 (depending on the cohesion in a stabilizer crystal) with its melting temperature T_m and molar mass .

Another aspect linked to stabilizer structure is illustrated by table 3.3: it seems that stabilizer performances to retain elongation at break (i.e. to inhibit oxidation process) are not linked to their performances to limit discoloration.

Table 3.3: Performances of stabilizer to retain elongation at break and limit color changes (t_{50} = time to 50 % of initial elongation at break, t_{10} = time to discoloration $\Delta E = 10$) [12].

T	AO	x (%)	f (g mol ⁻¹)	f	[AH] (mol l ⁻¹)	t _{50%} (h)	SE (h l mol ⁻¹)	t _{ΔE=10} (h)	SE (h l mol ⁻¹)
140°C	AO3	0.3	636	2	0.013	1500	1.1E+05	150	1.1E+04
	AO1	0.3	574	2	0.015	1500	1.0E+05	750	5.1E+04
	AO6	0.3	582	2	0.015	2500	1.7E+05	500	3.4E+04
	AO7	0.3	1090	3	0.012	750	6.4E+04	250	2.1E+04

This is linked to the nature of the reaction product between POO° and A° depending on the nature of 2, 4 and 6 substituent:

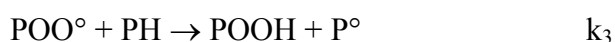
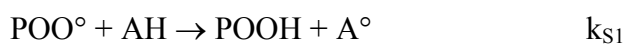


In other words, even if the rate of reaction with POO° is almost the same, these antioxidants have not the same effect on color changes because of the nature of formed products.

3.2.3.4. Kinetic parameters for stabilization

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At moderate temperature, when evaporation plays a negligible role, SE is very close for all stabilizers under study. This militates in favor of a very close k_{S1} value for all the members of the hindered phenol family, as suggested by Gur'yanova et al. [13] who calculated a rate constants ratio characterizing the stabilizer efficiency k_{S1}^2/k_6 . It seemed to us interesting to compare k_{S1} with k_3 , having in mind that:



are in competition. Estimated values are gathered in table 3.4.

Table 3.4: k_{S1} and k_3/k_{S1} at 60°C from the k_{S1}/k_6 value by [13] and k_3 and k_6 from [14].

	AO3	AO8	AO9	AO10	AO11	AO12
$k_{S1}/k_6^{1/2}$	3.2	2.5	0.6	5.3	4.5	8.53
k_6			3.6E+04			
k_3			5.9E-03			
k_{S1}	6.0E+02	4.7E+02	1.1E+02	1.0E+03	8.5E+02	1.6E+03
k_{S1}/k_3	1.0E+05	8.0E+04	1.9E+04	1.7E+05	1.4E+05	2.7E+05

The fact that kinetic parameters are very close for all these phenolic antioxidants could be explained by the fact that they react by giving a hydrogen to POO° radical as observed in other polymers [15]. The corresponding k_{S1} rate constant value is thus linked to BDE(O-H) in phenol and is almost independent of *ortho*, *meta*, *para* substituent nature.

As it will be seen later, some interactions exist with fillers, pigments and ultra violet radiation (UV) stabilizers.

3.3. Compounds reacting with secondary reaction products

To prevent further acidolysis (see ‘Chapter 11 - Chemical properties’), polyacetals and copolymers are protected by co-stabilizers being acid acceptors that react with formaldehyde to yield inert products. Suitable co-stabilizers are polyhydroxy compounds, melamine-formaldehyde condensation products [16], urea and its derivatives, amide and polyamides

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3.4. UV stabilization

3.4.1. Generality on UV stabilization

Let us describe the main effect of photo-oxidation as follows:



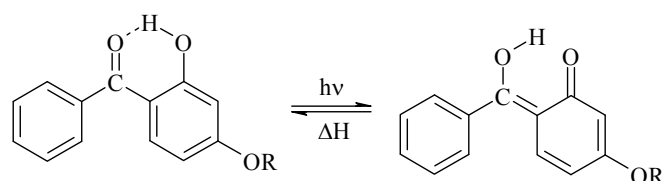
X being a chromophor of which direct photochemistry is a supplementary source of radical destabilizing the polymer. The aim is to decrease the rate constant k_{uP} for photochemically induced imitation. Polymers can be UV stabilized:

① by a mineral coating working as an UV shield [21]. This was not tried in the case of POM to our knowledge.

② by adding pigments, such as carbon black, decreasing the penetration of UV in polymers,

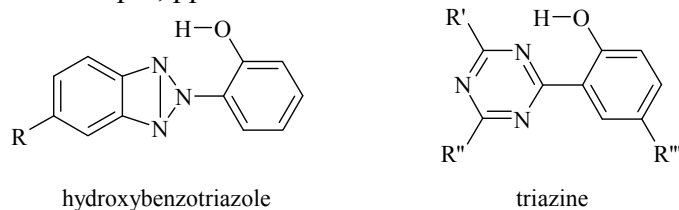
③ by adding chemicals in the bulk, of which properties are:

- a high molar absorptivity in the solar UV range (typically higher than $10^4 \text{ l.mol}^{-1}.\text{s}^{-1}$ in 300 nm to 400 nm wavelength range) which permits to absorb radiations even at low concentration (typically 0.001 g/g to 0.01 g/g).
- the ability to dissipate energy coming from UV light into heat without yielding radicals which is linked to the formation of isomers involving an intramolecular hydrogen bond as for example the case of hydroxybenzophenones:



Hydroxybenzotriazoles [22,23] and triazines are other current UV stabilizers:

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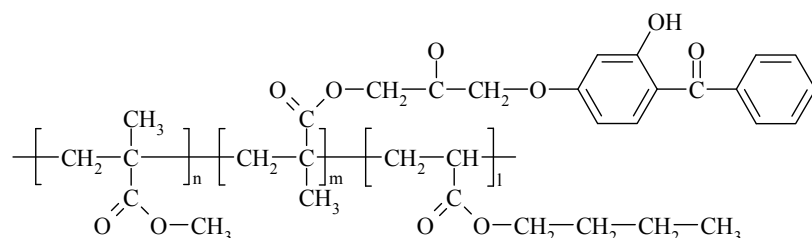
The performances of these molecules are compared in table 3.5 [24]:

Table 3.5: Typical lifetime (time for retaining 40 % elongation) of POM samples with various photostabilizers submitted to Xenotest 450 (29 min light, 1 min water spraying) or natural ageing (Frankfurt, Germany, 45° facing South).

	artificial ageing	natural ageing
without	0	5
1.5% hydroxybenzophenone	850	12
1.0 hydroxybenzotriazole	> 1000 (65%)	18
0.5% carbon black	> 1000 (85%)	> 36

Typical structures of UV absorbers are shown above. The nature of R- controls some key physical properties such as migration and physical loss. Wu et al [25] compared the stabilization by 2,4 dihydroxybenzophenone in the case of:

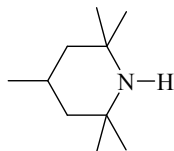
- grafting on an oligomer:



- simple mixing with the polymer matrix.

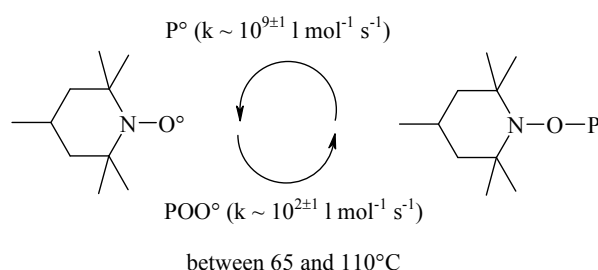
Their result showed a certain improvement in retaining mechanical properties when UV absorber is grafted instead of mixed, thus highlighting the already mentioned importance of volatility on stabilizer performances. They also showed that the UV stabilization could be improved if UV absorber was held by a core-shell polymer instead of a copolymer [26].

④ by adding chain breaking antioxidants such as Hindered Amine Stabilizers [24] that are molecules containing the 2,2,6,6 methyl piperidine group:



They have aroused a huge quantity of research work after which, even if the stabilization mechanism remains not totally elucidated, the following facts are widely accepted:

- >NH is converted into >N-O° radicals play a key role,
- >N-O° is converted into alkoxyamine >N-O-P or hydroxylamine >N-O-H able to trap POO° radicals and regenerating >N-O° [27]:



Let us emphasize that they are also expected to be efficient thermal antioxidants, even if Hindered Amine Light Stabilizer (HALS) efficiency is more often in conditions of light induced ageing than in thermal oxidation. Their stabilizing efficiency is thus due to the fact that they trap both P° and POO°, and that stabilizing forms (>N-O°, >N-O-P or >N-O-H) are regenerated contrarily to phenols, phosphites or sulfurs. According to Sedlář and Zahradníčková, HALS stabilization can be divided into four steps [28] (Fig. 3.1):

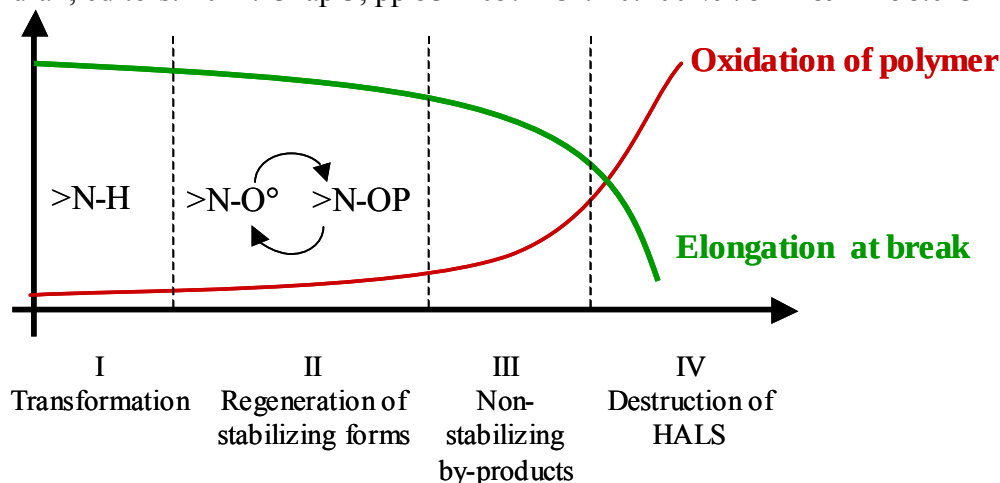


Figure 3.1: Stabilization by HALS.

- Phase I: amine reaction into $>\text{N-O}^\bullet$ radical.
- Phase II: regenerative cycle $>\text{N-O}^\bullet \rightleftharpoons >\text{N-O-P}$ or $>\text{N-O-H}$.
- Phase III: irreversible conversion of stabilizing forms into non stabilizing ones.
- Phase IV: total consumption of stabilizing forms and polymer oxidation and stabilization.

3.3.2. Performances of UV stabilizers in POM

Performances of several HALS and UV absorbers are reported in tables 3.6, 3.7 and 3.8 [38] for various accelerated ageing conditions.

Table 3.6: Time to chalking and corresponding SE factor for POM + stabilizer (Base stabilization: 0.3% stearate + 0.3% AO 2) submitted to Xenotest 1200 with black panel temperature equal to 53°C without water spraying. For HALS, M is the molar mass of repetitive unit of oligomeric stabilizer.

stabilizer	m/m	M (g mol ⁻¹)	c (mol l ⁻¹)	time to chalking (h)	SE (h l mol ⁻¹)
-	0	-	0	1400	0.00E+00
UVA 1	0.25 %	225	0.016	4000	1.65E+05
UVA 1	0.50 %	225	0.032	5000	1.14E+05
UVA 2	0.25 %	351	0.010	3800	2.37E+05
UVA 3	0.25 %	323	0.011	3800	2.18E+05
HALS 1	0.25 %	277	0.013	3200	1.40E+05
HALS 1	0.50 %	277	0.026	3200	7.02E+04
HALS 2	0.25 %	299	0.012	3600	1.85E+05
HALS 2	0.50 %	299	0.024	4000	1.09E+05

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Table 3.7: Time to crack of POM + several UV + HALS mixtures (base stabilization 0.1 % Ca stearate + 0.1 % Melamine + 0.15 % AO 1) submitted to 0.55 W m⁻² at 340 nm irradiation.

stabilizer	Y.I. (t = 0)	Y.I. (t = 896h)	% gloss loss	time to crack (h)
without	4.0	0.6 (320 h)	89.3 (384 h)	120
0.3% UVA 4 + 0.3% HALS 1	9.3	8.8	27.4	384
0.6% UVA 4 + 0.6% HALS 1	12.7	11.0	21.0	512
0.3% UVA 4 + 0.3% HALS 3	6.0	10.3	63.5	384
0.6% UVA 4 + 0.6% HALS 3	7.8	15.2	47.5	448
0.3% UVA 4 + 0.3% HALS 4	8.9	8.5	32.9	384
0.6% UVA 4 + 0.6% HALS 4	12.0	11.0	20.5	384
0.3% UVA 4 + 0.3% HALS 5	7.5	7.6	25.9	384
0.6% UVA 4 + 0.6% HALS 5	9.9	9.8	21.5	448

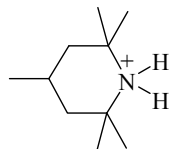
Table 3.8: Initial Yellow index, yellow index after ageing, relative gloss loss and estimated energy received to crack for stabilized POM samples (base stabilization: 0.1% Ca stearate + 0.15% AO1) submitted to natural exposure (Florida - 45°C South direct).

stabilizer	Y.I. (t = 0)	Y.I.	% gloss loss	Energy recieved to crack (h)
without	2.9	5.5	28.4	85
0.4% HALS 1	2.6	3.5	36.2	165
0.3% UVA 4	5.3	6.0	25.0	165
0.3% UVA 4 + 0.4% HALS 1	5.7	5.9	25.0	250

Identically to phenolic antioxidants (see ‘3.2. Antioxidants’ section), a SE value was determined in the case of simple polymer + stabilizers binary mixtures, showing that:

- Stabilizers efficiency seems to increase with molar mass, possibly because of stabilizer volatile loss.
- The SE decrease when increasing the stabilizer concentration can be due to physical limits of stabilization as for example a greater concentration than solubility limit.
- Changes in aspect properties (yellow index, gloss loss) are difficult to interpret.

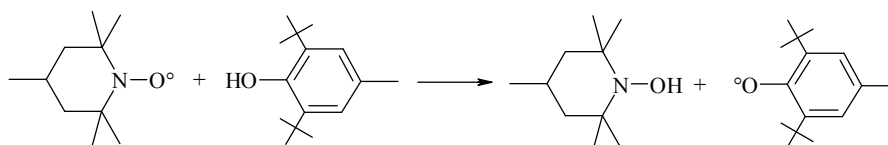
Possible negative interaction may occur with fillers [29] due to adsorption at the surface of filler. Antagonisms were also reported with halogenated flame retardants [30]. HALS are quite basic. They can hence react with acidic groups to form an inactive salt:



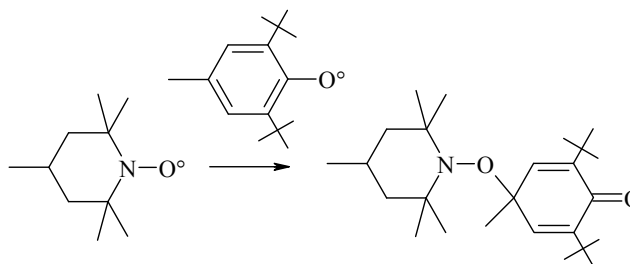
This problem can be avoided by replacing HALS with >N-H group ($pK_B = 4.3-7.4$) by HALS with >N-R (5.5-8.5) or >N-OR (9.8-10.0) [31] groups.

Last, let us mention that phenols may react with HALS by antagonistic mechanisms:

- abstraction of H by $NO^\bullet$ [32,33]:



- reaction between nitroxy and phenoxy leading to unstabilizing products [34]:



3.5. Impact modifier

Impact strength of a polymer is increased with temperature, broadness of molar mass distribution, and decreases with crystalline phase content and crystal size [35]. POM is a rigid and semi-crystalline polymer characterized by tough behavior but is notch sensitive, with a good resistance to crack initiation, but a poor resistance to crack propagation. Its impact strength can be improved by incorporating a rubber phase dispersed in the rigid matrix acting as a stress concentrator and forming a barrier to the extension of crazing.

Starting from a theory proposed by Wu [36], Kanai et al [37] showed that:

- Interparticle distance has a greater influence of on impact modification than particle size.
- Impact strength increase when average interparticle distance is below a critical value.
- The lower interparticle value is, the lower the brittle-tough temperature is.

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The performances of several additives to increase impact resistance are illustrated in figure 3.2.

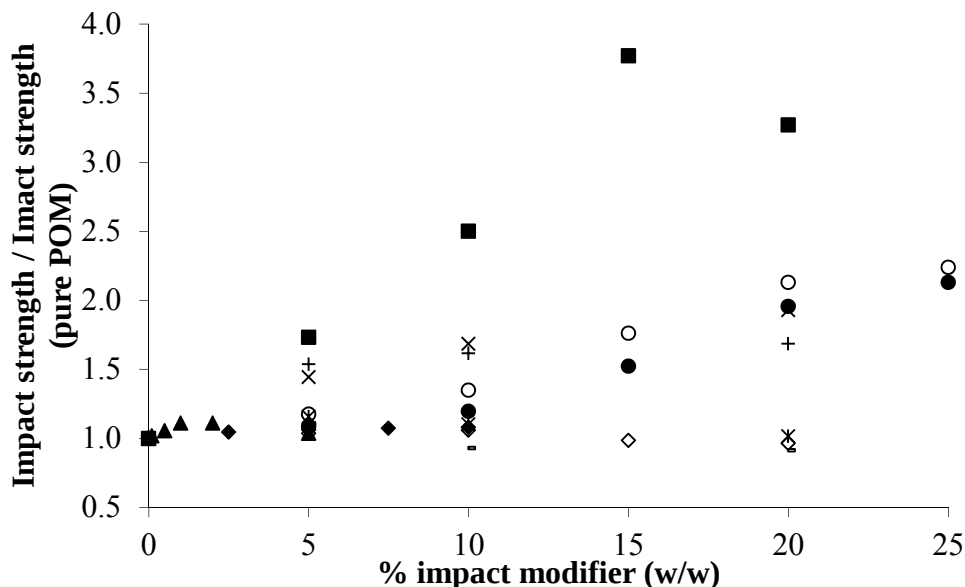
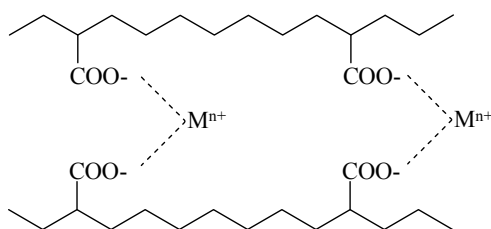


Figure 3.2: Changes of relative impact strength with impact modifier mass fraction: terpolymer of ethylene, metacrylate and acrylic acid (EAAT) (-), EAAT with 25 % of COOH neutralized with zinc acetate (x), EAAT with 50 % of COOH neutralized with zinc acetate (+), EAAT with 100 % of COOH neutralized with zinc acetate (*) [38], Ethylene methacrylic acid (EMA) with 5.35 % m/m Zn (●), EMA with 7.18 % Na (○) [39], Multiwall carbon nanotubes (MWCNT) (▲) [40], thermoplastic polyurethane (PUR) (■) [41], Ethylene Diene Rubber (EPDM) (◆) and EPDM grafted with maleic anhydride (◇) [42].

These results show that the linear relationship proposed by Hashemi et al [43]: $K_{c,POM/filler} = K_{c,POM} \cdot (1 + k \cdot \Phi_{filler})$ seems to be almost verified for a wide range of fillers.

Ionomers such as Na or Zn salts of ethylene-methacrylic acid copolymers are reported to be impact modified of POM and its blends [53]:



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Their reinforcement properties decrease when neutralizing carboxylate groups to form carboxylic acids because of the loss of intermolecular bonds $\text{--COO}^- \cdots \text{M}^{n+} \cdots \text{OOC--}$.

PUR is often mentioned in literature and is a reliable solution for POM toughening [35,41,44]. Mehrabzadeh [44] showed that the toughening was improved when polyurethane was crosslinked instead of linear. In the case of EPDM, a slight improvement was observed when EPDM was grafted with maleic anhydride, which acts as a compatibilizer [56].

Last, the impact strength improvement is counterbalanced by negative effect of impact modifiers on modulus changes (Fig. 3.3).

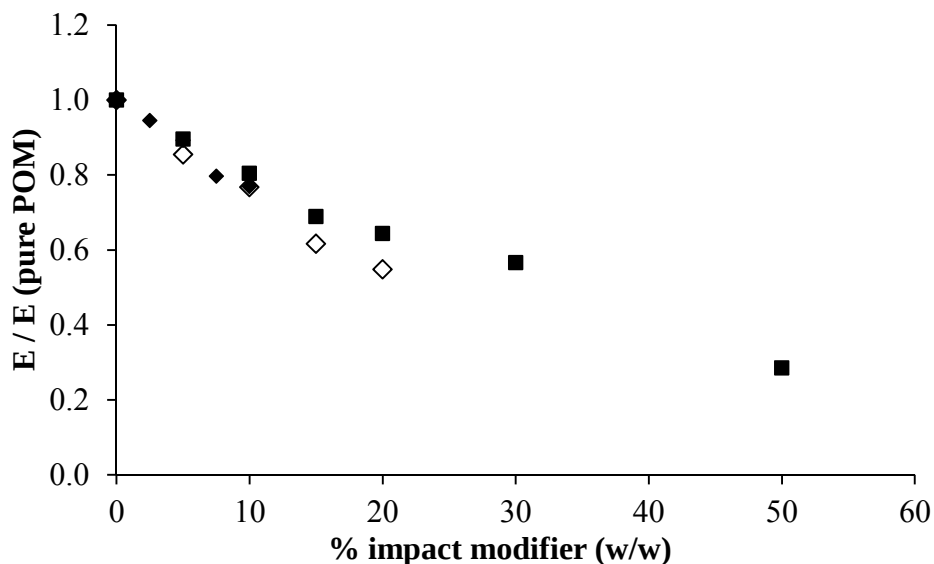


Figure 3.3: Changes of relative Young modulus with impact modifier mass fraction: thermoplastic polyurethane (■) [41], EPDM (◆) and EPDM grafted with maleic anhydride (◇) [42].

3.6. Nucleating agent

3.6.1. Theoretical recall on crystallization of polymers

The crystallization is the consequences of two phenomena: the nucleation and then the crystal growth. Nucleation can be:

- ① spontaneous,
- ② orientation induced,

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③ heterogeneous i.e. occurring at the interface of an extrinsic media on which chains align thus favoring crystallization. This is the case when nucleating agents are added. Let us recall some general features of these compounds:

- they contain both an organic group and a polar group,
- they are well dispersed in the polymer,
- they are insoluble,
- they have a common periodicity with the polymer crystal.

The polymer crystal itself can be thus considered as the ideal nucleating agent. The efficiency of a nucleating agent can be estimated from three distinct characteristics [45]:

① The Avrami constants expressing the progress of isothermal crystallization:

- In isothermal conditions:

$$x_C = 1 - \exp(-k.t^n)$$

The time to reach 50 % crystallization being equal to:

$$t_{1/2} = \left[\frac{\ln 2}{k} \right]^{1/n}$$

- In non-isothermal conditions:

$$x_C = 1 - \exp(-Z_t.t^n)$$

$$\ln Z_C = \frac{\ln Z_t}{\Phi}$$

Z_t being the rate of non-isothermal crystallization and Φ the temperature ramps value and n the Avrami exponent, depending on the mechanism and the geometry of crystal growth.

② The crystallization temperature from molten state (corresponding to peak temperature measured in DSC), which can be exploited to calculate the nucleating efficiency:

$$NE = \frac{T_{C,NA} - T_{C1}}{T_{C2,max} - T_{C1}} \times 100$$

Where:

- $T_{C,NA}$ is the peak temperature for the polymer crystallization in presence of nucleating agent.
- T_{C1} is the peak temperature for the pure polymer crystallization.
- $T_{C2,max}$ is the peak temperature for the self-nucleated polymer crystallization.

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③ The crystalline ratio and the thickness of crystalline lamellae, which is linked to the melting temperature by the Gibbs Thompson equation:

$$x_C = \frac{\Delta H_m}{\Delta H_{m100}}$$

$$l_C = \frac{2\gamma_E}{\Delta H_{m100}} \cdot \left(1 - \frac{T_m}{T_{m100}}\right)^{-1}$$

where :

- γ_E is the surface tension at the lamellae–amorphous phase interface equal to 0.125 J m^{-2} [46].
- ΔH_m and T_m are respectively melting enthalpy and melting temperature of polymer.
- ΔH_{m100} and T_{m100} are respectively melting enthalpy and melting temperature for a fictive 100 % crystalline polymer equal to $380.10^6 \text{ J m}^{-3}$ [46].

3.6.2. Effect of some nucleating agents in POM

Nucleating agents are efficient when polymer has an intermediary crystallization rate that can be easily increased. On the contrary, they are unnecessary if the polymer crystallizes spontaneously very fast (for example HDPE), or extremely slow (for example polycarbonate). It seemed to us interesting to compare the crystallization kinetics of POM with other semi-crystalline thermoplastics (table 3.9):

Table 3.9: Avrami’s parameters and corresponding half time for maximal crystallization of some thermoplastics [47,48,49].

$\Phi \text{ (}^\circ\text{C min}^{-1}\text{)}$	polymer	n	Z_C	Z_t	$t_{1/2} \text{ (min)}$
5	PP	4.8	0.54	0.05	1.75
	PE	2.3	1.44	6.19	0.39
	POM	4.89	0.67	0.14	1.40
10	PP	4.3	0.96	0.67	1.01
	PE	2.2	1.28	11.81	0.28
	POM	4.31	1.06	1.79	0.80

Table 3.9 suggests that the improvement in crystallization rate will not be as striking as it is for example in polypropylene (PP). The effect of several nucleating agents or additives can be appreciated by a short compilation of experimental results comparing the above-presented characteristics for POM and POM with additives (Tables 3.10, 3.11, 3.12 and 3.13).

Table 3.10: Effect of hydroxyapatite (HAP) on POM crystallization from molten state from DSC measurements. T_{onset} = temperature of crystallization start, T_{max} = temperature of maximal energy release, and T_{end} = temperature of end of transition.

	$T_{\text{onset}} (^{\circ}\text{C})$	$T_{\text{max}} (^{\circ}\text{C})$	$T_{\text{end}} (^{\circ}\text{C})$
POM	153.93	148.53	138.17
POM / 0.5%HAP	154.17	149.7	139.23
POM / 1.0%HAP	154.17	148.56	139.03
POM / 2.5%HAP	153.86	151.02	138.04
POM / 5.0%HAP	154.99	153.35	147.32

Table 3.11: Effect of polytetrafluorethylene (PTFE) on Avrami coefficients for non-isothermal crystallization [49].

$\Phi (^{\circ}\text{C min}^{-1})$	POM			POM + PTFE		
	n	Z_t	Z_c	n	Z_t	Z_c
5	4.89	0.13	0.67	3.51	0.12	0.65
10	4.31	1.78	1.06	3.85	1.53	1.04
20	3.95	9.57	1.12	3.3	5.69	1.09
40	3.75	43.85	1.1	3.65	31.84	1.09

Table 3.12: Effect of attapugite, diatomite, MultiWall Carbon NanoTubes (MWCNT) [54], Hexamethylene diamine-Formaldehyde condensate (HF) [50], attapugite and diatomite silicates [51], polyamide 12 (PA) [52] on Avrami coefficients for isothermal crystallization from molten state measured by DSC, *corrected with induction period of crystallization.

T (°C)	material	n	k	t _{1/2} (min)
151	POM	2.98	1.08E-04	18.95
151	POM + attapugite	3.08	1.52E-02	3.46
151	POM + diatomite	3.14	1.33E+00	0.81
152	POM	3.72	3.71E-04	7.71
152	POM + 0.2% PA	4.12	4.62E-04	6.35
152	POM + 0.4% PA	4.17	3.56E-03	3.62
152	POM + 0.6% PA	4.48	1.57E-02	2.39
152	POM	3	7.60E-04	7.9
152	POM + 0.05% HF	4.1	5.30E-03	4.5
152	POM + 0.2% HF	3.3	1.60E-03	4.9
152	POM + 0.5% HF	3.2	1.90E-03	6.20
154	POM	2.58	1.50E-02	8.74 *
154	POM + 0.5% MWCNT	2.33	1.03E+00	6.24 *
154	POM + 2% MWCNT	1.71	1.49E+00	6.18 *
154	POM + 5% MWCNT	1.5	1.54E+00	5.70 *

Table 3.13: Effect of MultiWall Carbon NanoTubes (MWCNT), Montmorillonite, polyvinylidenefluoride (PVDF) and polyamide (PA) on morphology of crystallized POM [54,63,65,66].

Material	T _C (°C)	$-H_C$ (J g ⁻¹)	x _C (%)
POM	142.90		48.3
POM + 0.5%MWCNT	146.10		49.4
POM + 5%MWCNT	147.70		49.4
POM + 5%MWCNT	148.60		48.6
POM	142.01	135.2	
POM + Na-MMT	143.39	125.2	
POM + organ-MMT	143.18	125.7	
POM	142.39	164.9	
POM + PVDF	144.52	131.0	
POM			72.8
POM + 0.2% PA			72.5
POM + 0.4% PA			81.2
POM + 0.6% PA			85.3

These tables call for the following comments:

- As expected considering the crystallization rate of pure polymer, the effect on T_C is generally relatively low compared for example with PP.
- Nucleating agents effect on Avrami's exponent is generally lower than on crystallization kinetic constant, consistently with the fact that they accelerate nucleation.

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- Under the same cooling rate, Z_C is found higher for POM than for POM/PVDF blend. It is indicated that the PVDF hinders the growth of POM crystallite under non-isothermal condition whereas it increases the peak temperatures and decreases crystallization. In other words, PVDF accelerate the nucleation but not the growth of crystalline zone.
- The effect of MWCNT is noticeably different from the other nucleating compounds because they seem to have a significant nucleating effect. Let us mention however that graphitized CNT are on the contrary reported to have no influence on crystallization [53]. The effect of Single wall CNT was shown to be improved in presence of supercritical CO_2 [54].
- Polyamide are both efficient nucleating agents [55] and thermal stabilizers.
- Last, in the case of PUR reinforced POM, those effect are less marked [56].

3.7. Pigments and dyes

The natural POM exhibits a translucent white color. It is colored using granular masterbatch, liquid concentrates and color compounds. Colorants are divided into two categories:

- Dyes, which are soluble.
- Organic and mineral pigments, which are insoluble.

Pigments and dyes are characterized by transparency, heat stability, light fastness, weather fastness, migration (Fig. 3.4) [57]:

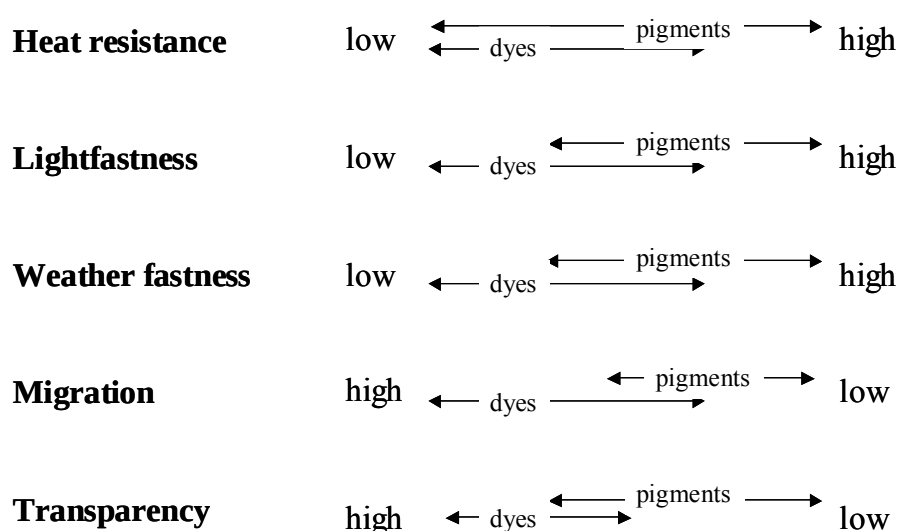


Figure 3.4: A comparison of properties of pigments and dyes.

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They are added to polymers by several ways:

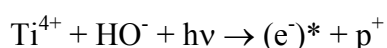
- Powder pigments, produced by chemical industry.
- Pigments granulates, compacted form of pigments.
- Masterbatches being carrier resin of similar chemical structure to the polymer to be colored.
- Liquid or solid concentrates, based on resins of broader compatibility and thus suitable for formulating concentrates for a wide variety of polymers.

In POM color compounds are generally produced by single pigments or broad compatibility monopigments concentrates, although custom color masterbatches are also available.

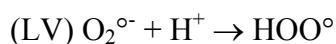
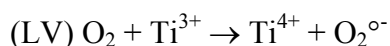
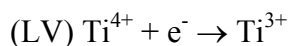
3.7.1. Mineral pigments

Common mineral pigments are TiO₂ anatase, rutile or brookite (white), FeOOH (yellow), Fe₂O₃ (red), Cr₂O₃ (green) CoO, Al₂O₃ (blue) and carbon black. Generally, pigments improve the light and thermal stability of unstabilized polymer [58]. However, their role may be much more complex as illustrated in the two following cases:

① TiO₂ may favor the oxidation of polymer by the so-called photocatalytic effect, of which mechanism is recalled in [59,60]. At TiO₂ surface, in presence of moisture, Ti⁴⁺HO⁻ is formed. At the lowest vacant conduction band:



(e⁻)* moves in the lowest vacancy band. The exciton (e⁻)* and the electronic hole p⁺ will react with the HO⁻ + H⁺ coming from water acidobasic equilibrium.

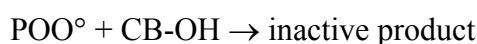


Ti⁴⁺HO⁻ is regenerated after having catalyzed the reaction: H₂O + O₂ → HOO[°] + HO[°], both radicals being highly reactive and able to initiate oxidation in polymer. The surface chemistry

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of TiO₂ influences this phenomenon: it is in particular well known [58,61] that this effect becomes negligible when TiO₂ is coated with Al₂O₃.

② Carbon black, that is a hyperconjugated structure of graphene groups with a surface chemistry depending on its elaboration process with the coexistence of hydroxyl and carbonyl groups. Carbon black may contribute to stabilization by two different ways [62]:

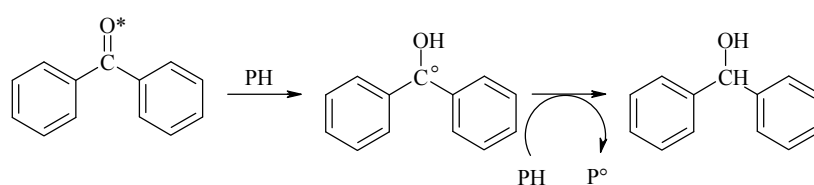
- The reaction between aromatic conjugated aromatic nuclei and radicals [63,64]:



- Hydroxyl and carbonyl groups present at the carbon black surface may adsorb stabilizers molecules [65], thus inhibiting their migration to the polymer superficial layers and subsequent reactions with their ‘targets’ (POO[°], POOH, etc.).

3.7.2. Organic pigments and dyes

Organic pigments display bright colors, lower heat stability. Their resistance to migration must be evaluated also. Some anthraquinone dyes are reported to favor photo-oxidation in the case of polyolefins because of the following photochemically induced process:



The choice of pigments involves a reverse engineering approach for the choice of UV stabilizers, which is the reason why UV absorbers or HALS stabilizers can be added to the masterbatch.

Several organic pigments can become partially soluble in very low concentrations leading to unstable shades. Soluble dyes are not recommended for coloring POM due to their potential to bloom from the polymer matrix. Care must be taken when selecting colorants for POM. When

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browsing pigments datasheets, one sees that pigments thermally and chemically stable in POM are suitable for example in polyolefins but the reverse is not necessarily true.

3.7.3. Conclusion

Despite the relative chemical instability of POM, a substantial number of suitable organic pigments is available and are generally preferred to soluble dyes and inorganic pigments.

For unstabilized polymers, pigments play a stabilizing role in photo-oxidation by increasing the opacity of polymer and also increase the thermal stability. Pigment-polymer-stabilizer interaction is much more complex (stabilizer must protect matrix and pigment without being adsorbed at pigment surface, which depends on pigment crystalline form and flocculating properties [29]) and much comprehensive works remain to be done to understand it better.

Residence time, shear, process temperatures and nozzles and screw parameters (speed, pressure) must also be chosen according to pigment heat stability, and possible color variations due to process induced granulometry changes for pigments.

Last, pigments must play the role of nucleating agents and their influence on shrinkage and dimensional stability must be evaluated for injection molding processed materials.

3.8. Flame retardants

3.8.1. Principles of combustion

The mechanism of combustion can be summarized by figure 3.5.

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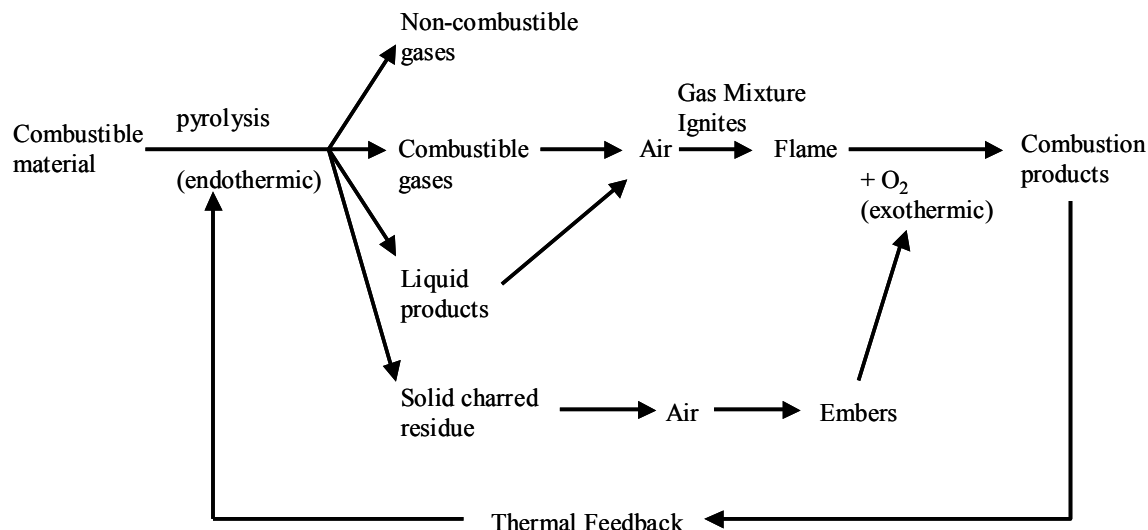


Figure 3.5: The four steps of the combustion process [66].

External heat generates volatile materials. Their combustion in gaseous phase releases heat that is transferred back to the polymer so that combustion goes on. The fire resistance of material is characterized by three sorts of data:

① The limiting oxygen index (LOI) which is the minimal oxygen fraction in N_2/O_2 mixtures for permitting combustion. POM has one of the lowest LOI (ca 15 %) among common polymers (table 3.14), and is hence one of the most difficult to be flame retarded.

Table 3.14: Oxygen Index of several polymers [67,68,69,70].

POM	PP	PS	PET	PA66	PVC	PVDC	PTFE
15.0	17.5	17.8	20.0	24.9	40.3	60.0	95.0

② The UL-94: a sample of specified dimensions is suspended over a surgical cotton. The sample is heated with a Bunsen burner for 10 seconds followed by 10 second after the first test sample flames extinguishes. Five specimens are evaluated. Samples are classified V-0, V-1 or V-2 based on the following criteria (table 3.15):

Table 3.15: Material ranking for UL-94 test.

	V0	V1	V2
afterflame time	< 10 s	< 30 s	< 30 s
sum of afterflame times (for 10 applications)	< 50 s	< 250 s	< 250 s
ignition of cotton by burning drips	no	no	yes
persistence of flame after 2d ignition	< 30 s	< 60 s	< 60 s

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 POM is generally not ranked which means that it behaves worse than V2 materials.

③ The results of a cone calorimetry measurement used to evaluate the flammability of samples under an external heat flux of 35 kW.m^{-2} , with specimen dimension of $100 \text{ mm} \times 100 \text{ mm} \times 3 \text{ mm}$ according to ISO 5660-1 standard. A typical curve is shown in Fig. 3.6.

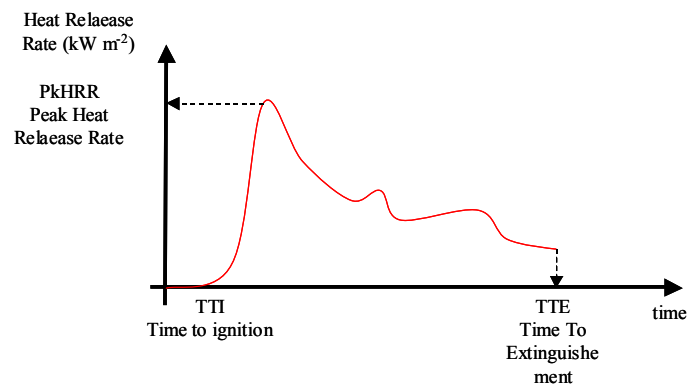


Figure 3.6: Heat release rate versus time for material combustion during cone calorimetry test.

The measured parameters of combustion performance include:

- time to ignition (TTI),
- time to extinguishment (TTE),
- peak heat release rate (PkHRR),
- average heat release rate (AvHRR),
- fire hazard risk index (the ratio of PkHRR to TTI, PkHRR/TTI),
- peak mass loss rate (PkMLR),
- total heat release (THR).

3.8.2. Strategies for improving flame resistance

Improving fire resistance of polymers can be achieved by:

① Decreasing temperature in the polymer using mineral fillers such as $\text{Al}(\text{OH})_3$. Its decomposition: $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ is endothermic and contributes to decrease the temperature in the burning zone [71].

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② Production of inert diluent gases: for example by the release of water (for example from $\text{Al}(\text{OH})_3$) or carbon dioxide, flame extinction will occur [71].

③ Creating a layer blocking the volatile transfer from polymer to the gaseous phase and acting as a barrier: intumescence additives or MMT nanocomposites [72].

④ Trapping radicals by halogen atoms using decabromodiphenylether or antimony trioxide (Sb_2O_3). Halogen flame-retardants are widely used for various polymers, but generally accelerate the decomposition of POM due to the catalytic action of the halide groups [73].

3.8.3. Examples of flame-retardants in POM

The effect of several combinations of flame-retardants on LOI, cone calorimeter tests and UL94 one are illustrated by tables 3.16, 3.17 and 3.18.

Table 3.16: Effect of aluminum trihydrate (ATH), Melamine (ME), Novolac, red phosphorus (Red Ph), ammonium polyphosphate (APP), melamine cyanurate (MC) and dipentaerythritol on LOI of POM based materials (*: [74], **: [75], ***: [76]).

POM	ATH	ME	Novolac	Red Ph	APP	MC	dipentaerythritol	LOI (%)	ref
100	0	0	0					< 16	*, **, ***
90				10				15.1	***
95		5						15.4	***
90			10					15.6	***
85		5	10					17.6	***
80			10	10				22.7	***
85			5	10				27.8	***
68					24	8		28.6	**
45	55	0	0					31	*
45	40	0	15					34	*
80		5	10	5				34.2	***
56					33	11		34.7	**
56			4		24	12	4	37.1	**
45	45	0	10					37.5	*
75		5	10	10				37.5	***
56			8		27	9		40.5	**
45	40	7.5	7.5					43	*
45	40	15	0					44	*
45	45	10	0					44.5	*
45	50	5	0					45.5	*
45	50	0	5					46	*
56			4		27	9	4	52.8	**

Table 3.17: Effect of ATH, Melamine, APP and Novolac on flame resistance measured by cone calorimetry (*: [74], **: [77]).

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POM	ATH	APP	ME	Novolac	TTI (s)	TTE (s)	THR (MJ m ⁻³)	PHRR (kW m ⁻²)	t _{HRR} (s)	Average HRR (kW m ⁻²)	ref
100					66	298	63.2	268.8	230	175.3	*
45	40		7.5	7.5	74		35.6	133	95	61.9	*
60		25	7	8	40	443		153.7		56.9	**

Table 3.18: UL Vertical Burning results of the flame retardant POM based materials (*: [91], **: [71], ***: [74]).

POM	Mg(OH) ₂	Al(OH) ₃	APP	ME	Novolac	TPP	UL94 level (3.2 mm)	ref
100							non rated	*
45	37			15		3	V2	**
45		45		5	5		V1	***
45		40		5	10		V1	***
45		40		7.5	7.5		V1	***
45		40		10	5		V1	***
60		40	25	7	8		V0	*
12	47				5	3	V0	**
45	35			15	5		V0	**
45	33			15	5	2	V0	**

Despite its intrinsic instability, POM can reach a satisfying level of flame resistance.

The role of Al(OH)₃ and Mg(OH)₂ was described in the ‘3.8.2. Strategies for improving flame resistance’. Novolac resin and ME could be explained by:

- The carbonized products of novolac resin could conglomerate the Al₂O₃ particles to form more continuous and consolidated char layers.
- Endothermic sublimation and decomposition of ME could further decrease the temperature of the burning zone.
- The produced gases from ME could effectively dilute oxygen and fuel gases.

Apart the case of red phosphorus, significant improve in flame resistance is obtained with a high amount of additive (50 % m/m Al(OH)₃ or Mg(OH)₂). It can provoke severe loss of mechanical properties: for example the notched Charpy impact of POM drops from 6.9 kJ.m⁻² to 2.2 kJ.m⁻² in the case of 45 % POM + 40 % ATH + 10 % ME + 5 % Novolac. Last, some of these additives may induce a decrease in thermal stability [75].

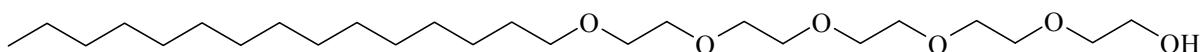
3.9. Antistatic agents

Plastics combine high electrical resistivity and low dielectric constant. They readily undergo charge build-up (static electricity) causing dust pick-up, handling problems, and/or electrical discharges giving electrical shocks. These problems can be solved using [78]:

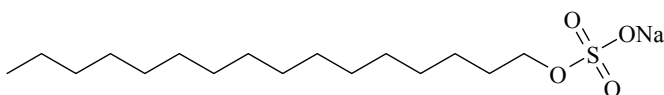
① External antistatic additives, coating polymer by spraying or immersion.

② Internal antistatic additives, incorporated into the polymer matrix and working as lubricants (see section ‘3.10. Lubricating agents’) reducing the friction induced static charge generation and migrating to the polymer surface with the generation of a thin water layer at the surface of polymer forming thus a conductive path. Some examples of internal antistatic agents are given below:

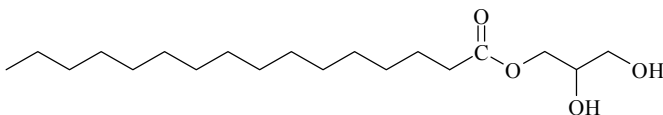
- Copolymers of ethylene oxide having certainly a structure close to ethoxylated alcohols:



- Sodium sec-alkane sulfonate:



- Molecular distilled high-mono carboxylate glyceride:



③ Conductive fillers such as carbon black, carbon fiber, carbon nanotubes or stainless steel fiber masterbatch.

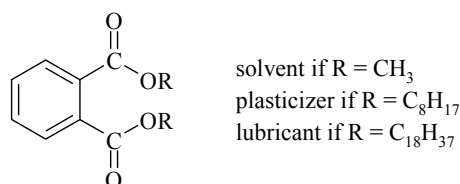
Antistatic additives are generally added to polymer matrix using a concentrated masterbatch permitting to attain a final mass fraction ca. 0.1% to 1 %.

3.10. Lubricating agents

Lubricants are used for decreasing viscosity at molten state and making processing easier at lower temperature. Two sorts of molecules with lubricating properties exist, depending on their compatibility (solubility) with polymer [79]:

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① Internal lubricants are soluble with the polymer melt and act as sort of plasticizers. The difference between plasticizers, and lubricants is illustrated in the case of phthalates in polyvinylchloride (PVC):



② External lubricants are on the contrary not compatible with molten polymer and form a film at the metallic surface of process tool-polymer interface.

For example, paraffin waxes are external lubricants for PVC and internal one for polyethylene (PE). A difference in the viscosity profile between internal and external lubricants is illustrated figure 3.7.

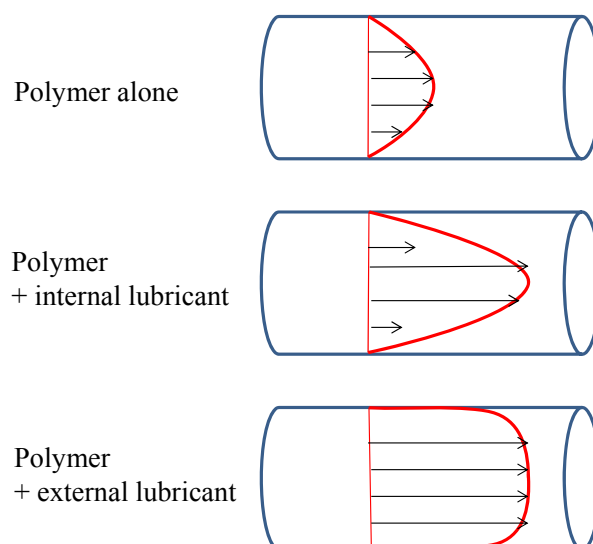


Figure 3.7: Difference in viscosity profile during processing for polymer, polymer with internal or external lubricant.

POM is processed mainly by injection molding. Its chemical reactivity makes it sensitive to acidic formulation constituent which restricts the use of carboxylic acids. Because of the high processing and service temperatures involved, suitable additives have to display good thermal stability and low volatility.

Montan waxes provide good release and flow properties, adequate compatibility, high thermal stability and good migration resistance. However, their use is limited by excessive loud cloud

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points or by intrinsic color which is not pure white. Micronized waxes [80], and synergistic blends of organic fatty amides, esters and glycerides [81] are met in technical literature.

The use of filler induces also a significant increase in viscosity in the molten state. The ratio of the viscosity of a suspension of spherical particles (η) to the viscosity of the pure liquid medium (η_0) is expressed using Einstein’s equation [82]:

$$\eta = \eta_0.(1 + k.\Phi)$$

Φ being the volume fraction of suspended particles. k is equal to 2.5 for incompressible spherical particles. Other models are reviewed by Hanemann and co-workers [83]. A term relative to filler-filler interaction is generally added, for example in Thomas model:

$$\eta = \eta_0.(1 + 2.5.\Phi + 10.05.\Phi^2 + P_1.\exp(P_2.\Phi))$$

The use of dispersants permits to decrease the filler-filler interaction and thus to reduce significantly the viscosity of the filled polymer melt and to ease the processing [84].

3.11. Fillers

Some general properties of common fillers are recalled in Appendix 2. Their effect on some engineering properties will be illustrated below.

3.11.1. Effect of fillers on thermal properties

3.11.1.1. Durability of materials submitted to thermal cycling

One of the key issues is the fiber-matrix decohesion for a material submitted to thermal cycling. A reasoning was proposed by Hancox [85]:

$$\sigma_L = -\frac{(\alpha_H - \alpha_L).\Delta T.E_L.V_H}{V_L \left[\frac{E_L}{E_H} - 1 \right] + 1}$$

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L subscript corresponds to filler and H to matrix. If $E_L \gg E_H$, and typically, $V_L = 1 - V_H \sim 0.5$:

$$\sigma_L = -(\alpha_H - \alpha_L) \cdot \Delta T \cdot E_H = -\sigma_H$$

In other words, fillers must fulfil the condition: $\sigma_H < \sigma_R$, σ_R being the POM stress at break.

3.11.1.2. Changes in transport and storage properties

Commonly used polymer materials are good electrical and thermal insulators. Recent applications of polymers as heat sinks in electronic packaging require new composites with relatively high thermal conductivity. Knowledge of heat transfer in polymer is also necessary for process simulation leading to improved processing equipment, materials design and reduced cycle times, elimination of hot spots causing material degradation, or excessive temperature gradients leading to internal stresses. We will here focus on two properties characterizing the thermal behavior of polymer:

- the specific heat capacity:
$$c_p = \frac{\partial}{\partial m} \left[\frac{\partial H}{\partial T} \right]_p \sim 1375 \text{ J.kg}^{-1} \cdot \text{K}^{-1} \text{ for POM}$$

- the thermal conductivity:
$$j_x = \frac{1}{A} \cdot \frac{dH}{dt} = -\lambda \cdot \frac{dT}{dx} \sim 0.35\text{-}0.39 \text{ W.m}^{-1} \cdot \text{K}^{-1} \text{ for POM}$$

- from which one can calculate the thermal diffusivity:

$$D_{th} = \frac{\lambda}{\rho \cdot c_p} \sim 1.8 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1} \text{ for POM}$$

Some examples of thermal conductivity or heat capacity changes with volume fraction of fillers like copper (Cu), cellulose fibers, graphite, carbon nanotubes (MWCNT) and polyethyleneglycol (PEG) are shown in figure 3.8.

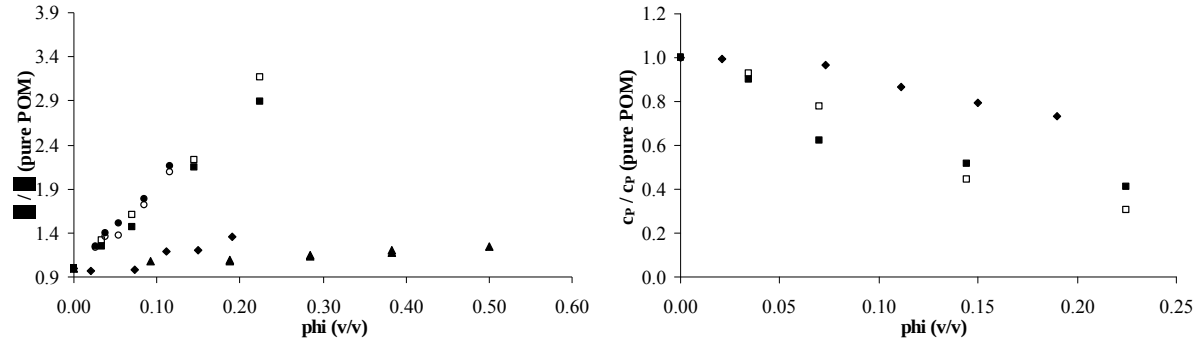


Figure 3.8: Relative changes in heat conductivity and heat capacity for POM + Cu (◆) [86], POM + cellulose fiber (▲) [87], nano and colloidal graphite (■), polyoxymethylene/graphite composites (□) [88], polyoxymethylene/carbon nanotubes compatilized with 10 % (●) and 15 % (○) PEG [89].

Graphite and MWCNT improve significantly thermal conductivity, having also the advantage of limit the mass increase compared for example to copper. All investigated additives involve a decrease in heat capacity, and in other word an increase in heat diffusion coefficient.

Several models are aimed at predicting the conductivity of a composite. Most of them were recently reviewed by [90]. One can propose models for serial or parallel elements:

$$\lambda_c = \lambda_m \cdot (1 - \phi_f) + \lambda_f \cdot \phi_f$$

$$\frac{1}{\lambda_c} = \frac{(1 - \phi_f)}{\lambda_m} + \frac{\phi_f}{\lambda_f}$$

where λ_c , λ_m and λ_f are respectively the thermal conductivity of composite, matrix and filler.

Other models exist [91,92] but it seems that these two models fit relatively well in coarse grain studies. The most refined equations versions are aimed at describing effect of filler geometry, as for example Hatta Taya model in the case of spherical inclusions [93]:

$$\frac{\lambda_c}{\lambda_m} = 1 + \frac{\phi_f}{\frac{1 - \phi_f}{3} + \frac{\lambda_m}{\lambda_f - \lambda_m}}$$

Practitioners also use the Agari's model [94]:

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$$\log \lambda_c = \Phi_f.C_2. \log \lambda_f + (1 - \Phi_f).\log(\lambda_m.C_1)$$

where C_1 is a factor related to the polymer microstructure and C_2 a factor related to the ease of filler percolation (table 3.19).

Table 3.19: Agari’s coefficient for POM grafted with MWCNT [89] and graphite [95].

	C1	C2
POM/MWCNT-g-PEG-10	1.045	0.928
POM/MWCNT-g-PEG-15	1.028	0.880
POM/colloidal graphite	1.120	0.666
POM/nanographite	1.040	0.655

The effect of drawing was in particular illustrated by Zhao et al. [88] in the case of POM/MWCNT: orientation induces a higher gain in thermal conductivity.

3.11.2. Effect of fillers on mechanical properties

3.11.2.1. On Young’s modulus and stress at break

Let us first mention that fillers will improves mechanical strength (Young’s modulus and yield stress) because of mixing laws, which will be detailed below. They may also favor the crystallization by an interfacial phenomenon was recently reviewed [96].

The elastic modulus of composite materials reinforced by discontinuous cylindrical fibers or lamellar shapes is expressed by the Halpin-Tsai equations [97]:

$$E = E_m \cdot \left[\frac{1 + \xi \eta \Phi}{1 - \eta \Phi} \right]$$

where:

- ξ is a measure of reinforcement geometry, which depends on loading conditions.

- And: $\eta = \frac{E_f / E_m - 1}{E_f / E_m + \xi}$

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Hashemi [43] used the following derived relationships in the case of tensile and flexural stress and modulus from POM filled with beads and fibers:

$$E_{\text{POM/filler}} = E_{\text{POM}} \cdot (1 + k_1 \cdot \Phi_{\text{filler}})$$

$$\sigma_{\text{POM/filler}} = \sigma_{\text{POM}} \cdot (1 + k_2 \cdot \Phi_{\text{filler}})$$

In the following, we will consider rather mass fraction, which is an engineering measure, instead of volume fraction. An example of curves for mechanical properties changes with filler content is shown in figure 3.9.

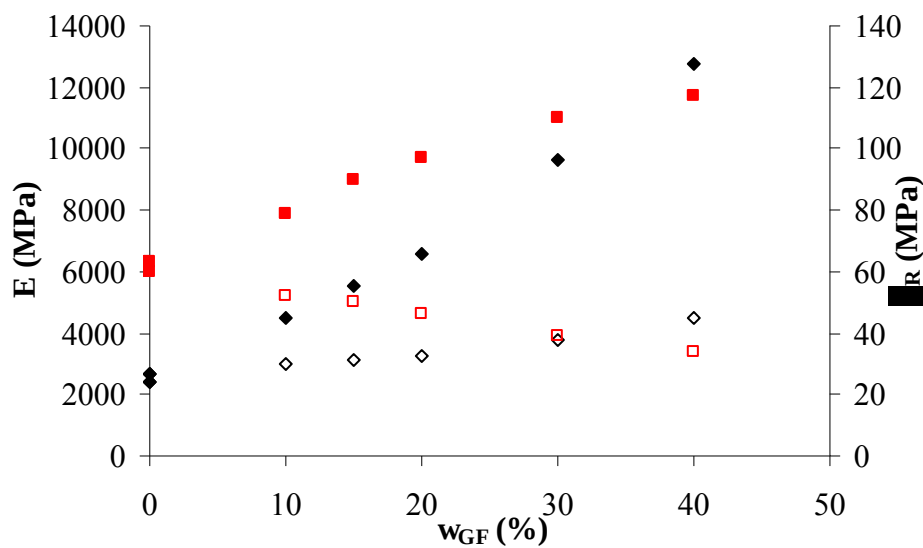


Figure 9. Young' modulus (◇,◆) and stress at break (■,□) for POM reinforced with glass beads (open symbols) and glass fibers (closed symbols) [98].

Literature illustrates the changes of Young's modulus with MWCNT ($k \sim 30$) [40], glass fibers ($k \sim 10$), cellulose ($k \sim 4$) [99], glass beads ($k \sim 2.5$) [57], ZnO ($k \sim 2$) [100], carbon fibers ($k \sim 1.5$) [101], and organoclays ($k \sim 0.5$) [102].

The compiled results call for the following comments:

- Bashtanik et al [103] illustrated the effect of organosilicon finishes on POM + cellulose fibers properties, showing an optimal mass fraction of finishes ca 1% (for a fiber mass fraction of 20 %).
- Adding low amount of SiO₂ can improve the properties of POM + 20 % carbon fibers, but an optimum is reached at ca 3 % for impact resistance.

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- Certain fillers have a negative impact on tensile properties, such as TiO₂ even at low mass percentage [100]. This effect seems particularly marked when decreasing particles size. Some fillers such as PUR having a positive effect on impact strength but decrease Young’s modulus and creep resistance as well [104].

- Stress at break values for POM filled with micro or nano-Cu particles or ZnO do not fit the above proposed relationships [105]. In the case of organoclays for example, the existence of an optimal filler mass fraction preceding a decrease in stress at break is shown [102].

3.11.2.2. On elongation at break

The effect of fillers on elongation at break is relatively complex to describe: curves displaying a maximum are generally observed in the case of MWCNT [40] or organoclays [102].

3.11.3. Effect of fillers on electrical properties

Electrical conductivity is defined by:

$$\sigma = \frac{1}{\rho} = \frac{1}{S \times R}$$

In the case of samples filled with additives improving the electrical properties, conductivity changes with filler content are illustrated in figure 3.10.

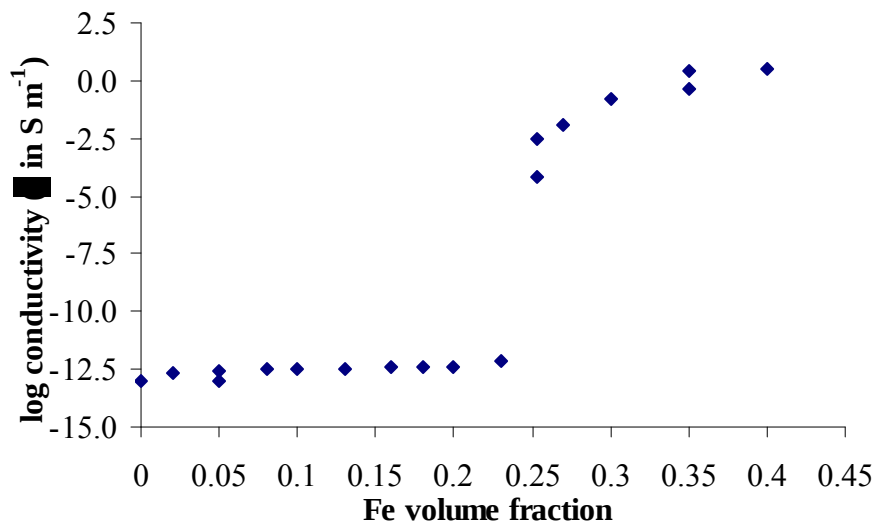


Figure 3.10: Typical conductivity changes with iron (Fe) volume fraction.

Curves have generally the following shape:

- At relatively low filler content, the electrical properties remain almost constant and very close to the ones of pure polymer.
- A percolation threshold is expected and corresponds to a sudden increase in electrical conductivity. The jump in electrical properties would correspond to the formation of the filler network in the polymer and in other words to a jump in rheological properties as well. A short literature review indicate that $\sigma_C \sim q \cdot \sigma_P$, with σ_P being the pure polymer conductivity, σ_C the conductivity at the saturation threshold and $q \sim 2-10$.
- Above the percolation threshold, conductivity increase with a negative curvature and plateaus at high filler content.

According to [106], the following equation can be ascribed:

$$\sigma = \sigma_C + (\sigma_M - \sigma_C) \cdot \left(\frac{\phi - \phi_C}{F - \phi_C} \right)^t$$

where:

- ϕ_C = percolation threshold
- σ_M is the maximal conductivity
- σ_C is the conductivity value at the percolation threshold
- F is the packing factor corresponding to filler volume fraction at the beginning of the plateau.

We have thus analyzed available experimental results for determining ϕ_C , σ_M , σ_C and F characterizing the filler performances in electrical properties improvement (table 3.20).

Table 3.20: Parameters of percolation law for electrical conductivity changes of POM with several additives (Fe [106], MWCNT [107,108]) σ_M and σ_C in $S \cdot m^{-1}$, Φ_C and Φ in volume fractions.

filler	Φ_C	σ_C	σ_M	F	t
CNT1	0,004	$2 \cdot 10^{-12}$	2,75	0,113	4,6
CNT2	0,004	$2 \cdot 10^{-12}$	2,4	0,05	3,76
Fe	0,24	$8 \cdot 10^{-13}$	6	0,113	3

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Fe permits the best improvement of electrical properties but with a high volume ratio (i.e. a significant increase in mass) whereas CNT significantly increase electrical properties at a low mass fraction (ca 1 %). However, they also induce a decrease in thermal stability [108].

3.11.2.4. Effect of fillers on tribological properties

Friction coefficient is the ratio of the tangential and normal force for a polymer sliding on a surface. One distinguishes:

- static friction coefficient, linked to the maximal force for permitting the motion.
- kinetic friction coefficient is linked to the average force during sliding.

The wear volume is defined as the volume of polymer which is removed when submitted to a material sliding on its surface:

$$V = k.F.L$$

Where:

- V is the wear volume.
- F is the normal load imposed to the sliding material
- L is the length of slide

Typical data are shown in table 3.21.

Table 3.21: Changes in friction and abrasion coefficient of POM with several additives - graphite (C), polyethyleneoxide (PEO) (*: [109], **: [110], ***: [111]).

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Material	μ	$k (10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1})$	Conditions	ref
POM	0.69	1.3	62.5 N - 0.3 m s ⁻¹	*
POM + 15% PTFE	0.24	0.6		
POM + 15% PTFE + 20% C	0.36	2.3		
POM + 15% PTFE + 20% glass	0.33	6.7		
POM	0.36	50	10 N - 0.1 m s ⁻¹ AISI-52100 hardened steel	**
POM + 20% glass fibers	0.35	40		
POM + 20% PTFE fibers	0.2	10		
POM + 20% PTFE micro powder	0.29	15		
POM	0.17	1.8	196 N - 0.4 m s ⁻¹	***
POM + 5% PTFE	0.165	1.5		
POM + 10% PTFE	0.14	1.3		
POM + 15% PTFE	0.13	1.25		
POM + 20% PTFE	0.12	1.2		
POM + 10% PEO	0.14	2.1		
POM + 15% PEO	0.145	2.25		

PTFE decreases friction coefficient and abrasion constant [112,113], despite some negative effects on mechanical properties. This can be improved if sodium etched PTFE is added to the mixture POM/PTFE, because sodium etching works as a compatibilization treatment [114].

Al₂O₃ [115] increases both friction coefficient and wear volume. MoS₂ was shown to be poorly effective even if a slight decrease in friction coefficient was observed when using nanoballs instead of microballs [116]. A combination of aromatic vinyl modified polyethylene and fatty acid ester can also be used for POM improving sliding performances [117]. On the contrary, cellulosic carbon fibers increase friction coefficient and wear volume [117].

3.11.2.5. On gas permeability

Fillers are expected to improve barrier properties of POM by two distinct ways:

① It was already shown (see ‘3.6. Nucleating agent’) that fillers help nucleation in POM. It is well known that gas is not soluble in it. Compañ [118] reported for example that if:

- $D^*(T)$ is the diffusion coefficient in a 100 % amorphous polymer,
- $D(x_{\text{am}}, T)$ is the diffusion coefficient in a semi-crystalline polymer (of crystallinity x_C)

One has:

$$\frac{D^*(T)}{D(x_{\text{am}}, T)} = \exp\left(-\frac{\Delta G_{\text{am}}^{++} - \Delta G^{++}}{RT}\right) = \exp\left(-\frac{\Delta G_{\text{am}}^{++}}{RT} \cdot x_C\right)$$

According to Compañ, this equation is consistent with Michael and Bixler [119] theory:

$$\frac{D^*(T)}{D(x_{am}, T)} = \beta \cdot \tau$$

Where :

- β is the factor expressing immobilization of amorphous phase by crystalline one

$$\beta = \exp\left(-\frac{\Delta H_{am}^{++} - \Delta H^{++}}{RT}\right)$$

- τ is the tortuosity linked to the presence of barriers blocking diffusion of gas molecules

$$\tau = \exp\left(\frac{\Delta S_{am}^{++} - \Delta S^{++}}{R}\right)$$

and [120,121]: $\ln \tau = -n \cdot \ln(1 - x_c)$

② Furthermore, clay nanoparticles induce a decrease in diffusion coefficient in amorphous phase of polymer by increasing the tortuosity i.e. working as barriers blocking the gas diffusion in amorphous phase, as observed for example by Gutierrez et al. [122] for PE.

The effect of some nanofillers on POM permeability to gas is illustrated in table 3.22.

Table 3.22: O₂ permability in bentonite filled POM [123].

	O ₂ permeability (cm ³ mm m ⁻² day ⁻¹ bar ⁻¹)	
POM	0.65	0.22
POM + NF5	0.44	0.06
POM + NF9	0.33	0.05
POM + KT	0.3	0.02

3.12. Processing aids

Polymer Process Aids (PPA) are specifically designed to enhance extrusion ability of plastics leading to productivity and / or quality improvement as for example:

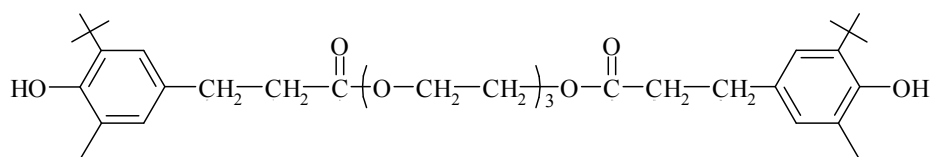
- Reduces / eliminates melt fracture.
- Eliminate sharkskin effect.

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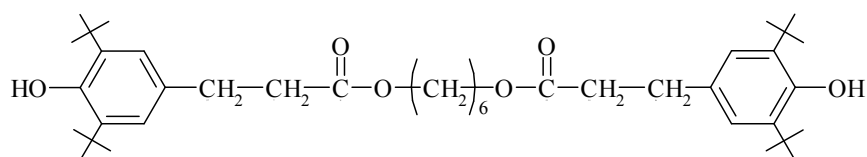
- Reduce or eliminate Gels and optical defects.
- Increase the output by up to 20 %.
- Reduce electricity consumption due to reduced back-pressure in the extruder.

Their role is not too far from the one of lubricants (see ‘3.10. Lubricants’). In fact, lubricants can be considered as processing aids, but some processing aids (for easing demoulding for example) are not lubricants. They are used as masterbatches formulated to form a microscopic dispersed phase within the polymer carrier.

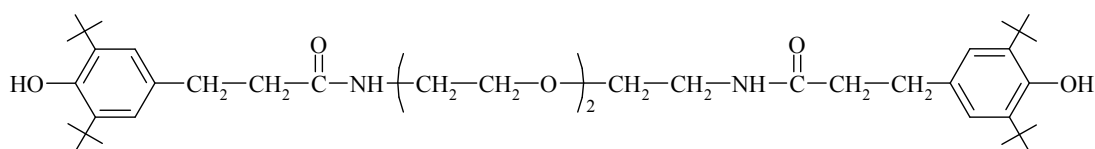
Silicones and silicone oil [124,125,126], acrylate copolymer [127], fluoroelastomer (Tecnoflon® NM FKM) or fluorinated thermoplastics (PVDF such as Solef® 11010) are evoked as possible processing aids for POM. During processing, these fluoropolymers coat the walls of the extruder and die, thus reducing the extruder backpressure to decrease.



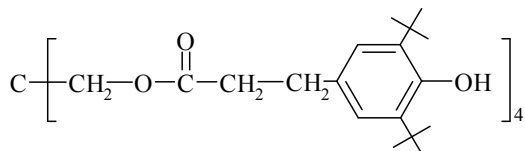
AO1: triethylene glycol-bis-3-(3-tertbutyl-4-hydroxy-5-methyl phenyl)propionate



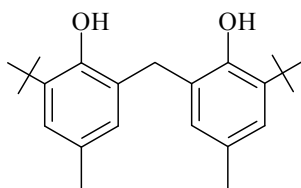
AO2: 1,6-hexamethylenebis-3-(3,5-ditertbutyl-4-hydroxyphenyl)-propionate



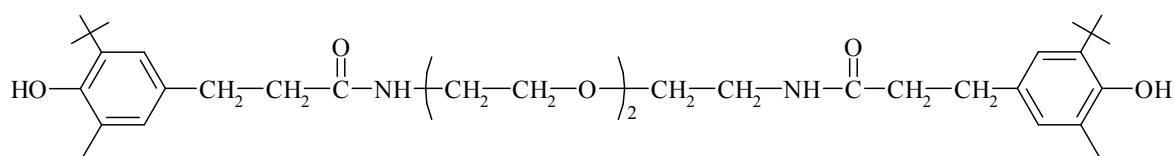
AO3: 1,6-hexamethylenebis-3-(3,5-ditertbutyl-4-hydroxyphenyl)-propionamide



AO4: pentaerythrityl-tetrakis-3-(3,5-ditertbutyl-4-hydroxyphenyl)-propionate

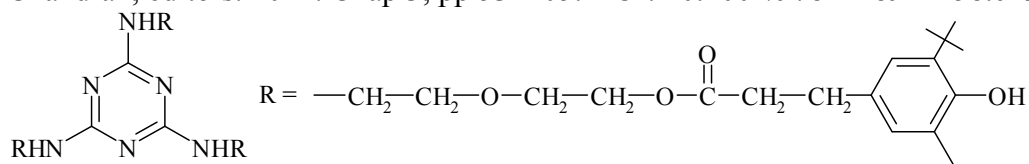


AO5: 2,2-methylene-bis-(4-methyl-6 tertbutyl phenol)

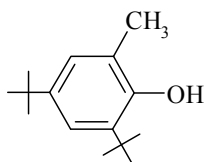


AO6: N,N'-triethylenedioxy-bis(3-tert-butyl-4-hydroxy-5methylhydroxycinnamide)

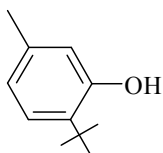
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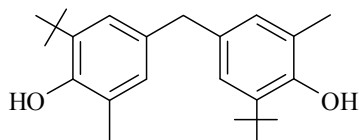
AO7: N,N',N''-tris[(3-tert-butyl-4-hydroxy-5-methylphenyl)-propionate-3-oxa-pentyl]melamine



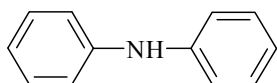
AO8. 2,4-di-tertbutyl phenol



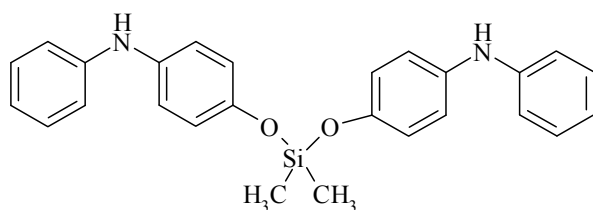
AO9. 6 tertbutyl-m-cresol



AO10. 4,4'-methylene-bis-(2-methyl-6-tert butyl-phenol)



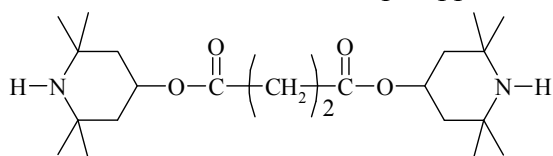
AO 11. diphenylamine



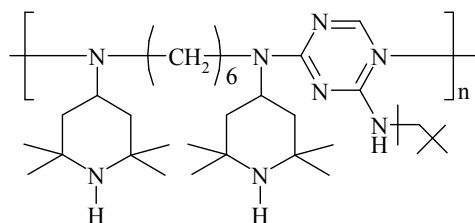
AO 12. dimethyldi-(phenylaminophenoxy)silane



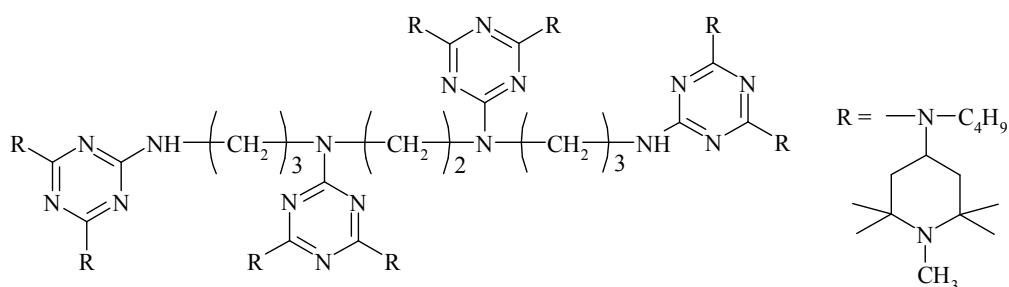
E Richaud . Polyoxymethylene Additives. In: “Polyoxymethylene Handbook: Structure, Properties, Applications and Their Nanocomposites”. Sigrid Lüftl, Visakh P.M., Sarath Chandran, editors. 2014. Chap 3, pp 53–105. DOI: 10.1002/9781118914458.ch3



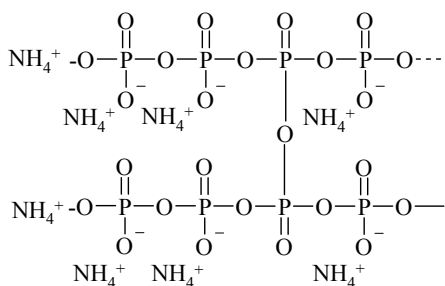
HALS 3



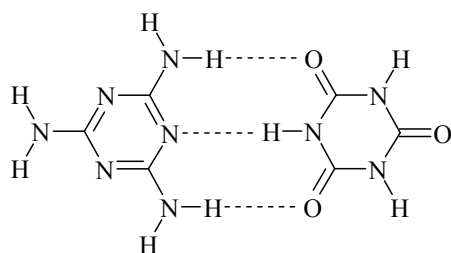
HALS 4.



HALS 5.

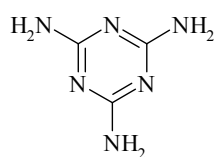


ammonium polyphosphate (APP)

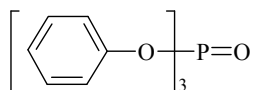


melamine cyanurate (MC)

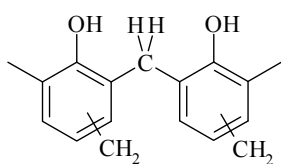
E Richaud . Polyoxymethylene Additives. In: “Polyoxymethylene Handbook: Structure, Properties, Applications and Their Nanocomposites”. Sigrid Lüftl, Visakh P.M., Sarath Chandran, editors. 2014. Chap 3, pp 53–105. DOI: 10.1002/9781118914458.ch3



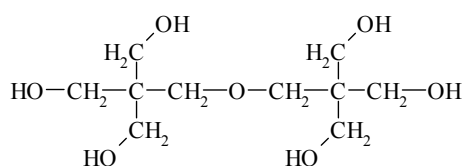
Melamine



Triphenylphosphate



Novolac



Pentaerythritol

E Richaud . Polyoxymethylene Additives. In: “Polyoxymethylene Handbook: Structure, Properties, Applications and Their Nanocomposites”. Sigrid Lüftl, Visakh P.M., Sarath Chandran, editors. 2014. Chap 3, pp 53–105. DOI: 10.1002/9781118914458.ch3
Appendix 2: Properties of some common fillers [128,129].

	filler	density	modulus (GPa)	thermal conductivity (W m ⁻¹ K ⁻¹)	specific heat capacity (J kg ⁻¹ K ⁻¹)	thermal expansion (K ⁻¹)	resistivity (Ω cm)
cubic and spheroidal fillers	CaCO ₃	2.7	35	2.5	866.5	10 ⁻⁵	10 ¹⁰
	Dolomite	2.87	35	2.7	840	10 ⁻⁵	5.10 ⁹
	MgCO ₃	3	35	2.2	820	10 ⁻⁵	5.10 ⁹
	BaSO ₄	4 - 4.5	30	2.5	460	10 ⁻⁵	-
	Glass beads	2.3	60	0.7	1130	8.6.10 ⁻⁶	10 ¹² - 10 ¹⁶
	SiO ₂	2.2	-	0.015	794	5.10 ⁻⁷	10 ¹³
	Al(OH) ₃	2.6	30	2.9	878	6.5.10 ⁻⁶	10 ¹⁰
	Carbon Black	1.7 - 1.9	-	2.5	866	5-11.10 ⁻⁵	10 ⁻¹ - 10 ²
	Wood Flour	0.4 - 1.35	10	0.25	1750	5.10 ⁻⁵	-
platy fillers	Talc	2.75	20	2.1	869.4	8.10 ⁻⁶	8.10 ⁻⁶
	Mica	2.75 - 3.2	17.2	2.5	878	2.5.10 ⁻⁵	2.5.10 ⁻⁵
	Kaolin - Clays	2.5 - 2.6	20-200	1.96-2.1	936-920	3.10 ⁻⁶ - 4.5.10 ⁻⁴	8.10 ⁻⁶ - 4.5.10 ⁻⁶
	Graphite	2 - 2.25	-	200	-	-	800 - 2500
acicular and fibrous fillers	Wollastonite	2.8 - 2.9	30	2.51	1003	6.5.10 ⁻⁶	-
				Glass fibers			
	A glass	2.46	74	0.7	1130	8.5.10 ⁻⁶	10 ¹² - 10 ¹⁶
	E glass	2.59	73	0.7	1130	5.10 ⁻⁶	10 ¹⁰ - 10 ¹⁷
	S glass	2.48	85.5	0.7	1130	5.9.10 ⁻⁶	10 ¹⁰ - 10 ¹⁶
				Aramid fibers			
	Low Modulus	1.45	80	0.05	1420	(-3.5).10 ⁻⁶	-
	High Modulus	1.45	120	0.05	1420	(-3.5).10 ⁻⁶	-
	UltraHigh Modulus	1.47	180	0.05	1420	(-3.5).10 ⁻⁶	-
				Carbon fibers			
	Low Modulus	1.78	240	17	710	-0.1	1.5.10 ⁻³
	Intermediate Modulus	1.76 - 1.80	325	17	710	-0.1	1.5.10 ⁻³
	High Modulus	1.79 - 1.90	400	17	710	-0.5	0.9.10 ⁻³
	UltraHigh Modulus	1.90 - 2.0	450	17	-	-	-

E Richaud . Polyoxymethylene Additives. In: “Polyoxymethylene Handbook: Structure, Properties, Applications and Their Nanocomposites”. Sigrid Lüftl, Visakh P.M., Sarath Chandran, editors. 2014. Chap 3, pp 53–105. DOI: 10.1002/9781118914458.ch3

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