



Additive blooming in polymer materials: Consequences in the pharmaceutical and medical field



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ABSTRACT

This article presents a comprehensive review of scientific literature concerning the blooming of additives on the surface of polymers, a phenomenon that depends on the solubility of an additive in a polymer and occurs in a time that depends on the diffusion coefficient of the additive in the polymer. Blooming is an important phenomenon as its occurrence can modify the material properties and lower its resistance to degradation. We report the parameters that influence the occurrence of blooming such as temperature, polymer morphology, additive shape and size. We also highlight the main fields in which the blooming was studied, the consequences of blooming on the material properties and the various characterization methods that are able to analyze the blooming phenomenon *in situ*. We focused next on the biomedical field, as blooming of additives on the surface of medical devices, especially those that are implanted or in contact with body fluids, can impact the device biocompatibility and represent a risk for the patient.

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Contents

1. Introduction	239
2. Physico-chemistry and evaluation of blooming	240
2.1. Species involved in blooming phenomenon	240
2.2. Mechanism of blooming: thermodynamic and kinetic factors	240
2.3. Parameters influencing the blooming	241
2.3.1. Solubility	241
2.3.2. Diffusion	242
2.3.3. Reported impact of different parameters on blooming occurrence	242
2.4. Methods of characterization for the blooming	242
3. Main fields in which the blooming has been studied	244
4. Blooming phenomenon in medical devices	244
5. Impacts of the blooming on material properties	245
6. Specific impact in the medical field	246
6.1. Toxicity aspect	246
6.2. Particulate contamination and its potential health risk	247
6.3. Surface modifications and consequences	247
7. Conclusion	248
Acknowledgement	248
References	248

1. Introduction

According to IUPAC « International Union of Pure and Applied

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Chemistry», blooming is defined as “the process in which one component of a polymer mixture, usually not a polymer, undergoes phase separation and migration to the external surface of the mixture” [1].

As known, polymers may contain additives (such as plasticizers, lubricants, stabilizers, antioxidants), which are added by the manufacturer to improve the process, the physical and chemical properties, or to prevent the discoloration and the loss of mechanical properties caused by the oxidation of polymers [2,3]. Most of these additives are compounds of low molecular weight (MW) and are added in a small amount (below 1% in most cases). These additives must be well incorporated into the polymer in order to ensure their intended functions. During polymer based materials fabrication, a melting process is performed to mix the additive(s) with the polymer prior to extruding or molding the material, followed by cooling to the room temperature.

Various states of the additive(s) within the polymer could result after this melt processing, and depending on their state, the material may or may not undergo blooming. Three cases are possible [4]:

- (i) The additive is not soluble or poorly soluble at room temperature and at the processing temperature: as a consequence, it will be dispersed as particles (for example pigment or filler) and only a very small amount of the additive will be dissolved in the material. In this case blooming will not be observed, but a phenomenon of chalking can occur. It refers to the formation of a loosely friable powder on the material surface as a result of polymer degradation. Chalking is encountered in lacquer, plastic films and weathering paint. It results from the gradual erosion of the coating film due to weathering: atmospheric and meteorological impact resulting from extended exposure to moisture or to rain [5,6].
- (ii) The additive is soluble at the processing temperature and at room temperature: in this case a molecularly dispersed solution is obtained. No blooming will occur.
- (iii) The additive is soluble at the processing temperature but not at room temperature (or much less so). Below a certain temperature, the polymer is supersaturated with the additive. However the additive generally does not crystallize inside the material, but the phase separation occurs on the polymer surface. This might be due to the high viscosity of the polymer that prevents the additive to crystallize and makes it remain in a metastable molecularly dispersed state.

Additives in plastic materials can also undergo other phenomena related to exudation associated with the additive solubility in the polymer [7]. These include:

- **Bleeding** [8]: this phenomenon mainly applies to liquid compounds, for example a plasticizer, whereby an oily film is formed on the polymer surface. Bleeding can also be encountered with polyolefins or with dyes in the case of PVC due to incompatibilities between the polymer and the dye.
- **Efflorescence**: mainly concerns dry paints with a migration of soluble salts onto the polymer surface.

2. Physico-chemistry and evaluation of blooming

2.1. Species involved in blooming phenomenon

Many species are concerned and subjected to this phenomenon, especially compounds with a low molecular weight (MW). Most examples of blooming are linked with polymer additives, however,

it can also occur with:

- Oligomers (polymers that consist of relatively few repeating units)
- Degradation products of the polymer and of the additives

Blooming has been widely studied for additives such as slip additives, antiblocking additives, antistatic agents, lubricants and release agents. Generally, these additives are unsubstituted amides of long chain fatty acids. For example; Rawls et al. [9] studied the erucamide blooming to the surface of linear low-density polyethylene (LLDPE) films where the erucamide is a preferred slip/release agent. The blooming of antiblock particulates on the surface of polymer films, together with bloomed amides, was also illustrated [10]: the study showed that the blooming of fatty acid amide was directly related to concentration within the film layer.

The blooming of numerous anti-oxidants (AO) additives has also been observed. It is quite a common phenomenon for phenolic antioxidants and phosphites. Blooming has been reported to occur with polyolefin antioxidants. For example, blooming of stabilizing antioxidants in polypropylene was illustrated by Spatafore et al. [11]. The migration of Santonox[®], a non-staining, non-discoloring hindered phenolic antioxidant widely used in polyethylene cables, has been reported [12]. The exudation of Irganox 1010[®] from the polyethylene to its surface in temperature below 70 C° and the blooming of Irganox 1330[®] from (polybutylene terephthalate) based polymer were also reported [13] and blooming of Irganox 1098[®] as a function of time and temperature was calculated by Dong et al. [14].

The blooming of flame-retardants to polymer surfaces has been widely studied and reported. For polypropylene (PP), numerous cases of incompatibilities between flame retardant additives and polymers were observed leading to blooming. Blooming can be a severe problem with monomeric halogen-containing additives; an example illustrated by Papazoglou [15] involves bromine-based flame retardant blooming associated with polystyrene and polyolefins. Furthermore, blooming was observed with high impact polystyrenes (HIPS) in which the fire retardant, 4,5,6,7-Tetrabromo-1,1,3-trimethyl-3-(2,3,4,5-tetrabromophenyl) indane was incorporated. This agent formed deposits of white material on the polymer surface, observed after variable time periods from production date [16]. Melamine (1,3,5-triazine-2,4,6-triamine) has been proposed as a flame retardant for polyamides [17], but with time, melamine or its decomposition products migrate from inside the molded article to the surface and exude in powder form [18]. Blooming of phosphate based flame retardants was also reported [19], and polymer compositions comprising both a borate and phosphorus containing anion component were particularly prone to blooming [20].

2.2. Mechanism of blooming: thermodynamic and kinetic factors

Many additives of low solubility have a high heat of fusion, whereby solubility rises very quickly with temperature allowing them to be dissolved at high concentrations at high temperatures while processing. However, these additives may migrate to the surface after cooling because of their poor compatibility.

Blooming will thus be a condition of the solubility of the additive molecule in the polymer plus its diffusion rate to the surface. Hence, the blooming of one additive is the product of both its solubility and its diffusion coefficient [21,22].

Solubility is a thermodynamic parameter which predicts whether blooming can occur; diffusion coefficient is a kinetic parameter that can indicate how much time it will take to bloom. The study of diffusion is more complex than solubility because it is

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