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The Role of Additives in Plastics

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PREFACE

The desire to compile this book was initiated partly by the author's experience in the teaching of plastics technology and partly as a result of a survey carried out among industrial technologists. A major difficulty experienced by students appeared to be associated with the lack of a comprehensive textbook on additives relating industrial practice to the underlying scientific principles. This is understandable to some extent since first, in technology many principles are not capable of accurate scientific explanation, (a situation which is also reflected in many sections of this book) and second, to fully understand the behaviour of plastics it often requires crossing the barrier of some quite distinct disciplines. A technologist can be guided however, by simple interdisciplinary models and mechanisms in his search for solutions to practical problems. This theme forms the basis on which this book was written, making maximum use of general principles which are applicable to industrial problems. Although the emphasis is on the benefits accrued from additives, some of the more important aspects of adverse interactions have been included.

This book is not intended primarily for specialists but for those wishing to acquire a basic knowledge of the use of additives in plastics materials, hence excessive literature review has been avoided and, to preserve the identity of a monograph, the information has been presented in a descriptive manner wherever possible.

The principles of mechanical property modifications have been emphasized to a greater extent than others since this is a major area in which chemists and engineers will have to share responsibility most for the successful advancement of plastics technology as a discipline comparable to metallurgy. The level of treatment in general is such that

it should be well within the grasp of both workers in industry engaged in development of polymeric compositions and students in technical colleges, polytechnics and universities, who study plastics technology as part of their general curriculum.

Finally, the subdivision of chapters has been made with the view that a reader may wish to concentrate on a particular group of additives without having to make frequent cross-references.

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1 GENERAL ASPECTS OF ADDITIVES FOR PLASTICS

Introduction

Since the very early stages of the development of the polymer industry it was realized that useful products could only be obtained if certain additives were incorporated into the polymer matrix. This process is normally known as 'compounding'. The term compounding was first used in the rubber industry and introduced by Goodyear in 1839 when he discovered that the addition of sulphur to a raw rubber stock gave much improved products.

About thirty years later a similar situation was experienced with the very first plastics product: cellulose nitrate. The use of large quantities of solvents was found to be necessary to shape the raw material, while the addition of camphor considerably improved the toughness of the finished products.

1.1 Definition and classification of additives

The term 'additives' is used here to describe those materials which are physically dispersed in a polymer matrix without affecting significantly the molecular structure of the polymer. Cross-linking agents, catalysts, etc., normally used in thermosetting systems are therefore excluded.

Additives used in plastics materials are normally classified according to their specific function, rather than on a chemical basis. It is also convenient to classify them into groups and to subdivide them further

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according to their more precise function:

- | | |
|--|---|
| (i) Additives which assist processing | { (a) Processing stabilizers
(b) Lubricants { Internal
External
(c) Processing aids and flow promoters
(d) Thixotropic agents |
| (ii) Additives which modify the bulk mechanical properties | { (a) Plasticizers or flexibilizers
(b) Reinforcing fillers
(c) Toughening agents |
| (iii) Additives used to reduce formulation costs | { (a) Particulate fillers
(b) Diluents and extenders |
| (iv) Surface properties modifiers | { (a) Antistatic agents
(b) Slip additives
(c) Anti-wear additives
(d) Anti-block additives
(e) Adhesion promoters |
| (v) Optical properties modifiers | { (a) Pigments and dyes
(b) Nucleating agents |
| (vi) Anti-ageing additives | { (a) Anti-oxidants
(b) U.V. stabilizers
(c) Fungicides |
| (vii) Others | { (a) Blowing agents
(b) Flame retardants |

1.2 Technological requirements of additives

(a) *Compatibility and mobility of additives*

The most important requirement of any additive is that it should be effective, for the purpose for which it has been designed, at an economic level.

Improvements in one property can, however, lead to deteriorations in others and, consequently it is the overall performance of an additive in a given formulation which determines the final choice.

Furthermore, the effectiveness of compounding additives depends also on the correct procedure of incorporation into the polymer matrix. The appropriate physical form of the additive in the polymer matrix depends in turn on the mechanism by which it exerts its function.

Complete compatibility (i.e. mutual miscibility at molecular level) and mobility or diffusibility of the additive molecules within the polymer matrix are essential if the action of the additive is such that any or all the molecules of the system are to interact with each other.

Total incompatibility and immobility of the additive molecules are desirable when the additive exerts its function at a supermolecular level, i.e. the action of the additive is derived from its intrinsic physical properties in the bulk or macroscopic form.

Partial compatibility is required when a strong affinity between polymer and additive is to be exerted at the interface. This is best achieved when at the interface the physical properties change smoothly from those of the polymer to those of the additive, even if such a change is to take place over small distances, e.g. a few molecular layers.

The compatibility and diffusibility of additives in polymeric compositions is normally assessed by 'trial and error' methods; a practice which is still likely to be used for some time in the future. The principal reason for this situation is to be attributed to the lack of sound scientific alternatives. The theories put forward so far, in fact, have been primarily developed for solvent/polymer systems and may have limited applicability to the case of additive/polymer mixtures, where the polymer is normally the major constituent.

In addition to this, the number of additives available and their possible combinations in polymeric systems are enormous and their compositions are continually changing. However the basic principles of solution thermodynamics can be used to provide a rough guide for the assessment of the relative compatibility of additives and polymers. It is intended to give here only a brief account of this and consequently oversimplifications will be made.

Entropy of mixing This can be obtained by constructing a lattice model consisting of additive and polymer molecules of equal size and shape so that their position in the lattice is interchangeable. Using the Boltzmann equation, we can obtain an approximate expression for the

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entropy in terms of the respective volumetric fractions of the two components,

$$\Delta S_M = k \ln \Omega \quad (1.1)$$

where k is the Boltzmann constant, and Ω is the total number of possible arrangements for the additive and polymer molecules.

If, n_0 = total number of molecules

n_1 = number of polymer molecules

n_2 = number of additive molecules

then

$$\Omega = \frac{n_0!}{n_1! \cdot n_2!} \quad (1.2)$$

and, therefore

$$\Delta S^M = k \ln \frac{n_0!}{n_1! \cdot n_2!} = k (\ln n_0! - \ln n_1! - \ln n_2!) \quad (1.3)$$

Using the Sterling approximation, $\ln n! = n \ln n - n$, and substituting in the above equation we obtain

$$\Delta S^M = k [n_0 \ln n_0 - n_1 \ln n_1 - n_2 \ln n_2] \quad (1.4)$$

In terms of molar volumetric fractions, where

$\varphi_1 = n_1/n_0$ molar volumetric fraction of the polymer

$\varphi_2 = n_2/n_0$ molar volumetric fraction of the additive

the above equation becomes:

$$\Delta S^M = k [n_0 \ln n_0 - n_1 \ln n_0 - n_1 \ln \varphi_1 - n_2 \ln n_0 - n_2 \ln \varphi_2]$$

and since $(n_0 - n_1 - n_2)/n_0$ is zero, then

$$\Delta S^M = -k [n_1 \ln \varphi_1 + n_2 \ln \varphi_2] \quad (1.5)$$

Heat of mixing The heat of mixing can be obtained by considering the changes in internal energy (ΔE_{12}), which take place when the additive and polymer are mixed together, relative to their respective internal energy in their pure state.

According to Hildebrand and Scott¹ this energy change can be obtained from the expression

$$\Delta E_{12}^M = (n_1 v_1 + n_2 v_2) \left[\left(\frac{E_1^v}{v_1} \right)^{1/2} - \left(\frac{E_2^v}{v_2} \right)^{1/2} \right]^2 \varphi_1 \varphi_2 \quad (1.6)$$

where v_1 is the volume of one polymer molecule, v_2 is the volume of one additive molecule, the quantities $\Delta E^v/v$ are the respective energy of vaporization per unit volume, and the values of $(\Delta E/v)^{1/2}$ are called 'solubility parameters' and denoted by the symbol δ .

If V_1 is the volume occupied by the polymer and V_2 is the volume occupied by the additive, equation (1.6) can be re-written as

$$\Delta E_{12}^M = \varphi_1 \varphi_2 V_1 (\delta_1 - \delta_2)^2 \quad (1.7)$$

since $V_1 \gg V_2$.

If the mixing process is considered to take place without changes in volume, $\Delta V^M = 0$, and since $\Delta H^M = \Delta E^M + P\Delta V^M$, then equation (1.3) also represents the heat of mixing, i.e. $\Delta H^M = \Delta E^M$.

Free energy of mixing This quantity can now readily be computed from the entropy and heat of mixing equations,

$$\begin{aligned} \Delta F^M &= \Delta H^M - T\Delta S^M \\ &= \varphi_1 \varphi_2 V_1 (\delta_1 - \delta_2)^2 - kT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2) \end{aligned} \quad (1.8)$$

According to the second law of thermodynamics, mixing (like any other spontaneous process) occurs if there is a decrease in free energy, i.e. ΔF^M must be negative or ΔF^M positive.

In the solid state when the concentration of additive is small we can only expect a small increase in entropy. It follows, therefore, that these restrictions will only allow a relatively small increase in ΔH . Hence δ_1 and δ_2 will have to be as close as possible. Somewhat larger differences in δ values are allowable when there is possibility of H -bonding between the two components, since this would result in a decrease in ΔH .

We have now reached the conclusion that it is possible to obtain a rough indication of whether an additive is miscible in the polymer considered from a knowledge of the relative values of the heat of mixing or from a knowledge of their solubility parameters δ_1 and δ_2 . Solubility parameters for a variety of polymers and additives, plasticizers in particular, are now becoming available in the literature and handbooks, and it may be useful to consult these when selecting additives for plastics compositions.

(b) *Migration and consumption of additives*

The additive must neither volatilize out of the matrix during processing

nor exude to the surface during service. This implies that the additive must have a low vapour pressure at high temperatures and must not aggregate, i.e. precipitate or crystallize out of the polymer matrix, on ageing, and leave behind a fine film of additive deposits. This phenomenon is called 'chalking'. The additive must not be extractable by liquids with which the host polymeric composition may come into contact during finishing operations, neither must it exude out during its life in service. The two latter phenomena are known as 'bleeding' and 'blooming' respectively. Not only would these phenomena produce aesthetically objectionable effects and contaminate liquids and other products in contact with the plastics component, but the loss of additives from the system would inevitably reduce its efficiency.

Bleeding and blooming phenomena are obviously related to the kinetics of diffusion and consequently are dependent on parameters such as compatibility of the additive with the polymer, molecular size of the additive, physico-chemical interactions between additive and polymer molecules, configuration of polymer chains and intermolecular voids etc.

Hence insoluble inorganic additives, such as pigments, fillers etc. are unlikely to bleed or bloom, whereas soluble low-molecular-weight plasticizers are more likely to exude to the surface during processing and subsequent ageing and may even constitute a vehicle for the migration of other soluble additives such as processing stabilizers.

When the additive in question functions by interacting with either the polymer, another additive or environmental agents, it would be desirable if it could be made auto-regeneratable so that its effectiveness would not depend on its previous history. There are indications that, to some extent, an auto-regeneration mechanism operates with some 'synergistic' stabilizer systems (see later).

(c) *Health hazards of additives*

An additive must not have any damaging effects on the health of the personnel engaged in compounding and processing operations nor on that of the consumer, especially when the plastics component is intended for packaging of food products or for toys. Legislation is particularly stringent with respect to protection of consumers against toxic effects derived from extracted additives.

The British Plastics Federation has laid down certain recommenda-

tions for the plastics industry, which may be summarized as follows³:

- (1) If an ingredient of a plastics material cannot be extracted by foodstuff with which it is in contact, it does not constitute a toxic hazard.
- (2) If a material is found in a food as a result of its contact with plastics it may constitute a toxic hazard if in itself it is toxic in the biological sense.
- (3) Acute toxic levels are unlikely to be realized in practice. It is possible, however, that injurious effects may be produced by repeated small doses of material extracted from plastics and therefore it is the accumulative effect which should be used in assessing the hazard.
- (4) The toxic hazard is a function of the chronic toxicity and of its extractability from a plastics material under service conditions.
- (5) Extractability tests must be carried out with the foodstuffs themselves or a range of representative extractants under the most severe conditions likely to be incurred in practice. The results must then be combined with the data on chronic toxicity expressed by their 'toxicity-factor' and a given 'toxicity quotient', which is a measure of the hazard.
- (6) As an additional safety factor all 'Schedule I' poisons should never be in contact with foodstuffs.

The results of tests are expressed by

$$Q = \frac{E \times 1000}{T}$$

where (1) Q = toxicity quotient; (2) T = toxicity factor of the extracted material, which is a figure assessed by the Federation on the examination of available data and approximates to the maximum daily oral dose expressed in mg/kg body weight which can be tolerated for 90 days by groups of animals without producing any detectable toxic effect; (3) E = weight in grams of extracted material per specific volume or surface area of the original sample depending on whether this is a thick or thin section of material.

A plastics material is considered satisfactory for use in contact with foodstuffs if the sum of all 'toxicity quotients' of extracted ingredients is less than 10.

The extractants usually used are:

Distilled water, 5% Na_2CO_3 , 5% acetic acid, 50% ethyl alcohol, olive oil + 2% oleic acid or paraffin oil, 5% citric acid.

Extraction tests are carried out under three conditions:

- (a) 45 °C for 24 hours – intermittent contact
- (b) 60 °C for 10 days – prolonged contact
- (c) 80 °C for 2 hours – intermittent contact with food

1.3 Unavoidable side-effects of additives: deterioration of dielectric properties

It is often the case that a combination of additives are incorporated into plastics to produce from a few basic polymers a wide range of 'grades', in order to meet all the service requirements which a product may demand.

It is not surprising, therefore, that chemical and physical interactions which would lead to undesirable side-effects may take place among the various additives. Some of these interactions will be dealt with in later chapters by reference to specific examples. Furthermore there are certain polymer properties which are invariably impaired as a result of additive interactions; notably among these are the dielectric properties. This point will be illustrated by considering the effects on dielectric losses and electric break-down voltage.

1.3.1 Dielectric losses

The disturbance of electric charges within a material and the resultant surface charges when the material is subjected to an external electric field is described in terms of dielectric constant ϵ and polarization P .

The polarization of a material is defined as the change in charge density on the plates of a condenser when the material is used as the dielectric in place of vacuum, i.e. $P = q_{(\text{vac})} - q_{(\text{diel})}$. Within the material the displacement of charges will neutralize one another, and therefore polarization occurs only at the two surfaces in contact with the plates of the condenser. The dielectric constant, on the other hand is defined as the relative increase in capacitance (C) of the condenser or the relative decrease in voltage gradient (V) when the charge density is kept constant, i.e.

$$\epsilon = \frac{C(\text{diel})}{C(\text{vac})} = \frac{V(\text{vac})}{V(\text{diel})} \quad (1.9)$$

Thus as a result of introducing the material between the plates of the condenser instead of vacuum, the field strength is reduced inversely proportionally to its dielectric constant, i.e. $E_{(\text{vac})} = \epsilon \cdot E_{(\text{diel})}$. The total polarization P is the algebraic sum of several components known respectively as 'interfacial' or 'space-charge polarization' P_i , 'dipolar' or 'orientation polarization' P_d , 'atomic polarization', P_a , and 'electronic polarization' P_e .

Interfacial polarization arises from macroscopic movements of ions within the material. Orientation polarization arises from the distortion and rotation of permanent dipoles, which in the case of polymers consist of asymmetric pendant side groups or portions of the molecular backbone chains.

Atomic polarization arises from very small movements of atoms within a molecular structure, and finally, electronic polarization is associated with movements of electrons.

All polarization processes are time dependant owing to constraints on the various displacements imposed by neighbouring constituents of the structure of the material. This time dependance can be described by exponential equations of the type $P = P_0(1 - e^{-t/\tau})$ where τ is a characteristic 'relaxation time' for each particular charge displacement. Relaxation times are very small for atomic and electronic polarization ($\cong 10^{-13}$ and $\cong 10^{-15}$ s)⁴, but are considerably larger for dipolar and interfacial polarizations ($\cong 10^{-8}$ and 10^{-2} s respectively). In alternating electric fields, polarization also varies periodically with time but the internal constraints to rapid movements of charges causes a dissipation of energy, normally in the form of heat. So whereas in vacuum the electric current would form a phase angle of 90° with the voltage, polarization of the dielectric will decrease *pro-rata* the phase angle, as shown in Fig. 1.1. Consequently the effective electric current I has an imaginary component I_i , in phase with the voltage, known as the loss current, and a real component I_c which corresponds to the current intensity in absence of any losses (e.g. in vacuum) and it therefore forms a 90° phase angle with the voltage.

From Fig. 1.1 we obtain $\tan \delta = I_i/I_c$, which is called the 'loss tangent'.

Accordingly we can represent the dielectric constant in complex form $\epsilon^* = \epsilon' - j\epsilon''$, where ϵ'' is called the 'loss factor', and it can be shown that $\epsilon''/\epsilon' = \tan \delta$.

The power losses which occur in dielectrics are proportional to ϵ''

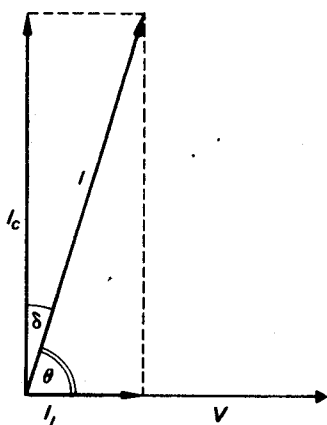


Fig. 1.1 Vector diagram showing the phase angle θ and the loss angle δ (I_l is in phase with V).

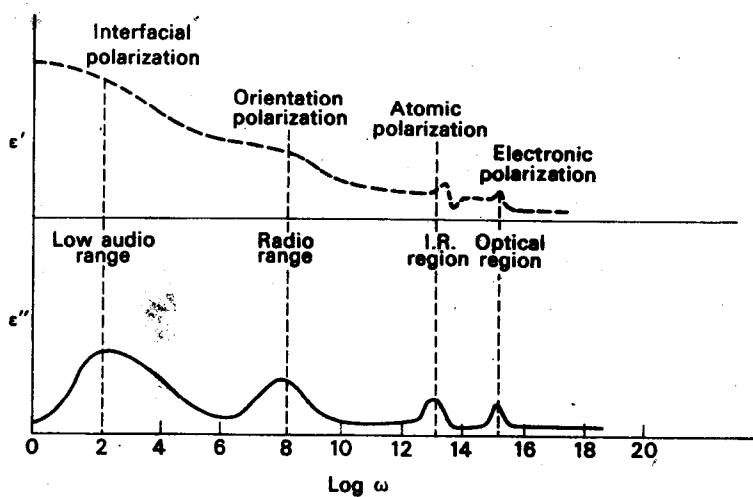


Fig. 1.2 Relative contributions to overall polarization and dielectric losses⁶.

and $\tan \delta$, from which the terms loss factor and loss tangent are derived. Both ϵ'' and ϵ' are frequency dependant and vary in magnitude according to the type of polarization which takes place as shown in Fig. 1.2. In electrical applications one is normally concerned with frequencies less than 10^{10} Hz and therefore there will be no contribution from both atomic and electronic polarizations to dielectric losses. Hence it is the orientation and interfacial polarization which must be minimized to obtain high quality insulating materials

Consequently most polymers used in plastics, in their 'pure' state and at relatively low temperatures, are not likely to give rise to appreciable losses in the low audio frequency range and with non-polar polymers, such as polyolefines, there will be relatively low losses over the whole range of frequencies of practical importance

1.3.2 Dielectric strength

The dielectric strength of an insulating material is expressed in terms of minimum voltage which causes a permanent loss of dielectric properties (by converting it into a conductive material) under specified conditions. This results from a breakdown in the chemical structure of the material mainly as a result of thermal and environmental degradation processes.

The heat generated as a result of dielectric losses can raise the temperature of polymers (owing to their low thermal diffusivity) to levels at which there will be sufficient thermal energy to cause molecular cleavage (see p. 25). This can lead to the formation of double bonds and ultimately to conjugated macromolecular structures.

Both temperature rise and chemical structure breakdown will increase the conductivity of the material which will eventually lose completely its insulating characteristics.

Plastics based on phenolic materials e.g. PF's, polycarbonates etc., can produce⁷ readily conductive paths by forming highly conjugated graphitic structures

Environmental agents, air, moisture or other ionic species present either on the surface or in the bulk of the polymer can accelerate the rate of temperature rise and structure breakdown and, therefore, will reduce the dielectric strength of the material.

Since the temperature will rise at different rates and the chemical breakdown process is obviously also rate dependant, it is to be expected that the dielectric strength of a plastics material is not constant. Neither

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would it be surprising to find the a.c. breakdown voltages to be appreciably lower than the d.c. voltage values measured under similar conditions.

1.3.3 Adverse effects of additives

It was shown in the preceding sections that it is the polarity of the constituent groupings of polymer molecules and the presence of mobile ionic species which are mostly responsible for the dielectric losses of materials and, which at the same time, will contribute to dielectric breakdown.

Additives may increase losses either because of their intrinsic ionic and/or polar nature or because they may absorb water, which increases further the dipolar and ionic constituents of the system. Their adverse effect on dielectric breakdown may result from the higher losses which will increase the rate of temperature rise, and if they are hygroscopic they may accelerate the decomposition of polycondensate systems, e.g. heterochain linear polymers and thermosets.

Incompatible additives, especially those with a high surface free-energy (e.g. inorganic fillers and pigments) may increase the interfacial polarization by adsorption and immobilization of ionic and polar species which will in turn decrease the effective internal charge neutralization. Furthermore they may give rise to the formation of irregular microvoids at the interface, which may trap harmful gaseous matter such as oxygen, water, etc. At the same time on the asperities of these microcracks there will be a high charge density which constitute points of weakness regarding the initiation of the breakdown process. Oxygen, in fact, ionizes and forms ozone under these conditions, which causes a very rapid thermal oxidative breakdown. Although it is generally believed that non-hygroscopic and contamination-free fillers such as mica flakes, etc., may improve the dielectric strength of phenolic compounds by interrupting the continuity of the conductive path through the material, this is only likely to be true when very high filler loadings are used and the compound is cured under very high pressures. Otherwise the interfacial discharge breakdown will predominate and the dielectric strength will therefore be reduced⁵.

1.4 Methods of incorporation of additives into polymer matrices

The manner in which additives and polymers are blended together or 'compounded' is determined by the following factors: