



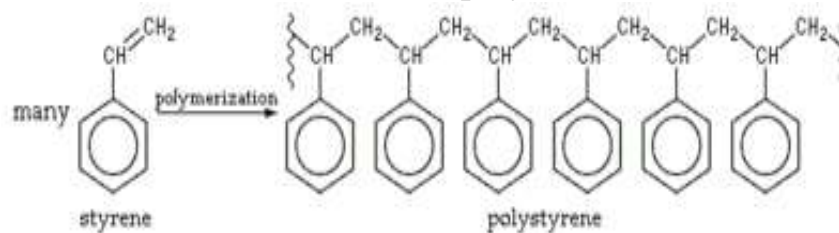
Polymeric implant materials:

Synthetic polymeric materials have been widely used in medical disposable supply, prosthetic materials, dental materials, implants, dressings, extracorporeal devices, encapsulants, polymeric drug delivery systems, tissue engineered products, and orthoses as that of metal and ceramics substituents. The main advantages of the polymeric biomaterials compared to metal or ceramic materials are ease of manufacturability to produce various shapes (latex, film, sheet, fibers, etc.), ease of secondary processability, reasonable cost, and availability with desired mechanical and physical properties. The required properties of polymeric biomaterials are similar to other biomaterials, that is, biocompatibility, sterilizability, adequate mechanical and physical properties, and manufacturability.

Polymerization and Basic Structure:

POLYMERIZATION

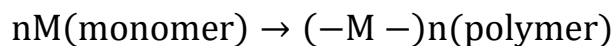
Polymerization is a process of reacting monomer molecules together in a chemical reaction to form 3D networks or polymer chains.



- ✓ The methods of polymeric synthesis are divided in two major groups.
 - Addition polymerization or Chain growth polymerization
 - Condensation polymerization or Step growth polymerization.

Addition (Chain growth) polymerization:

- ✓ Chain growth polymerization is a polymerization technique where unsaturated monomer molecules add on to a growing polymer chain one at a time.
- ✓ It can be represented with the chemical equation:



Where n is the degree of polymerization.

- ✓ The addition polymers are obtained by subjecting olefinic compounds to polymerization.
- ✓ Addition polymerization involves only rearrangements of bonds.
- ✓ The backbones of addition polymers consist only of carbon-carbon bonds.
- ✓ Chain growth polymerization involves the linking together of molecules incorporating double or triple chemical bonds.



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- ✓ These unsaturated monomers have extra internal bonds that are able to break and link up with other monomers to form the repeating chain.
- ✓ Chain growth polymerization is involved in the manufacture of polymers such as polyethylene, polypropylene, and polyvinyl chloride (PVC).
- ✓ A special case of chain growth polymerization leads to living polymerization.
- ✓ In the radical polymerization of ethylene, its pi bond is broken, and the two electrons rearrange to create a new propagating center like the one that attacked it.
- ✓ The form this propagating center takes depends on the specific type of addition mechanism.
- ✓ There are several mechanisms through which this can be initiated. The free radical mechanism was one of the first methods to be used.
- ✓ Free radicals are very reactive atoms or molecules that have unpaired electrons.
- ✓ Taking the polymerization of ethylene as an example, the free radical mechanism can be divided into three stages:
 - Chain initiation
 - Chain propagation
 - Chain termination
- ✓ Free temperature radical addition polymerization of ethylene must take place at high temperatures and pressures, approximately 300°C and 2000 atm.
- ✓ While most other radical polymerizations do not require such extreme temperatures and pressures, they do tend to lack control.
- ✓ One effect of this lack of control is a high degree of branching. Also, as termination occurs randomly, when two chains collide, it is impossible to control the length of individual chains.
- ✓ A newer method of polymerization similar to free radical, but allowing more control involves the Ziegler – Natta catalyst, especially with respect to polymer branching.
- ✓ Other forms of chain growth polymerization include cationic addition polymerization and anionic polymerization.
- ✓ While not used to a large extent in industry yet due to stringent reaction conditions such as lack of water and oxygen, these methods provide ways



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to polymerize some monomers that cannot be polymerized by free radical methods such as polypropylene.

- ✓ Cationic and anionic mechanisms are also more ideally suited for living polymerizations, although free radical living polymerizations have also been developed.
- ✓ Chain growth polymerization and addition polymerization (Poly addition) are two different concepts (not always identical).
- ✓ In fact polyurethane polymerizes with addition polymerization (because its polymerization don't produce any small molecules, called "condensate"), but its reaction mechanism concern to a step growth polymerization.

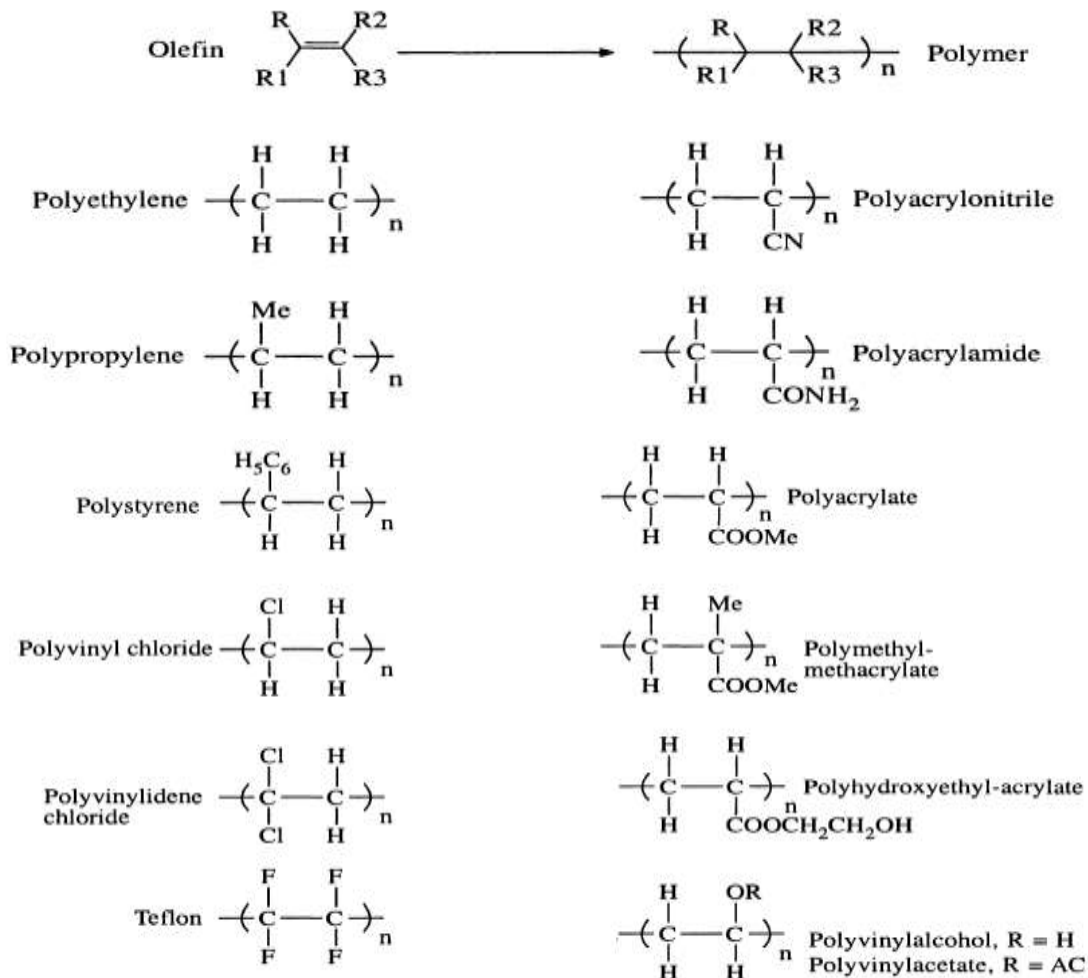


Fig. 5.1 Repeating units of addition polymers. (Homopolymers)

Condensation (Step growth) polymerization:

- ✓ Step growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomers.



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- ✓ Most step growth polymers are also classified as condensation polymers, but not all step growth polymers release condensates.
- ✓ Step growth polymers increase in molecular weight at a very slow rate at lower conversions and reach moderately high molecular weights only at very high conversion (i.e. >95%).
- ✓ To alleviate inconsistencies in these naming methods, adjusted definitions for condensation and addition polymers have been developed.
- ✓ A condensation polymer is defined as a polymer that involves elimination of small molecules during its synthesis, or contains functional groups as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded.
- ✓ A series of condensation steps take place whereby monomers or monomer chains add to each other to longer chains.
- ✓ This is termed condensation polymerization or step growth polymerization, and occurs for example in the synthesis of polyesters or nylons.
- ✓ It may be either a homopolymerization of a single monomer A-B with two different end groups which condense, or a copolymerization of two comonomers A-A and B-B.
- ✓ Condensation polymers form more slowly than addition polymers, often requiring heat.
- ✓ They are generally lower in molecular weight. Monomers are consumed early in the reaction; the terminal functional groups remain active throughout and short chains combine to form longer chains.
- ✓ A high conversion rate is required to achieve high molecular weights.
- ✓ The condensation polymers are typically formed from reactions of alcohols and acids to form polyesters, reactions of acids or esters with amines to form polyamides or reactions of alcohols or amines with isocyanates to form polyurethanes or polyurea respectively.
- ✓ Small molecules are generated during condensation.
- ✓ The backbones of condensation polymers contain carbon-hetero atom bonds in the main chain. Silicone polymers have silicon-oxygen bonds in the backbone.

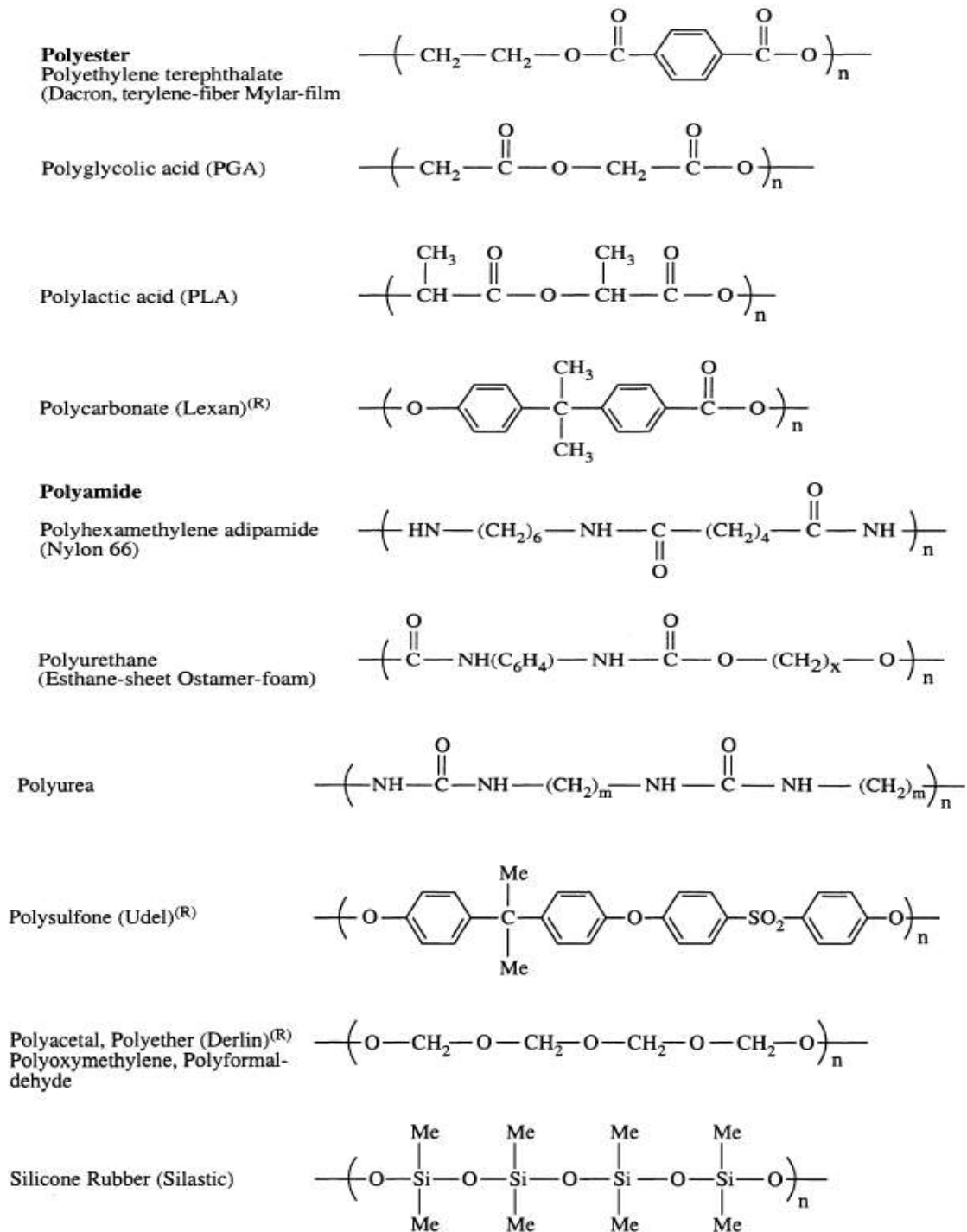


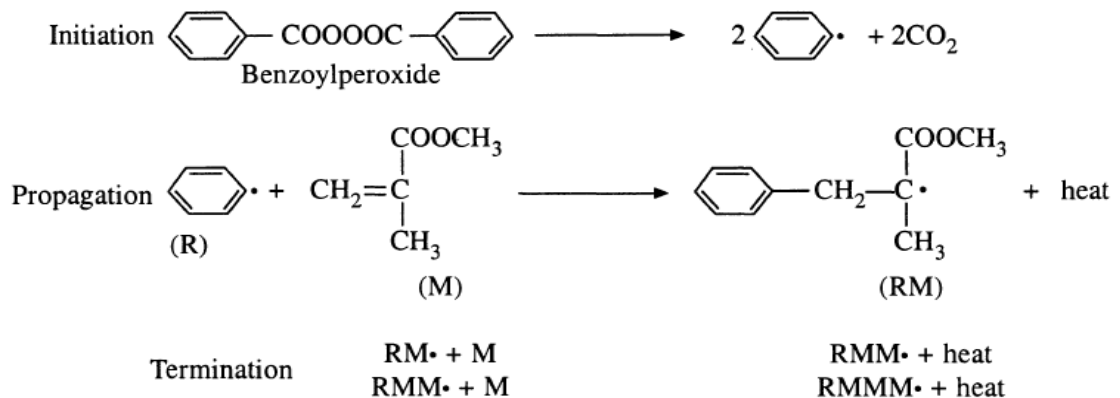
Fig. 5.2 Repeating units of some condensation polymers.

- ✓ Polymerization reactions involve initiation, propagation and termination steps. Heat, ultraviolet light or chemicals can activate the initiation. These chemicals may involve free radicals, cations, anions or metal ions for the



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purpose. For example a free radical (R') can react with olefin monomer to initiate polymerization, the resulting radical can react with another monomer, thus the chain continues to grow. These steps are called propagation, and the chains are finally terminated by a combination of radicals or transfer or disproportionation processes. Radical chain-growth polymerization reactions are considerably more important industrially than either cationic or anionic chain-growth reactions.



Combining two free radicals or additions of a terminator.

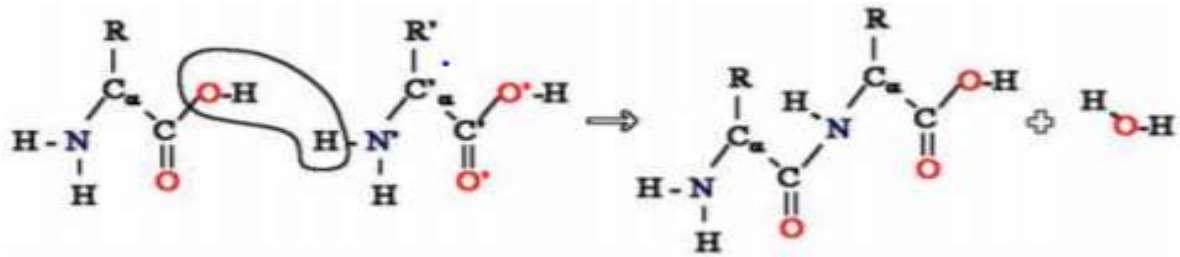
POLYAMIDE

A polyamide is a polymer containing monomers joined by peptide bonds. They can occur both naturally, examples being proteins, such as wool and silk, and can be made artificially, examples being Nylons, Aramids, and sodium poly(aspartate).

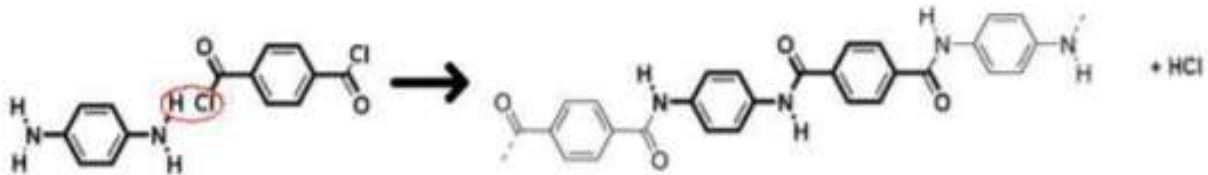
Production from monomers

The amide link is produced from the condensation reaction of an amino group and a carboxylic acid or acid chloride group. A small molecule, usually water, ammonia or hydrogen chloride, is eliminated. The amino group and the carboxylic acid group can be on the same monomer, or the polymer can be constituted of two different bifunctional monomers, one with two amino groups, the other with two carboxylic acid or acid chloride groups.

Amino Acids can be taken as examples of single monomer (if the difference between R groups is ignored) reacting with identical molecules to form a polyamide:



The reaction of two amino acids. Many of these reactions produce long chain proteins. Aramid (pictured below) is made from two different monomers which continuously alternate to form the polymer and is an aromatic polyamide:



The reaction of 1,4-phenyl-diamine (para-phenylenediamine) and terephthaloyl chloride to produce Aramid.

ACRYLIC POLYMER:

Acrylic is a generic term denoting derivatives of acrylic and methacrylic acid, including acrylic esters and compounds containing nitrile and amide groups. Polymers based on acrylics were discovered before many other polymers that are now widely employed. Optical clarity is an important quality in medical devices or diagnostic equipment that rely on visual inspection and therefore require a high level of transparency.

Acrylic, the common name for polymethyl methacrylate (PMMA), has long been used in the manufacture of cuvettes, tubing connectors, speculums, and many other medical devices requiring impact strength, chemical resistance, biocompatibility, and clarity. Acrylic polymers thus occupy a prominent place in the market for clear, disposable plastics--only glass transmits light as well. Acrylic also is commonly used in the manufacture of reading glasses, due to its superior optical qualities. The properties of acrylic materials and compares them with other thermoplastics competing for a share of the medical market.

Benefits to both the manufacturer and the end-user are highlighted, as are applications for which acrylic is well suited and those for which it is not recommended. In addition, the paper discusses acrylic's chemical resistance and performance after sterilization, along with disposal, recycling, and other environmental issues. Design and processing guidelines for manufacturers are also included as is a case study of a specific application.

Overview of Acrylic



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Acrylic polymer, derived from the monomer methyl methacrylate (MMA), was first developed more than 60 years ago. General-purpose acrylic grades contain a co-monomer, added during the polymerization process, to facilitate flow during injection molding and extrusion. Specialty grades are formulated to perform in applications requiring high impact strength and heat resistance.

UV-light-transmitting formulations are also available, and are specified for certain critical diagnostic equipment in which even slight UV absorption or variation in material flow could be detrimental.

Easily processed and assembled, acrylic has been used in medical and health-care applications since its introduction. One of the first uses of acrylic sheet was for incubators. The first intraocular acrylic prosthesis was implanted in 1955, and ever since acrylic has been used in contact with human tissue. Its biocompatibility led to the adoption of acrylic for aircraft canopies during World War II: pilots suffered fewer infections from shards of acrylic than they had from glass.

The leading applications of acrylic in the medical industry today are for cuvettes and tubing connectors, but it is also used to produce test kits, syringes, luers, blood filters, and drainage wands as well as flowmeters, blood-pump housings, fluid silos, surgical-blade dispensers, incubators, and surgical trays. Acrylic polymers are resistant to many biological and chemical agents.

The use of acrylic polymers in the medical industry has been steadily increasing over the past several years. This is especially noticeable in the area of diagnostics, due to the fact that acrylic is an inert material that does not react with the reagents used in testing. For medical devices, special impact-modified grades formulated to resist breaking and cracking are employed more often than standard grades.

Physical Properties

Acrylic offers light transmittance of 92%--theoretically the maximum obtainable--with particular clarity at lower wavelengths of 270 to 350 nm.

For example, acrylic is the material of choice for disposable cuvettes, used to contain blood and other fluids, through which a spectrum of UV light is passed for analysis. Although quartz glass can be used for the most demanding applications, since it transmits light as low as 220 nm, it is not cost-effective in an application that increasingly favors disposable plastics.

Other prominent physical properties of acrylic include good mechanical strength and dimensional stability; along with high tensile and flexural strength. Medical-grade acrylic can be supplied for intricate, thin-wall applications in which maximum optical clarity is required: it offers excellent injection molding flow properties (13 g/10 min) and a tensile strength of 10,600 psi.

Acrylic also provides good surface hardness for scratch resistance, an important quality in medical applications. Because acrylic is a rigid material, standard grades do not provide high



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impact resistance. Therefore, impact-modified grades--softer and less rigid than standard formulations--are specified for applications that typically require increased toughness.

Acrylic is not recommended for applications that demand very high impact resistance or those that put surfaces under high pressure. Acrylic does perform well in electrical applications, due to its insulating nature; an increase in absorbed moisture makes it more conductive. As temperatures increase, acrylic becomes more flexible and exhibits less flexural strength. Under sustained loading, strain on the material can induce excessive molecular movement that increases with time under load and higher temperatures and results in the phenomenon known as creep that is common to all thermoplastics.

Chemical Resistance

Acrylic is resistant to a wide range of chemicals including salts, bases, aliphatic hydrocarbons, fats and oils, most common gases and inorganic chemicals, dilute mineral and organic acids, and dilute and concentrated solutions of most alkalis. It is attacked by strong acids, chlorinated and aromatic hydrocarbons, ketones, alcohols, ethers, and esters.

Sterilization Effects

Acceptable sterilization technologies for acrylic are E-beam or gamma irradiation or dry ethylene oxide gas. While gamma sterilization has a tendency to discolor (yellow) most acrylics, this yellowing is temporary and recovery can be complete, with the parts retaining their original integrity. The higher the radiation dosage, the greater the yellowing and the longer the required recovery time.

Material Selection

The failure of plastic parts can often be traced to mistakes in design, production methods, or material choice. Selecting the material for a particular application involves careful consideration of the end-use environmental conditions and functional requirements of the part. Basing the selection on incorrect criteria can lead to overdesigning the part or specifying a material with properties that exceed the demands of the application, often at the expense of scratch or chemical resistance, clarity, or other desirable qualities.

Environmental conditions that figure into the selection include chemicals likely to be encountered, sterilization methods, humidity, temperature, and thermal cycling. Other important factors are mold and part design, processing requirements, and assembly methods.

In selecting the best grade of acrylic to use, these same factors must be considered. Higher-molecular-weight grades are more resistant to crazing from chemical exposure and mechanical stress, but have lower melt-flow rates. As the level of impact modifier is increased in impact-grade acrylic, other properties such as clarity, light transmission, and tensile strength often diminish.

Processing requirements can be difficult to predict. Flow patterns and mold-filling problems can result from large part surfaces, deep ribs or flanges, asymmetrical geometries, and unbalanced thick and thin sections.



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Experimenting with several different grades in the prototype tool is recommended. Molds designed for acrylic, ABS, and polycarbonate parts typically accommodate a shrinkage level of 0.006 in./in., allowing for convenient trial runs of acrylic in molds used for ABS or polycarbonate parts. Direct comparison of the parts molded from different materials can help determine the best one for the application.

Processing Considerations

Compared with other polymers, acrylic is relatively easy to process. It can be molded with little or no residual stress and is available in formulations specifically designed for injection molding or extrusion in a wide range of melt-flow rates.

Under normal processing conditions, acrylic produces melts that are typically higher in viscosity than those of many other thermoplastic polymers. The higher-molecular-weight grades are generally recommended for extrusion.

Because of acrylic's higher- viscosity flow properties, injection molding runners and sprues used to process it need to have larger diameters than those handling polystyrene or polyethylene. Large injection-molded parts or parts with thin-wall geometries may require a high meltflow rate.

When acrylic is processed in molds built for polycarbonate or polyester, lower injection pressures should be used, as it is less likely to warp than polyesters and is more forgiving in molds not designed with well-balanced gates. 6 Because acrylic has a higher melt viscosity than polystyrene or styrenic alloys, it requires higher injection pressures when selected in place of those materials. Higher clamping forces may also be required.

A hygroscopic material, acrylic absorbs water and must be dried prior to molding: if molded while wet, it exhibits moisture splay, leaving streaks, bubbles, and a rough surface on the part. Typical wall thicknesses for acrylic parts range from 0.040 to 0.500 in. Thicker or thinner parts can be achieved with special designs or processing methods such as injection/ compression molding. Consistency is the key; any changes in thickness should be gradual, and feature radiused edges.

Vertical walls should be the same thickness as the rest of the part to avoid pressure variations on the flow front, which can lead to stressed areas and voids caused by trapped air. Moderate residual stress does not affect part performance, but high levels of stress can reduce impact strength and resistance to chemical or heat crazing, and can undermine the dimensional stability of the molded part. Before the part and mold design are completed, a mold-flow analysis should be performed to help avoid costly mistakes and downtime.

Bonding Systems



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Acrylic parts can be fastened by chemical bonding, ultrasonic welding, and heat staking. Two types of agents are commonly used to chemically bond acrylic: solvents and polymerizable adhesives.

Solvents such as dichloromethane dissolve the surfaces of two acrylic parts, which harden after the solvent evaporates and bond to one another. Solutions of acrylic polymer dissolved in a solvent or methyl-methacrylate monomer work similarly.

Two-part polymerizable adhesives contain a viscous acrylic resin base and a liquid catalyst that when mixed together provide a strong joint. Ultrasonic welding is an efficient method of fusing two parts made from the same material. Both contact (near-field) welding and transmission (far-field) welding can be used for joining acrylic parts.

However, materials with different melting points are not good candidates for ultrasonic welding, since even a few degrees difference can result in one material melting before the other reaches its melting point, preventing a fusion between the parts.

Mechanical fastening, which concentrates loads at fastening points, is not recommended for acrylic parts, as the act of drilling holes or torquing fasteners can introduce potentially damaging stress. Holes should be cored out rather than drilled.

Acrylic Case History

Selecting the wrong grade of acrylic can lead to unsatisfactory results. Recently, a manufacturer of a blood-clot analyzer experienced early production problems with several complex parts molded from a general-purpose grade of acrylic.

With the formulation initially chosen, parts developed stress cracks upon ejection from the tools, primarily because of complicated geometries that included sharp corners, edges, and points. Streaking also occurred. It was determined that additional toughness and impact strength were required, in a high-flow grade that would fill the molds. An impact-modified, gamma-resistant acrylic--which is supplied in injection-grade pellets--was then selected and found to solve some tricky molding problems.

High tensile strength and impact resistance were critical; since the parts are used in the assembly of a cassette intended to contain blood, they must be resilient enough to resist cracking if accidentally dropped. Dimensional precision was also important, given the complexity of the processes that occur under pressure inside the cassette during blood analysis.

A third requirement was UV transmissability, which was necessary for curing the adhesive used in the cassette assembly. Molded from the impact-modified grade, the cassette parts have proven to be sufficiently durable, both during fabrication and in use. The acrylic material provides the requisite impact strength as well as a high degree of optical clarity and scratch resistance, and presents a pleasing, glossy surface finish. After use in the blood-clot analyzer, the disposable cassettes are incinerated with other medical waste. Disposal and Recycling Acrylic burns extremely clean, providing virtually smokeless combustion with end products of carbon dioxide and water.



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In addition, the material offers superior recyclability: acrylic can be reground and reused, which results in less material waste during molding. Another characteristic of acrylic is its ability to be depolymerized back to its monomer, thoroughly purged of impurities, and repolymerized back into PMMA. Commercial processing facilities set up for this process typically use a molten lead bath to vaporize the acrylic material. The vapors are captured and recondensed into MMA, while eliminating any biomedical waste. This is a true recycling process, taking the polymer back to its monomer, whereas most other "recycling" processes involve crushing the material and using it in applications with lower specifications.

For environmental reasons, commercial molten lead baths are no longer operated in the United States, but do exist in England, India, and several other countries. Used in medical applications for many years, acrylic offers a number of advantages compared with other clear thermoplastic materials traditionally specified for diagnostic equipment and medical devices. Benefits include unsurpassed clarity, superior toughness, rapid gamma recovery, excellent UV-light transmittance, biocompatibility, and good chemical and scratch resistance. Acrylic is easily processed and assembled and offers the potential to be recycled back to its monomer and used again, an important property as the pressure to recycle increases.

Acrylic resin can be custom formulated to meet the requirements of a broad range of medical applications. Since it can be processed in molds designed for polycarbonate and other thermoplastics, manufacturers using those materials should consider trial runs with acrylic. Direct comparisons between parts molded with acrylic and with competing thermoplastics may reveal potential cost savings as well as unexpected side benefits such as improved surface finish, transparency, processing, and part performance.