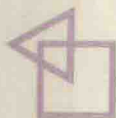


INJECTION MOLDING OF THERMOPLASTICS MATERIALS

VOL. 2

Tony Whelan

John Goff



POCKET GUIDES
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PLASTICS

Injection Molding of Thermoplastics Materials 2

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藏书章

Tony Whelan and John Goff

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Preface

Over the years 1984 to 1989, we published a series of articles on the molding of thermoplastics, and of thermosetting materials, in the monthly magazine *British Plastics and Rubber* (B P & R). These articles were very well received and we also received a large number of requests for reprints. The articles were also translated into languages other than English.

In order to cater for what is obviously a need in both the thermoplastics, and the thermosetting, molding industries, we therefore brought the information together and produced it in book form. To make the material easier to handle we produced it in the form of several books and this is one of them. We can only hope that the information so presented, serves you well and that you find the information useful. We in turn would like to thank the editor of the magazine B P & R for helping us in this matter.

Thanks are also due to our many friends and colleagues throughout the molding industry for their useful help and advice: in particular, the company Moldflow (Europe) Limited deserve a special mention as they allowed us to extract information from their extensive data base.

The information presented in this publication is intended to give the reader an over view of the processing and properties of the materials listed in the index of this book. More detailed information, on specific grades or applications, should be obtained from the manufacturers of the material or, from the suppliers. We therefore suggest that, the user of such materials, seek and adhere to, the manufacturers or suppliers current instructions for the handling of each grade or type of material they use. Any determination of the suitability of the material for any use contemplated by the user, and the manner of processing and use, is the sole responsibility of the user who must satisfy himself/herself that the material as processed meets the needs of a particular product or use.

The information presented in this publication was based on our knowledge and experience and represents the opinions of us, the authors, and not necessarily the opinions of any other person or organization. To the best of our knowledge the information is accurate; however we do not assume any liability whatsoever for the accuracy or completeness of such information. Such information is given in good faith but in view of the many factors that affect processing and properties, the data so presented does not relieve processors from the responsibility of carrying out their own tests and experiments: neither does the data presented imply any legally binding assurance of certain properties, ease of

processing or, of suitability for a given purpose. It is also not our responsibility to ensure that proprietary rights are not infringed and to ensure that relevant legislation is observed.

To the extent that any hazards may have been mentioned in this publication, we neither suggest nor guarantee that such hazards are the only ones which exist. We strongly recommend that anyone intending to rely on any suggestion or recommendation (or to use any equipment, processing technique or material mentioned in this publication) should satisfy himself/herself that all applicable safety and health standards can be met. Remember, there is a need to reduce human exposure to many organic materials to the lowest practical limits, in view of possible long-term adverse effects.

John Goff and Tony Whelan.

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PLASTICS AND POLYMERS

The polymers which are processed by melt processes, such as molding and extrusion, may be divided in various ways, for example, they may be divided into thermoplastics, thermosetting plastics and, into elastomers. Each type of material may, in turn, be extensively modified by, for example, the use of fillers.

THERMOPLASTIC MATERIALS

A thermoplastics material is one which softens on heating and hardens on cooling: this heating and cooling process can be repeated a large number of times. Approximately 80% of all plastics used throughout the world are thermoplastics: this important group of materials has been divided into four groups:-

- i) commodity or bulk thermoplastics;
- ii) engineering thermoplastics; and,
- iii) thermoplastic elastomers or rubbers, and,
- iv) blends or alloys.

At one time everybody seemed to know what these terms meant but now, because of materials modification, the position is far less clear with, for example, plastics such as PP (see Table 1 and Table 2 for a list of abbreviations and, for letters used to modify abbreviations) sometimes included in a definition of engineering plastics and sometimes not. Even this simple example illustrates a very important point: it is possible to lift, or move, a plastics material from one category to another. In the case of PP, a commodity plastics material, it can be changed into an engineering plastics material by materials enhancement.

The practice of materials modification is as old as the polymer industry itself. For example, sulfur is added to cross-link rubber; rubber is added to polystyrene (PS) and, the effect is remarkable as it changes PS from a material with poor impact strength to one which is good enough for the manufacture of stiletto shoe heels. In both cases there is not a simple addition; one material is chemically grafted, or bonded, to another. In the case of the second example however, the new polymer (high impact polystyrene, HIPS or, TPS or, IPS) can be reprocessed as it is a thermoplastics material. Cross-linked rubber cannot be easily reprocessed as the chemical links are not thermally labile i.e. not capable of being broken on heating. What is required is a material which can be processed like a thermoplastic and yet, has many of the properties of a cross-linked plastics material: this is one reason for the current interest in polymer alloying.

COMMODITY OR BULK MATERIALS

This group of materials covers the major materials such as polypropylene, polyvinyl chloride, polystyrene and polyethylene (PP, PVC, PS and PE). Each of these divisions covers a number of sub-divisions, for example PP covers homopolymers and copolymers, PVC covers rigid and plasticized, PS covers general purpose PS and toughened PS (TPS, or IPS, or HIPS) and PE covers LDPE, LLDPE and HDPE. The importance of bulk thermoplastics cannot be over-emphasized; approximately 70% of all plastics used fall into this category.

These materials are used so extensively because the raw materials on which they are based are relatively cheap and, conversion into plastics which have useful properties is fairly easy. It is also now being realized that the properties of this class of materials can be up-graded so that they compete with other more exotic, and therefore more expensive, plastics. A case in point is UPVC; because of the inherent flame resistance of this material, it has been developed so that it can now compete with engineering thermoplastics in some applications.

ENGINEERING THERMOPLASTICS

Engineering plastics are a group of polymers which offer a combination of some of the following, high strength, stiffness, toughness and, resistance to wear, chemical attack and heat.

Any discussion of engineering thermoplastics must concentrate on materials such as polyamides, acetals, polycarbonates, thermoplastic polyesters and modified polyphenylene oxide (also known as modified polyphenylene ether or PPE). Greater than 90% of all the engineering plastics used in the world, fall into one of these categories (approximately 8% of all plastics usage is accounted for by these five categories). Other materials such as the sulfones and the modified polyimides only account for a very small percentage (approximately 1 to 2%) of the total usage of engineering plastics. This relatively low consumption occurs, because most of the engineering plastics use, is in metal replacement where exotic property (and therefore expensive property) characteristics, are not required. The 'tonnage', engineering thermoplastics are used in a wide range of applications even though they have comparatively low heat resistance (below 150°C or 302°F) and relatively low creep resistance especially at high, or elevated, temperatures.

THERMOPLASTIC ELASTOMERS

Those materials which are referred to as 'thermoplastic elastomers' (TPE) or, as 'thermoplastic rubbers' (TPR) are a comparatively new group of materials but already they have become sig-

nificant in terms of both tonnage and in terms of value. This is because they are creating new markets as well as replacing both plastics and traditional rubbers in some of their applications. They exhibit some of the properties associated with traditional, or vulcanized, rubbers, but they also exhibit the speed, and ease, of processing of thermoplastics; the ability to be re-processed is also important. Of major importance is the wide color range possible from this type of material. TPEs may be based on specifically manufactured polymers (e.g. styrene butadiene styrene or polyether ester elastomer - SBS and PEEL) or, they may be based on blends of rubbers and plastics. For example, a widely used material is that obtained by mixing PP with an ethylene propylene rubber. A two phase material results in which there is a plastics phase and a rubber phase. In the simplest cases, the rubber is not crosslinked or vulcanized but, is simply dispersed throughout the plastics material. There are other materials which also contain a dispersed rubber phase but, in this case, the rubber is partially vulcanized: these may be known as thermoplastics vulcanizates (TPV).

It is believed that the usage of TPEs will increase to such an extent that they will displace traditional rubbers from many applications. Such traditional elastomers/rubbers will continue to be used for applications requiring high temperature resistance and dynamic performance but TPEs will serve better for all other applications.

The reasons cited for the anticipated decline of traditional rubbers, in favor of TPEs, include the availability of a variety of TPEs of consistent quality, the elimination of customer formulation and compounding, easy and rapid processing, elimination of non-reusable scrap and, the often superior resistance of TPEs to chemical attack: it is often possible to replace a range of rubber mixes by one TPE because of the superior chemical resistance of the TPE.

BLENDS

There are a number of reasons for blending materials and these include the generation of unusual materials, extending the performance of existing plastics, extending this performance quickly, extending the performance cheaply and, re-using plastics materials. Both time and cost are against the development of new plastics. It may, for example, take fifteen years to develop a new plastic and cost many millions of dollars: a new blend can be produced for a fraction of this cost. The other factor is that new polymers, as envisaged by the manufacturers, have rarely satisfied the market for very long and, once original markets have developed, demands usually arise for performance improvements.

The blends which result are often produced on twin screw

extruders using what is called reaction compounding. As many twin screw machines are modular in design, their construction can be tailored to suit a particular resin blend thus facilitating production and giving the all-important, blend consistency. Because of the relatively poor performance of many engineering plastics in some applications, and/or because of their high price, recent attention has focussed on engineering polymer blends (EPB).

Engineering polymer blends (EPB) can be roughly divided into blends of an engineering plastic or resin (ER) with a commodity plastic, blends of an engineering plastic with another engineering plastic, blends of an engineering plastic with an elastomer and, blends which contain three or more polymers. We can therefore get combinations such as PPO/PS; PPO/PA; PC/ABS; PET/PBT; PBT/PC/SAN etc.; each of the blends may in turn be filled. When blends are made the objective is to simultaneously optimize blend formulations, in respect of several properties important for a particular application, sacrificing those which are not important.

THERMOSETTING PLASTICS

A thermosetting plastic, or a thermoset, may be defined as a material which once shaped by heat and pressure is incapable of being re-processed by further applications of heat and pressure. This is because during the shaping process, cross-links, or crosslinks, are introduced between the molecules which make up the basic resin or plastic. It is these cross-links which make the cured material insoluble and infusible as they stop the molecules slipping past each other and so prevent re-softening. This does not mean to say that these plastics are chemically inert: as will be seen, they are swollen by some chemicals and attacked by others.

Materials such as polyethylene may be cross-linked, after they have been shaped as a thermoplastic, but such materials will not be considered as thermosetting materials in these guides. Those materials which will be treated as thermosets are those which are traditionally known as thermosets - such as phenolics and amino-plastics: these materials are processed by the application of fairly high pressures in processes such as compression molding, transfer molding and injection molding. Also included in this category of materials are epoxides and, molding compositions based on an unsaturated polyester, for instance DMC.

ELASTOMERS

An elastomer (a rubber) may be defined as a material which may be stretched by 100% and on release of the stretching force it retracts, or springs back, rapidly. This elasticity was always associated with vulcanized (cross-linked) rubber and, is due to the

structure of that type of material. Now, thermoplastics materials can be made rubber-like.

The long chain molecules on which rubbers are based, prefer to exist in a random, or coiled, configuration. However, the same, long chain molecules are not rigid structures but can untwist (or unwind) around the carbon to carbon bonds, on the application of a stretching force - provided the material is above its glass transition temperature. The chain is not stretched it is simply made to adopt a different configuration, or layout, but it always remembers that it would prefer to exist in a random, or coiled, state. So, when the stretching force is removed, back it goes to a random, coiled state. (A rubber molecule may be likened to a steel spring which, because of the way that it is constructed, may be easily stretched).

The crosslinks serve to stop the chains slipping past each other when they are stretched. If they were not there, then the chains would find it easier to untangle, orientate in the direction of force application, and then move past each other: this would cause the material to separate into pieces.

MATERIALS MODIFICATION

It is generally understood in the plastics molding industry that the materials used, as injection molding materials, may contain small amounts of additives. Such additives may include stabilizers and lubricants. Materials modification usually means the addition of larger amounts of additives. Such additives may include elastomers, flame retardants and fillers.

Materials modification, such as with fibers or with fillers, is extensively adopted with thermosetting plastics, and now with engineering plastics, so as to obtain a desirable combination of properties. It is not done simply to save money as often a molding, made from a filled compound, is the same price as one made from the unfilled plastics material. This is because of the high density of most fillers and because of the high compounding costs. Many of the fillers used are fibrous fillers as the use of such materials improves properties such as modulus.

INJECTION MOLDING OF THERMOPLASTICS

1 COMMON NAMES

Most thermoplastics begin with 'poly' and then this term, which means 'many' is followed by the old fashioned name for the monomer from which the plastic is derived i.e the name is source-based. Because of this practice we get names such as polystyrene and polyethylene for homopolymers. When the plastics material has more than one word in the name, parentheses, or brackets, may be put around the words so that we get poly(vinyl chloride). However this practice is not universal and so we also meet the same term without the brackets i.e. polyvinyl chloride. Source-based nomenclature is not however, universally used and so names such as 'acetals' and 'cellulosics' are also encountered. Other, more logical systems of nomenclature have been proposed but as yet, they have not been adopted,

2 ABBREVIATION(S)

Because of the complex, chemical names used to describe polymers, they are nearly always referred to by abbreviations. Such abbreviations take the form of a short string of capital letters; each capital letter refers to a part of the common name. If the plastics material begins with 'poly' then the first letter is P: the other letter(s) are derived from the monomer unit. Names such as polystyrene and polyethylene are thus shortened to PS and PE respectively (see table 1).

SOME RELEVANT STANDARDS

Many standards organizations, for example, the British Standards Institution (BSI), the International Standards Organisation (ISO) and the American Society for Testing and Materials (ASTM) issue standards which specify what letters shall be used. See ASTM standard D1600-86 (that is standard number D1600 revised/published in 1986) and called 'Standard abbreviations of terms related to plastics. There was a British standard published in 1978 - see BS 3502 1978: the corresponding ISO standard is ISO 1043 1978. There is now another ISO standard ISO 1043-1 which was published in 1987 and which is called 'Basic polymers and their special characteristics'. It has the number ISO 1043-1 : 1987 (E). (The nomenclature of rubbers and latexes are described in ISO 1629).

STANDARD AND-NON STANDARD ABBREVIATIONS

It must be appreciated that both standard and non-standard abbreviations are used. Often materials appear, and become used, before the standards committee has issued its suggestion. By this time a 'non standard' abbreviation has become established or more than one abbreviation may 'appear' for the same material. The thermoplastic elastomer, known as polyether ester elastomer, may be referred to as PEEL or, as COPE (from copolyester) or, as TEEE (thermoplastic elastomer ether ester) or, as YBPO (an American suggestion).

GENERALLY ACCEPTED RULES

Because of the possibility of confusion it is suggested that when abbreviations are used in publications that their first occurrence in the text should be enclosed in parentheses i.e. brackets, and preceded by the written word being abbreviated. So, for the first time, polystyrene would appear in an article as polystyrene (PS). Subsequent references to such words in the publication can then be by means of the abbreviation.

One practice which does seem to be growing, particularly within companies, is that of increasing the number of letters used to identify plastics, to a minimum of three; this is apparently to suit the needs of common electronic data processing (EDP) systems. If asked to abstract information from a data base, then the request can be made more specific if, for example, polypropylene is given an extra letter, for example R or N so as to make the terminology PPR or PPN, rather than PP. With some systems there is a danger of pulling out everything which begins with PP (for example, PPE and PPO as well as PP) if only PP is asked for. However, this practice should be used with caution as R is used to denote a random copolymer so, strictly speaking, PPR means a random copolymer of PP - these materials are being used in blow molding. Polystyrene may be referred to as general purpose polystyrene GPPS or as PS-GP.

Another practice which seems to be growing, again to suit EDP, is that of not putting anything before the abbreviation for the plastic; for example in this system, low density polyethylene would be referred to as PE LD and not LDPE. In practice, a hyphen is inserted between the groups of letters so that PE LD becomes PE-LD.

ABBREVIATION MODIFICATION

By standard, and by general usage, additional letters may be used to modify those used as abbreviations (see table 2). For example, PE-UHMW therefore stands for ultra high molecular weight

polyethylene. As ASTM 1600-86 suggests that GP stands for 'general purpose', PS-GP stands for general purpose polystyrene. In the thermoplastics world, G stands for glass and F stands for fibre/fiber i.e. GF stands for glass fiber.

What a particular letter stands for sometimes depends on the context as individual letters can have more than one meaning, for example, M: when used in GMT it stands for 'mat' and so, GMT stands for a 'glass mat thermoplastics' material. Because of the growth of oriented plastics products, the letter O is put in front the abbreviation for a particular material so, oriented PVC becomes OPVC: this means that a container is made from that oriented material.

Please note that if a letter is not being used in table 2b then, it does not mean that it is not being used in another branch of the plastics industry. (See also the draft ISO standards which are referred to as ISO/DIS 1043/2 and ISO/DIS 1043/3).

POLYAMIDES

By standard, and by general usage, PA stands for 'polyamide'. Numbers after the PA, designate plastics prepared from various condensation units in an homologous series. Of the large number of polyamides possible, two are of great commercial significance; these are PA 6 (polymer of ϵ -caprolactam) and PA 66 (polymer of hexamethylenediamine and adipic acid). By an extension of the abbreviation system, PA 66, GF 35 means that the material being referred to is 'polyamide 66 with 35%, by weight, of glass fiber'.

COPOLYMERS

If two monomers are used to make a plastics material then, the resultant product is known as a copolymer. It may be referred to by means of initials which represent the monomers used i.e. without a 'p' for 'poly'. For example, the copolymer (bipolymer) made from styrene and acrylonitrile, is referred to as styrene acrylonitrile copolymer or, as SAN. It is now suggested that an oblique stroke / be placed between the two monomer abbreviations e.g. E/P for an ethylene propylene copolymer. However, this suggestion is not universally adopted as SAN is still SAN: the oblique strokes may be omitted when common usage so dictates according to ISO 1043-1 : 1987 (E).

The major ingredient/monomer is usually mentioned first and the other polymer is often only mentioned if it is above a certain percentage, for example, 5%. (Some, so-called homopolymers are in actual fact copolymers but the second monomer is only present in minor amounts).

BLENDS OR ALLOYS

Because of their ease of manufacture, using (for example, twin-screw compounding extruders) there is a lot of interest in blends of plastics or, in blends of plastics with elastomers: either may be modified with fillers or glass fibre/fiber. When mixtures are made from two or more polymers (blends or alloys), it is further suggested that the symbols for the starting polymers be separated by a plus sign, and the whole be placed in parentheses i.e. (A + B). If styrene acrylonitrile copolymer or, SAN is blended with the copolymer made from ethylene and vinyl acetate or, E/VAC then it would be represented as (SAN + E/VAC) in the 'standard' system i.e. by ISO 1043-1 1987 (E). More commonly however, it would be referred to as SAN/EVA or, as SAN/EVAC. The major ingredient is usually mentioned first and the other polymer is often only mentioned if it is above a certain percentage, for example, 5%. If below this figure it is regarded as an additive and these are not often mentioned in commonly used systems.

In the case of both copolymers and blends, it would seem reasonable to indicate the percentage by weight of each ingredient, for example, 70:30, but this information is not often not, readily available.

MORE COMPLEX CODING

A data block system is available, for example in ASTM, to classify, or codify, plastics materials so that, the material description says if the material is, for example, a copolymer based on specified monomers, the intended processing method, whether the material contains additives which modify its basic behavior and, information on its properties. However, many users do not appreciate that such information exists and may be obtained from raw material suppliers.

ABBREVIATIONS USED FOR VULCANIZED ELASTOMERS

Rubbery materials, and compositions based upon them, are commonly referred to by a number of letters which refer to the monomers on which the polymer is based. The standard recommended practice (D1418-72A) issued by the American Society for Testing Materials (ASTM) is the most widely used for the nomenclature of elastomers (rubbers) and lattices. This practice recommends that the elastomers be grouped and coded into a number of classes according to the chemical composition of the polymer chain. Of the various types, the "R" and "M" classes are the most commercially important.

The "M" class includes:-

CM - Chloro-polyethylene.

EPDM - Terpolymer of ethylene, propylene and a diene with the residual unsaturated portion of the diene in the side chain.

EPM - Copolymers of ethylene and propylene.

The "R" class is defined by inserting the name of the monomer(s) before the word "rubber" from which it was prepared (except for natural rubber). The letter immediately preceding the letter R signifies the diolefin from which the rubber (elastomer) was prepared - except for natural rubber. Any letter(s) preceding the diolefin letter signifies the comonomer(s). Commonly encountered members of this class are:-

BR - butadiene rubber (BR is also known as polybutadiene);

CR - chloroprene rubber (CR is also known as polychloroprene);

IIR - isobutene-isoprene.

IR - isoprene synthetic (IR is also known as cis-polyisoprene);

NBR - nitrile-butadiene (NBR is also known as acrylonitrile butadiene rubber or, as nitrile butadiene rubber);

NR - natural rubber; and,

SBR - styrene-butadiene rubber.

ABBREVIATIONS FOR THERMOPLASTIC ELASTOMERS

The rubbery materials, which are processed as thermoplastics, are usually treated as thermoplastics and identified in the same way. However, they are sometimes referred as TPE (which stands for thermoplastic elastomer) and then, these letters are followed by another letter which identifies the type of TPE. For example, TPE-A means that it is amide based, TPE-U means that is urethane based and, TPE-O means that it is olefin based.

3 ALTERNATIVE NAMES

Many plastics are known by more than one name, for example, acetals may be known as polyformaldehyde or, polyoxymethylene. When this is so then the alternative name(s) should be listed so that cross-referencing is possible. The use of trade names is also prevalent - some of these are shown in Table 3.

4 SOME SUPPLIERS

These are not necessarily the manufacturers as like any other commodity, plastics are bought and sold on a world-wide basis: some companies also specialize in making plastics compounds

by, for example, adding fillers and in such a case, the resultant compound may be marketed under their own trade name. See table 3 for a list of some abbreviations and trade names/trade marks.

5 TRADE NAMES OR TRADE MARKS

Where possible the name associated with a particular Company's polymer should be known- this is because in some molding shops, plastics are often only known by their trade name or trade mark. An alphabetical list of some commonly encountered trade names/trade marks, their abbreviations and suppliers, is given in table 4.

6 MATERIAL PROPERTIES

In this section an appreciation of the properties of this particular type of plastic will be given. However, because each of the plastics discussed is, in effect, a family of materials which differ in, for example, molecular weight and molecular weight distribution, then the advice should only be regarded as a general guideline. The properties of plastics may also be dramatically changed by the processing conditions employed and by the use of additives.

PLASTICS AND POLYMERS

Most commercial plastics, also known as resins in North America, are based on the element carbon and are synthesized, or made, from simple, oil-based raw materials. These starting materials are called monomers and these simple, low molecular weight materials are put together, by a process known as polymerization (polymerisation), so as to form polymers. This term means that the final product consists of many identical, repeat units. Because the final molecular weight, or mass, is so large the material may also be referred to as a 'high polymer' or, as a 'macromolecule'.

All plastics are polymers but not all polymers are plastics. Cellulose is a polymer but it cannot be processed like a plastics material unless it is modified.

A plastic is a polymer, which is capable of being shaped or molded under conditions of moderate temperature and pressure. There are two main categories of plastic and these are thermoplastics and thermosetting plastics (thermosets). Thermoplastic products, for example an injection molding, may be softened and reshaped whereas a thermoset product cannot. In terms of tonnage thermoplastics are by far and away the most important. Many plastics are based on one monomer and are known as