23 Plastics Additives

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23.1 Introduction

Plastics make useful complex shapes as well as inexpensive high-volume items. In order to meet these diverse demands, commercial polymers are modified with additives to make plastics.

Compounding of polymers with additives and modifiers to make commercially useful plastics is a business that is constantly changing due to new materials, price changes, improved processing machinery, changing customer needs, environmental laws and concerns, etc. Some needs are persistent such as the requirement to fabricate parts, ways to upgrade properties, how to correct for problems introduced by the use of additives to accomplish the first two items, and controlling costs. The following remarks deal with additives from these points of view. No perfect solutions exist, so polymer additives and modifiers is a truly dynamic field of study.

23.2 Overview

Polymers as made are usually not suitable for industrial use as plastics, so industry uses additives and modifiers to adjust the properties of the as made polymers to make most of the plastics used today. The first polymers that became available are natural products like cellulose, natural rubber, or simple chemicals like phenol and formaldehyde that make "bakelite." In order to shape cellulose—the most abundant polymer on earth—into useful products, two things must happen.

First cellulose is modified by chemicals like acetic or nitric acid to make it easy to process. Then these chemically modified cellulose materials are cast into thin sheets or films, but thick shapes will crack, and even the thin forms have stiffness problems. Plasticizers like camphor and fillers like sand or sawdust corrected these problems.

Many thermoset materials like the phenolics (bakelite) have large shrinkage that will cause cracking. Fillers reduce this shrinkage and solid crack-free parts can be fabricated.

Based on these examples and many similar ones, polymer additives or modifiers are necessary to perform three essential functions. First, additives are required in order to process or fabricate many polymers. Several as made polymers have thermal stability limitations that force the producers to find and utilize stabilizers that allow melt processing.

Once this obstacle is addressed, room temperature storage can be a concern. Many polymers must be stabilized from the effects of oxygen, ozone, and other gases in the air. Exhaust gas from forklift trucks has been associated with odor problems in polypropylene food contact items.

Another example involves some polymers (and monomers) that will not wet reinforcing glass fibers; so wetting agents are used, in order to process the mixture into a useful plastic. These additives are usually put onto the glass by the glass manufacturer. Sometimes, the plastic compounder adds his own wetting agent to gain a competitive advantage, but in all cases, these additives are necessary to make the plastic function properly.

The second type of additive is for property enhancement. In the above example, a wetting agent may be necessary to process the polymer, but a coupling agent can be added as an enhancement to provide long-term durability. Fillers improve the flexural modulus and DTUL (deflection temperature under load). Color, odor, surface gloss, and other properties are improved by additives of this second category. Rubber improves impact resistance. Fibers improve both impact and modulus in many cases. Flame retardants enhance properties of a plastic and make it more valuable. Additives of this second type pay for themselves by giving much more performance value than the added cost of the additive.

The third type or class of additive corrects the flaws of the first two classes. Plasticizers are required to fabricate flexible PVC. Some of these plasticizers provide food for organisms like mildew and fungus. An additive is needed to correct this.

Additives are the essential ingredients that convert raw polymers into commercially useful plastics. Plastics that are fabricated into complex and useful shapes that meet so many needs of the modern world would not be possible without additives.

23.3 Thermal Stabilizers

23.3.1 Overview

Some synthetic polymers have chemical bonds that are less thermally stable than the chemically pure backbone of the perfect structure. These "weak links" often fail during

melt processing and lead to reduced performance of the resultant plastic part. Some commercial polymers contain chemical impurities like catalyst residues and thermal decomposition products that further reduce thermal stability of the backbone chain of atoms that create the polymer.

Thermal stabilizers minimize molecular weight (MW) change during melt processing by blocking the adverse effects of polymer flaws and impurities. The most thermally sensitive polymers are PVC, PP, and POM (polyoxymethylene), but even HDPE can change MW during melt processing.

23.3.2 PVC

Several different chemical classes of additives are used for thermal stabilization of PVC. These include divalent lead compounds, tin and antimony based chemicals, and mixed compounds of cadmium/barium, calcium/zinc, and many others. In general, the lead based thermal stabilizers are used in electrical applications, the tin based ones are used for external uses in siding and other extruded shapes, and mixed compounds are used in plastisols and injection molded parts.

Thermal stabilization of PVC is complex because:

- different base polymers are used commercially
- use of various plasticizers alters the amount and type of stabilizer
- processing conditions change thermal stabilizer needs (twin screw vs. single screw for example)
- toxicity of the additive package
- cost, etc.

All of these topics are considered in detail in *Handbook of Vinyl Formulating*, second edition, Wiley-Interscience, edited by Richard F. Grossman.

23.3.3 Polyolefins

Polypropylene (PP) and high-density polyethylene (HDPE) represent two extreme cases of a wide variety of commercially important polymers. PP and HDPE behave differently when thermally stressed during the melting process. PP decomposes to low MW products and HDPE crosslinks; increasing MW. Both polymers have carbon chain backbones and hydrogen is the only other atomic species: the difference is in chemical structure.

HDPE is a linear chain of carbon and hydrogen in the form of methylene ($-CH_2-$) groups. There is a methyl group (CH_3) on the chain ends. PP is like HDPE, but every other hydrogen in the chain is replaced by a methyl group.

This change makes a big difference in thermal stability and many other properties as well. Considering only thermal stability, PP will undergo carbon-to-carbon chain breaks that accelerate with temperature. At the melting point, chains break so rapidly that the process results in a solid polymer

becoming a wax, liquid, or even a gas. All this is related to the structural differences between HDPE and PP. In short, PP cannot survive melt processing without thermal stabilization.

HDPE does not decompose like PP. HDPE carbon chains are not destabilized by methyl groups; so the HDPE resists decomposition by heat better than PP. On the other hand, because the carbon chain is so stable, it will undergo crosslinking. Hydrogen atoms will be replaced by carbon chains, both short and long. This results in an increase in MW. To minimize this, HDPE must be stabilized against this type of change. In short, HDPE needs some thermal stabilization.

If the same thermal stabilizers are used for both polymers, the amounts required to survive one melting cycle without excessive change of MW are quite different; PP takes three to ten times the stabilizer, as does HDPE. Polymers that are between PP and HDPE in the number of side groups (methyl or alkyl groups that behave like methyl) require amounts of thermal stabilizers between the extremes noted.

The companies that manufacture these hydrocarbon based polymers are well aware of these thermal stability concerns and more. The additional concerns involve color, odor, surface, etc., problems related to the specific polymer and materials used in the synthesis. Catalyst residues can have major effects on these other properties and they must be handled accordingly. There are two methods: elimination and/or quenching with additives.

Hindered phenolic antioxidants are useful in addressing some of these concerns. Each manufacturer has different standards and needs related to the exact polymer and its synthesis conditions. This is why there are many different thermal stabilizer systems in use for this large class of hydrocarbon based polymers. The best sources of current information are patents along with analytical results. Even this is not perfect because some additives might undergo chemical changes during thermal processing of the material that they are protecting.

23.3.4 Polyoxymethylenes (POM polyacetals)

The chemistry of the POM family of polymers and copolymer makes them extremely sensitive to acids, excessive heat, and many different types of impurities including many additives (colorants, fillers, etc.). Some grades are also sensitive to bases. Manufacturers of these useful engineering polymers warn processors and end users about these concerns. So long as processors and end users observe the guidelines for each specific grade, there will be no need for additional additives in most cases.

23.4 Nucleating Agents

Nucleating agents are used with polymers that can crystallize in order to speed cycle times. After melting, it is solidification rate of the plastic into a useful shape that

controls processing and cycle time. Both amorphous and crystalline polymers are subject to molded-in stresses that are a result of the tool geometry. These are the concerns of injection molding and extrusion experts since they are controlled largely by tool geometry and processing conditions.

Crystalline polymers have an additional concern. When they cool, they also crystallize. The amount of crystallization and the type of crystals formed are controlled by thermal history, cooling rate, and additives. There are specific additives that will speed or slow crystal formation and they will also affect the exact crystal that forms.

Fast crystallization allows faster molding cycles or clearer extruded thin film. Nucleation speeds this crystallization process. Crystallization is a complex subject because there can be a downside as well as immediate economic advantage. Many different types of chemicals can nucleate crystallization. The effect is specific for the polymer and the chemical. Glass fibers, pigments, talc, etc. can nucleate crystallization for some polymers.

If crystallization is too fast, crystal size will be small. This is desirable for clear film but for some polymers in time, there will be a growth of crystallite size along with a change of properties.

There is another meaning for nucleating agent that must not be confused with crystal nucleation described above. In the foaming process, dissolved fluids in the polymer must come out of solution, form a gas bubble and create a foam cell. In this application, the number of nucleating agents can control cell size. Shock nucleation is a mechanical process that is generally independent of material nucleating agent. All of this applies to the foaming process and not crystallization.

Some polymers crystallize in more than one crystal type. This leads to different properties from the same polymer. For example, PP has three well known crystal forms; The alpha (α) is the usual form with a melting point of 164 °C. Special nucleating agents will produce the beta (β) form with a MP of 150 °C. This crystal form is more ductile and impact resistant than the alpha but it is thermodynamically less stable, so it reverts to alpha. The third form is gamma (γ) and it is formed by crystallization after high sheer in a thin section. It is the "living hinge" that is so important in PP items with moving parts. Flexing immediately after molding is a factor in some products. Other crystalline polymers have different types of crystals that might be commercially useful.

23.5 Antioxidants

23.5.1 Primary Antioxidants

Antioxidants (AO) function in the environment and protect polymers for long times at ambient conditions. Several different chemical types of antioxidants serve different polymers and different functions. Some that are in commercial use are discussed below.

Phenolic type AOs are very effective as thermal stabilizers as well as providing long term environmental protection. The chemistry of this class of AOs is based on the well known food additive butylated hydroxy toluene (BHT). BHT is an effective AO for many polymers but its low MW and poor solubility in many polymers limits use. These limitations are overcome by the wide range of chemical structures all based on BHT that are commercially available. Cost of this class of AOs is falling as the various types come off patent and production in Asia steps up to meet demand.

23.5.2 Secondary Antioxidants

Secondary AOs extend the life of the more expensive phenolic type primary AOs. They also delay onset of color from used up phenolic type AOs. As phenolic primary AOs react with oxygen, they form different chemical structures that are yellow to tan in color. These quinone type structures are not AOs and they are expensive, having formed from expensive primary AOs. Chemists have dealt with this problem by developing secondary antioxidants that keep quinones from forming until all the secondary AOs are consumed.

There are two different chemical types of secondary AOs. Both have the common properties of low cost relative to primary and the ability to be oxidized to colorless materials before the quinones can form from primary AOs. Organic phosphite and organic sulfur compounds modified to fit the needs of specific polymers are the chemicals that are used.

Sulfur based secondary AOs sometimes have odor problem but they are very effective in rubber based plastics. They will react with phosphites, so mixed secondary AOs are never used.

Phosphite type secondary AOs sometimes have water sensitivity, so there are many different materials offered for each specific polymer and end use. Some of the newer secondary AOs of this class approach or exceed primary AOs in cost, but this is justified by reduction of color and falling cost of some primary AOs.

Interaction of the sulfur and phosphorus types of chemicals can be a problem in recycling. If it is suspected that these two different types of chemicals are present in a mixed recycling blend, additional secondary AO of one type should be added in excess to provide long environmental life without color formation. The same is true when using these systems as thermal stabilizers.

23.5.3 Hindered Amine Light Stabilizers (HALS)

Hindered amine light stabilizers (HALS) were developed as photostabilizers and/or metal deactivators. It was soon determined that the oxime structure functioned as an AO as well. In fact, these AOs are almost self-regenerating so they last for long times. They also serve their original functions,

thus they often do double and even triple duty. These additives are responsible for high performance PP used in artificial turf that is expected to perform for up to a decade and more.

HALS are used whenever high performance is desired and the chemistry of the plastic allows. HALS cannot be used with halogen containing compounds such as PVC or halogenated flame retardants. Based on the success of HALS, other oxime based AOs are under development. They may be less expensive than HALS in some cases.

23.5.4 Lactones

Lactones are similar to HALS in some of their chemistry but their nitrogen free chemistry allows use in the presence of halogens. Some natural products have lactone structures and they function as food antioxidants. Lactones are becoming the AOs of choice in some plastics as their popularity grows.

23.5.5 Vitamin E

Also known as, $d\ell$-α-tocopherol, vitamin E is an antioxidant that is used commercially in polymers. The synthetic form of vitamin E will function as well as the natural product in polymers; most of these uses involve food contact or biodegradable polymers.

23.5.6 Carbon Black

Carbon blacks come in many different varieties. Some grades have AO properties especially in high concentrations. Many grades of plastics that are stored or used out of doors contain high levels of these blacks and lesser amounts of conventional more costly AOs perform satisfactorily. In some cases, the AO can be eliminated altogether.

23.5.7 Thin Films

When thin films are extruded, special care must be taken to avoid loss of additives by sublimation. The high surface area and high temperatures of extrusion make this a critical issue for all high surface parts exposed to high temperatures. This is the reason that some AO molecules have very high molecular weights to keep them from volatilizing. Other parts of the AO molecule improve compatibility with the polymer that they are designed to protect. This is why some AO molecular structures look so big and complex; they have to be that way to function.

23.6 Flame Retardants

23.6.1 Halogen Free

Halogen free flame retardant systems are highly desirable because they have fewer toxicity and regulatory issues than the sometimes more effective halogen systems. This is an active area for research, and new additives and tests are appearing with increased frequency. Some halogen free systems use phosphorus or nitrogen chemistry and others are based on inorganic minerals.

23.6.2 Inorganic Flame Retardants

The least expensive, most used, and possibly least toxic flame retardant (FR) is aluminum trihydrate (ATH) and similar inorganic hydrates. These materials must be used at very high loadings (sometimes exceeding 60% by weight) so they function as fillers as well as FR materials. They function by decomposing to liberate water at temperatures exceeding the melt processing temperatures of many polymers, so they are not used in many of the high temperature thermoplastics such as PA, PBT, PC, etc. Even PP is beyond the limits of ATH. When ATH decomposes, steam results. If this happens during melt processing, the polymer is foamed. ATH is used in polyethylene wire and cable (W&C) formulations as well as thermoset polymers like epoxy and thermoset polyesters. So long as the temperature does not exceed 200 °C, ATH is safe to use (but check first before doing large scale processing).

Magnesium hydroxide is an inorganic hydrate that is more thermally stable than ATH. It can be used in PP and similar high melting thermoplastics. Like ATH, $Mg(OH)_2$ must also be used at high concentrations to achieve good FR performance.

These high concentrations of FR minerals tend to increase part density and brittleness. Some polymers can react with them as well. Thermoplastic polyester like PBT cannot be used with them for this reason. The big advantage of these inorganic materials is low cost as well as their white or light color and the non-toxic benefits. Sometimes they are used at low concentrations with other FR materials as cost savings additives. Sometimes they provide other benefits in certain electrical applications like ion sequestration.

23.6.3 Other Halogen Free Systems

Additives based on melamine, phosphorus, and other char making materials are finding use in specific FR systems. The phosphorus based systems appear to function best with oxygen containing polymers. The char is believed to be a complex phosphorus oxide based coating that blocks oxygen from coming into contact with monomer or other flammable materials. The melamine based systems form chars that are based on nitrogen as well as phosphorus in the case of melamine phosphate systems.

Nano particles dispersed in polymers are presumed to block or slow down the contacts between oxygen and fuel. This reduces burning rate and allows other flame retardants to extinguish the fire. This binary system approach can be cost effective by reducing the amounts of FR materials required. This also allows maintenance of many physical properties that otherwise would be altered by larger amounts of additives as often happens with the other FR systems.

Some polymers have some unique chemistry that allows the use of relatively low amounts of additives that catalyze a molecular rearrangement that provide some flame resistance. Polycarbonate (PC) is an example. It is a polymer based on para orientation of chemical bonds. These para bonds can be changed to meta bonds by traces of sulfonic acids. Meta linkages are less flammable than the original para ones. Of course, some other properties are changed as well. Other aromatic based polymers take advantage of this chemistry. "Nomex" is a meta bonded form of the better known "Kevlar." Kevlar with para bonds has better properties but Nomex is more flame resistant and is used by firefighters worldwide.

23.6.4 Halogen Systems

Traditional antimony/halogen systems are still in wide use because they are proven by years of successful applications in the electronic and electrical markets. There are many applications where thin sections (<1 mm) must be flame retarded to meet UL V-0 or V-5 standards where only halogen systems are effective.

One of the more popular systems is decabromodiphenyl ether (DECA) and antimony trioxide. DECA has been under attack but so far, it seems to be less toxic than several closely related bromated aromatic compounds that have been banned in Europe and elsewhere. Some of the concern about DECA occurred when decabromodiphenyl accidentally got into the human food chain. The similarity between the two different chemical names (decabromodiphenyl and decabromodiphenyl ether) is not easily detected by those who have not studied chemistry, and this may have contributed to some of the concern. On the other hand, there are real toxicity concerns about many brominated organic chemicals.

High melt processing temperatures require more thermal stability in the FR systems and this usually means the more expensive bromine compounds. Remember, the FR system must be stable at processing conditions and decompose to extinguish the fire at temperatures slightly above the highest processing temperature. When the thermal properties of the polymer allows, chlorine based compounds are used with antimony oxide, because they usually decompose at lower temperatures and they are usually less expensive than their bromine counter parts.

Halogen based flame retardants are special chemicals. They are required to be relatively non-corrosive, low toxicity, and yet, liberate corrosive halogen compounds that react with antimony oxide at fire temperatures. Some of these chemicals have chemistry similar to PVC and, thus, sometimes they require thermal stabilizers to withstand thermal processing.

PVC and other highly halogenated polymers are useful in construction applications (sometimes, after they are upgraded with antimony oxide) such as siding, windows, and electrical systems including commercial W&C uses. Some of these PVC type polymers are used in blends with more flammable polymers to make flame resistant business machine housings with stringent FR specifications. These are excellent materials that make use of several properties of PVC as a blending additive. ABS, SBR, and similar polymers are blended with PVC for these applications.

23.7 Color and Colorants

Pigments are solid materials that scatter as well as absorb light. Dyes are soluble materials that absorb light but do not scatter it. Thus, the color from dyes is often brighter, sharper, transparent, or cleaner than that from pigments.

Most plastics use pigments for color in spite of the above because pigments, in general, are more thermally stable, more stable to exposure to light, and not prone to "bleeding" or exuding out of the plastic to discolor objects in close contact. Pigments produce opaque colors in thick sections and translucent ones in thinner sections. Most colors in a common series look better if they all have similar degrees of translucency at the same thickness. Therefore, depth of color or opacity as well as color must be matched when working with pigments in plastics.

When it was determined that some colorants might hurt the environment, they were no longer available or they were manufactured at off shore locations. Some colorants are safe under all end use conditions but can be a problem when discarded at the end of their useful life. Other colorants might be a problem in fires or when incinerated.

Because of this concern, today some dyes are used as pigments by converting the soluble dyes to insoluble pigments. There can be processing problems with these materials because sometimes they can dissolve or melt in the polymer carrier at high temperature. When these pigment dyes come out of solution upon cooling, they crystallize in different sizes and/or shapes than intended, thus altering color. This alters color and transparency leading to customer problems.

Color is a most interesting field of study. An introductory course of several days' length is offered by SPE and it is useful even for plastics professionals not directly involved with color.

Some of the reasons that certain colorants are more expensive than others are worth a little investigation. Copperphalocyanine (CPC) blues and greens are relatively non-toxic colorants, but they are manufactured overseas for the most part because the process has many byproducts that are hard on the environment. Cadmium colors (reds, oranges and yellows) are manufactured from cadmium compounds that are highly toxic. The colorants (cadmium sulfoselinides) are non-toxic but their products of incineration are toxic. All of these concerns and others apply to several classes of polymer additives and modifiers that themselves are only mildly toxic.

23.8 Fillers

Calcium carbonate comes from natural sources such as bone, limestone, shells, or it can be made synthetically. It can

be pure enough to take as medicine (anti-acid), or it can be ground up rock with many impurities (also used as anti-acid). It may be the most widely used filler. (A similar claim can be made for carbon black or carbon in all its many forms.) Calcium carbonate is widely used in PVC as an acid acceptor, in polypropylene as a filler, and in many thermosets and thermoplastics as an inexpensive filler.

Precipitated grades as well as the pulverized ones can be surface modified. The precipitated calcium carbonate that is used in polypropylene (and other similar thermoplastic resins) is usually surface modified with stearic or isostearic acid.

$CaCO_3$ is an extremely important commercial material for a few large volume polymers; both thermoplastic and thermoset. If one grade does not work in your application, ask your vendor as well as other vendors for alternatives. There will be two or three grades for most applications, but only one or two will generally give superior performance. As in all additive situations, keep looking and asking until you get the results you want!

Carbon black provides a black color that protects many thermoplastic polymers from the damaging effects of sunlight (UV) by absorbing the damaging energy. Certain carbon blacks will function as antioxidant materials and others are used as jet black pigments. Still other grades function as conductive fillers for EMI shielding.

Carbon blacks are made from many different raw materials including natural gas, petroleum, coconut shells, and other varied organic materials both natural and synthetic. Fibers like polyacrylonitrile, bamboo, cotton, etc. are the sources of other interesting forms of carbon fibers and filaments. Other carbon forms are becoming available from special gas phase chemistry yielding fullerenes and tube forms. These are small scale at the present time, but the future might be very bright for these dark materials. Reinforcing carbon blacks are essential ingredients in many elastomers used in car and truck tires.

The structure of carbon black involves size, shape, and connection of fundamental particles into high levels of structure that gives the reinforcement. Carbon blacks have surface areas measured in tens to many hundreds of square meters per gram. For this reason, intensive mixing is often required for ultimate dispersion. Degree of mixing can be judged by viewing a thin film against a strong light. Dispersion measurement requires a microscopic inspection of thin film or a pressure drop test with an extruder, screen pack, and differential pressure gauge.

Research on carbon based materials like the fullerenes (buckey balls), single wall nano tubes (SWNT), and graphene (single layer of graphite) is leading to many new and improved products for electromagnetic shielding (cell phones) and advanced computer flexible folding flat screens.

Silica occurs in different crystal forms and impurity levels. Its low cost and widespread availability are offset by its density (2.65 g/cc), hardness (7 on mho scale), and concern about toxicity of some but not all grades. Its wide geographic distribution makes it available in all parts of the world. So it is widely used. The crystalline form of silica causes silicosis or white lung when inhaled in excess as occurs in some mining operations and machining crystalline silica filled plastics.

Clay is another common material of wide ranging properties. Like all fillers, just because one grade or type does not perform satisfactorily does not mean that all grades will fail. Some time with your vendor's technical department can pay off here in finding inexpensive filler with unique value to your application. Clay is becoming important in some nano composites because it can be exfoliated into nano thin platelets.

Talc is white and soft, so it is a valuable filler. The flat shape of talc particles adds reinforcing value in addition to simply acting as a filler. Asbestos does occur in some talc deposits, so the location of the talc mine from where your talc supply comes could be important in some demanding applications.

Mica can vary in color, but this is offset by better physical properties than talc in some filler applications. There are many forms of this widely distributed mineral. The naturally thin sheets of mica can be exploited by exfoliation to the nano thickness range.

Wood and nut shell flours are natural products that serve as both fillers and reinforcements due to their fiber structure. Moisture levels are a problem in many applications. These materials may become much more important in the future as recycled wood products become abundant. Public concern as well as technology may get involved in some of the applications, and it is becoming politically correct to use some renewable resource in your compounding.

Fly ash is another product that comes from an increasing awareness of our environment. Some applications have been found in polymers for fly ash and in time there will be more. Modern technology is involving public relations and environmental issues more and more. Whenever these issues can be turned into commercial benefit for your company or organization that should be the direction of research when the cost can be justified. Quality products must never be sacrificed, however. *Slag* is also being processed into filler form for plastics. Inexpensive fillers like slag, fly ash, etc. must be carefully evaluated for toxicity.

Wollastonite is a mineral that has enjoyed some success as an asbestos replacement as well as finding niche markets on its own. The shape is elongated so there is reinforcement as well as filler applications. A large use is in asbestos replacement applications.

Glass spheres are a product of ground up glass from bottles and jars, as well as special grades that are made for specific applications. The major use of this product is in reflective paints (those reflective white stripes on black top roads are due to this material). In polymer applications, glass beads impart geometrically flat surfaces in injection molded

parts along with good color. Glass beads are used with glass fibers and thus balance reinforcement and warping.

Hollow glass and mineral spheres have all the advantages of solid glass spheres, plus lower density. The increased cost may be completely offset by the reduced density (when volume or area pricing is used). Replacing expensive resin with hollow spheres of lower density is often a very good trade off. Most applications are in thermosets, where the spheres do not have to withstand high compressive forces. Furniture manufacturers make extensive use of hollow low-density fillers in syntactic foam for legs, arms, and even tops. These materials have found wide use in aerospace applications as well.

Injection molding pressures range between about 10,000 and 30,000 psi, and this will crush most hollow spheres. In general, the lower the density, the lower the compressive strength of the hollow spheres; so only low pressure fabrication can be used.

Recycled materials of many types are coming onto the market. Some companies may even choose to make polymers specifically as compatibilizing additives for selected types of recycled materials. The construction, pipe, and transportation industries are candidates for many of these applications. Ground thermosets with high filler loadings will be an important source of new fillers and manufacturers may be required to use these products in some applications. Recycled textile fibers can serve as reinforcements, which add value to composites if they can be collected in usable forms.

Portland cement is inexpensive, widely available, and water curable. It has been tested in several polymers as an additive that causes the composite to harden with time of exposure to moisture, turning a thermoplastic into a more durable thermoset.

23.9 Reinforcements

23.9.1 Overview

Reinforcing fibers for plastics are used in several ways. They can be wrapped around polymer tubes, laminated between polymer surfaces, laminated to the surface, woven into complex shapes containing polymer as an adhesive matrix, extruded as long or short fibers into polymer composites, and blended with polymers to make carpets with fiber reinforced backings. This discussion is limited to mostly short fibers (under about 2 cm) that are used in thermoplastics that are intended for melt processing applications.

Reinforcing fibers are used for improving the strength of composites. The vector direction(s) of the strength improvements, the value of those improvements, application and manufacturing techniques, and special needs must be considered when selecting the fiber for the application. If very smooth surfaces must result, random short fiber injection molding material may not be adequate. Rocket casings must be lightweight and reliable, so special fabrication

techniques and fibers are used. Electrical and thermal conductivity can be the reason for choosing a certain construction over a less expensive one.

Glass fibers have proved themselves in many difficult applications. This was not always the case, but surface modification of various grades of glass fibers over the past 50 years has led to a wide variety of fibers for many different applications.

E glass is most common in thermoplastic composites. The E stands for glass that has superior electrical properties, C is for glass with the best chemical resistance, and S is for highest strength glass formulation.

S glass is the strongest and it tends to be used in thermoset plastics where filament winding or pultrusion is used; these maximize the strength, nickel coated glass is conductive, and hollow fibers with improved strength to weight ratios are still being tested for cost/benefit in many composites.

There are still concerns about the use of glass fiber for some applications, like high temperature fluoropolymers that might liberate hydrogen fluoride (HF) during processing, acetal resins that are sensitive to trace amounts of impurities, polymers that are processed at temperatures too high for many usual surface modifiers for glass, and some durability issues concerning thermosets (crazing, weathering, etc.).

Even with all these concerns, glass fibers are the standard against which other fibers are compared. Glass fibers and indeed all rigid fibers have a tendency to introduce some warping in thermoplastic composites. This warping is related to the fiber, which is stiff and non-shrinking, and the plastic melt which is initially soft but later hardens. When this occurs with some degree of bonding between the fiber and the resin, there will be molded in forces that can result in warpage in the part. Some work with glass fibers that have three lobes has led to a reduction in this type of warpage. Another approach to the problem is to mix fibers and fillers (glass spheres) to reduce the warpage.

An experimental low melting glass fiber will soften at the processing temperature of the engineering plastic like polyether ether ketone (PEEK). Then, as the resin cools, the glass will move a bit to accommodate the shrinkage of the matrix resin. In theory, this will provide strength enhancement without molded-in stresses normally found with conventional fiber glass reinforcements.

The latest new development in glass fiber innovation is a commingled glass and polymer fiber. This morphology allowing close contact of the two materials is offered in hopes of improving the wetting of the glass more completely.

Graphite or carbon fibers are very high modulus materials that are conductive (electrical and thermal) and withstand flexing within their elastic limits very well. The surface is inert so it is difficult to modify. As a result, the full value of these materials is seldom realized in many applications unless the fibers are placed individually to maximize their value. An immense amount of work has been done on this surface modification problem by some excellent scientists,

but progress has been slow. Current interest in fullerenes and micro tubes (SWNT) may help in this area.

The very high flexural modulus and the light weight make carbon fibers the material of choice for many aerospace parts and high tech sports equipment. With just a slight improvement in surface adhesion, the use could skyrocket. So far this problem has not been solved, but many small improvements are upgrading the value of carbon fibers constantly.

Kevlar® is a high temperature polymeric fiber that is tough. Surface bonding is a concern but less than in the case of carbon fibers because Kevlar is more flexible. Price will drop as supply is increased and more manufacturers come into the business. Many of the applications that might have gone to carbon will go to Kevlar because it can be modified to meet end use requirements easier than carbon fibers.

Polyethylene can be spun in the gel form (5% UHMWPE in decahydronapthalene) to a very high strength fiber on the basis of the free-breaking length. (Free-breaking length is the height to which a fiber can be lifted before breaking under its own mass.) The best UHMWPE fibers have a free-breaking length value of 336 km compared with Kevlar of 193 km, carbon of 171 km, and steel with a value of 37 km. This measure of strength to weight is truly impressive for polyethylene. The low melting point (145 °C) and the difficulty of modifying the surface to make it reactive with coupling agents are serious limitations that are yielding slowly to research efforts. Special applications in body armor justify the current price of $45−85/kg.

Stainless steel is an excellent conductor of electricity. Very fine diameter SS fibers can be added to many polymer composites without loss of mechanical strength or toughness. This has led to their use in injection moldable electrically conductive RFI/EMI shielding applications.

Cotton and cellulose fibers like s*isal* have good high temperature properties (equal to or even above nylon). Some cotton fibers are as long as 4 in. Water removal is a problem in the use of natural fibers, but benefits including renewable resource may offset the difficulties. Polymer coated cotton fabric is widely used in many different applications. Some excellent work on recycled wood and natural fiber composites for use in construction is being done at the USDA Forest Products Laboratory in Madison, WI.

Wood flour (sawdust) is used in PE or PVC to make the popular grades of plastic lumber that competes with pressure treated wood. Plastic lumber is maintenance free and colorable, giving it a big advantage over lumber in several specific applications like outdoor decking.

Woven and non-woven synthetics are finding use in many niche markets; some of which are quite large. Kevlar is growing so fast that it is mentioned by itself, but there are many other materials just looking for problems that they alone can solve. PTFE fibers have been used in low friction acetal resin for example and PTFE covered glass is used in domed stadiums.

Mineral fibers are coming onto the market place every so often. They tend to be brittle but inexpensive. Some must be checked for toxicity (asbestos type). As new applications arise, the user of these (and other) fibers must remain alert to new developments in toxicity concerns.

23.10 Impact Modifiers and Impact Modification

One theory holds that failure begins at a flaw. If flaws are kept below a certain critical flaw size, failure will be prevented. This is seldom possible, so rubber particles are used to dissipate the point of the crack so that the crack can no longer propagate through the brittle matrix resin. According to this view of why plastics fail in impact or stress situations, rubber particles must be placed in the path of the crack to prevent failure. The questions to be answered concern the amount of rubber and the size of the particles. Apparently, there are some flaws that require many small rubber particles and there are some flaws that require fewer but larger rubber particles. For each polymer matrix there is an optimum size or sizes of particles. These rubber particles do not have to be spherical, but they frequently are. The rubber phase is not compatible with the plastic phase and this can lead to uneven distribution of the elastomer in the resin matrix. There are several ways to overcome this fundamental problem.

The rubber phase can be in a copolymer that has blocks of elastomer and blocks of matrix polymer. This will make the elastomer compatible with the continuous polymer phase. Many polymers of the A-B, A-B-A, A-B-C, etc. exist.

The rubber phase can be grafted to the polymer phase. The rubber toughened nylons are a spectacular example of this technology. A variation consists of polymers grafted to elastomers to provide a three dimensional interface. The rubber phase can be encapsulated inside of a particle rich in the matrix resin.

Sometimes, the rubber particles are mixed with the plastic without special compatibilizers due to an unusual affinity between the two phases; one of which is crosslinked and the other is not. Some thermoset systems are formulated in this fashion.

The above discussion assumed that a propagating flaw was the cause of failure. It would be better if the flaw never existed. Many modern impact modifiers are designed to prevent the formation of the flaw. The approach here is to prevent the polymer phase from yielding by extending the elastic range of the polymer by control of monomers.

The above discussion points the need for different types of impact modifiers. Some are used to prevent flaws, and some minimize the effects of these flaws even though they do not prevent flaws. Some impact modifiers modify the effects of flaws that are caused by other additives. There are many materials to serve these many different functions.

- Thermoplastic elastomers
- Random copolymers
- Vulcanized or thermoset elastomers
- Polymers grafted to elastomers
- Elastomers grafted to polymers
- Block polymers
- Plasticizers

In addition to serving as impact modifiers, many of the above materials can also function as compatibilizers. This is because all of them have two different phases with the exception of the vulcanized or thermoset elastomers. At least one of the phases must be compatible with a known polymer in order for these materials to be commercially useful. If the other phase is compatible with a different commercial polymer, then you have a compatabilizer that is also an impact modifier. Because of the similarity of technology and growing interest in both impact modification and compatabilization, there will be more materials appearing every year for the next decade or longer.

23.11 Miscellaneous

23.11.1 Coupling Agents

Coupling agents chemically bond dissimilar materials together even in challenging environments. When plastic composites are made with inorganic reinforcements, wood fibers, or other fillers, these materials tend to separate from the plastic and make the composite weak if they are not compatible with the plastic. *Coupling agents increase the time that it takes for dissimilar materials to fail in service.* The improvements are measured in orders of magnitude. Many of our modern high performance plastics would not exist without coupling agents. There are some special cases where polymeric coupling agents can react with metal oxides, amines, or with themselves to form crosslinked composite structures that have commercial value as well as great scientific interest. The best coupling agents for many polymers are based on silane chemistry. Some other materials are claimed to act as coupling agents. These products must be carefully checked for durability (especially in wet or humid environments) because they do give some short term property and even processing improvements, but they may not last as well as true durable coupling agents.

23.11.2 Surface Modifiers

Surface modifiers change the physical chemistry of mineral and fiber surfaces. Hydrophilic surfaces, as commonly found with many mineral fillers, can be made hydrophobic by surface modification. Mineral and glass fibers can be treated so that the polymers they reinforce will wet their surfaces. Surface modifiers are chemically bound to one surface and physically attracted to another surface or material. They unite dissimilar materials with physical and chemical bonds, where the physical bond is not permanent and the chemical bond is. Again, silanes are very effective in these applications, but so are some titanates, and chemicals like stearic acid.

23.11.3 Wetting Agents

Wetting agents have a physical attraction for both surfaces involved. Wetting agents have no permanent chemical bond to the surfaces that they wet. Therefore, wetting agents are easily extracted from composites by means of solvents and, consequently, they are not permanent. They cannot survive in water or high humidity because they are extracted or the water comes between the wetting agent and the hydrophilic surface, thus destroying the temporary bond. Many titanates and organic surfactants (both ionic and non-ionic) are examples of additives that function in this application.

23.11.4 Biocides

Most synthetic polymers are of little or no food value to bacteria, mold, mildew, etc. The exceptions appear to be polymers that contain nitrogen like nylon or polymers that contain plasticizers that are appetizing to the microbes involved.

Additives used for biological defense cover the spectrum from ones with odors that offend rodents to toxic materials that kill mold and mildew. There is a wide range available but there are still reports of squirrels electrocuted while biting through power lines.

Plasticizers for PVC are a special problem that must be carefully considered when making formulations for shower curtains and other applications that involve good growth conditions for mildew and fungus. There are many additives to consider for each application and the user has a wide field from which to select. Quaternary ammonium salts prevent bacterial attack. A very old and well known biological control agent is coming back into popularity.

Silver salts are well known to inhibit many kinds of biological species. This technology is currently the material of choice for many plastics.

23.11.5 Plastizers

Plasticizers are a high volume class of additive mainly used in just one polymer, PVC. There may be as many as three hundred or more simple chemicals and polymers that have been used commercially over the past decades.

Acrylic polymers are used in outdoor applications of rigid PVC formulations. Other ABS and SBR polymers are used in less demanding applications.

The workhorse for flexible PVC is DOP (Dioctyl phthalate, bis-2-ethylhexyl phthalate, and several other names). Questions about toxicity have been raised and addressed, but some concerns still exist. This has led to DNP (Dinonyl

phthalate), citric acid esters, and many other substitutes. Many of these are more expensive and less effective than DOP, but safety concerns keeps them on the market, especially in toy applications.

Some FR grades of flexible PVC use phosphorus based plasticizers. There are special plastizers for non-skid vinyl floor tile. These applications illustrate many of the specialized needs of PVC that require specialty plasticizers.

23.11.6 Mold Release Agents

Some mold release agents are sprayed directly onto the tool steel of the mold. These include among others some silicone and some fluorocarbon based materials. Other mold release agents are coated or sprayed onto the surface of the molding powder. This is done in batch blenders just before pack out to avoid passage through an extruder. Most release agents that are melt blended with polymer can be applied in this alternative fashion.

Mold release agents function by coming to the surface between plastic and tool. Some like certain fluoropolymers do not mix or dissolve well in the polymer but they do have a good affinity for the die or mold surface. Other mold release agents dissolve in hot polymer but come out of solution during the extrusion or molding process.

Mold release agents may have more than one function. Some stay on the plastic surface and lubricate the plastic. Others bring other additives with them as they go the shape or part surface. This is useful for surface active additives like biocides and some UV stabilizers.

Sometimes mold release agents function too well and interfere with printing, gluing, and painting. Changing from a calcium salt of a fatty acid to barium or zinc salt can make all the difference. A good metal deactivator such as calcium stearate is a mold release agent, but it might hurt printability of the part surface in some systems.

When mold release agents dissolve in the melt, they can reduce melt viscosity and function as a processing aid. Many processing aids also function as mold release agents.

Since the class of chemicals that function as mold release agents is broad (salts, amides, polymers, etc.), many individual members can have more than one function. Function varies with polymer type as well as chemistry of the mold release agent.

23.11.7 Others

There are dozens of other additives that are used occasionally. Along with these additives comes special processing techniques like grafting an additive to a polymer to keep it immobile. Small amounts of polymers like polymethylmethacrylate (PMMA) will often improve surface appearance. Traces of PA 6 will make PA 6, 6 a bit easier to process and a bit of recycled PET will reduce the cost of some polyesters like PBT. Many of the major additives discussed in this article are important enough to have books written about their use. Some of the books that this author uses are noted below.

Polymer Modifiers and Additives, by John R. Lutz and Richard F. Grossman. Marcel Dekker, Inc. 2000 ISBN 0824799496.

Coloring of Plastics Fundamentals second edition by Robert A. Charvat. Wiley-Interscience 2003 ISBN 0471139068.

Plastics Additives third edition by R. Gächter and H. Muller. Hanser Publishers 1990 ISBN 3466156801.