Additives in Polymers

Industrial Analysis and Applications

J.C.J. BART

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Foreword

Loss of knowledge is an acute threat to companies. The crucial question is how existing knowledge and new technologies can be harnessed as a corporate resource. A major problem facing industry is retaining knowledge within the company, in particular in times of acceleration of innovation. Moreover, in industrial research there is an unmistakable shift from generating knowledge and solving problems by experimental work towards detecting, selecting and absorbing knowledge from the external knowledge infrastructure and adapting it to specific situations. This book contributes a great deal to preserving and critically evaluating knowledge in the field of the analytics of polymer additives.

Additives play a leading role in the success of commercial plastics, elastomers, rubbers, coatings and adhesives. Without additives, many polymers would simply be of limited use. Although polymer additive analysis claims a history of use spanning at least half a century it is, nevertheless, still a continuously evolving research area with new and modified procedures related to increasingly sophisticated products. In many ways, this has led to a plethora of traditional and new chemical, physico-chemical and physical techniques and applications that are confusing to the specialist and beginner alike. An overview of developments across all areas of polymer additive analysis is lacking and a unified approach should therefore be of considerable assistance. This work shows that industrially relevant polymer additive analysis has developed into a very broad and complex field, in retrospect at the limit for one single author and problem holder. Also, despite the many advances direct polymer additive analysis has not yet displaced conventional wet chemical routes. In this respect, current state-of-the-art ends up in a draw. This book makes a substantial contribution to the current literature on the analytics of polymer additives, follows up an earlier industrial tradition and lays a foundation for the future. It will be of great value to a broad readership comprising industrial and academic (analytical) chemists, polymer scientists and physicists, technologists and engineers, and other professionals involved in R&D, production, use and re-use of polymers and additives in all areas of application, including manufacturers, formulators, compounders, end users, government legislators and their staff, forensic scientists, etc.

With a rapidly developing field as this one, this book can only be considered as a work in progress. Hopefully, this monograph will help users to avoid reinventing the classical analytical wheel, and abandon obsolete, old practices, to redirect their efforts eventually towards more appropriate, though sometimes complicated equipment, to become sufficiently proficient to solve real-life analytical problems efficiently and with confidence, or even to devise innovative and challenging new directions. Certainly, this book will save significant time and effort for those analysts faced with cracking complex polymer additive cocktails. As nothing holds true for ever, it will be most appropriate to review the field again within the next decade.

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Preface

Whenever textbooks on polymer chemistry deal with polymer analytical aspects, macromolecular characterisation is usually overemphasised giving the unsuspecting reader the incorrect impression that polymers and formulated polymeric materials are one and the same thing. This treatise, which attempts to remedy such an oversight, is concerned with the characterisation of additives embedded in a broad variety of polymeric matrices. The topic is particularly relevant in view of the impressive growth in the use of synthetic polymeric materials and significant analytical advances in terms of sample preparation, chromatography, detection systems, hyphenation and computation in the last two decades. In every field of science and engineering, it is convenient to have at one's disposal an up-to-date handbook to provide specialists with a broad collection of technical details about the individual elements of the field. This has now come true for polymer/additive analysis.

The purpose of this monograph, the first to be dedicated exclusively to the analytics of additives in polymers, is to evaluate critically the extensive problem-solving experience in the polymer industry. Although this book is not intended to be a treatise on modern analytical tools in general or on polymer analysis *en large*, an outline of the principles and characteristics of relevant instrumental techniques (without hands-on details) was deemed necessary to clarify the current state-of-the-art of the analysis of additives in polymers and to accustom the reader to the unavoidable professional nomenclature. The book, which provides an in-depth overview of additive analysis by focusing on a wide array of applications in R&D, production, quality control and technical service, reflects the recent explosive development of the field. Rather than being a compendium, cookery book or laboratory manual for qualitative and/or quantitative analysis of specific additives in a variety of commercial polymers, with no limits to impractical academic exoticism (analysis for its own sake), the book focuses on the fundamental characteristics of the arsenal of techniques utilised industrially in direct relation to application in real-life polymer/additive analysis. The analyst requires *expert knowledge*, i.e. understanding of the strengths, weaknesses and limits of application of each technique and how they relate to practical problems. Therefore, the chapters are replete with selected and more common applications illustrating why particular additives are analysed by a specific method. By understanding the underlying principles, the mystery of the problem disappears. Expertise, of course, requires more than understanding of the principles alone. Consequently this book does not serve to become overnight expert in the area of polymer/additive analysis. Rather, it helps the emerging generation of polymer analysts to obtain a rapid grasp of the material in minimal time but is no substitute for personal experience.

Additives in Polymers: Industrial Analysis and Applications fulfils a need and provides information not currently available from another single literature source. This book is different from other books on polymer analysis in a number of ways. Instrumental methods are categorised according to general deformulation principles; there is more emphasis on effective problem solving and promoting understanding than on factual information or instrumental capabilities without focus on any specific analyte or polymer class. The tools of the trade are introduced when appropriate in the deformulation strategy, not on the basis of their general properties only. In particular, the author has tried to emphasise the importance of employing rational methods to laboratory, *in situ* and on-line polymer/additive analysis. The present text is an appraisal of the literature and methodology currently available (tool description), from which the inexperienced 'deformulator' can select those means necessary to tackle his own problem and finally write his own recipe and clear procedures in compliance with local instrumental possibilities. The critical evaluation of methods also indicates what still needs to be done. From an industry perspective, it is clear that above all there is a need to improve the quantitative aspects of the methods.

Although wide-ranging, the author does not claim to present a collection of 10 comprehensive reviews. Instead, *illustrative* examples, drawn from closely related fields (polymers, rubbers, coatings, adhesives), are given to outline the ranges of applicability. The value of the book stays in the applications. No book is perfect and no doubt equally deserving papers have been omitted and some undeserving ones have been included. However, with the number of techniques much greater than originally planned the text should be kept within reasonable bounds. The reader may keep in mind the lines

For what there was none cared a jot.
But all were wroth with what was not.

Theory and practice of polymer/additive analysis are not a regular part of analytical education, and usually require on-the-job training. The intention in writing this text was to appeal to as wide an audience as possible. Using an instructional approach, this reference book helps orienting chemists and technicians with little or no background in polymer/additive analysis who would like to gain rapidly a solid understanding of its fundamentals and industrial practice. Seasoned analysts of polymer formulations may use the text to quickly understand terms and techniques which fall outside of their immediate experience. The author has attempted to bring together many recent developments in the field in order to provide the reader with valuable insight into current trends and thinking. Finally, this book can also serve as a modern textbook for advanced undergraduate and graduate courses in many disciplines including analytical chemistry, polymer chemistry and industrial chemistry.

In planning this book the author has chosen a monograph in decathlon fashion. This allows critical comparisons between methods and has the advantage of a unified structure. The disadvantage is that no individual can have specialist knowledge in all fields equal to that of the sum of the experts. To overcome this drawback extensive peer review has been built in. For each individual technique more excellent textbooks are available, properly referenced, albeit with less focus on the analysis of additives in polymers. However, the steep growth curve during the past two decades has made reporting on this subject an almost elusive target.

Each chapter of this monograph is essentially self-contained. The reader can consult any subchapter individually. Together they should give a good grounding of the basic tools for dealing with the subject matter. The reader is well advised to read the two introductory chapters first, which define the analytical problem area and general deformulation schemes. The next chapters tackle polymer/additive deformulation strategically in an ever-increasing order of sophistication in analytical ingenuity. Conventional, indirect, polymer/additive analysis methods, mainly involving wet chemistry routes, are described in Chapters 3 to 9. The book is concluded with prospects in Chapter 10. Extensive appendices describe additive classes; a glossary of symbols, and databases. To facilitate rapid consultation the text has been provided with *eye-catchers*. Each chapter concludes with up-to-date references to the primary literature (no patent literature). Contributions from many of the top industrial research laboratories throughout the world are included in this book, which represents the most extensive compilation of polymer/additive analysis ever. Once more it comes true that most research is being carried out beyond one's own R&D establishment.

The author has not tried to include a complete *ab-initio* literature search in any particular area. The majority of references in the text are from recent publications (1980–2003). This is not because excellent older references are no longer relevant. Rather, these are frequently no longer used because: (i) more recent work is a fine-tuned extension of prior work; (ii) the 'classic' texts list extensive work up to 1980; and (iii) older methods are frequently based on inferior or obsolete technology and thus direct transfer of methods may be difficult or impossible. Readers familiar with the 'classics' in the field will find that almost everything has changed considerably.

As most (industrial) practitioners have access to rapid library search facilities, it is recommended that a literature search on the analysis of a *specific* additive in a given polymer be carried out at the time, in order to generate the most recent references. Consequently, the author does not apologise for omitting references to specific analyses. However, every effort has been made to keep the book up-to-date with the latest methodological developments. Each chapter comprises a critical list of recommended general reading (books, reviews) for those who want to explore the subjects in greater depth.

This book should convince even the most hardened of the 'doubting Thomases' that polymer/additive analysis has gone a long way. With a developing field such as this one, any report represents only work in progress and is not the last word.

Geleen
December 2003

About the Author

Jan C.J. Bart (PhD Structural Chemistry, University of Amsterdam) is a senior scientist with broad interest in materials characterisation, heterogeneous catalysis and product development who spent an industrial carrier in R&D with Monsanto, Montedison and DSM Research in various countries. The author has held several teaching assignments and researched extensively in both academic and industrial areas; he authored over 250 scientific papers, including chapters in books. Dr Bart has acted as a Ramsay Memorial Fellow at the Universities of Leeds (Colour Chemistry) and Oxford (Material Science), a visiting scientist at Institut de Recherches sur la Catalyse (CNRS, Villeurbanne), and a Meyerhoff Visiting Professor at WIS (Rehovoth), and held an Invited Professorship at USTC (Hefei). He is currently a Full Professor of Industrial Chemistry at the University of Messina.

He is also a member of the Royal Society of Chemistry, Royal Dutch Chemical Society, Society of Plastic Engineers and The Institute of Materials.

Acknowledgements

This book summarises the enormous work done and published by many scientists who believe in polymer analysis. It is humbling to notice how much collective expertise is behind the current state-of-the-art in polymer/additive analysis and how little is at the command of any individual. The high degree of creativity and ingenuity within the international scientific community is inspiring. The size of the book shows the high overall productivity. Even so, only a fraction of the pertinent literature was cited.

Any project has its supporters and opponents, ranging from those faithful who repeatedly encourage to others who actively discourage. The author wishes to thank DSM from CTO to operational managers at DSM Research BV for providing foresight and generous resources for monitoring developments in this field of interest, for stimulating the work and granting permission for publication. This monograph was finalised during a sabbatical year granted only half-heartedly by the Faculty of Science of the University of Messina. The end-product may convince academic sceptics that a book marks a more permanent contribution to transfer of know-how from industry to academia than a standard one-semester course for ever-dwindling flocks of students.

The author thanks colleagues (at DSM Research) and former colleagues (now at SABIC Euro Petrochemicals) for taking on the difficult job of critically reading various chapters of the book. Reviewing means lots of work and not much appreciation from the general public. Information Services at DSM Research have been crucial in providing much needed help in literature search. Each chapter saw many versions, which needed seemingly endless word-processing. Without the expert help and patience of Mrs Coba Hendriks, who cared repeatedly about every dot and dash, it would not have been possible to complete this work successfully. A special word of thanks goes to Mihaela and David for their hospitality and endurance during the many years of preparation of this text.

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Jan C.J. Bart
Geleen
December 2003

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Contents

CHAPTER 1

Search before Research

Introduction

The successful use of plastic materials in many applications, such as in the automotive industry, the electronics sector, the packaging and manufacturing of consumer goods, is substantially attributable to the incorporation of additives into virgin (and recycled) resins. Polymer industry is impossible without additives. Additives in plastics provide the means whereby processing problems, property performance limitations and restricted environmental stability are overcome. In the continuous quest for easier processing, enhanced physical properties, better long-term performance and the need to respond to new environmental health regulations, additive packages continue to evolve and diversify.

Additives can mean ingredients for plastics but they play a crucial role also in other materials, such as coatings, lacquers and paints, printing inks, photographic films and papers, and their processing. In this respect there is a considerable overlap between the plastics industry and the textiles, rubber, adhesives and food technology industries. For example, pigments can be used outside the plastics industry in synthetic fibres, inks, coatings, and rubbers, while plasticisers are used in energetic materials formulations (polymeric composite explosives and propellants). Additives for plastics are therefore to be seen in the larger context of *specialty chemicals*. 'Specialties' are considered to be chemicals with specific properties tailored to niche markets, special segments or even individual companies. Customers purchase these chemicals to achieve a desired performance. Polymer and coatings additives are ideal specialty chemicals: very specific in their application and very effective in their performance, usually with a good deal of price inelasticity. The corresponding business is associated with considerable innovation and technical application knowledge. Research and development are essential and global operation is vital in this area.

Plastics additives now constitute a highly successful and essential sector of the chemical industry. Polymer additives are a growing sector of the specialty chemical industry. Some materials that have been sold for over 20 years are regarded today as commodity chemicals, particularly when patents covering their use have expired. Others, however, have a shorter life or have even disappeared almost without trace, e.g. when the production process cannot be made suitably economic, when unforeseen toxicity problems occur or when a new generation of additive renders them technically obsolete.

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1.1 ADDITIVES

It is useful at this point to consider the definition of an additive as given by the EC: an additive is a substance which is incorporated into plastics to achieve a technical effect in the finished product, and is intended to be an essential part of the finished article. Some examples of additives are antioxidants, antistatic agents, antifogging agents, emulsifiers, fillers, impact modifiers, lubricants, plasticisers, release agents, solvents, stabilisers, thickeners and UV absorbers. Additives may be either organic (e.g. alkyl phenols, hydroxybenzophenones), inorganic (e.g. oxides, salts, fillers) or organometallic (e.g. metallocarboxylates, Ni complexes, Zn accelerators). Classes of commercial plastic, rubber and coatings additives and their functionalities are given in Appendices II and III.

Since the very early stages of the development of the polymer industry it was realised that useful materials could only be obtained if certain additives were incorporated into the polymer matrix, in a process normally known as '*compounding*'. Additives confer on plastics significant extensions of properties in one or more directions, such as general durability, stiffness and strength, impact resistance, thermal resistance, resistance to flexure and wear, acoustic isolation, etc. The steady increase in demand for plastic products by industry and consumers shows that plastic materials are becoming more performing and are capturing the classical fields of other materials. This evolution is also reflected in higher service temperature, dynamic and mechanical strength, stronger resistance against chemicals or radiation, and odourless formulations. Consequently, a modern plastic part often represents a high technology product of material science with the material's properties being not in the least part attributable to additives. Additives (and fillers), in the broadest sense, are essential ingredients of a manufactured polymeric material. An additive can be a primary ingredient that forms an integral part of the end product's basic characteristics, or a secondary ingredient which functions to improve performance and/or durability. Polypropylene is an outstanding example showing how polymer additives can change a vulnerable and unstable macromolecular material into a high-volume market product. The expansion of polyolefin applications into various areas of industrial and every-day use was in most cases achieved due to the employment of such speciality chemicals.

Additives may be monomeric, oligomeric or high polymeric (typically: impact modifiers and processing aids). They may be liquid-like or high-melting and therefore show very different viscosity compared to the polymer melt in which they are to be dispersed.

Selection of additives is critical and often a proprietary knowledge. Computer-aided design is used for organic compounds as active additives for polymeric compositions [1]. An advantage of virtual additives is that they do not require any additive analysis!

Additives are normally present in plastics formulations intentionally for a variety of purposes. There may also be unintentional additives, such as water, contaminants, caprolactam monomer in recycled nylon, stearic acid in calcium stearate, compounding process aids, etc. Strictly speaking, substances which just provide a suitable medium in which polymerisation occurs or directly influence polymer synthesis are not additives and are called polymerisation aids. Some examples are accelerators, catalysts, catalyst supports, catalyst modifiers, chain stoppers, cross-linking agents, initiators and promoters, polymerisation inhibitors, etc. From an analytical point of view it is not relevant for which purpose substances were added to a polymer (intentionally or not). Therefore, for the scope of this book an *extended definition* of 'additive' will be used, namely anything in a polymeric material that is not the polymer itself. This therefore includes catalyst residues, contaminants, solvents, low molecular components (monomers, oligomers), degradation and interaction products, etc. At most, it is of interest to estimate on beforehand whether the original substance added is intended to be transformed (as most polymerisation aids).

Additives are needed not only to make resins processable and to improve the properties of the moulded product during use. As the scope of plastics has increased, so has the *range of additives*: for better mechanical properties, resistance to heat, light and weathering, flame retardancy, electrical conductivity, etc. The demands of packaging have produced additive systems to aid the efficient production of film, and have developed the general need for additives which are safe for use in packaging and other applications where there is direct contact with food or drink.

The number of additives in use today runs to many thousands, their chemistry is often extremely complex and the choice of materials can be bewildering. Most commercial additives are single compounds, but some are oligomeric or technical mixtures. Examples of polymer additives containing various components are Irgafos P-EPQ, Anchor DNPD [2], technical grade glycerylmonostearate [3] and various HAS oligomers [4]. Polymeric hindered amine light stabilisers are very important constituents of many industrial formulations. In these formulations, it is often not just one component that is of interest. Rather, the overall identity, as determined by the presence and distribution of the individual components, is critical. The processing stabiliser Irgafos P-EPQ consists of a mixture of seven compounds and the antistatic agent *N*,*N*-bis-(2-hydroxyethyl) alkylamine contains five components [5]. Similarly, the antistat Atmos 150 is composed of glycerol mono- and distearate. Ethoxylated alcohols consist of polydisperse mixtures. 'Nonyl phenol' is a mixture of monoalkyl phenols with branched side-chains and an average molecular weight of 215 [6]. Commercial calcium stearate is composed of 70 % stearate and 30 % palmitate. Also dialkylphthalates are technical materials as well as the high-molecular weight (MW) release agent pentaerythritoltetrastearate (PETS). Flame retardants are often also mixtures, such as polybromodiphenyl ethers (PBDEs) or brominated epoxy oligomers (BEOs). Surfactants rarely occur as pure compounds.

It is also to be realised that many additives are commercialised under a variety of *product names*. Appendix III shows some examples for a selection of stabilisers, namely a phenolic antioxidant (2,2′-methylene-bis-(6-*tert*-butyl-4-methylphenol)), an aromatic amine (*N*-1,3-dimethyl-butyl-*N*′-phenyl-paraphenylene-diamine), a phosphite (trisnonylphenylphosphite), a thiosynergist (dilaurylthiodipropionate), a UV-absorber (2-hydroxy-4-*n*-octoxybenzophenone), a nickel-quencher ((2,2′-thio-bis-(4-*tert*-octylphenolato)-*n*-butylamine)-nickel), a low-MW hindered amine light stabiliser or HALS (di-(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate) and a polymeric HALS compound (Tinuvin 622). Various commercial additive products are binary or ternary blends. Examples are Irganox B225 (Irganox 1010/Irgafos 168, 1:1), Ultranox 2840 (Ultranox 276/Weston 619, 3:2), and Tinuvin B75 (Irganox 1135/Tinuvin 765/Tinuvin 571, 1:2:2).

It may be seen from Appendix II that the tertiary *literature* about polymer additives is vast. Books on the subject fall into one of two categories. Some provide commercial information, in the form of data about the multitude of additive grades, or about changes in the market. Others are more concerned with accounts of the scientific and technical principles underlying current practice. This book gives higher priority to promoting understanding of the principles of polymer/additive deformulation than to just conveying factual information.

1.1.1 Additive Functionality

Additives used in plastics materials are normally classified according to their intended *performance*, rather than on a chemical basis (cf. Appendix II). For ease of survey it is convenient to classify them into groups with similar functions. The main functions of polymer additives are given in Table 1.1.

Generally, polymer modification by additives provides a cost-effective and flexible means to alter polymer properties. Traditionally, however, the use of an additive is very property-specific in nature, with usually one or two material enhancements being sought. An additive capable of enhancing one property often does so at the cost of a separate trait. Today many additives are *multifunctional* and combine different additive functionalities such as melt and light stabilisation (e.g. in Nylostab® S-EED) or metal deactivation and antioxidation (e.g. in Lowinox® MD24) (cf. Table 10.14). Dimethyl methyl phosphonate (DMMP) is a multifunctional molecular additive acting as an antiplasticiser, processing aid and flame retardant in cross-linked epoxies. In a variety on the theme, some multifunctional antioxidants, such as the high-MW Chimassorb 944, combine multiple functions in one molecule. Adhikari *et al.* [7] have presented a critical analysis of seven categories of multifunctional rubber additives having various combinations of antidegradant, activator, processing aid, accelerator, antioxidant, retarder, curing agent, dispersant, and mould release agent functions.

In analogy to plastics additives, paper coating additives are distinguished in as many as twenty-one functional property categories (for dispersion, foam and air entrainment control, viscosity modification, levelling and evening, water retention, lubricity, spoilage control, optical brightness improvement, dry pick improvement, dry nub improvement and abrasion resistance, wet pick improvement, wet rub improvement, gloss-ink hold-out, grease and oil resistance, water resistance, plasticity, fold endurance, electroconductivity, gloss improvement, organic solvent coating additives, colouring), even excluding those materials whose primary function is as a binder, pigment or vehicle [8].

Typical technology questions raised by plastic producers and manufacturers and directed at the additive supplier are given in Table 1.2, as exemplified in the application of injection moulding of polyamides. These problems may be tackled with appropriate addition of chain extenders and cross-linking agents, nucleating agents and lubricants, release agents, reinforcements, etc.

There are now far more categories of additives than a few decades ago. The corresponding changes in additive technology are driven partly by the desire to produce plastics which are ever more closely specified for particular purposes. The *benefits* of plastics additives are not marginal. As outlined before, they are not simply optional extras but essential ingredients, which make all

Table 1.1 Main functions of polymer additives

Polymerisation/chemical modification aids	
Accelerators	Cross-linking agents
Chain growth regulators	Promoters
Compatibilisers	
Improvement in processability and productivity (transformation aids)	
Defoaming and blowing agents	Release agents
Flow promoters	Surfactants
Plasticisers	Thixotropic agents, thickening agents
Processing aids	Wetting agents
Slip agents and lubricants (internal and external)	
Increased resistance to degradation during processing or application	
Acid scavengers	Metal deactivators
Biostabilisers	Processing/thermal stabilisers
Light/UV stabilisers	
Improvement/modification of mechanical properties	
Compatibilisers	Impact modifiers (elastomers)
Cross-linking agents	Nucleating agents
Fibrous reinforcements (glass, carbon)	Plasticisers or flexibilisers
Fillers and particle reinforcements	
Improvement of product performance	
Antistatic agents	Friction agents
Blowing agents	Odour modifiers
EMI shielding agents	Plasticisers
Flame retardants	Smoke suppressants
Improvement of surface properties	
Adhesion promoters	Lubricants
Antifogging agents	Slip and antiblocking agents
Antistatic agents	Surfactants
Antiwear additives	Wetting agents
Coupling agents	
Improvement of optical properties	
Nucleating agents	Pigments and colorants
Optical brighteners	
Reduction of formulation cost	
Diluents and extenders	Particulate fillers

Table 1.2 Technology questions related to injection moulding of polyamides

- Short cycle times
- Better mould release
- Plate-out and deposits on moulds and plastics surfaces
- Feeding problems
- Increased dimensional stability, less shrinkage
- Processing protection against depolymerisation and yellowing
- Better melt flow
- Improved surface of glass-reinforced parts
- Better strength of flow lines in moulded parts
- Higher molecular weight
- Rise of impact strength and elongation at break

the difference between success and failure in plastics technology. Typically, PVC is a material whose utility is greatly determined by plasticisers and other additives. The bottom line on the use of any additive is a desired level of performance. The additive package formulation needs to achieve cost effectively the performance required for a given application. In this respect we recall that early plastics were often unsatisfactory, partly because of inadequate additive packages. In the past, complaints about plastics articles were common. Use of additives brings along also some potential *disadvantages*. Many people have been influenced by a widespread public suspicion of chemicals in general (and additives in particular, whether in foods or plastics). Technological actions must take place within an increasingly (and understandably) strict environment which regulates the potential hazards of chemicals in the workplace, the use of plastics materials in contact with foodstuffs, the possible side-effects of additives as well as the long-term influence of the additives on the environment when the product is recycled or otherwise comes to final disposal.

Concerns are expressed by legislation and regulations, such as:

• General Health & Safety	Fitness for purpose (food/water contact materials, toys, medical)
• Montreal Protocol	Blowing agents for foams
• EU Directives	Food contact
• Landfill Directives	Disposal, recycling
• Life Cycle Analysis	Realistic evaluation of product use (flame retardants, volatiles, etc.).

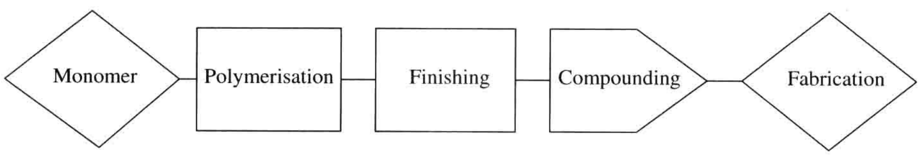
All additives are subject to some form of regulatory control through general health and safety at work legislation. From an environmental and legislative point of view three additive types in particular experience pressures, namely halogen-containing flame retardants (actions pending), heavy metals (as used in pigments and PVC stabiliser systems), and plasticisers. The trend towards the incineration of plastics, which recovers considerable energy for further use, leads to concern and thought about the effects of any additives on the emissions produced. Environmental issues often have beneficial consequences. The toxicity of certain pigments, both in plastics and in paints, has been a driving force for the development of new, safer pigments with applications in wider areas than those originally envisaged. Where food contacts are the issue, the additives used must be rigorously tested to avoid any tainting of the contents of the packaging. On the whole, the benefits of additives far outweigh the disadvantages.

1.2 PLASTICS FORMULATIONS

Plastic additives are a diverse group of specialty chemicals that are either incorporated into the plastic product prior to or during processing, or applied to the surface of the product when processing has been completed. To a great extent, the selection of the appropriate additive is the responsibility of the plastic processor or the compounder carrying out the modification. Scheme 1.1 illustrates the use of typical additives in the process from polymerisation to product manufacturing.

Figure 1.1 describes the interrelationships between the players in plastic materials manufacturing, which is considerably more complex than for the coating industry. The product performance specifications are defined by the end-users. Specialty additives demand is nowadays migrating to compounders, converters and distributors.

The *rubber industry* was the original user of additives. Rubber is a thermosetting polymer, which classically requires curing (peroxides), in a reaction which must be controlled by initiators (e.g. sulfur compounds), accelerators (e.g. aniline), retarders, etc. The whole compounding and moulding process is to be controlled by antioxidants and antiscorch agents to prevent decomposition. Plasticisers are added to improve processability, and adhesion promoters may be added to improve the bonding with reinforcement. To protect cured rubber products during lifetime, other additives are introduced into the compound to confer resistance to ozone, ultraviolet and internal heat build-up (hysteresis) as the compound is stressed. Other vital components of a final rubber compound are fillers as reinforcing agents, pigments, and extenders (essentially low-cost fillers).



Inhibitors	Initiators	Slip agents	Foaming agents	Foaming agents
	Catalysts	Antioxidants	Antioxidants	Slip agents
	Co-catalysts	Lubricants	Coupling agents	Lubricants
	Stereo modifiers	Mould releases	Impact modifiers	Mould releases
	Mineral oil	Antistats	Lubricants	Curing agents
	(catalyst carriers)	Plasticisers	Antistats	
			Flame retardants	

Scheme 1.1 Exemplified application of additives in various stages of the production process of a polymeric material