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.).

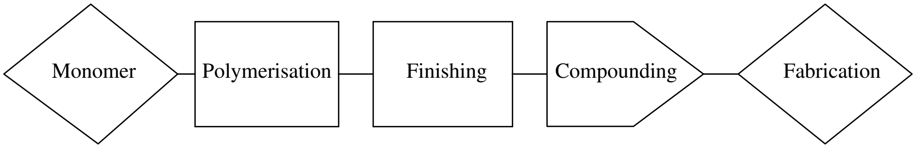
All additives are subject to some form of regulatory control through general health and safety at work legislation. From an environmental and legislative point of view three additive types in particular experience pressures, namely halogen-containing flame retardants (actions pending), heavy metals (as 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 (catalyst carriers)	Antistats	Lubricants	Curing agents
		Plasticisers	Antistats	
			Flame retardants	

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

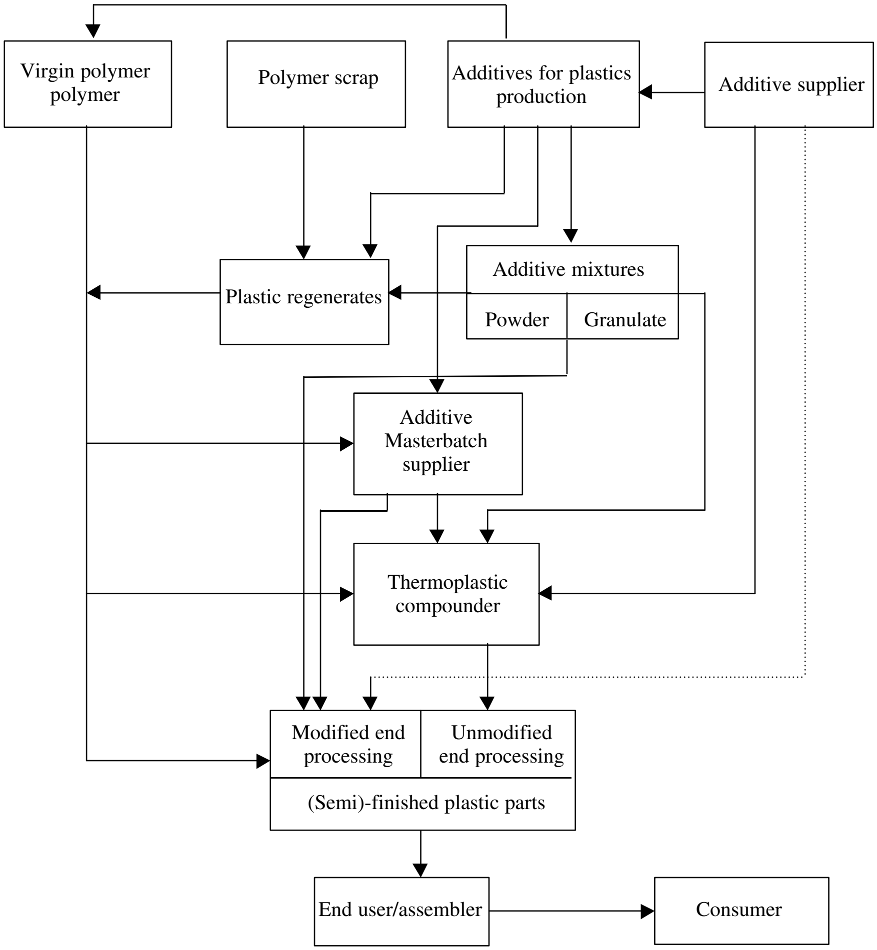


Figure 1.1 Methods of manufacturing plastic materials. After Titzschkau [9]. Reproduced by permission of Intertech Corporation, Portland, MN

The compounded rubber is therefore a highly complex chemical system, difficult to analyse (cf. Section 2.2).

Table 1.3 shows the build-up of a typical recipe for PP grades. It is important to take into account possible incompatibilities, such as co-additive interactions leading to undesired effects.

Typical additive packages for *engineering thermoplastics* have been described by Titzschkau [9], such as processing aids for PA, PP, or PET/PBT, three-component additive packages for polyamides and polyesters (nucleating agent, lubricant and process heat stabiliser) and coated copper stabilisers for polyamides. Additive packages or combinations of up to five or more additives are quite common. A typical white window PVC profile formulation comprises an acrylic impact modifier, TiO_2, $CaCO_3$, calcium stearate, a processing aid, polyethylene wax, oxidised polyethylene wax, an external/internal lubricant and lead stabilisers. Not surprisingly, the additives largely determine the cost price of PVC. Typical fibre formulations comprise primary and secondary process stabilisers, a

Table 1.3 Basic additive formulation for polypropylene

- Long-term stabiliser (always for Z/N PP, usually phenolic AOs)
- Melt stabiliser (phosphite or phosphonite)
- Acid scavenger (always for Z/N PP)
- Slip and antiblocking agents (for film)
- Nucleators, clarifiers, antistatics (for specific injection moulding applications)
- Specific antioxidants (for fibres; nonvolatiles, gas-fading)
- UV absorbers (for automotive)

neutraliser, UV additive, pigment, optical brighteners and a flame retardant.

1.2.1 Supply Forms

Various physical supply forms for product formulation exist: powders, irregular flakes, beads/prills, granulate (highly extruded or compacted), lenses, pastilles, spheres, emulsions and liquids. The majority of the additives are *solids*. Product shape is strongly influenced by the production method of the additive, typically extrusion, (strand) pelletising, grinding, spraying, flaking, or pastillating. The main concern of the additive producer is always to have a defined throughput (kg/h) of pellets with a specific average diameter (mm) from a given material. A current trend is the re-working of traditional workhorse grades of some additive classes into environmentally more acceptable product forms, which offer greater safety and are easier to handle and to mix. Traditional additives in powder form emit dust and tend to flow erratically in feeder equipment causing worker hygiene and handling problems [10,11]. Priority challenges in the field of product form performance of additives are dust reduction, dosing optimisation and dispersion improvement. Conventional approaches to meet these goals are based on mechanical compaction or mechanical treatments, using large compression forces and significant amounts (approximately 20–60 %) of processing aids causing secondary deterioration effects. Additives in the *ideal physical form* have a spherical product shape ($d_{50} = 500\text{–}1500\,\mu\text{m}$), exhibit the same performance as the original powder, ensure high homogeneity and dispersibility rate, are mechanically resistant, show no segregation in the polymer and are more suitable for feeding, dosing and blending. Some relevant milestones in additive development in the past 25 years have been the introduction of dust-free formulations of light stabilisers (1979), free-flowing antioxidants, light stabilisers and compounds (1983), free-flowing beads of oligomer light stabilisers (1989), free-flowing/dust-free oligomer light stabilisers and antioxidants (1991), durable dust-free antioxidants and compounds (1995) and customised additives (one-packs, in powder form, as dust-free compacted granules or as masterbatches). Free-flowing silica fillers have been created by dispersion of siloxane gums [12]. Additive concentrates are also available in granulate form (e.g. Morstille 18, a pastille form of DSTDP from Morton Performance Chemicals). Compared to masterbatches, these formulations have the advantage that they can be prepared at very low temperatures and the additives are thus likely to be virtually intact. Some innovative spherical particle systems with narrow size distribution have recently been introduced, such as drop process pelletising with industrial applications for waxes, saponified fatty acids, metal stearates, metal soaps, stabilisers and colour concentrates [13], and continuous fluidised bed (FB) spray granulation, as demonstrated for carbon-black (CB), TiO_2, flame retardants (FR), colour pigments, organic based stabilisers (OBS) and light stabilisers [14]. Drop process pelletising of low-viscosity plastics and additives is applicable to materials available as liquids or melts with viscosities below 500 cP.

The last 15 years have witnessed a constantly increasing impact of *additive masterbatches* (concentrates containing a higher level of additives dispersed in the parent polymer), e.g. for antistatics [15], foaming agents, flame retardants, impact modifiers, antimicrobials, modifier masterbatches for surface improvement and shear reduction, colour masterbatches [16], etc. The use of concentrated additive masterbatches and sophisticated material delivery systems gives high confidence in polymer compounding. Other important reasons for choosing additive masterbatches instead of pure additives are the physical form, dosability, ease of handling, homogeneous mixing, safety, additive protection and improvement of performance, influence of carrier system, supplier experience and cost. Porous polyolefin carriers offer masterbatch suppliers an inexpensive and simple way of producing high concentrates without having to use an extruder. Pure additives usually require specific handling. In fact, some additives have to be dispersed like pigments to avoid agglomeration; some others need to be intensively kneaded. It is difficult to choose processing conditions that offer simultaneously an optimum on mixing/dispersing/kneading/dissolving efficiency as required for processing of additives with very different properties. Masterbatches go some way to overcome these problems. An additive producer or a masterbatch supplier may carry out additive selection and production of the mixture.

Blending and/or custom blending is another current trend. *One-pack systems* may offer antioxidant activity, processing aid and lubrication or anticorrosive activity in one package, usually in a low- or nondusting product form. A proprietary database [17] mentions already some 140 commercial binary and ternary phenol-phosphite blends, HALS-containing blends and miscellaneous blends. As most polymer processing requires both primary and secondary antioxidant addition, 'one-pack' blends containing these components are another obvious development. Antioxidant blends are combinations of primary hindered phenolic and secondary organophosphite antioxidants, which synergistically act together to provide excellent performance in the prevention of thermo-oxidative degradation of the polymer. Examples are Ciba Specialty Chemicals Irganox B series additive blends (e.g. Irganox B561 is Irganox 1010 and Irgafos 168 in 1:4 parts) and Great Lakes Chemical No Dust Blends (NDB) [18–20]. The move to multicomponent packages takes away the risk of operator error, leads to productivity benefits, aids ISO protocols and good housekeeping. Other *advantages* are ease of dosage, reduction in concentration variability during polymer production (quality control, less off-spec product), in logistics and in analytical costs (analysis only of the easiest detectable component). By controlling the composition of the NDB with analytical instruments the precision has been found to be of the same order of magnitude as the tolerance of the used analytical methods. However, because the weighing operation is carried out by an electronic balance, the achieved precision level is always higher than the one detectable with common analyses. Dosing/homogeneity accuracy affecting stabiliser additivation has been addressed by Sasselli [18].

For the purpose of cost reduction, it is sometimes dangerous practice to limit analysis of the components of dry-blends or other mixtures to the determination of one ‘critical’ component only. As shown by Pahl and Grosse-Aschhoff [21] various degrees of dispersion may easily invalidate such conventional assumptions. Techniques do exist (e.g. near-infrared spectroscopy) which simultaneously determine all components and can therefore cope with problems of heterogeneity. Main disadvantages of one-pack systems are loss of flexibility and price. A trend towards uniformity and streamlining of the product range nowadays applies especially to producers of polyolefins and PVC; however, the situation is different for engineering thermoplastics where it is virtually impossible to avoid producing tailor-made product modifications.

Only a few additives are *liquids* (e.g. Vitamin E), which require different handling. A recent development is incorporation of the (viscous) liquid and low-melting additives in high concentration in high-porosity carriers, such as LDPE (Stamypor®, $d = 925\,\mathrm{kg/m^3}$) [22]. Such nonhygroscopic holey beads can successfully be used for the production of polyolefin concentrates with liquid and low-melting polar and nonpolar additives, such as antistats, anticondensation agents, slip agents, mould-release agents, lubricants, antioxidants, UV stabilisers, pigments, polyisobutylene, pastes and fragrances; temperature-sensitive reactants such as silanes, peroxides and chain extenders offer safety and efficiency improvements. Due to its spherical shape, Stamypor® remains a free-flowing product even after high liquid loading (exceeding 50 %), allowing good dispersion. The loading process just requires a low-speed mixer. Similarly, AKZO’s microporous carriers (Accurel), based on PP, HDPE, LDPE, EVA, PC, ABS, SAN and nylon, have a load capacity of up to 70 %.

The *concentration* of additives in a polymer depends on the intended function. Each additive has specific concentration ranges in which it does not affect the properties of the matrix. Additive levels amount to at least some 100 ppm (e.g. Vitamin E as a melt processing stabiliser), although catalyst residues and unintentional contaminants may show lower levels. Typical antioxidant levels to inhibit thermal oxidation in polyolefins are of the order of 0.1 wt%. However, in applications of LDPE, LLDPE, HDPE and PP calling for very good toughness or high deformability of the material the filler content easily amounts to 30–40 wt% [23]. There are many nominally organic plastics articles which actually consist of considerably less than 50 % organic polymer, the remainder being largely inorganic additives. For example, in general spumific flame retardant additives are less efficient in polyamides than either halogenated or intumescent additives and much higher loading levels, typically 50–60 wt%, are then required in order to prevent dripping and to obtain the same levels of flame retardancy that can be achieved with typically 10–25 wt% of a halogenated or an intumescent additive. Some other highly filled compounds are cross-linked PMMA/72 wt% SiO_2 (Silgranit), PMMA/62 wt% Si (Silacron), PMMA/62 wt% $Al(OH)_3$ (Corian). The Japanese manufacturer Kanebo Gosen has developed a heavily metal-filled PA resin for production of electronic and automotive components with a specific gravity of $13\,\mathrm{g/cm^3}$ (compared with 11.3 of lead). Composite polymeric materials containing high percentages of nonpolymeric materials are used extensively in the fabrication and engineering industries. Twin-screw systems are configured to continuously mix very high levels of metal fillers (90 wt% +) with various polymer binders. Obviously, at such high loading levels a distortion of the balance of mechanical properties of the base polymer results, but this may be acceptable (e.g. 70 wt% of fused silica properly balances the coefficient of thermal expansion in an epoxy moulding resin) [24]. Similarly, a large proportion of automotive dashboard skins has a high plasticiser content (ca. 70 phr). PVC is almost unique in its ability to accept addition of very high plasticiser levels (up to 100 phr and above) while still retaining useful mechanical properties. Also for processing of cellulose acetate it is necessary to incorporate relatively high levels of a polar plasticiser (typically

50 phr) to lower the softening temperature below the decomposition temperature.

1.2.2 Additive Delivery

Additives can be incorporated into the polymer at several stages: (i) during the polymerisation stage (directly during production of the plastic in the reactor); (ii) addition to the finished granulate in a subsequent processing (compounding/mixing) stage, or in the processing machine itself. Finally, additives may be applied to the finished part surface. Much depends on the type of additive and polymer. Automated powder sampling systems have been described [25] and handling of solid additives has been reviewed [26]. A crucial aspect is to obtain a completely homogeneous mixture of polymer and additive – a difficult technological target, as shown by microscopy and chemiluminescence studies. Additives such as stabilisers can be introduced at the raw material manufacturing stage, whereas performance-critical additives (such as flame retardants) are introduced at the compounding stage. Additives to confer special technical properties are usually introduced in a secondary compounding stage.

To facilitate in-plant compounding, most suppliers have developed systems which efficiently and reproducibly deliver a controlled additive ‘package’ to a compound, using either a specialised concentrate or a masterbatch formulation. Some of the polymer manufacturers have also made available *advanced additive delivery* systems, which they have often developed originally for their own use (e.g. Eastman, Montell).

In the most sophisticated operations, there are facilities for *reactive compounding*, in which reactive additives are chemically bound as an integral part of the polymeric structure. Thus it is possible to produce hundreds of very differentiated modified plastics from very few basic plastic types and the range of recipes and possible varieties is virtually inexhaustible.

1.3 ECONOMIC IMPACT OF POLYMER ADDITIVES

Plastic and rubber additives are both commodity chemicals and specialties. The *Handbook of Plastic and Rubber Additives* [27] mentions over 13 000 products; antioxidants and antiozonants amount to more than 1500 trade name products and chemicals [28], flame retardants to some 1000 chemicals [29] and antimicrobials to over 1200 products [30].

In the past decades, polymer materials have been continuously replacing more traditional materials such as paper, metal, glass, stone, wood, natural fibres and natural rubber in the fields of clothing industry, E&E components, automotive materials, aeronautics, leisure, food packaging, sports goods, etc. Without the existence of suitable polymer materials progress in many of these areas would have been limited. Polymer materials are appreciated for their chemical, physical and economical qualities including low production cost, safety aspects and low environmental impact (cf. life-cycle analysis).

Plastic additives account for 15–20 wt% of the total volume of plastic products marketed. Estimates of the size of the *world additives market* vary considerably according to classification. Table 1.4 shows

Table 1.4 The global additives business (various estimates and forecasts)

	Global				USA	Western Europe		
	1996^{a} (%)	1996^{a} (kt)	1996^{a} (US\$m)	1996^{b} (kt)	1995^{b} (US\$m)	1996^{b} (US\$m)	2001^{b} (US\$m)	2000^{c} (kt)
Fillers	n/a					1020	1060	
Plasticisers						1930	1960	
Colorants						1200	1370	
Flame retardants	31	843			718	580	670	375
Heat/light stabilisers	17	462		295		530	620	
Impact modifiers	17	462						
Lubricants	16	435						
Antioxidants	7	190		88		370	480	
Others	12	326				1000	1190	
Europe	26		4100					
North America	23		3700					
Asia/Pacific	39		6200					
Rest of world	12		1900					
Total		2720	15 900			6630	7350	

Source: ^{a} Phillip Townsend Associates; ^{b} Business Communications Co.; ^{c} Schmidt [31].

some marked differences in the estimates of the global additives business volume (depending upon definition of 'additive'). According to Phillip Townsend Associates Inc. [32] the world market for performance additives (modifiers, property extenders and processing agents), thus excluding commodity materials such as fillers and pigments but including plasticisers, was worth nearly US$15.9 billion or 7.9 mt/yr in 1996. Recent figures for 2001 are 14.6 billion (by region: US 28 %, EU 26 %, AP 38 %, ROW 10 %) or 8.0 mt/yr [33] denoting a reduction in the growth rate, shrinking value (Asian crisis, WTC effect), and margin compression for material suppliers and compounders. Plastics additives are a highly competitive business.

Table 1.5 is a breakdown of the consumption by additive class. Total EU additive consumption is reported as 6989 kt (1997) growing up to 9031 kt (2002), with fillers 4346 kt, plasticisers 940 kt and colourants 728 kt (in 1997) being the main classes. Additive consumption by polymer classification for Europe is given in Table 1.6.

Worldwide consumption of performance additives (excluding plasticisers) grew from just over 2.7 mt in 1996 to 3.6 mt in 2001. Flame retardants make up 31 % of the volume and stabilisers, impact modifiers and lubricants each account for around 16–17 %. Flame retardant markets (construction, E&E devices, automotive) are headed for unprecedented development and change, being threatened by environmental, health and safety issues. The global demand for mineral-based FR compounds will increase dramatically.

Table 1.5 Consumption of plastic additives by type (1998)

Plasticisers	32 %	Organic peroxides	6 %
Flame retardants	14	Lubricants/mould release agents	6
Heat stabilisers	12	Light stabilisers	3
Impact modifiers/ processing aids	10	Others	8
Antioxidants	9	Total	US$14.9 billion

Source: Townsend's Polymer Services & Information (T-PSI). Reproduced by permission.

Table 1.6 Additive consumption by polymer classification in Europe

Class	1997	2002	1997	2002
Commodity thermoplastics	4500 kt	5500 kt	62.2 %	59.5 %
Engineering plastics	1050	1900	15.3	20.7
Thermosets	1500	1600	22.5	19.8

After Dufton [34]. Reproduced by permission of Rapra Technology Ltd.

The total bulk volume of additives derives from modifiers, while the value comes from relatively small volumes of increasing high-performance chemicals, for stabilising, curing/cross-linking, colouring and flame-retarding various types of plastics, both thermoplastics and thermosets. More precisely, a breakdown of the 1999 world market (totalling 7.6 mt and US$15.0 billion) shows modifiers (coupling agents, impact modifiers, nucleating agents, organic peroxides, chemical blowing agents, plasticisers) at 69 % of total volume and 51 % of total value, property extenders (antioxidants, preservatives, light and heat stabilisers, antistatic agents, flame retardants) at 23 % of total volume and 41 % of total value, processing aids (mould release agents, lubricants, antiblocking agents, slip agents) at 8 % of total volume and 8 % of total value [35].

The plastic additive market is characterised by a highly fragmented global market. Nevertheless, global customers, a maturing technology and expiring patents are fuelling the field. Each of the additive classes is favoured by a different customer group. Modifiers are largely purchased by fabricators, who account for 69 % of the modifier consumption (volume). Resin manufacturers or captive compounders capture 16 % and merchant compounders purchased the remaining 15 % of the modifiers. In 1994, resin manufacturers consumed 1.9 billion pounds of property extenders, merchant compounders 28 %, and fabricators the remaining 7 %. The processing aids are the most evenly consumed class of polymer additives. Fabricators lead with 44 % of total volume, followed by resin manufacturers with 33 % and merchant compounders consuming the remaining 23 %. The average cost of the polymer additive classes varies widely.

Demand for the different classes of polymer additives varies by resin. Modifiers and processing aids rely heavily on PVC while the property extenders are primarily used in non-PVC resins. PVC is by far the largest *consuming resin* for polymer additives (excluding fillers), accounting for some 80 % of the world-wide volume or 60 % in total value. Polyolefins are a distant second accounting for 8 % and 17 %, respectively [36].

The European consumption of plasticisers (as the main modifier) is gradually increasing, as shown in Table 1.7, with an expected growth of 2.7 % for 2001–2006. The total European market for flame-retardant chemicals (percent of revenues by product type – forecast for the year 2003) is as follows:

Table 1.7 European consumption of plasticisers (kt)

Plasticiser type	1993	1997	2000
DOP	484	522	562
DINP/DIDP	371	454	490
Other phthalates	78	91	100
Other plasticisers	147	171	184
Total	1080	1239	1336

Source: CDC.

Table 1.8 Plastic additives – expected global growth rates 1999–2004[a]

Highest growth (6–7 %)	*Medium growth (4–5 %)*
Coupling agents	Antiblocking agents[b]
Light stabilisers[b]	Antioxidants[b]
Nucleating/clarifying agents	Antistatic agents
	Chemical blowing agents
Lowest growth (3 % or less)	Flame retardants[b]
	Heat stabilisers[b]
Biocides	Impact modifiers/processing aids[b]
Plasticisers[b]	Lubricants/mould release agents[b]
	Organic peroxides
	Slip agents

[a] Not corrected for WTC effect.
[b] Additives most affected by environmental.
After Galvanek *et al.* [35]. Reproduced by permission of Rapra Technology Ltd.

phosphorous-based chemicals (38.2 %), inorganic compounds and melamine (36.2 %), halogen-based chemicals (25.6 %). The volume of halogenated flame retardants in Europe has not declined. The European market for additives (plasticisers, light and heat stabilisers, flame retardants and antioxidants) is expected to grow from US$2.2 billion (1998) to 2.6 billion (2005) [37]. *Global growth rates* for plastics additives are given in Table 1.8, with some performance additives showing 'above-average' potential.

Light stabilisers are the fastest-growing sector of the US additives market. Large amounts of stabilisers are also used for the protection of various petroleum products, foods, sanitary goods, cosmetics, and pharmaceuticals. The most extensive development, however, is addressed to the field of polymer stabilisation. The global consumption of light stabilisers in plastics in 1996 amounted to 24.8 kt world-wide, namely PP 45 %, PE 29 %, styrenics 5 %, EP 7 %, PVC 9 % and other polymers 5 %. Similar figures for antioxidants are 206.5 kt world-wide with PP 40 %, PE 25 %, styrenics 15 %, EP 10 %, PVC 5 % and other polymers 5 % (source: Phillip Townsend Associates Inc.). More than 200 users worldwide consume over US$400 million of light stabilisers. Much lower growth is predicted for plasticisers [38]. For the seven main types of plasticiser – phthalates, aliphatics, epoxidised vegetable oils (EPOs), phosphates, trimellitates, citrates and polymerics – the predicted growth rate is 2.8 % for the period 1999–2004 for a global demand of 4.6 mt in 1999. Factors affecting plastic additive growth are given in Table 1.9.

Table 1.9 Factors affecting plastic additives growth

- Resin demand/mix changes
- End use demand and requirements
- New technologies
- Interpolymer competition
- Regional growth patterns
- Substitution of traditional materials
- Lifetime shortening
- Miniaturisation
- Drive for shareholder value
- Focus on the customer ('one stop shopping')
- Environmental regulatory issues

On the whole, the amount of additive per pound weight of resin is decreasing as more efficient materials are developed, cost reduction is attempted and, in some cases the concentration of potentially toxic substances is cut. Excluding the filler market (largest in size: 50 vol%; 15 % of total value), there are over 400 suppliers of performance polymer additives (antiblocking/slip agents, antioxidants, antistatics, coupling agents, chemical blowing agents, flame retardants, heat stabilisers, impact modifiers, light stabilisers, lubricants, mould-release agents, nucleating agents, organic peroxides, plasticisers and preservatives) worldwide, including already over 200 producers of colour masterbatches only in Europe [32].

Figure 1.1 shows that the methods of manufacturing (semi-)finished plastic parts involve various players: equipment manufacturers, polymer producers, additive suppliers, compounders and final processors. It can be safely assumed that the compounder will continue to be the main customer for additives and additive concentrates also in the future. Finally, the recently established Plastics Additive Museum (Lingen, Bavaria), by a pioneer in PVC additives (Bärlocher GmbH), shows that the business is coming to age.

1.4 ANALYSIS OF PLASTICS

In contrast to low-MW substances, which are composed of identical molecules (eventually apart from isomers), macromolecules constitute a statistical assembly of molecules of different molecular weight, composition, chain architecture, branching, stereoregularities (tacticity), geometric isomerism, etc. Examination of polymer systems requires determination of several types of polydispersity, such as molecular weights $\langle M_n \rangle$, $\langle M_w \rangle$, molecular weight distribution (MWD), compositional homogeneity, functionality distribution, etc. Various chromatographies, such as size-exclusion chromatography (SEC), high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC), are helpful in these analyses. Yet, even with this much of effort a polymer is not fully characterised as other 'details' are of great practical importance, such as rest monomer (e.g. styrene in PS), oligomers, or volatiles (such as water in nylons). Catalyst residues are another inherent, and important, impurity in a polymer, especially in relation to stability. Consequently, full characterisation of an unknown polymer is a challenging task. However, this is more child's play in comparison to the requirements of extensive chemical analysis of a *polymeric material*, constituted of a formulation of the aforementioned statistical assembly of macromolecules with organic and/or inorganic additives, fillers, etc. *Textbooks* on various aspects of the determination of the complex structure of polymers (in particular macromolecular characterisation in terms of molar mass, chemical composition, functionality and architecture) [39–57] outnumber those covering *analysis of additives* in polymers [41,50,54,55,58–63] or textbooks dealing with the in-service aspects of the materials [58,60]. Actually, in industrial practice these problems are usually treated separately as different interests are addressed. This does not mean to say that no polymer/additive sample will ever be examined both to characterise the polymer and the additive composition. However, frequently the chemical nature of the polymeric matrix of a formulated polymeric material is already known (but usually not for rubbers). Eventually, for additive analysis only the nature of the polymer needs to be assessed (mainly for solvent choice), but not its polydispersity or other structural details. Consequently, and in view of the considerable spread of the analytical topics, it is not surprising that few authors dare deal in depth with molecular characterisation of polymers and polymer/additive analysis in one monograph [41,50,52,54,55]; the latter are also fairly dated. The required *level of analysis* is often not merely that of the identification of the additives of Appendix II (relatively simple), but a full analysis of all active ingredients present in a polymeric matrix, both qualitatively (not straightforward) and quantitatively (difficult), and sometimes even in a spatially resolved fashion (very difficult). Representative sampling is obviously of immediate concern. Basic needs in polymer/additive analysis are given in Table 1.10.

Table 1.10 Basic needs in polymer/additive analysis

- Qualitative identification of a particular additive in a sample
- Quantitative determination of the additive concentration
- Reliability, accuracy
- Sensitivity (down to 0.01 wt% or less)
- Short analysis time (e.g. simultaneous analyses, automation)

Industrial analytical laboratories search for methodologies that allow high quality analysis with enhanced sensitivity, short overall analysis times through significant reductions in sample preparation, reduced cost per analysis through fewer man-hours per sample, reduced solvent usage and disposal costs, and minimisation of errors due to analyte loss and contamination during evaporation. The experience and criticism of analysts influence the economical aspects of analysis methods very substantially.

The ability to reproducibly determine the additive package present in polymers is of major concern to resin manufacturers, converters (compounders), end-users, regulators and others. Qualitative and/or quantitative knowledge of compounding ingredients, to be obtained by additive analysis, may be needed in various stages of a *product lifecycle* (Table 1.11).

Analytical support is required throughout for base polymers, compounds, additives, polymer-based products and manufacturing sector products and components. Product development (e.g. surface active additives, such as antistatics, slip and antiblocking additives) leading to better performing products requires an in-depth understanding of the mechanism of action. Polymer/additive analysis contributes to this understanding. Apart from polymer microstructural analysis, polymer/additive analysis is the only way to investigate the effects of processing conditions on a polymer at the molecular level. The determination of factors affecting additive consumption can lead to an improved understanding of how to process polymers both cost effectively and with maintenance of final product properties as a goal. However, in order to determine additive consumption and draw valid conclusions, the technologist requires reliable and reproducible methods for additive level determination.

It is equally important for the manufacturer and regulator to know the level of additives in a polymer material to ensure that the product is fit for its intended purpose. Additive analysis marks sources of supply, provides a (total) process signature and may actually be used as a *fingerprint* of a polymeric material, in particular as molecular characterisation of the polymer

Table 1.11 Analytical product lifecycle

Development

- Materials selection
- Product development (structure/property relationships)
- Improved product design specification
- Improvement of product quality
- Compound formulation
- Testing (stability, flame retardancy, etc.)
- Process development
- Vendor and competitor additive package analysis (reverse engineering)
- Countertyping
- Research applications
- Application development
- Food contact (toxicology)
- Migration studies (compliance with regulations, blooming, staining; medical)
- Service life prediction

Production

- Assessment of raw materials (purity; ‘hidden’ ingredients; supplier monitoring)
- Quality control of intermediate and end-products (plant support; process deviations)
- Manufacturing problems (compounding or processing errors)
- Spy on production process (via low-MW by-products)
- Deposit compositions (dosing problems, caking, etc.)
- Contamination
- Process improvements
- Technical specification compliance
- Standardisation of semimanufactured and intermediate products (SPC, GLP)
- Additive depletion during polymer processing
- Industrial troubleshooting (defect and failure analysis at polymer, additive and masterbatch producers, or at polymer processors)
- Occupational safety and hygiene

In-service

- Failure diagnosis (degradation of product performance)
- Customer support
- Product recall (complaints, substandard batches)
- Compliance testing
- Taste, odour, discoloration problems (yellowing, mystery contaminants)
- Emission of VOCs and decomposition products
- Additive depletion or degradation during materials lifetime
- Post-mortem analysis
- Materials changes (ageing, dynamic loading, etc.)
- Grade detection (ownership; materials recognition, markers)
- Government regulations
- Environmental
- Claims, litigation
- Expert witness service
- Forensic investigation
- Recycling (characterisation, restabilisation)

is often less selective in fair discrimination. Important problems, both for the additive producer and user, are the determination and control of impurities in additives (determination via chromatographic methods). It is equally important to be able to determine the concentration of adventitious volatiles in polymers (arising from the manufacturing method), which usually range from a few tens of ppm to several hundred ppm. Volatile residues may affect the processability and mechanical properties of polymers, or may cause tainting in case of foodstuff- or beverage-packaging grades of polymers. Residual volatiles are often indicative of the production process (and therefore play a role in product protection). Typically, oligomer extracts often provide a fingerprint permitting to establish the origin of a polymeric material (e.g. of polycarbonate). In both cases a broad knowledge of competitor products is required. Obviously, for a detailed insight in the differences of the fingerprints further identification (e.g. by means of LC-MS) is necessary. ‘Tracers’, based on uncommon elements (e.g. strontium stearates), are increasingly being used by polymer manufacturers as a rapid means of screening ‘complaint’ polymer samples, in order to ascertain the ownership of the material.

Apart from *routine quality control* actions, additive analysis is often called upon in relation to testing additive effectiveness as well as in connection with food packaging and medical plastics, where the identities and levels of potentially toxic substances must be accurately known and controlled. Food contact plastics are regulated by maximum concentrations allowable in the plastic, which applies to residual monomers and processing aids as well as additives [64–66]. Analytical measurements provide not only a method of quality control but also a means of establishing the loss of stabilisers as a function of material processing and product ageing.

Additive analysis is also beneficial in the identification of reaction or transformation products, as well as of odorants or irritants that evolve from a polymeric material during processing or use, in dealing with problems involving migration and diffusion phenomena, in the *deformulation* of unknown additive cocktails, and in solving the origin of complaints (e.g. regarding discoloured or early aged materials), etc. Moreover, inadvertent contaminants may often pose considerable practical problems as sources of yellowing or discoloration. Consequently, some applications require a quick semiquantitative analysis to support production while in other circumstances the analytical chemist must act as a detective to determine which additives are incorporated into a sample and then quantify them. Unless the analyst is sufficiently familiar with the type of sample to be tested, it makes good sense to apply a specific test for

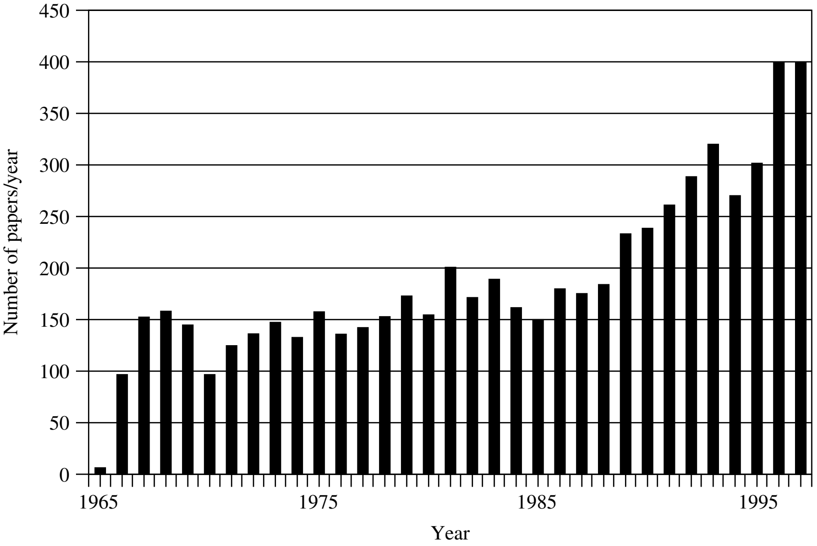


Figure 1.2 Number of scientific publications per year on polymer/additive analysis. Source: *Chem. Abstr.*

the presence of specific additives before embarking upon the involved determination of something that might not be there. Gabriel and Mulley [67] have detailed a range of such tests for anionic surfactants. However, in some cases it is imperative that a complete characterisation of a system of additives in a polymer is made, e.g. if a product is not meeting performance expectations.

Nothing is more difficult than screening for the general unknown (nontargeted analysis). Identification and/or verification and quantification of a complete additive package, consisting in the best case of fairly low-MW organics in a polymeric matrix, is a considerable analytical challenge. The detection of an additive in a polymer is determined by the following parameters: (i) chemical nature of additive and polymer matrix; (ii) concentration; and (iii) thermal stability (fragmentation). The analytical problem becomes even considerably more complex for *polymeric* additives, in case of interaction between additive and polymer backbone (grafted functionalities), or in the presence of degradation phenomena. Analysis of polymeric additives such as Chimassorb 944 is notoriously difficult (cf. Sections 4.4.2.2 and 4.4.2.3). The same analytical misfortune may be bestowed on a polymer material supplier who stealthily tries to build up some knowledge of competitor products (either in a ‘me too’ approach or with more refined objectives). The task is the more demanding as it is not acceptable from an analytical point of view that fragmentation occurs during analysis. This may easily be the case in handling thermally labile compounds. For instance, both mass spectrometry and thermal analysis indicate initial fragmentation resulting in the loss of 2-hydroxybenzophenone from a 2-hydroxybenzophenone based phosphite, or of 4-amino tetramethylpiperidine from a novel phosphite stabiliser based on a bis-hindered phenolic moiety coupled to a 4-aminotetramethylpiperidine chromophore [68].

The need for complete compositional analysis of additive packages in industrial plastics for both research and quality control applications has led to the development of numerous analyte-specific test procedures in recent years.

Table 1.12 and Figure 1.2 give a fair idea of the vast amount of polymer/additive analysis *literature* published in the last three decades and the effort spent on each technique. It is clearly not the purpose of this book to deal with analytical methods for any class of additives in particular, even less so to describe all reported analytical procedures for a given additive. Rather, those general analytical procedures are highlighted which have been used in the past and are still being applied nowadays, and especially those which may be expected to have an increasing impact in the near future. Over 90 % of all reported polymer/additive investigations have been concerned with polyolefins and polyesters.

Table 1.13, which lists the main techniques used for polymer/additive analysis, allows some interesting observations. Classical extraction methods still score very high amongst sample preparation techniques; on the other hand, not unexpectedly, inorganic analysis methods are not in frequent use; for separation purposes

Table 1.12 Scientific publications on analysis and determination of additives and additive classes in polymers and plastics

Class	No. entries	Class	No. entries
Additives	1647	Lubricants	437
Antioxidants	829	Metal deactivators	4
Antiozonants	34	Nucleating agents	47
Antistatics	86	Optical brighteners	10
Blowing agents	127	Photoinitiators	113
Cross-linking agents	442	Plasticisers	713
Emulsifiers	186	Quenchers	43
Fire/flame retardants	132	Stabilisers	530
Free radical scavengers	22	Surfactants	917
Hydroperoxide decomposers	16	UV-absorbers	100
Impact modifiers	32	Total	5792

Source: *Chem. Abstr.* 1968–1997.

Table 1.13 Scientific publications on analytical methods for the qualitative and quantitative determination of additives and additive classes of Table 1.12

Sample preparation techniques: extraction (776), Soxhlet (33), ultrasonics (24), microwave (21), SFE (22), Soxtec® (–), ASE® (2)
Chromatographic techniques: chromatography (1024), GC (424), HS-GC (6), GC-MS (102), (HP)LC (321), (HP)LC-FTIR (31), (HP)LC-MS (30), SEC (39), SFC (34), SFE-SFC (14), CE/CZE (32)
Spectroscopic techniques: spectroscopy (567), UV (478), (FT)IR (727), NIRS (15), NMR (247), SFE-SFC-FTIR (2)
Mass spectrometric techniques: mass spectrometry (387), CI (20), EI (7), ESP-MS (12), FAB (15), FD (11), FTICR-MS (44), MALDI-ToFMS (12), others (APCI, DCI, DI, DP, DT, FI, LSIMS, PB, PD, PSP, TSP) (4)
Thermal techniques: thermal analysis (357), pyrolysis (201), PyGC (97), PyMS (65), PyGC-MS (42)
Inorganics: AAS (16), AED (3), ICP (8), XRF (23)
Various: direct analysis (29), LD (24), ToF-SIMS (32), ISE (49)

Source: *Chem. Abstr.* 1968–1997.

chromatography (especially GC and HPLC) and thermoanalytical techniques are being relied upon; for detection much trust is laid upon (FT)IR, UV, NMR and MS, with the latter detection method being divided up into a bewildering number of subdisciplines. Hyphenated techniques are holding the future. Direct (in-polymer) analytical methods are still rather few but constitute a growth area.

Despite continuing improvements in instrumental methods for chemical analysis, the reliable analysis of organic (and inorganic) additives in polymers remains a formidable task because of the complexity of commercial polymer formulations [69,70]. Frequently more than one method may perform an analysis. An example of such a *multiple choice* is the quantitative analysis of a nonpolymeric component in a polymer matrix, such as dioctylphthalate (DOP) in PVC. If DOP is the only carbonyl containing material present, IR is feasible with suitable calibration. An alternative is quantitative analysis by GC, LC or SEC. Usually a multitechnique approach is necessary. A good *multidisciplinary analysis* is the study of performance of antistatic and slip additives in polyolefins, as studied by means of XPS, PA-FTIR, IR, TLC, NMR, potentiometry and chemiluminescence [71]. It is the added value of the analyst to apply those techniques that are most likely to provide a rapid answer.

In compliance with EURACHEM/CITAC Guide 2 [72] polymer/additive analysis can be considered as a collection of discrete subtasks (Figure 1.3), each consisting of a number of unit processes, themselves composed of modules containing routine unit operations. The unit processes are characterised as being separated by natural dividing lines at which work can be interrupted and the test portion can be stored without detriment before the next step.

Critical expert forums for all aspects related to the analytics of additives in polymers are the ACS Analytical Division, SPE Polymer Analysis and Polymer Modifiers & Additives Analysis Divisions or the German Arbeitskreis Polymeranalytik (cf. homepage DKI).

1.4.1 Regulations and Standardisation

The additive content of polymers needs to be monitored for quality and regulatory reasons. Examples of regulations with limits are food-contact rubber articles intended for repeated use (21 CFR 177.2600) and food-contact packaging for irradiated food (21 CFR 179.45). Unfortunately, the additive composition is not usually disclosed to the analysts of the food packaging industries, nor to those of food surveillance programmes. In the framework of control of materials and articles a systematic approach to such control has been elaborated in The Netherlands to meet *Dutch Regulations* [73] in existence before Directive 90/128/EEC. Practical application of this approach for over a decade has shown that analysis of the type of polymer used in a given food-contact situation, and of the additives and other constituents that might be present requires great experience. The Dutch test method is subject of discussion by the CEN working

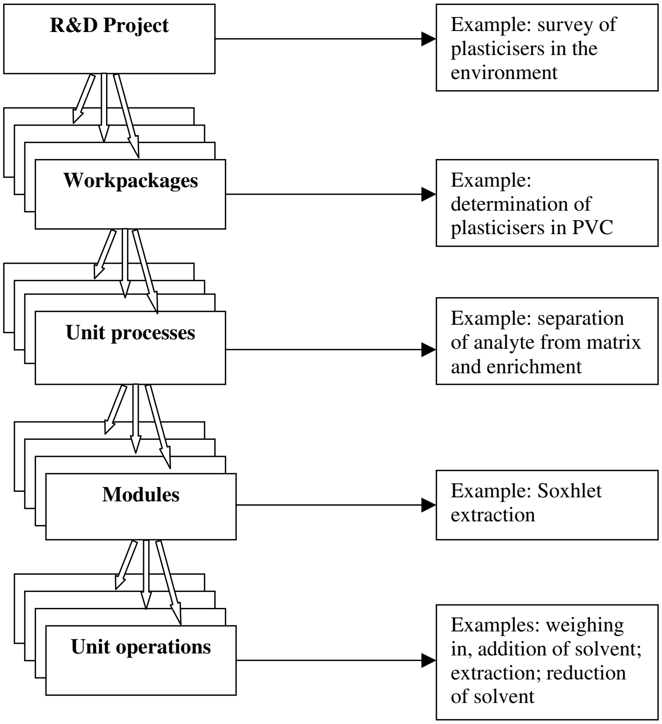


Figure 1.3 Breakdown of a polymer/additive analysis project into unit operations

group WG 2 of Technical Committee TC 194; a CEN standard is in preparation [74]. The Dutch method is applied in its original or slightly modified form by a number of government laboratories in Denmark, Greece, Norway, Sweden and Switzerland and in industrial test laboratories (especially by converters).

It should be mentioned that the Food Additives Analytical Manual (FAAM) [75] provides analysts with FDA evaluated methodology (partly subjected to collaborative study) needed to determine compliance with food additive regulations, including procedures for indirect food additives, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *t*-butylhydroxyquinone (TBHQ), dilaurylthiopropionate (DLTDP), fatty acid methyl esters (FAME), sodium benzoate, sorbitol, and others.

Analysts in industry prefer in many cases to maintain consistent methods for their analyses. Recommended ASTM analytical procedures are quite well developed in the rubber and polymer industry. As an example, we mention the standard test method for determination of phenolic antioxidants and erucamide slip additives in LDPE using liquid chromatography [76]. However, the current industry standard test methods (ASTM, AOAC, IUPAC, etc.) use a large number of solvents in vast quantities whereas spent solvent waste stream disposal has become an important issue.

National and *supranational (EEC) regulations* are being enforced to exercise control on the use of a list of additives used for the production of food contact plastics (Synoptic Document N.7 of the Commission of the European Communities [77]), but often without adequate analytical support. Moreover, industry has generated its own *company-specific standards* and (validated) analytical procedures for polymer/additive analysis. For reasons of compliance the polymer producers (chemical industry) are well advised to take good notice of company-specific norms of their end-users, e.g. document D 40 5271 (PSA) regulates extraction of plasticisers and additives, instruction D 40 1753 (PSA) [78] concerns the quantitative evaluation of the principal components of vulcanised rubbers by means of thermogravimetric analysis, document PV 3935 (Volkswagen/Seat/Škoda/Audi) [79] describes an analytical method for the determination of polymer type and additives by means of pyrolysis - gas chromatography/mass spectrometry (PyGC-MS), whereas instruction PB VWT 709 (Daimler Benz) [80] regulates the determination of gaseous and condensable emissions in car interiors by means of thermodesorption.

For standard or proprietary polymer additive blends there is the need for analytical certification of the components. Blend technology has been developed for two- to six-component polymer additive blend systems, with certified analytical results [81]. Finally, there exist physical collections of reference additive samples, both public [82] and proprietary. The Dutch Food Inspection Service reference collection comprises 100 of the most important additives used in food contact plastics [83–85]. Reference compounds of a broad range of additives used in commercial plastics and rubber formulations are generally also available from the major additive manufacturers. These additive samples can be used as reference or calibration standards for chromatographic or spectroscopic analysis. DSM Plastics Reference Collection of Additives comprises over 1400 samples.

1.4.2 Prior Art

As shown in Appendix II there is a multitude of books concerning various aspects of additives in polymers (either commercial information or technical/scientific principles). However, in the past, only a fairly restricted number of contributions in *textbooks* has devoted attention to the analysis of additives in plastics. The field of polymer/additive analysis has grown steadily since its inception in the late 1950s.

Leadership in many branches of chemistry resides outside the traditional academic boundaries. In many areas, including polymer/additive analytics, industrial laboratories have assumed the leadership. This is not surprising because of the geography of the problem. Haslam *et al.*'s classic textbook [54] on the identification and analysis of plastics, reflecting the considerable analytical experience of the ICI Plastics Division, has been *the* established working reference source for industrial chemists concerned with plastics analysis in the 1965–1983 period (though limited to literature up to 1970 only). However, the authors deal mostly with the molecular characterisation of (co)polymers, such as vinyl resins, polyesters, nylons, polyolefins, fluorocarbon polymers, rubbers, thermosetting rubbers, and natural rubbers, with limited attention to the analysis of plasticisers, fillers and solvents. Whereas in the first edition (1965) attention was restricted mainly to IR methods, the state-of-the-art techniques in 1970 had broadened considerably to include UV/VIS, IR, NMR, GC, PyGC, GC-IR, AAS, AES, XRF and automated titrations. Although now dated and obviously light on modern instrumental methodology this book contains a wealth of information on polymer/additive analysis. In the German language area early books on polymer analysis by Schröder *et al.* [55] and on rubber analysis by Ostromow [61] should be mentioned. Krause *et al.* [86] have also briefly described chemical analysis of additives (limited to fillers, stabilisers, dyes and pigments), and have compiled an extensive and useful index to ASTM and DIN standards for analysis and characterisation of polymers, resins, rubbers, plastics and fibres. In the past, chromatographic, spectral, mass spectrometric, electrochemical and radioisotopic methods were most widely employed for the determination of additives [87].

Crompton [88,89] has regularly provided detailed accounts of the scientific principles underlying current practice, targeted mainly at the experienced industrial technologist. An extensive review on polymer/additive analyses (period 1960–1980) is contained in Crompton [52]. More recently, the same author [41] has described polymer analysis (polymer microstructure, copolymer composition, molecular weight distribution, functional groups, fractionation) together with polymer/additive analysis (separation of polymer and additives, identification of additives, volatiles and catalyst residues); the monograph provides a single source of information on polymer/additive analysis techniques up to 1980. Crompton described *practical analytical methods* for the determination of classes of additives (by functionality: antioxidants, stabilisers, antiozonants, plasticisers, pigments, flame retardants, accelerators, etc.). Mitchell [53] has covered many aspects of polymer analysis and characterisation, including analysis of additives, residual monomers and oligomers, moisture and adventitious impurities. Gooch [59] has recently addressed the analysis and deformulation of a variety of polymeric materials (paints, plastics, adhesives and inks).

In a later manual of plastics analysis Crompton [50] deals with *all* aspects of polymer analysis, including the polymer structure (compositional analysis), as well as deliberately added nonpolymeric processing chemicals used during manufacture, chemicals added to improve the polymer properties during service life and impurities, such as water and processing solvents, unreacted monomers, etc. If any criticism is allowed, only a modest and very selective share (20 %) of references *post* 1980 is included in this textbook, which therefore cannot claim to be an up-to-date or complete review of the world literature on the subject of polymer/additive analysis. Some 108 detailed experimental procedures, again largely dated (1950s 3 %, 1960s 27 %, 1970s 30 %, 1980s 7 %, previously unpublished 33 %), were included. In this respect the *current text*, organised by clusters of analytical techniques dressed up with applications, is a more rational rather than a descriptive approach, apart from being dedicated *exclusively* to polymer/additive analysis and more up-to-date (up to end 2002). Scheirs [58] has described a range of techniques and strategies for the compositional and failure analysis of polymeric materials and products, with applications of analytical methods for troubleshooting industrial problems. This practical description (with literature coverage up to 1997) is complementary to the current more analytical approach. Forrest [63] has recently touched on techniques and methods used to characterise and carry out QC work on plastics, deformulation of plastic compounds and investigation of failure of plastic products (both molecular characterisation and additive analysis). The same author [90] has described analytical aspects of the characterisation of rubber polymers, with emphasis on the determination of the principal components in rubber compounds and product deformulation.

The recent literature also contains a number of *reviews* more limited in scope and frequently outside the English language area (Table 1.14). Several papers are worth mentioning. Squirrell [139] has reviewed ICI's approach towards the analysis of additives and process residues in plastics materials (state-of-the-art 1981); Scrivens and Jackson [111] have described current MS practice. Lattimer and Harris [105] have put emphasis on the extraction of additives from polymers, MS analysis of the extracts, GC-MS and LC-MS as well as on direct mass spectral analysis of polymer additives, including thermal desorption and pyrolysis. Developments in techniques, instrumentation and problem solving in applied polymer analysis and characterisation up to 1987 have been described by Mitchell [134]. Later Foster [140] has addressed analytical methods in relation to testing of oxidation inhibition, and Rotschová and Pospíšil [130] have published an excellent review covering both indirect and direct analysis methods of stabilisers (state-of-the art 1989). A fairly comprehensive overview of the literature on additive analysis (restricted to some protective agents, such as antioxidants and UV stabilisers) has been published by Freitag [133] in 1993 with emphasis on sample preparation (Soxhlet and reflux extraction, dissolution/precipitation), TLC, HPLC, GC and various spectroscopic techniques. Other reviews are more specific. Munteanu [98] has reported an excellent account of the analysis of antioxidants and light stabilisers in polyolefins by HPLC. Newton [94] has reviewed wet chemical analysis of additives in various polymers (PP, PVC, PTFE and polyamides). Thomas [131] has presented a general overview of the analytical techniques available to qualitate and quantify the primary and secondary additive stabilisers (antioxidants, processing and light stabilisers) in polyolefin substrates. Berger [100] has examined the use of SFC in the analysis of polymer additives. Bataillard *et al.* [132] have recently given

Table 1.14 Selected reviews concerning polymer/additive analysis

Topic(s)	Reference(s)
Sample preparation (SFE, chromatographic analysis)	[91,92]
Extractions	[93]
Separation and analysis of additives in polymers	[94]
Qualitative/quantitative analysis (GC)	[95]
Qualitative/quantitative analysis (surface micro analysis)	[96]
Vulcanised rubbers (HS-GC)	[97]
Polyolefins, antioxidants and light stabilisers (LC)	[98]
TLC applications	[99]
SFC applications	[100]
Pyrolysis-GC applications	[101]
PP pellets, additives (NIRS)	[102]
PVC, plasticisers, stabilisers, fillers (IR, GC)	[103]
Volatile additives (direct mass spectrometry)	[104]
Organic additives (qualitative MS analysis, TD, PyMS, GC-MS, LC-MS)	[105]
LC-MS applications	[106]
FAB-MS applications	[107,108]
LDI applications	[109]
LD FTICR-MS applications	[110]
Direct and indirect analysis (FD-MS, MALDI, LSIMS, TD-GC-MS)	[111]
Inorganic additives	[112]
Thermal analysis, applications	[24,113,114]
Thermal evolution techniques, applications	[115]
Blends of monomeric and polymeric additives, separations	[116]
Polymer/additive analysis; general; softeners	[96]
Additives in plastics and rubbers (instrumental analysis)	[117–124]
HALS (chromatographic and spectroscopic methods)	[125]
Low-MW organic additives (extraction)	[126]
Radioactive tracers in stabilisation technology	[127]
Packaging materials, residual monomers	[95]
Cable insulating compounds, additives	[128]
Surface modifying additives, siloxane surfactants	[129]
Identification and determination of stabilisers of oxidation processes	[130]
Stabilisers (chromatography, analytical artefacts)	[6]
Polyolefins, antioxidants, processing and light stabilisers	[131–133]
Additives, impurities, degradation products	[134]
Rubbers, sulfur-containing additives	[135]
Antimicrobials	[136]
Antioxidants	[137,138]

broad coverage of polymer/additive analytics. Gouya [141] has recently reviewed dispersion and analytical methods of a variety of polymer additives (plasticisers, lubricants, stabilisers, coupling agents, photocatalysts, surfactants, vulcanisation and cross-linking agents). Finally, Hummel [62] has described the application of vibrational (FTIR, UV, Raman) and mass spectrometries for identification and structure elucidation of plastics additives (mainly antioxidants, stabilisers, plasticisers, pigments, fillers, rubber chemicals). Other reviews are mentioned under the specific headings of the following chapters. Many analytical tools are more capable of compound *class* identification than of specific compound analysis.

Progress in the field of polymer/additive analysis in the last three decades can best be illustrated by an old recipe for the direct determination of organotin stabilisers in PVC [142]:

> *PVC (200 mg) was dissolved in 20 mL THF and precipitated with 50 mL EtOH. Several drops of 0.1 % pyrocatechol violet solution were added to the heated filtrate until a blue colour appeared. This solution was titrated with 0.001 M EDTA until the change via green to yellow. In the presence of Mg, Ca, and Zn, Eriochrome Black was added before titration.*

Physico-chemical instrumental analysis nowadays has greatly suppressed such chemical handwork. An internet website disseminates methods of analysis and supporting spectroscopic information on monomers and additives used for food contact materials (principally packaging).

1.4.3 Databases

Access to databases provides one of the most critical tools for polymer/additive analysis, as it greatly determines the efficiency (and cost) of the overall operations (cf. Table 1.15). The literature provides a wealth of *spectral information*, available in bound volumes of illustrations or in a computer format (e.g. on CD ROMs), such as the Bio-Rad Sadtler, Aldrich, Bruker-Merck, Nicolet and Rapra collections of FTIR and/or NMR spectra of organic compounds, additives (including plasticisers, flame retardants, surfactants), rubber chemicals, polymers and inorganics (including minerals). Typically, on-line IR (and Raman) data files comprise approximately 200 000 spectra of pure compounds (Sadtler with 1740 polymer additives, 1480 plasticisers, 590 flame retardants, 3070 dyes and pigments, 700 curing agents, 850 basic surfactants as specific products), 7000 ('Hummel'), 18 500 (Aldrich) [143], 3000 (Merck) [144], 3000 (coatings), 1000 (inorganics) and 576 spectra (Rapra Collection of Infrared Spectra of Rubbers, Plastics and Thermoplastic Elastomers) [145]. Over 50 000 FTIR, NIR and Raman spectra of polymers and related compounds are available. Important support has been provided by Scholl [146] in 1981 with a spectroscopic atlas of fillers and processing additives and later more extensively (analytical methods and spectroscopy) by Hummel. The 'Hummel/Scholl infrared databases' (now Chemical Concepts) include fillers, processing aids and surfactants [146–150], with typically 1520 auxiliaries and additives, and 1570 monomers and low-MW substances. The atlas of industrial surfactants comprises 1082 FTIR spectra [149]. Infrared spectra of plasticisers have also been collected [151]. Library searching of SFC/FTIR spectra can be carried out with reference to the Sprouse Library of Polymer Additives [152], as distributed by Nicolet. This library contains 325 reference spectra recorded either neat, as chloroform casts, or as nujol mulls. A recent atlas of plastics additives contains 772 FTIR spectra [62]. However, e-databases are more efficient than those in printed format. As to the distribution of reference spectroscopic databases, cf. Davies [153], Hummel [154] has illustrated the possibilities and limitations of computer-based searching with special FTIR libraries (additives, surfactants, monomers, etc.).

As public libraries are far from being complete as to (newly introduced) commercial polymer additives various *proprietary databases* have been created. In this respect, ICI keeps a company database on polyolefin stabilisers with over 4000 records [155]. The Hoechst IR and Raman spectroscopic database (80 000 entries) contains some 500 internal reference data for polymer additives [156]. DSM Research has developed a more general customised polymer additive reference database for analytical purposes running on Windows 98 and NT and comprising over 1000 of the most common industrially used additives with molecular and structural formula, molecular weight, systematic chemical name, and commercial brand names, CAS Registry number, commercial names, GC, HPLC, NMR, UV, IR, Raman, MS and ToF-SIMS data, some chemical and physical properties (such as melting point, density, etc.) and safety data [157]. DSM also disposes of a proprietary trade mark/chemical structure database for over 250 antioxidants, light and heat stabilisers (with some 1100 entries [17], cf. Appendix III). It is noticed that this database has grown considerably in the last 5 years. Ciba-Geigy has issued positive lists of additives for plastics, elastomers and synthetic fibres [158] and of additives used in the PVC industry [159], both for food contact applications.

Additive analysis also greatly benefits from the new NIST 02 release of the NIST/EPA/NIH Mass Spectral Library, containing 143 000 verified spectra and almost complete coverage with chemical structures [160]; the Wiley library contains 230 000 mass spectra. However, all mass spectra are not created equal. Consequently, secure comparison of mass spectra for positive compound identification requires attention to the ionisation mode. In relation to PyGC-MS analysis the Shimadzu/VW additive mass spectra library is of interest [161]. The 1993 publication *Spectra for the Identification of Monomers in Food Packaging* [162,163] presents FTIR and MS information on monomeric substances and other starting substances listed in Directive 90/128/EEC [65], which restricts the range of compounds that can be used for the production of plastics materials and articles intended for food contact applications. Reference [164] contains other spectra for the identification of additives in food packaging. The handbook *Spectra for the Identification of Additives in Food Packaging* [84] compiled with EC funding under the SM&T programme, contains a collection of spectra for the identification of 100 of the most important additives used in plastics packaging and coatings. Infrared and mass spectra are presented, together with ^{1}H NMR spectra and GC data. This file is accessible via an internet website (*http://cpf.jrc.it/smt/*) [82]. In another recent compilation nearly 400 fully assigned NMR spectra of some 300 polymers and polymer additives are collected [165].

Obviously, use of such databases often fails in case of interaction between additives. As an example we mention additive/antistat interaction in PP, as observed by Dieckmann *et al.* [166]. In this case analysis and performance data demonstrate chemical interaction between glycerol esters and acid neutralisers. This phenomenon is pronounced when the additive is a strong base, like synthetic hydrotalcite, or a metal carboxylate. Similar problems may arise after ageing of a polymer. A common request in a technical support analytical laboratory is to analyse the additives in a sample that has prematurely failed in an exposure test, when at best an unexposed control sample is available. Under some circumstances, heat or light exposure may have transformed the additive into other products. *Reaction product identification* then usually requires a general library of their spectroscopic or mass spectrometric profiles. For example, Bell *et al.* [167] have focused attention on the degradation of light stabilisers and antioxidants in chemical and photo-oxidising environments. HPLC-UV/VIS, FTIR, and GC-MS were found to be suitable techniques to follow the degradation chemistry of the additives. On the other hand, the study of the chemistry of benzotriazoles turned out to be more difficult because of the insolubility of the resinous degradation products.

The importance of adequate support by database reference material is well illustrated with the following case. After chromatographic separation (TLC, CC), the combination of ^{1}H/^{13}C NMR, DI-MS (EI), FTIR and HPLC (UV/VIS, DAD and MS) a flame retardant in a Japanese polypropylene TV cabinet on the European market was identified as tetrabromobisphenol-*S*-bis-(2,3-dibromopropyl ether) (TBBP-S) [168]. The result was verified by synthesis of reference material; the product was finally identified as Non Nen #52 from Marubishi Oil Chemical Co., Ltd (Osaka), not registered in any spectral database.

1.4.4 Scope

As the structure of additives for polymers becomes evermore complex, there is an increasing need for good reliable analysis of additives to meet more exacting performance demands. High-quality analytical methods are needed for high-quality products. As the rate of accumulation of scientific knowledge accelerates, it becomes increasingly difficult for scientists to find relevant information quickly and effectively and to put it in the proper context. This certainly holds for such a broad field as the analytics of polymer additives. This book provides comprehensive coverage of the current status of the (qualitative and quantitative) analysis techniques for additive determination in commercial polymers at the lowest level of analytical sophistication (bulk analysis). No technique will suit every need. Emphasis is laid on understanding and applicability. As additive analysis is typically an *industrial problem solving* area particular attention is paid to cost effective, real-life, analytical approaches. In particular, the prospects of analysis conducted after separation of the additives from the polymer are compared. Recent years have seen an almost quantum increase in the range of analytical techniques, particularly involving hyphenated chromatography, spectroscopy and mass spectrometry. This book draws them all together, in a comprehensively up-dated version with specific applications. Limitations of current additive analysis methodology are indicated.

The main goal of this book is to set the scene for ‘Analytical Excellence’ in the field of polymer/additive analytics, not unlike Manufacturing or Operational Excellence programs in industry. Table 1.15 shows the necessary ingredients. For product analysis a mix of analytical technique specialists and product specialists is ideal. Some industrial analytical departments are structured in this fashion [169]. The key to the successful analysis of additives in a polymer for a specific application not only requires a comprehensive understanding of commercial additives but also knowledge of the polymer matrix and its targeted application, as well as the required tests to be passed for that specific application [170,171]. For in-polymer additive analysis already Crompton [52] had stressed the importance of familiarity with the chemical and physical properties of additives. For this purpose the reader is referred to Appendix II.

An adequate measurement technique is not sufficient for good analytical results. Analyses are operated under ISO 9001 and carried out according to validated analytical protocols. Deviations from such protocols are to be given as amendments (a priori) or as deviations (a posteriori). Moreover, under no conditions the analyst should change the analyte.

Table 1.15 Requirements for Analytical Excellence

Feature	Action(s)
Analytical strategy	Clear-cut corporate strategy
Product analysis	Technique and product specialists
Operator competence	Analyte specific physico-chemical background
Standardisation	Norms, validated analytical procedures, certification
State-of-the-art	Instrumentation, method development, current awareness
Multidisciplinary approach	Standard Operating Procedures
Quality control	Calibration, (certified) reference materials
Efficiency	Databases, benchmarking, 'Best Practice'
Profitability	Excellent knowledge infrastructure, automation, low cost
Analytical information management	Central repository for analytical data
Analytical sample management	LIMS
Quality assurance	ISO 9001
Reproducibility	SPC
Reliance	No dependence on one analysis technique
Bureaucracy	Fewer analytical chemists than analytical problems
Proficiency testing	Round-robins
Health, safety, and environment	Responsible Care

It is clearly not the *purpose* of this monograph to deal with analytical methods for any class of additives in particular. Also, this book is not intended to be a manual for reported analytical procedures for a given additive. Yet, in order to comply with the primary value of reporting particular method developments and applications in the literature, namely that the reader knows that at least someone was successful with a particular analyte in a particular matrix, extensive referencing is included. Literature was covered as comprised in *CA Selects^{SM} Plastics Additives* up to the end of 2002. In this text those analytical procedures in particular are highlighted which have been used in the (recent) past and are still being applied today and especially those which may reasonably be expected to have an increasing impact in the near future. Relevant techniques are detailed up to the point that the applications may be rationalised and understood. Although the devil is often in the detail, a deeper level of abstraction of the numerous analytical tools utilised (Figure 1.4) would have led to an unmanageable amount of experimental data for which the original literature is the most suitable source of information. By describing many real applications, the author tries to alert the reader to the opportunities of the various techniques. For the selection of the many citations in this monograph, next to their information content, their topicality and availability also played a role. No claim is made to comprehensive coverage.

This highly specific book is not a collection of independent reviews, but promotes understanding and emphasises development of problem-solving ability. It is just the tip of the iceberg of the field. Expecting to use cookbook methods does not necessarily work. In fact, such methods are unavailable for most analyte–matrix pairs anyway, and actually are pretty dangerous for the unaware. This book just provides the routing (Figure 1.5). Those applying the calibration equation coefficients of a published method and expecting to get immediately good quantitative results may easily get disillusioned. Such an approach only works well when the application is very well defined and adhered to.

It should be understood that the reported practices of polymer/additive analysis, being the focus of this book, equally well apply to additive analysis of rubbers, textile fibres, surface coatings, paints, resins, adhesives, paper and food, but specific product knowledge gives the edge. Both fresh and aged materials may be analysed, as well as those of both industrial and forensic origin.

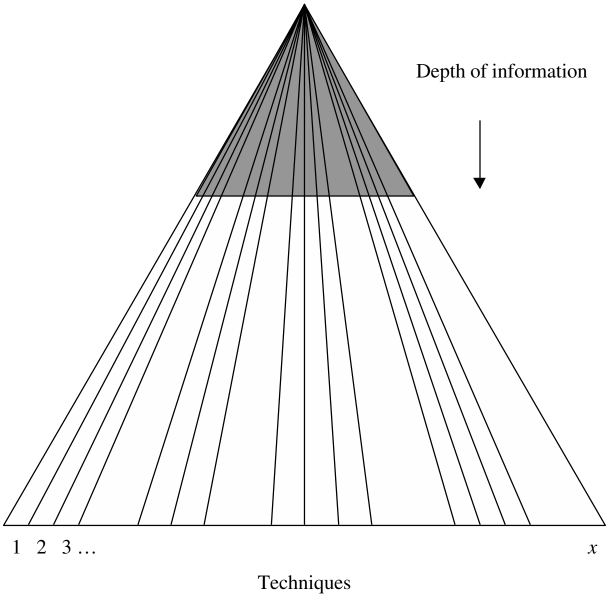


Figure 1.4 Level of abstraction of analytical tools on additives in polymers with delimitations adopted in the text (shaded)

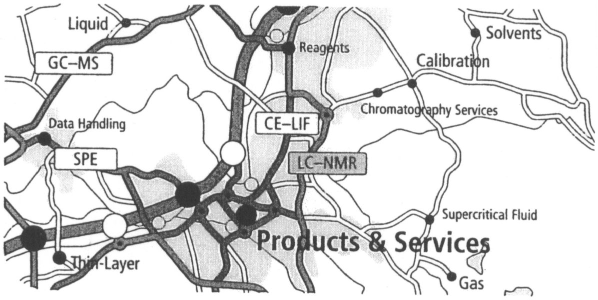


Figure 1.5 Road map of polymer/additive analysis. Reprinted with permission from *LC.GC Europe*, Vol. 14, Number 8, August 2001. LC.GC Europe is a copyrighted publication of Advanstar Communications Inc. All rights reserved

This book, being the first one *entirely* dedicated to analysis of additives in polymers, is closely targeted to R&D units, manufacturers, compounders, leading end-users, universities and colleges, government/independent testing and certification bodies. It is expected to contribute to the development of recognised analytical procedures for the determination of constituents of plastics, as aspired to by various organisations ranging from forensic institutions to Greenpeace [172] and others.

Many polymer companies have not maintained a cadre of experts on the analysis of additives in polymers. Consequently, there is a need to train a new generation of people about additives and methods of deformulating them. Outsourcing of polymer/additive analysis is usually not an option for the reasons mentioned (unfamiliarity with the underlying chemistry). Today, there are also more sophisticated compounders who formulate their own products. Along with the increased popularity of blended, pelletised and compacted mixtures of additives, this suggests that there should be broad interest in the topics of this book among formulators of concentrates and additive producers.

1.4.5 Chapter Overview

Methods of analysis are either chemical or physical in nature. Chemical methods of analysis are based on the selective interaction of materials (chromatographic media, etc.) with analytes. Physical methods of analysis are based on the direct interaction of materials (analyte) with electromagnetic waves; corpuscular beams, such as electrons and neutrons; or electric, magnetic, and gravimetric fields. It is important to appreciate that various methods of instrumental analysis, including all kinds of spectroscopies, have completely changed the nature of chemical research. Physical and chemical methods are not clearly separated. The goal of Chapter 2 is to familiarise the reader with general reverse engineering schemes proposed for polymers and rubbers. Industrial practice and developments are illustrated for the 1980–2002 period.

Conventional polymer/additive analysis by wet chemical means is described in seven chapters. Chapter 3 describes the separation of the polymer from the additive components. Consequently, emphasis is both on classical liquid–solid extractions and modern pressurised extraction methods. Digestion techniques and depolymerisation approaches to polymer/additive analysis are also treated. Chapter 4 provides a critical review of modern chromatographic separation techniques for additive analysis, based on the solvent extracts according to Chapter 3, or evaporative losses. The main techniques and applications covered are GC, HS-GC, HPLC, SEC, GPEC®, TLC and CE. The power of specific detection modes is evaluated. Different spectroscopic methods (UV/VIS, mid-IR, luminescence and NMR), applicable to additives in extracts before and after chromatographic separation, are described in Chapter 5 and are critically evaluated. Chapter 6 summarises the power of the most important organic mass spectrometric techniques for direct and indirect additive analysis. In Chapter 7 use and power of a great variety of (multi)hyphenated and multidimensional techniques (sample preparation–chromatography–detection) for polymer/additive analysis of extracts are assessed. The applications of multidimensional spectroscopy are outlined. The reader is given detailed insight in the possibilities and limitations of these sophisticated analytical techniques for the specific applications of interest. This chapter reflects the explosion of procedures in the last few years. Both conventional and more modern element analytical protocols for extract and in-polymer additive analysis are illustrated in Chapter 8, including inorganic MS and radioanalytical methods. The limited usefulness of electrochemical techniques for this purpose is pointed out. Chapter 9 addresses the prospects for direct chromatographic, spectroscopic and mass spectrometric methods of deformulation of polymer/additive dissolutions without prior separation of the components.

The final chapter summarises the book with special emphasis on the future of polymer/additive analysis. The methods, results and their evaluation presented in this chapter encompass all material developed in the book's previous chapters. Three appendices contain lists of symbols, describe the functionality of common additives (as a reminder) and show an excerpt of an industrial polymer additive database.

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