CHAPTER 34
POLYMERIC OPTICS

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34.1 GLOSSARY

- $A_{\text{H2O}}$: water absorption
- $K$: thermal conductivity
- $T_s$: maximum service temperature
- $\alpha$: thermal expansion coefficient
- $\rho$: density

34.2 INTRODUCTION

A small number of carbon-based polymeric materials possess some of those qualities which have made glass an attractive optical material. Most of these polymeric materials do exhibit certain physical deficiencies compared to glass. But, despite the fact that “plastic optics” has acquired an image as a low-end technology, it may nonetheless be a better choice, or even the best choice, in certain applications.

Selection Factors

Virtually all of the polymers having useful optical properties are much less dense than any of the optical glasses, making them worthy of consideration in applications where weight-saving is of paramount importance. Many of them exhibit impact resistance properties which exceed those of any silicate glass, rendering them well-suited to military applications (wherein high “g” loads may be encountered), or ideal for some consumer products in which safety may be a critical consideration.

Though the physical properties of the polymers may make them better matched to certain design requirements than glass, by far the most important advantage of polymeric optics is the considerable creative freedom they make available to the optical and mechanical design effort. While the design constraints and guidelines governing glass optics design and fabrication are fairly well defined, the various replication processes which may be put to use in polymer optics fabrication make available unique opportunities for the creation of novel optical components and systems which would be unthinkable or unworkable in glass. Oftentimes, the differences in the engineering approach, or in the production processes themselves, may make possible very significant cost reductions in high-volume situations.
34.3 FORMS

Thermoset Resins

Optical polymers fall into basically two categories—the thermoset resins and the thermoplastic resins. The thermoset resin group consists of chemistries in which the polymerization reaction takes place during the creation of the part, which may be produced by casting, or by transfer replication. The part which has been created at completion of the reaction may then be postprocessed, if desired, by machining. In general, the thermoset resins cannot be melted and reformed.

The most commonly encountered thermoset optical resin is that used to produce ophthalmic lenses for eyewear. The monomer, which is stored in liquid form at reduced temperature, is introduced into a mold, where the polymerization reaction takes place, forming a part which assumes the shape of the cavity containing it. Alternatively, epoxy-based chemistries have been used with some success to form replicated reflecting surface shapes by a transfer process, and to produce aspheric figuring (at relatively modest expense) upon spherical refractive or reflective substrates.

Thermoplastic Resins

With the possible exception of eyewear, most polymeric optics are executed in thermoplastic materials which are supplied in already-polymerized form. These materials are normally purchased in bulk as small pellets. These pellets are heated to a temperature beyond the softening point, so that they flow to become a single viscous mass. This mass is then formed to assume the shape desired in the final part.

Parts may be created by the injection molding process, in which the heated polymer is squirted into a mold at high pressure and allowed to cool in the shape of the desired component. Or the pellets may be directly heated between the two halves of a compression mold, and the mold closed to effect formation of the part. Hybrid molding technologies combining these two processes are recently experiencing increasing popularity in optical molding applications, and have produced optical surface figures of very high quality.

The capability of modern molding technology to produce optics having very good surface-figure quality has made possible the creation of polymeric optical components for a wide variety of applications. Among these are medical disposables, intraocular lenses, a host of consumer products, military optics, and a number of articles in which optical, mechanical, and electrical functions are combined in a single part.

34.4 PHYSICAL PROPERTIES

Density

Optical glass types number in the hundreds (if all manufacturers worldwide are counted). The glass types available from the catalogs cover a wide range of optical, physical, thermal, and chemical properties. The density of these materials varies from about 2.3 g/cm$^3$ to about 6.3 g/cm$^3$. The heaviest optically viable polymer possesses a density of only about 1.4 g/cm$^3$, whereas the lightest of these materials will readily float in water, having a density of 0.83 g/cm$^3$. All other things being equal, the total element count in an optical system may often be reduced (at modest cost penalty) by the inclusion of nonspherical surfaces. All things considered, then, polymeric optical systems may be made much less massive than their glass counterparts, especially if aspheric technology is applied to the polymer optical trains.
Hardness

Although cosmetic blemishes rarely impact final image quality (except in the cases of field lenses or reticles), optical surfaces are customarily expected to be relatively free of scratches, pits, and the like. Ordinary usage, especially cleaning procedures, are likely to result in some scratching with the passage of time. Most common optical glasses possess sufficient hardness that they are relatively immune to damage, if some modest amount of care is exercised.

The polymeric optical materials, on the other hand, are often so soft that a determined thumbnail will permanently indent them. The hardness of polymeric optics is difficult to quantify (in comparison to glass), since this parameter is not only material-dependent, but also dependent upon the processing. Suffice it to say that handling procedures which would result in little or no damage to a glass element may produce considerable evidence of abrasion in a polymeric surface, particularly in a thermoplastic. In fact, the compressibility of most thermoplastic polymers is such that the support for hard surface coatings is sufficiently low that protection provides immunity against only superficial abrasion. These deficiencies are of no particular consequence, however, if the questionable surfaces are internal, and thereby inaccessible.

Rigidity

A property closely related to hardness is the elastic modulus, or Young’s modulus. This quantity, and the elongation factor at yield, are determinants of the impact resistance, a performance parameter in which the polymers outshine the glasses. These properties are, again, dependent upon the specified polymeric alloy, any additives which may be present, and processing history of the polymer, and cannot be dependably quoted. The reader is referred to any of several comprehensive references listed herein for mechanical properties data. Those properties which create good impact resistance become liabilities if an optical part is subjected to some torsion or compressive stress. Since optical surface profiles must often be maintained to subwavelength accuracy, improper choice of the thickness/diameter ratio, or excessive compression by retaining rings, may produce unacceptable optical figure deformations.

Polymer chemistry is a complex subject probably best avoided in a discussion of polymer optics. Carbon-based polymers have been synthesized to include an extensive variety of chemical subgroups, however. Unfortunately, relatively few of these materials are actually in regular production, and only a handful of those possess useful optical properties for imaging purposes.

Service Temperature

Any decision involving a glass/plastic tradeoff should include some consideration of the anticipated thermal environment. While the optical glasses may exhibit upper service temperature limits of from 400 to 700°C, many of the glass types having the most interesting optical properties are quite fragile, and prone to failure if cooled too quickly. These failures are mostly attributable to cooling-induced shrinkage of the skin layer, which shatters because the insulating properties of the material prevent cooling (and shrinkage) of the bulk material at the same rate.

The polymeric materials, on the other hand, have much lower service temperature limits, in some cases no higher than about 60°C. The limit may approach 250°C for some of the fluoropolymers. The thermal conductivity of many of these polymers may be as much as an order of magnitude lower than for the glasses and the thermal expansion coefficients.
TABLE 1  Physical Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$</th>
<th>$\alpha$</th>
<th>$T_c$</th>
<th>$K$</th>
<th>$\Delta H_{\text{f.o}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-methylmethacrylate</td>
<td>1.18</td>
<td>6.0</td>
<td>85</td>
<td>4–6</td>
<td>0.3</td>
</tr>
<tr>
<td>P-styrene</td>
<td>1.05</td>
<td>6.4–6.7</td>
<td>80</td>
<td>2.4–3.3</td>
<td>0.03</td>
</tr>
<tr>
<td>NAS</td>
<td>1.13</td>
<td>5.6</td>
<td>85</td>
<td>4.5</td>
<td>0.15</td>
</tr>
<tr>
<td>Styrene acrylonitrile (SAN)</td>
<td>1.07</td>
<td>6.4</td>
<td>75</td>
<td>2.8</td>
<td>0.28</td>
</tr>
<tr>
<td>P-carbonate</td>
<td>1.25</td>
<td>6.7</td>
<td>120</td>
<td>4.7</td>
<td>0.2–0.3</td>
</tr>
<tr>
<td>P-methyl pentene</td>
<td>0.835</td>
<td>11.7</td>
<td>115</td>
<td>4.0</td>
<td>0.01</td>
</tr>
<tr>
<td>P-amide (Nylon)</td>
<td>1.185</td>
<td>8.2</td>
<td>80</td>
<td>5.1–5.8</td>
<td>1.5–3.0</td>
</tr>
<tr>
<td>P-arylate</td>
<td>1.21</td>
<td>6.3</td>
<td>7.1</td>
<td>2.5</td>
<td>0.26</td>
</tr>
<tr>
<td>P-sulfone</td>
<td>1.24</td>
<td>2.5</td>
<td>160</td>
<td>2.8</td>
<td>0.1–0.6</td>
</tr>
<tr>
<td>P-styrene co-butadiene</td>
<td>1.01</td>
<td>7.8–12</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>P-cyclohexyl methacrylate</td>
<td>1.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-allyl diglycol carbonate</td>
<td>1.32</td>
<td></td>
<td>100</td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>1.20</td>
<td></td>
<td></td>
<td>4.0–8.0</td>
<td></td>
</tr>
<tr>
<td>P-ethersulfone</td>
<td>1.37</td>
<td>5.5</td>
<td>200</td>
<td>3.2–4.4</td>
<td></td>
</tr>
<tr>
<td>P-chloro-trifluoroethyline</td>
<td>2.2</td>
<td>4.7</td>
<td>200</td>
<td>6.2</td>
<td>0.003</td>
</tr>
<tr>
<td>P-vinylidene fluoride</td>
<td>1.78</td>
<td>7.4–13</td>
<td>150</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>P-etherimide</td>
<td>1.27</td>
<td>5.6</td>
<td>170</td>
<td></td>
<td>0.25</td>
</tr>
</tbody>
</table>

characterizing the polymers are often an order of magnitude larger than those associated with optical glasses. Consequently, subjecting any polymeric optical element to a significant thermal transient is likely to create more severe thermal gradients in the material, and result in significant thermally-induced optical figure errors. Again, it is suggested that the interested reader consult the plastic handbooks and manufacturer’s literature for a complete listing of this behavior, as additives and variation in molecular weight distribution may significantly affect all of these properties. Some of the most important physical properties of the more readily available optical polymers are tabulated in Table 1.

Conductivity (Thermal, Electrical)

Most materials which exhibit poor thermal conductivity are also poor electrical conductors. Since many unfilled polymers are very effective electrical insulators, they acquire static surface charge fairly easily, and dissipate it very slowly. Not surprisingly, these areas of surface charge quickly attract oppositely charged contaminants, most of which are harder than the plastic. Attempts to clear the accumulated particles from the surfaces by cleaning can, and usually do, result in superficial damage. Application of inorganic coatings to these surfaces may do double duty by providing a more conductive surface (less likely to attract contaminants), while improving the abrasion resistance.

Outgassing

In contrast to glass optical parts, which normally have very low vapor pressure when properly cleaned, most polymers contain lubricants, colorants, stabilizers, and so on, which may outgas throughout the life of the part. This behavior disqualifies most plastic optical elements from serving in space-borne instrumentation, since the gaseous products, once lost, surround the spacecraft, depositing upon solar panels and other critical surfaces. Some, but few, thermoset resins may be clean enough for space applications if their reaction stoichiometry is very carefully controlled in the creation of the part.
Water Absorption

Most polymers, particularly the thermoplastics, are hygroscopic. They absorb and retain water, which must, in most cases, be driven off by heating prior to processing. Following processing, the water will be reabsorbed if the surfaces are not treated to inhibit absorption. Whereas only a very small amount of water will normally attach to the surfaces of a glass optical element, the polymer materials used for optics may absorb from about 0.003 to about 2 percent water by weight. Needless to say, the trapped water may produce dimensional changes, as well as some minor alterations of the spectral transmission. Physical properties of some of the more familiar optical polymers are listed in Table 1.

Additives

Polymers are normally available in a variety of “melt flow” grades—each of which possesses viscosity properties best suited to use in parts having specific form factors. A number of additives are commonly present in these materials. Such additives may, or may not, be appropriate in an optical application. Additives for such things as flame retardancy, lubricants, lubrication, and mold release are best avoided if not included to address a specific requirement. Frequently, colorants are added for the purpose of neutralizing the naturally occurring coloration of the material. These additives create an artificial, but “clear,” appearance. The colorants must, of course, absorb energy to accomplish this, resulting in a net reduction in total spectral transmission.

Radiation Resistance

Most of the optical polymers will be seen to exhibit some amount of fluorescence if irradiated by sufficiently intense high-energy radiation. High-energy radiation of the ultraviolet and ionizing varieties will, in addition, produce varying amounts of polymer chain crosslinking, depending upon the specific polymer chemistry. Crosslinking typically results in discoloration of the material, and some amount of nonuniform energy absorption. Inhibitors may be added to the polymeric material to retard crosslinking, although, oddly enough, the polymers most susceptible to UV-induced discoloration are generally the least likely to be affected by ionizing radiation, and vice versa.

Documentation

Although polymeric materials suffer some shortcomings in comparison to glass (for optical applications), distinct advantages do exist. The major obstacle to the use of polymers, however, is the spotty and imprecise documentation of many of those properties required for good engineering and design. In general, the resin producers supply these materials in large quantity to markets wherein a knowledge of the optical properties is of little or no importance. With luck, the documentation of optical properties may consist of a statement that the material is “clear.” In the rare case where refractive index is documented, the accuracy may be only two decimal places. In these circumstances, the optical designer or molder is left to investigate these properties independently—a complex task, since the processing itself may affect those properties to a substantial degree.

Unfortunately, optical applications may represent only a small fraction of a percent of...
the total market for a given resin formulation, and since these materials are sold at prices ranging from less than two dollars to a few dollars per pound, the market opportunity represented by optical applications seems minuscule to most polymer vendors.

### 34.5 OPTICAL PROPERTIES

#### Variations

It is only a fortuitous accident that some of the polymers exhibit useful optical behavior, since most all of these materials were originally developed for other end uses. The possible exceptions are the materials used for eyeglass applications (poly-diallylglycol), and the materials for optical information storage (specially formulated polycarbonate). Citation of optical properties for any polymeric material must be done with some caution and qualification, as different melt flow grades (having different molecular weight distribution) may exhibit slightly different refractive index properties. Additives to regulate lubricity, color, and so on can also produce subtle alterations in the spectral transmission properties.

#### Spectral Transmission

In general, the carbon-based optical polymers are visible-wavelength materials, absorbing fairly strongly in the ultraviolet and throughout the infrared. This is not readily apparent from the absorption spectra published in numerous references, though. Such data are normally generated by spectroscopists for the purpose of identifying chemical structure, and are representative of very thin samples. One can easily develop the impression from this information that the polymers transmit well over a wide spectral range. Parenthetically, most of these polymers, while they have been characterized in the laboratory, are not commercially available. What is needed for optical design purposes is transmission data (for available polymers) taken from samples having sufficient thickness to be useful for imaging purposes.

Some specially formulated variants of poly-methylmethacrylate have useful transmission down to 300 nm. Most optical polymers, however, begin to absorb in the blue portion of the visible spectrum, and have additional absorption regions at about 900 nm, 1150 nm, 1350 nm, finally becoming totally opaque at about 2100 nm. The chemical structure which results in these absorption regions is common to almost all carbon-based polymers, thus the internal transmittance characteristics of these materials are remarkably similar, with the possible exception of the blue and near-UV regions. A scant few polymers do exhibit some spotty narrowband transmission leakage in the far-infrared portion of the spectrum, but in thicknesses suitable only for use in filter applications.

#### Refractive Index

The chemistry of carbon-based polymers is markedly different from that of silicate glasses and inorganic crystals in common use as optical materials. Consequently, the refractive properties differ significantly. In general, the refractive indices are lower, extending to about 1.73 on the high end, and down to a lower limit of about 1.3. In practice, those materials which are readily available for purchase exhibit a more limited index range—from about 1.42 to 1.65. The Abbe values for these materials vary considerably, though, from about 100 to something less than 20. Refractive index data for a few of these polymers, compiled from a number of sources, is displayed in Table 2. In the chart,
TABLE 2  Refractive Index of Some Optical Polymers

<table>
<thead>
<tr>
<th>Line ID</th>
<th>Wavl., nm</th>
<th>PMMA</th>
<th>P-styr</th>
<th>P-carb</th>
<th>SAN</th>
<th>PEI</th>
<th>PCHMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>1014.0</td>
<td>1.4831</td>
<td>1.5726</td>
<td>1.5672</td>
<td>1.5519</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>796.5</td>
<td>1.4878</td>
<td>1.5820</td>
<td>1.5768</td>
<td>1.5601</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>656.3</td>
<td>1.4892</td>
<td>1.5849</td>
<td>1.5799</td>
<td>1.5627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C'</td>
<td>643.9</td>
<td>1.4896</td>
<td>1.5858</td>
<td>1.5807</td>
<td>1.5634</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>589.3</td>
<td>1.4917</td>
<td>1.5903</td>
<td>1.5853</td>
<td>1.5673</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>587.6</td>
<td>1.4918</td>
<td>1.5905</td>
<td>1.5855</td>
<td>1.5674</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>546.1</td>
<td>1.4938</td>
<td>1.5950</td>
<td>1.5901</td>
<td>1.5713</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>486.1</td>
<td>1.4978</td>
<td>1.6041</td>
<td>1.5994</td>
<td>1.5790</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F'</td>
<td>478.0</td>
<td>1.4983</td>
<td>1.6052</td>
<td>1.6007</td>
<td>1.5800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>435.8</td>
<td>1.5026</td>
<td>1.6154</td>
<td>1.6115</td>
<td>1.5886</td>
<td></td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>404.7</td>
<td>1.5066</td>
<td>1.6253</td>
<td>1.6224</td>
<td>1.5971</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>365.0</td>
<td>1.5136</td>
<td>1.6431</td>
<td>1.6432</td>
<td>1.6125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abbe number</td>
<td>57.4</td>
<td>30.9</td>
<td>29.9</td>
<td>34.8</td>
<td>18.3</td>
<td>56.1</td>
<td></td>
</tr>
<tr>
<td>$dn/dT \times 10^{-5}/^\circ C$</td>
<td>$-1.05$</td>
<td>$-1.4$</td>
<td>$-1.07$</td>
<td>$-1.1$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the familiar glass map \((n \text{ vs. } v)\), shows the locations of some of the more familiar polymers. Note that these materials all occupy the lower and right-hand regions of the map. In the Schott classification system, the polymers populate mostly the FK, TiK, and TiF regions of the map.\(^{16}\)

**Homogeneity**

It must be kept constantly in mind that polymeric optics are molded and not mechanically shaped. The exact optical properties of a piece cannot, therefore, be quantified prior to manufacture of the element. In fact, the precise optical properties of the bulk material in an optical element are virtually certain to be a function of both the material itself, and of the process which produced the part. Some materials, notably styrene and butyrate resins, are crystalline to some degree, and therefore inherently birefringent. Birefringence may develop in amorphous materials, though, if the injection mold and process parameters are not optimized to prevent this occurrence. Likewise, the bulk scatter properties of a molded optical element are a function of the inherent properties of the material, but are also strongly related to the cleanliness of the processing and the heat history of the finished part.

**34.6 OPTICAL DESIGN**

**Design Strategy**

Virtually all optical design techniques which have evolved for use with glass materials work well with polymer optics. Ray-tracing formulary, optimization approaches, and fundamental optical construction principals are equally suitable for glass or plastic. The generalized approach to optical design with polymeric materials should be strongly medium-oriented, though. That is, every effort must be made to capitalize upon the design flexibility which the materials and manufacturing processes afford. Integration of form and function should be relentlessly pursued, since mechanical features may be molded integral with the optics to reduce the metal part count and assembly labor content in many systems.

**Aberration Control**

The basic optical design task normally entails the simultaneous satisfaction of several first-order constraints, the correction of the monochromatic aberrations, and the control of the chromatic variation of both first-order quantities and higher-order aberrations. It is well known that management of the Petzval sum, while maintaining control of the chromatic defects, may be the most difficult aspect of this effort.\(^{17,18}\) It is also widely recognized that the choice of optical materials is key to success. While the available polymer choices cover a wide range of Abbe values, insuring that achromatization may
be accomplished in an all-polymer system, the refractive index values for these materials are not well-positioned on the “glass” map to permit low Petzval sums to be easily achieved.

Material Selection

Simultaneous correction of the Petzval sum and the first-order chromatic aberration may, however, be nicely accomplished if the materials employed possess similar ratios of Abbe number to central refractive index. This implies that the best material combinations (involving polymers) should probably include an optical glass. Also implied is the fact that these hybrid material combinations may be inherently superior (in this respect) to all-glass combinations. Ideally, the chosen materials should be well-separated (in Abbe value) on the glass map, so that the component powers required for achromatization do not become unduly high. This condition is satisfied most completely with polymers which lie in the TiF sector of the glass map, coupled with glasses of the LaK, LaF, and LaSF families.

Most lens designers would prefer to utilize high-refractive-index materials almost exclusively in their work. Optical power must be generated in order to form images, and because the combination of optical surface curvature and refractive index creates this refractive power, these two variables may be traded in the lens design process. Since it is well known that curvature generates aberration more readily than does a refractive index discontinuity, one generally prefers to achieve a specified amount of refractive power through the use of low curvature and high refractive index. From this perspective, the polymers are at a distinct disadvantage, most of them being low-index materials.

Aspheric Surfaces

An offsetting consideration in the use of polymeric optical materials is the freedom to employ nonspherical surfaces. While these may be awkward (and very expensive) to produce in glass, the replication processes which create plastic optical parts do not differentiate between spherical and nonspherical surfaces.

As any lens designer can attest, the flexibility that aspheric surfaces make available is quite remarkable. Spherical surfaces, while convenient to manufacture by grinding and polishing, may generate substantial amounts of high-order aberration if used in any optical geometry which departs significantly from the aplanatic condition. These high-order aberrations are often somewhat insensitive to substantial changes in the optical prescription. Thus, profound configurational alterations may be necessary to effect a reduction in these image defects.

On the other hand, the ability to utilize surface shapes which are more complex than simple spheres permits these high-order aberration components to be moderated at their point of origin, which may in turn reduce the amount of “transferred aberration” imparted to surfaces downstream in the optical train. In a multielement optical system, especially one employing cascaded aspheric surfaces, the required imagery performance may be achieved using fewer total elements. And due to the fact that the surface aberration contributions are diminished, the sensitivity to positioning errors may also be reduced, with the result that an aspheric optical system may actually be more forgiving to manufacture than its spherical counterpart.

In practice, the use of aspheric surfaces in polymer optical elements appears to more than compensate for the handicap imposed by low refractive index values. Using aspheric surfaces, it is possible to bend, if not break, many of the rules which limit design with
spherical surfaces. Aspherics create extra leverage to deal with the monochromatic aberrations, and with the chromatic variation of these image defects. A designer experienced with aspherics, given a capable set of software tools, can frequently create optical constructions which deliver high performance, despite the fact that they appear odd to those accustomed to the more “classical” spherical surface configurations. Quite often, unfavorable design constraints such as an inconvenient aperture stop location, may be handled with less difficulty using aspherics.

Athermalization

The thermal behavior of the polymers, mentioned previously, may cast a shadow upon some applications where the temperature is expected to vary over a significant range, but the focal surface location must be fixed in space. In such cases, the variation of refractive index usually accounts for the largest share of the variation, with the dimensional changes playing a secondary role. In such situations, the thermally induced excursions of the focal surface may be compensated by modeling these functions and designing mechanical spacers of the proper material to stabilize the detector/image location.

Alternatively, the optical system may be designed to exhibit inherently athermal behavior over the operational temperature range. Unfortunately, this is not strictly possible using only polymeric materials, as the thermo-optic coefficients display so little variation among themselves that the component powers would be absurdly high.

In combination with one or more glass elements, however, very nicely athermalized design solutions may be obtained with polymer elements. Athermal designs may be generated by modeling the optical system in multiconfiguration mode in the lens design software, much as one would develop a zoom lens. The parameters to be “zoomed” in this case are the refractive indices at two or more temperatures within the operating range. The resulting designs frequently concentrate most of the refractive power in the glass elements, with the polymer elements functioning to achieve achromatism and control of the monochromatic aberrations. See also Vol. I, Chap. 39 of this Handbook.

Processing Considerations

In much the same manner that optical design with polymer materials is different from optical design with glass, the treatment of the fabrication and assembly issues are also quite different matters. The major issues requiring examination are those related to the materials themselves. While it is possible to characterize the glass for an optical system with complete certainty prior to performing any fabrication operations, with polymers, one’s knowledge of the starting materials is only a rough indication of the properties of the finished optical parts.

When optical properties data are offered by the polymer supplier, it should be realized that these numbers apply only to measurement samples which have been predried to specification, have experienced a specified residence time in the extrusion barrel under specific temperature conditions, have been injected into the mold cavity at specific rates and pressures, and so on. Consequently, it is unlikely that the refractive properties of a polymer element will conform closely to catalog values (if such values are indeed supplied). Moreover, homogeneity, bubble content, scatter properties, and so on, are all process-dependent. So while the melt sheets may fix the optical properties of glass materials very precisely, the uncertainty associated with the polymers demands that
refractive variations be allocated a significant portion of the fabrication and assembly error budget.

**Manufacturing Error Budget**

Other constructional parameters, conversely, may be implemented with great precision and repeatability in plastic. The molding process, executed by means of modern equipment, can be exceedingly stable. Vertex thickness, curvature, and wedge may often be maintained to a greater level of precision, with greater economy than is possible with glass fabrication technology. It is not unusual to see part-to-part variations in vertex thickness of less than 0.01 to 0.02 mm over a run of thousands of parts from a single cavity.

**Multiple Cavities**

The economic appeal of injection molding is the ability to create several parts in one molding cycle. In a multicavity scenario, the parts from different cavities may exhibit some small dimensional differences, depending upon the level of sophistication of the tool design and the quality of its construction. Cavity variations in axial thickness, fortunately, may be permanently minimized by implementing small tooling adjustments after the mold has been exercised. Consequently, part thickness variation rarely consumes a significant fraction of the constructional error budget.

**Dimensional Variations**

Surface radii, like axial thickness, may be replicated with great repeatability if the molding process is adjusted to a stable optimum. Radius errors, if they are present, are usually attributable to incorrect predictions of shrinkage, and may be biased out by correcting the radii of the mold inserts. Thus, the consistency of surface radii achievable with glass may often be equaled in plastic. Thus, radius errors, as well as axial thickness errors, frequently constitute a small portion of the polymer optics manufacturing error budget.

Element wedge, like axial thickness, may be minimized by careful attention to precision in the tool design and construction. It is quite possible to achieve edge-to-edge thickness variations of less than 0.01 mm in molded plastic lenses. With polymer lenses, the azimuthal location of the part gate may be used, if necessary, to define rotational orientation of the element in the optical train. Consequently, rotational alignment of plastic optical parts may be easily indexed.

**Optical Figure Variations**

Control of optical figure quality is obviously key to the successful execution of a good optical design. In glass, achievement of subfringe figure conformance is accomplished routinely, albeit at some cost penalty. In polymeric optics, the nonlinear shrinkage, surface tension, and other processing-related effects cause surface figure errors to scale with part
size, sometimes at a rate proportional to some exponent of diameter. This limits the practical size range for polymeric optics, although capable optics molders may routinely produce elements in the 10-mm-diameter range to subfringe accuracy.\textsuperscript{23}

On one hand, it can probably be stated that processing-induced variations in properties, and a dearth of dependable optical data, preclude any serious discussions of such things as apochromatic polymeric optics, or of large polymeric optics operating at the diffraction limit. On the other hand, the consistency with which some dimensional parameters may be reproduced in quantity, and the design freedom and flexibility afforded by molded aspherics, make possible the satisfaction of some design requirements which would be out of range for conventional glass optics.\textsuperscript{24,25}

**Specification**

Given the fact that the guidelines and restrictions for design and implementation are very different for glass and polymeric optics, it is not surprising that the approach to specification of polymer optical parts and systems should be tailored to the materials and processes of polymer optics. Attempts to convert a glass optics concept to plastic are frequently unsuccessful if the translation overlooks the fundamental themes of the molding and tooling technologies involved. Much as optimum tube and solid-state electrical circuit topologies should be significantly different, so must the execution of a conceptual optical system, depending upon whether glass or polymer material is the medium.

It follows naturally that manufacturing drawings for polymer optics may contain annotations which seem unfamiliar to those versed in glass optics manufacture. Furthermore, some specifications which are universally present on all glass optics drawings may be conspicuously absent from a polymer optics print.

For example, thermal and cosmetic damage considerations preclude the use of the familiar test glasses in the certification of polymeric optics. Figure conformance, then, need only be specified in “irregularity” or asphericity terms, since the alternative method, use of a noncontacting interferometer, implies that the focus error (fringe power in test plate language) will be automatically removed in the adjustment of the test setup.

References to ground surfaces may be omitted from polymer optics drawings, since no such operation takes place. Discussions of “chips” inside the clear aperture, staining, and the like are also superfluous. Beauty defect specifications do apply, although such imperfections are almost always present in every sample from a specific cavity, probably implying the need to rework a master surface.

In general, the lexicon of optics, and that of the molding industry, do not overlap to a great extent. Molding terms like flash and splay are meaningless to most optical engineers. Those endeavoring to create a sophisticated polymeric optical system, anticipating a successful outcome, are advised to devote some time to the study of molding, and to discussions with the few experts in the arcane field of optics molding, before releasing a drawing package which may be unintelligible to or misunderstood by the vendor.

### 34.7 **PROCESSING**

**Casting**

As mentioned above, polymeric optics may be produced by any of several processes. These include fabrication, transfer replication, casting, compression molding, injection molding, and some combinations of the aforementioned.\textsuperscript{26} The earliest polymeric optical parts were probably produced by fabrication or precipitation from solution. Large military tank
prisms have been made by both processes. In the latter case, the polymer (typically PMMA) was dissolved, and the solvent then evaporated to produce a residue of polymer material in the shape of the mold—a very inefficient technique indeed.

Many of the polymers may be fabricated by cutting, grinding, and polishing, much as one would deal with glass materials. The thermoset resin tradenamed CR-39 (polydiallylglycol) was formulated specifically to be processed using the same techniques and materials as those used to fabricate glass optics. And this material does indeed produce good results when processed in this manner. It is used extensively in the ophthalmic industry to produce spectacle lenses. The processing, in fact, usually involves casting the thermoset resin to create a lens blank which emerges from the mold with the optical surfaces polished to final form. More conventional fabrication techniques may then be utilized to edge the lens, or perhaps to add a bifocal portion.

**A abrasive Forming**

Unfortunately, the softness of most of the polymers, coupled with their poor thermal conductivity, complicates the achievement of a truly high quality polish using conventional methods. Even in the case of CR-39, which is relatively hard for a polymer material, some amount of “orange peel” in the polished surface seems unavoidable. Many thermoplastics, most of them softer than CR-39, may be conventionally ground and polished to give the appearance of an acceptable optical surface. Closer examination, however, reveals surface microstructure which probably does not fall within the standards normally associated with precision optics. Nonetheless, fabrication of optical elements from large slabs of plastic is often the only viable approach to the creation of large, lightweight refractive lenses, especially if cost is an issue.

In general, the harder, more brittle polymers produce better optical surfaces when ground and polished. PMMA and others seem to fare better than, say, polycarbonate, which is quite soft, exhibits considerable elongation at the mechanical yield point, but is in great demand due to its impact resistance.

**Single-point Turning**

An alternative approach to fabrication, one that is especially useful for the production of aspheric surfaces, is the computer numerical control (CNC) lathe turning of the bulk material using a carefully shaped and polished tool bit of single-crystal diamond or cubic boron nitride. See also Vol. I, Chap. 41, this Handbook. The lathe required to produce a good result is an exceedingly high precision tool, having vibration isolation, temperature control, hydrostatic or air bearings, and so on. On the best substrate materials (PMMA is again a good candidate), very good microroughness qualities may be achieved. With other materials, a somewhat gummy character (once more, polycarbonate comes to mind) may result in microscopic tearing of the surface, and the expected scatter of the incident radiation.

The diamond-turning process is often applied in conjunction with other techniques in order to speed progress and reduce cost. Parts which would be too large or too thick for economical stand-alone injection molding are frequently produced more efficiently by diamond-turning injection molded, stress-relieved preforms, which require minimal material removal and lathe time for finishing. Postpolishing, asymmetric edging, and other postoperations may be performed as necessary to create the finished part. Optics for illumination and TV projection applications are often produced by some combination of
these techniques. Given the fact that the technology in most widespread use for the production of plastic optics involves some form of molding (a front-loaded process, where cost is concerned), diamond-turning is often the preferred production method for short production runs and prototype quantities.

**Compression Molding**

Most high-volume polymeric optics programs employ a manufacturing technology involving some form of molding to produce the optical surfaces, if not the entire finished part. Of the two most widely used approaches, compression molding is best suited to the creation of large parts having a thin cross section. In general, any optical surface possessing relief structure having high spatial frequency is not amenable to injection molding, due to the difficulty of forcing the material through the cavity, and due to the fact that the relief structure in the mold disrupts the flow of the polymer. In addition, the relief structure in the master surfaces may be quite delicate, and prone to damage at the high pressures often present in the mold cavity.

The compression molding process is capable of producing results at considerably lower surface pressure than injection molding, and as long as the amount of material to be formed is small, this molding technology can replicate fine structure and sharp edge contours with amazing fidelity. Since the platens of a compression molding press are normally heated using steam or electrical heaters, most compression molded parts are designed to be executed in polymers having a relatively low temperature softening point, and materials like polyethersulfone are rarely utilized.

**Injection Molding**

Optical parts having somewhat smaller dimensions may be better suited to production by the injection molding process. This is probably the preferred polymer manufacturing technology for optical elements having a diameter smaller than 0.1 m and a thickness not greater than 3 cm. Not only do the economics favor this approach in high production volume, but if properly applied, superior optical surfaces may be produced.

It should be kept firmly in mind that the basic injection molded process (as it is known to most practitioners) requires a great deal of refinement and enhancement in order to produce credible optical parts. Unfortunately, very few molders possess either the molding know-how, or the testing and measurement sophistication to do the job correctly. Given a supply of quality polymer material, the molding machine itself must be properly configured and qualified. Relatively new machinery is a must. The platens to which the mold halves are mounted must be very rigid and properly aligned. And this alignment must be maintainable on a shot-to-shot basis for long periods. The screw and barrel must be kept scrupulously clean, and must be carefully cleaned and purged when switching materials. The shot capacity, in ideal circumstances, should be more carefully matched to the part volume than for non-optical parts. The process control computer must be an inordinately flexible and accurate device, able to profile and servo a number of operational functions that might be of little importance if the molded part were not optical in nature.

Since much of the heating of the injected polymer resin occurs as a result of physical shear and compression (due to a variable pitch screw), the selection of these machine characteristics is critical to success. In addition, the energy supplied to the machine barrel
by external electric heaters must be controlled with more care than in standard industrial applications. A failure of a single heater, or a failure of one of the thermal measurement devices which close that servo loop, may result in many defective parts.

Vendor Selection

The injection mold itself requires special attention in both design and execution in order to produce state-of-the-art molded lenses. A number of closely held “trade tricks” normally characterize a mold designed to produce optical parts, and these subtle variations must be implemented with considerably greater accuracy than is normally necessary in ordinary molding. The mold and molding machine are often designed to operate more symbiotically than would be the case in producing non-optical parts. Control of the mold temperature and temperature gradients is extremely critical, as is the control bandwidth of those temperatures and the temperature of the molding room itself. The most important conclusion to be drawn from the preceding paragraphs is that the molding vendor for polymer optical parts must be selected with great care. A molding shop, no matter how sophisticated and experienced with medical parts, precision parts for electronics, and so on, will probably consume much time and many dollars before conceding defeat with optical parts.

Although success in molding optical elements is a strong function of equipment, process control, and engineering acumen, attention to detail in the optical and mechanical design phases will consistently reduce the overall difficulty of manufacturing these items. An awareness of the basic principles of injection molding procedures and materials is very helpful here, but it is necessary to be aware that, in the optical domain, we are dealing with micrometer-scale deformations in the optical surfaces. Thus, errors or oversights in design and/or molding technique which would totally escape notice in conventional parts can easily create scrap optics.

Geometry Considerations

The lens design effort, for best results, must be guided by an awareness of the basic physics of creating an injection molded part, and of the impact of part cross section, edge configuration, asymmetry, and so on. In general, any lens having refractive power will possess a varying thickness across its diameter. Unfortunately, meniscus-shaped elements may mold best due to the more uniform nature of the heat transfer from the bulk. Positive-powered lens elements will naturally shrink toward their center of mass as they cool, and it may be difficult to fill the mold cavity efficiently if the edge cross section is only a small fraction of the center thickness.

Negative lenses, on the other hand, tend to fill in the outer zones more readily, since the thinner portion of the section (the center) tends to obstruct flow directly across the piece from the part gate. In extreme circumstances, it is possible that the outer zones of the lens element will be first to fill, trapping gases in the center, forming an obvious sink in molding terminology. Parts designed with molded-in bores may exhibit the ‘weld-line’ phenomenon, which is a visible line in the part where the flow front of the molten plastic is divided by the mold cavity obstruction forming the bore. In the case of both negative and positive lens elements, it is good policy to avoid element forms wherein the center-to-edge thickness ratio exceeds three for positive elements, or is smaller than 0.3 for negative elements.
Shrinkage

Surface-tension effects may play a significant role in the accuracy to which a precision optical surface may be molded. Particularly in areas of the part where the ratio of surface area/volume is locally high (corners, edges), surface tension may create nonuniform shrinkage which propagates inward into the clear aperture, resulting in an edge rollback condition similar to that which is familiar to glass opticians. Surface tension and volumetric shrinkage may, however, actually aid in the production of accurate surfaces. Strongly curved surfaces are frequently easier to mold to interferometric tolerances than those having little or no curvature. These phenomena provide motivation to oversize optical elements, if possible, to a dimension considerably beyond the clear apertures. A buffer region, or an integrally molded flange provides the additional benefit of harmlessly absorbing optical inhomogeneities which typically form near the injection gate. Figure 2 depicts several optical element forms exhibiting favorable (a–e) and unfavorable (f–j) molding geometries. In some cases, a process combining injection and compression molding may be used to improve optical figure quality. Several variants of this hybrid process are in use worldwide, with some injection molding presses being specifically fitted at the factory to implement this procedure.

Mechanical Assembly

In order to appreciate fully the design flexibility and cost-saving potential of polymer optics, it is necessary to modify one’s approach to both optical and mechanical design. A fully optimized polymeric optical system not only makes use of aspheric technology and integrally molded features in the optical elements, but embodies an extension of this design philosophy into the lens housing concept and assembly strategy. These issues should ideally be considered in concert from the very beginning, so that design progress in one aspect does not preclude parallel innovation in other facets of the development process.

It is important to resist the urge to emulate glass-based optomechanical design approaches, since the polymer technology permits design features to be implemented which would be prohibitively expensive (or even impossible) in metal and glass. Spacers
required to separate elements may be molded as part of the elements (Fig. 2), reducing the metal part total, and simplifying assembly operations. See also Vol. I, Chap. 37, of this Handbook. Housings may be configurations which would be either improbable or unmanufacturable using machine tool technology. The collet-and-cap design shown in Fig. 3 is one such example. Joining might be accomplished by ultrasonic bonding. The clamshell concept shown in Fig. 4 may be designed so that the two halves of the housing are actually the same part, aligned by molded-in locating pins. Joining might be performed by a simple slip-on C ring.

Whereas lens assemblies in glass and metal are normally completed by seating threaded retaining rings, their plastic counterparts may be joined by snap-together pieces, ultrasonic bonding, ultraviolet-curing epoxies, expansion C rings, or even solvent bonding. Solvent bonding is dangerous, however, since the errant vapors may actually attack the polymer optical surfaces.
Following the basic polymeric optics philosophy, the lens element containment and assembly approach should probably not even consider the disassembly option in the event of a problem. In order to maximize assembly precision, and minimize unit cost, the design of the lens cell should evolve alongside that of the optical system, and this cell should be visualized as an extension of a fixture conceived to minimize the labor content of the assembly.

An in-depth treatment of optical mold design and tooling technology is obviously beyond the scope of this discussion. Many of the methods and procedures parallel those in use in the molding industry at large. However, a number of subtle and very important detail differences do exist, and these are not extensively documented in the literature. Issues having to do with metallurgy, heat treatment, chemical passivation, metal polishing, and so on, have little to do with the actual design and engineering of a polymeric optical system. In a modern tool design exercise, though, the flow behavior of the polymer material in the mold, and the thermal behavior of that mold, are carefully modeled in multinode fashion, so that part quality may be maximized, and cycle time minimized. A nodding awareness of these methods, and the underlying physics, may be helpful to the person responsible for the engineering of the polymer optical system.

Testing and Qualification

In the process of implementing any optical system design, the matters of testing and certification become key issues. In molded optics, the master surfaces, whose shapes are ultimately transferred to the polymer optical parts, must be measured and documented. A convenient testing procedure for the optical elements replicated from these surfaces must likewise be contrived, in order to optimize the molding process and insure that the finished assembly will perform to specification. The performance of that assembly must itself be verified, and any disparities from specification diagnosed.

In general, mechanical dimensions of the polymer parts may be verified by common inspection tools and techniques used in the glass optics realm. The possibility of inflicting surface damage, however, dictates that noncontact interferometric techniques be used in lieu of test glasses for optical figure diagnosis. This is a straightforward matter in the case of spherical surfaces, but requires some extra effort in the case of aspherics. See also Vol. II, Chap. 30, of this Handbook.

Obviously, aspheric master surfaces must be scrupulously checked and documented, lest the molder struggle in vain to replicate a contour which is inherently incorrect. The verification of the aspheric masters and their molded counterparts may be accomplished in a variety of ways. Mechanical gauging, if properly implemented, works well, but provides reliable information through only one azimuthal section of the part. Measurement at a sufficient number of points to detect astigmatism is awkward, very time consuming, and expensive. And this is not exactly consistent with the spirit of polymer optics.

Null Optics

An optical null corrector permits the aspheric surface to be viewed in its entirety by the interferometer as if it were a simple spherical surface. This is a rapid and convenient procedure. The null optics consist of very accurately manufactured (and precisely aligned) spherical glass elements designed to introduce aberration in an amount equal to, but of opposite sign from, that of the tested aspheric. Thus, interspersing this device permits aspherics to be viewed as if they were spherical. Since there exists no simple independent test of the null compensator, one must depend heavily upon the computed predictions of correction and upon the skill of the fabricator of the corrective optics. See also Vol. II, Chap. 31, of this Handbook.
The concept of greatest importance regarding the use of aspheric surfaces is that successful production of the total system is cast into considerable doubt if a surface is present which is not amenable to convenient testing. While some aspheric optics may be nulled fairly easily, those which appear in polymer optical systems are frequently strong, exhibiting significant high-order derivatives. If the base curves are strong, especially strongly convex, there may exist no practical geometry in which to create a nulling optical system. And if a favorable geometry does exist, several optical elements may be necessary to effect adequate correction. One can easily approach a practical limit in this situation, since the manufacturing and assembly tolerances of the cascaded spherical elements may themselves (in superposition) exceed the theoretical correction requirement. The bottom line is that one should not proceed with cell design, or any other hardware design and construction, until the aspheric testing issues have been completely resolved.

34.8 COATINGS

Reflective Coatings

Given the fact that optical polymers exhibit specular properties similar to those of glass, it is not surprising that optical coatings are often necessary in polymeric optical systems. The coatings deposited upon polymer substrates fall mostly into four general categories. These include coatings to improve reflectivity, to suppress specular reflection, to improve abrasion resistance, and to retard accumulation of electrostatic charge.

Reflective coatings may be applied by solution plating, or by vacuum-deposition. These are most often metallic coatings, usually aluminum if vacuum-deposited, and normally chromium if applied by plating. The abrasion resistance and general durability of such coatings is rather poor, and susceptibility to oxidation quite high, if no protective coating is applied over the metal film. In some applications, especially involving vacuum deposition, the overcoat may be a thin dielectric layer, deposited during the same process which applies the metal film. If the reflective coating has been applied by plating, the overcoat may be an organic material, perhaps lacquer, and may be deposited separately by spraying or dipping. Not surprisingly, the quality of a surface so treated will be poor by optical standards, and probably suitable only for toy or similar applications.

Antireflection Coatings

Antireflection coatings are frequently utilized on polymer substrates, and may consist of a single layer or a rudimentary multilayer stack yielding better reflection-suppression performance. Due to the stringent requirements for control of the layer thicknesses, such coating formulations may be successfully deposited only in high-vacuum conditions, and only if temperatures in the chamber remain well below the service temperature of the substrate material. Elevated temperatures, necessary for baking the coatings to achieve good adhesion and abrasion resistance, may drive off plasticizing agents, limiting the “hardness” of the chamber vacuum. Such temperatures can ultimately soften the optical elements, so that their optical figure qualities are compromised. Relatively recent developments in the area of ion beam-assisted deposition have made possible improvements in the durability of coatings on polymer materials without having to resort to significantly elevated chamber temperatures. See also Vol. I, Chap. 42, of this Handbook.
Antiabrasion Coatings

In general, many polymeric optical systems which could benefit from application of coatings are left uncoated. This happens because the expense incurred in cleaning, loading, coating, unloading, and inspecting the optical elements may often exceed that of molding the part itself. Some optics, particularly those intended for ophthalmic applications, are constantly exposed to abuse by abrasion, and must be protected, cost notwithstanding. Antiabrasion coatings intended to provide immunity to scratching may be of inorganic materials (normally vacuum-deposited), or may be organic formulations.

Inorganic antiabrasion coatings may be similar to those used for simple antireflection requirements, except that they may be deposited in thicknesses which amount to several quarter-wavelengths. The practical thickness is usually limited by internal stress buildup, and by differential thermal expansion between coating and substrate. In general, the inorganic coatings derive their effectiveness by virtue of their hardness, and provide protection only superficially, since sufficient pressure will collapse the underlying substrate, allowing the coating to fracture.

Organic coatings for abrasion resistance normally derive their effectiveness from reduction of the surface frictional coefficient, thereby minimizing the opportunity for a hard contaminant to gain the purchase required to initiate a scratch. These coatings are often applied by dipping, spraying, or spinning. Coatings thus deposited usually destroy the smoothness which is required if the piece is to be qualified as a precision optical element.

Antistatic Coatings

Coatings applied for the purpose of immunization against abrasion, or suppression of specular reflection, often provide a secondary benefit. They may improve the electrical conductivity of the host surface, thus promoting the dissipation of surface static charge, and the accumulation of oppositely charged contaminants. In circumstances where antireflection or antiabrasion coating costs cannot be justified, chemical treatments may be applied which increase conductivity. These materials typically leave a residue sufficiently thin that they are undetectable, even in interferometric testing.

34.9 REFERENCES