The Complete Technology Book on Industrial Polymers, Additives, Colourants and Fillers
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The Indian plastic and polymer industry has taken great strides. In the last few decades, the industry has
grown to the status of a leading sector in the country with a sizable base. The material is gaining notable
importance in different spheres of activity and the per capita consumption is increasing at a fast pace.
Numerous plastics and fibers are produced from synthetic polymers; containers from propylene, coating
materials from PVC, packaging film from polyethylene, experimental apparatus from Teflon, stockings from
nylon fiber, there are too many to mention them all. The reason why plastics are popular is that they may
offer such advantages as transparency, self lubrication, light weight, flexibility, economy in fabricating and
decorating. Properties of plastics can be modified through the use of fillers, reinforcing agents and chemical
additives. Silicones are by far the most important industrial polymers and are based on silicon, an element
abundantly available on our planet. Polymers are classified in three broad groups; addition polymers,
condensation polymers and special polymers. It is well known that the major consumption of additives is in
PVC compounds. Approximately 80% of additives are being used in PVC; however the left over 20% is
consumed in compounding of other thermoplastics. Plastic master batches and fillers have their own
importance in plastic processing industries. Colorants are the materials that give colour and opacity to
plastics are chemically characterized as either pigments or dyes. Pigments are finely pulverized natural or
synthetic particles which may be of inorganic or organic origin and insoluble in the matrix in which they are
dispersed. Permanent red 2B is a mono azo pigment that is widely used in thermoplastics because it is
inexpensive and has high tinting strength and good bleed resistance. Fillers are commonly employed in
opaque PVC compounds to reduce cost and to improve electrical insulation properties, to improve
deforation resistance of cables, to increase the hardness of a flooring compound and to reduce tackiness
of highly plasticized compounds. Various calcium carbonate are used for general purpose work, china clay
is commonly employed for electrical insulation, and asbestos for flooring applications. Also employed
occasionally are the silicas and silicates, talc, light magnesium carbonate and barites (barium sulfate).
Polymer Energy system is an award winning, innovative, proprietary process to convert waste plastics into
renewable energy. Polymers are the most rapidly growing sector of the materials industry. No wonder
polymers are found in everything from compact discs to high tech aerospace applications. On the basis of
value added, Indian share of plastic products industry is about 0.5% of national GDP.
Some of the astonishing fundamentals of the book are industrial polymers, addition polymers
polyolefins, polyethylene, chlorinated polyethylene, cross linked polyethylene, linear low density
polyethylene (LLDPE), high molecular weight polyethylene, high density polyethylene, ultrahigh molecular
weight polyethylene, polypropylene, poly(vinyl chloride), stabilizers, plasticizers, extenders, mineral filled or
glass bead/milled glass grades, antistatic/electro conductive grades, electroplatable grades, etc.
The present book enlightens the processing of industrial polymers, additives, colourant and fillers. This
book is an invaluable resource to new entrepreneurs, technocrats, researchers, professionals etc.

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Polyethylene, High Density (HDPE)

INTRODUCTION
For normal molecular weight polyethylenes (melt index \[ 0.5\]), the density of homopolymer HDPE is fixed at 59.9-60.2 lb/ft³ (0.960 to 0.965 g/cm³), depending on the manufacturing process. However, HDPE spans the density range of 58.7-60.3 lb/ft³ (0.941 to 0.967 g/cm³) by the use of copolymers that add side-chain branches and thus reduce the density. The density of HDPE is controlled in the manufacturing process by the amount of comonomer added to the reactor. Typical comonomers used with ethylene in HDPE are propylene, butene, hexene, and octene. As the molecular weight of polyethylene increases, the longer polymer chains do not crystallize as readily and the lower amount of crystallinity further reduces the density of a HDPE homopolymer (melt index \[ 0.5\]).

CATEGORY
HDPE is a partially crystalline, partially amorphous thermoplastic material. The degree of crystallinity depends on the molecular weight, the amount of comonomer present, and the heat treatment given. The crystallinity of a given HDPE resin can be varied over a wide range by the rate of cooling from the molten state; slower cooling rates favor crystalline growth. The range of crystallinity for HDPE is normally 50-80%. A density value normally quoted on data sheets for HDPE is determined by a compression molded sheet that has been cooled at the rate of 27°F (15°C) per minuted. Most commercial fabrication processes cool from the melt at much faster rates; as a result, an article fabricated from HDPE rarely reaches the density quoted on a data sheet. Because the amount of crystallinity in HDPE is variable, HDPE can be considered as an amorphous polymer having a variable amount of crystalline filler.

HISTORY
The introductory section on polyethylenes provides historical information on HDPE.

POLYMERIZATION
HDPE is manufactured by a low pressure process; by comparison, low density polyethylene (LDPE) is manufactured by a high pressure process. The pressure used in manufacturing HDPE is below 2000 psi (14 MPa); in many cases, it is below 1000 psi (7 MPa). [In manufacturing LDPE, pressures commonly exceed 10,000 psi (70 MPa)].

There are three major commercial processes used for polymerization of HDPE: solution, slurry, and gas-phase processes. The catalysts used in the manufacture of HDPE are usually either a transition metal oxide type or a Ziegler/Natta type. It is important to note that the performance of HDPE resins having identical melt indexes, densities, and molecular weight distributions (MWDs) can vary if the resins are produced by different processes. These differences normally are seen only in critical applications having very narrow processing windows. For most applications, HDPE resins selected from more than one supplier will perform adequately, even if the resins are made by different processes.

As mentioned, along with melt index and density, MWD is a distinguishing property of HDPE. As HDPE is polymerized, polymer molecules of many different lengths (molecular weights) are produced. If an HDPE resin has a narrow range of molecule lengths, it is said to have a narrow MWD. Conversely, an HDPE having a broad range of molecule lengths is said to have a broad MWD. The MWD is a plot of molecular weight versus the number or frequency of a given molecular weight. As the MWD of an HDPE is broadened, the processibility and melt strength increase, while impact strength, low-temperature toughness, and warpage resistance decrease. The MWD of HDPE is largely controlled by the type of catalyst used in polymerization and by the type of manufacturing process employed.

DESCRIPTION OF PROPERTIES
In HDPE, the properties of tensile yield strength, stiffness, creep resistance, impermeability, abrasion...
resistance, mold shrinkage, and hardness increase with increasing density. On the other hand impact strength, flexibility, and environmental stress crack resistance (ESCR) increase with decreasing density. As the average molecular weight of HDPE increases, the polymer's molten flow decreases. The standard test for measuring the molten flow of HDPE is called the melt index. Melt index is inversely proportional to the average molecular weight. The properties of ESCR, impact strength, tensile strength, elongation, melt strength, and die swell improve with decreasing melt index (and with increasing average molecular weight). The properties of processibility, melt drawdown, and optics decrease with decreasing melt index. As the average molecular weight of HDPE increases, there is more shrinkage and warpage present in the molded parts.

These brief comments on melt index and density indicate that it is not possible to maximize all of the properties of HDPE in a single resin. Therefore, compromises are necessary in designing any HDPE resin. For that reason, most manufacturers of HDPE offer many different HDPE resin grades in their product mix. Selection of an HDPE resin for a given application involves careful evaluation of the application requirements, in order to select the HDPE resin that most closely satisfies the most important requirements. The glass-transition temperature $T_g$ of polyethylene is well below room temperature. This gives polyethylene its more rubbery nature (compared to a polymer such as polystyrene which has a glass-transition point above room temperature). The rubbery nature of HDPE also limits its service temperature compared to that of a polymer having a $T_g$ above room temperature. The $T_g$ for HDPE has been assigned several different values by different measuring techniques and is the subject of much controversy. There are three temperature ranges commonly assigned as the glass-transition point for polyethylene: $-207$ to $-171^\circ F$ ($-133$ to $-113^\circ C$), $-126$ to $-99^\circ F$ ($-88$ to $-73^\circ C$), and $-45$ to $9^\circ F$ ($-43$ to $-13^\circ C$). (5)

Because HDPE is rubbery, its creep modulus is more important than, for example, its flexural modulus in determining the in-service strength of a part fabricated from it. In designing an HDPE part that is intended to bear a load for an extended period of time (greater than one hour), flexural or tensile modulus cannot safely be used to calculate the strength of the fabricated part. Instead, the designer should refer to creep data and select a creep modulus that corresponds to the maximum service time under load for the part. The creep modulus should be employed in strength calculations instead of the flexural and tensile modulus.

Failure to consider creep when parts are designed in HDPE is an invitation to premature part failure. Creep resistance improves in HDPE with increasing density and increasing average molecular weight. Creep resistance can also be improved by the use of such cross-linking techniques as irradiation and chemical cross-linking.

APPLICATIONS

HDPE is used for many food packaging applications because it provides excellent moisture barrier properties. However, HDPE, like all polyethylenes, is limited to those food packaging applications that do not require an oxygen barrier. In film form, HDPE is used in snack food packages and cereal box liners; in blow-molded bottle form, for milk and some non-carbonated beverage bottles; and in injection-molded tub form, for packaging margarine, whipped toppings, and deli foods.

Because HDPE has good chemical resistance, it is used for packaging many household as well as industrial chemicals. Examples of such injection-molded applications include 5-gal pails of floor cleaner, 1-gal pails of paint, and construction containers of spackling paste. Blow-molded applications include 55-gal HDPE drums of antifreeze.

Although HDPE has good chemical resistance, it is prone to environmental stress cracking (ESC), commonly from such agents as detergents and surfactants. HDPE can still be used to package these items if the designer carefully selects an HDPE with a time-to-ESC-failure longer than the required shelf life of the product. Resistance to ESC for HDPE increases with decreasing density and melt index. Although there are many tests for ESC resistance, there is no substitute for field experience with a given product.
HDPE does not provide good barrier resistance to lower molecular weight hydrocarbon solvents such as kerosene, and it is not recommended for nonvented packages of such solvents. HDPE is used for some noncritical gasoline containers where the loss of gasoline through the wall can be tolerated and the container is vented. It can be used for critical gasoline containers, such as automotive gas tanks, if a barrier is added-by surface sulfonation and fluorination treatments, for example.

General uses of HDPE include injection-molded beverage cases, bread trays, and dunnage trays as well as films (which have wide and growing use in merchandising and grocery sacks). Another interesting HDPE application is extruded sheet that is subsequently thermoformed into such articles as canoes and pickup truck bed liners. HDPE can readily be thermoformed but not as easily as styrenics.

In sum, HDPE is a versatile thermoplastic enjoying many successful applications that maximize its properties.

ADVANTAGES/DISADVANTAGES
The performance attributes of HDPE have earned this resin family significant commercial uses. Compared to LDPE and LLDPE, HDPE provides greater stiffness and rigidity.

**Advantages**
- Good moisture barrier properties beneficial in many packaging applications (inner-liner films in paperboard cartons, molded end caps for caulking tubes)
- Good stiffness adequate for some structural applications (beverage crates, tote bins, pallets)
- Load-bearing applications when creep is factored correctly in the part design (load-bearing capabilities improve with increasing molecular weight; ultra-high molecular weight HDPE affords the greatest load-bearing capabilities)
- Relative chemical inertness (can be used to package some chemicals)
- Good thermal stability over a range of -40 to 600°F (-40 to 316°C).

**Disadvantages**
- Relatively high gas transmission rates (would not protect a packaged product from oxygen penetration)
- The creep propensity of HDPE prevents it from being considered a true engineering plastic; the load-bearing capability of conventional molecular weight HDPE decreases rapidly with increasing environmental temperature
- Some chemicals may cause premature failure of HDPE parts because of ESC. Prior to packaging chemicals in containers fabricated of HDPE, testing is recommended as some solvents will penetrate and soften HDPE
- Higher temperatures may cause degradation of HDPE unless an antioxidant is added to the resin

**PROCESSING TECHNIQUES**
HDPE can be made into film using both the extrusion blown film and cast film processes. It is efficiently extruded into sheet and profiles and is readily injection molded, blow molded, and rotationally molded. When a blowing agent is added, HDPE can be fabricated into foamed products. HDPE can also be compression molded, although it is rare to find a commercial system doing so. HDPE can be forged and molded at temperatures below its melting point, but this is not done commercially. Promising developmental work is under way on the production of fibers from HDPE.

As HDPE is fabricated into film and other articles, orientation-influenced properties become very significant. The crystalline structure of HDPE is oriented during the fabrication process; as a result, films or articles exhibit characteristically anisotropic physical properties.

For example, the impact properties a test specimen cut from an injection-molded part parallel to the line of major flow of plastic into the mold would be significantly different from those of a test specimen cut perpendicular to the major line of flow into the mold. This anisotropic behavior must be considered in HDPE part design. If the fabrication process cannot minimize the anisotropic behavior of fabricated HDPE, then
the film or article should be designed to take advantage of the orientation. Fabrication methods commonly used with HDPE are listed in the Master Material Outline.

Most fillers and reinforcing agents can be used with HDPE. The addition of a filler usually improves flexural strength, creep resistance, and hardness, but such gains in physical properties may be offset by reduced impact strength, tensile elongation, and processibility. The addition of a filler can also increase the density of HDPE, and increased density can be a detriment rather than a gain.

Most HDPE resins are sold by the pound by resin producers to fabricators, who, in turn, sell the fabricated articles by the part, not by the pound. The resin producer is concerned with weight, while the seller of fabricated parts is concerned with weight and volume. This relationship of weight and volume can become critical when the density of HDPE (volume per pound) is increased by adding a filler. Any increase in density means that a fabricator must buy (or process) more pounds of filled HDPE to make the same number of parts. This can result in a hidden cost to the fabricator for filled HDPE.

Compounding is another cost factor in filled HDPE systems. Most fillers cannot simply be blended with HDPE and used on normal fabrication equipment. The HDPE and the filler must be compounded by extrusion, intensive mixers, or both, before fabrication, which can add 6 to 12 cents per pound to the cost of filled HDPE. Because of the relatively low cost of unfilled HDPE, and the hidden costs of increased density and compounding, it is difficult to add a filler to HDPE and improve economics. This would not be so, of course, if the cost of HDPE exceeded $1 per pound or if the natural density of HDPE were greater than 62 lb/ft³ (1 g/cm³). Some fillers used with HDPE are talc, calcium carbonate, and mica.

**Processability of HDPE**

<table>
<thead>
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<th>Process</th>
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<td>B</td>
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<tr>
<td>C</td>
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**Injection Molding**

X

**Extrusion**

X

**Thermoforming**

X

**Foam Molding**

X

**DIP Slush Molding**
Rotational Molding

X

Powder Fluidized-Bed Coating

Reinforced Thermoset Molding

Compression/Transfer Molding

X

Reaction Injection Molding (RIM)

Mechanical Forming Casting

X

A = Common processing technique.
B = Technique possible with difficulty.
C = Used only in special circumstances, if ever.

Standard design chart for HDPE

- Recommended wall thickness/length of flow, mm
  Minimum __________ for ______________ distance
  Maximum __________ for ______________ distance
  Ideal __________ for ______________ distance
- Allowable wall thickness variation, % of nominal wall 10%
- Radius requirements
  Outside: Minimum 150% w Maximum 175% w
  Inside: Minimum 50% w Maximum 75% w
- Reinforcing ribs
  Maximum thickness 80% w
  Maximum height 24% w
  Sink marks: Yes X No_____
- Solid pegs and bosses
  Maximum thickness 80% w
  Maximum weight 160% w
  Sink marks: Yes X No_____

- Strippable undercuts
  Outside: Yes_____No X
  Inside: Yes X No____
- Hollow bosses: Yes X NO_______
- Draft angles
  Outside: Minimum 1°/side Ideal 2°/side
  Inside: Minimum 1°/side Ideal 2°/side
- Molded-in inserts: Yes X
  No____
- Size limitations
  Length: Minimum_____Maximum_____Process_____
  Width: Minimum_____Maximum_____Process_____
- Tolerances
- Special process- and materials-related design details
  Blow-up ratio (blow molding) 1:1 to 3:1
  Core L/D (injection and compression molding) 1:1 to 10:1
  Depth of draw (thermoforming) 1.4 to 1.5:1
  Other__________________

The reinforcing material most commonly added to HDPE is glass fiber. (Glass fiber is considered to be a reinforcing material while talc, calcium carbonate, and mica are considered to be fillers because there is more strength gained per pound of glass fiber than per pound of talc, calcium carbonate, or mica.) Glass-fiber-filled HDPE has excellent stiffness and higher temperature service than unreinforced HDPE. The chief drawbacks to using glass fiber in HDPE are increased cost and the abrasiveness of glass to the fabrication equipment. With the cost of surface-treated glass fibers being over $1 per pound, an HDPE so reinforced is much more expensive than unreinforced HDPE.

In deciding whether or not to add a filler or reinforcing agent to HDPE, the designer should consider the following criteria.
- Is there a property requirement in the application that is not met by natural HDPE?
- Can the requirement be met by adding a filler or reinforcing agent?
- Can the application support the additional cost of the filled system?
- Can another polymer (other than HDPE) offer the required properties in an unfilled state as economically as a filled HDPE system?

RESIN FORMS
HDPE can be purchased from resin suppliers in pellet, granular, or powder form. The most common mode of shipment is by bulk railcar. Bulk truck, 1000-lb and 500-kg cartons, and 50-lb and 25-kg bags shipments also are used. In quantities less than truckload, HDPE is generally sold by brokers or resellers rather than by resin manufacturers.

SPECIFICATION OF PROPERTIES

Master Outline of Materials Properties

<table>
<thead>
<tr>
<th>Material HDPE</th>
<th>Property</th>
<th>Test Method</th>
<th>English Units</th>
<th>Value</th>
<th>Metric Units</th>
<th>Value</th>
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<tr>
<td></td>
<td>Density</td>
<td>D792</td>
<td>1b/ft³</td>
<td>58.7-60.3</td>
<td>g/cm³</td>
<td>0.941-0.967</td>
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<td>Property</td>
<td>Method</td>
<td>Unit 1</td>
<td>Unit 2</td>
<td>Unit 3</td>
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<tr>
<td>--------------------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>D638</td>
<td>psi</td>
<td>2700-4400</td>
<td>MPa</td>
<td>18.6-30.3</td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>D638</td>
<td>psi</td>
<td></td>
<td>Mpa</td>
<td></td>
<td></td>
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<tr>
<td>Flexural Modulus</td>
<td>D790</td>
<td>psi</td>
<td>100,000-240,000</td>
<td>Mpa</td>
<td>689-1654</td>
<td></td>
</tr>
<tr>
<td>Elongation To Break</td>
<td>D638</td>
<td>%</td>
<td>100-1000</td>
<td>%</td>
<td>100-1000</td>
<td></td>
</tr>
<tr>
<td>Notched Izod At Room Temp</td>
<td>D256</td>
<td>ft-lb/in.</td>
<td>0.5-3.0</td>
<td>J/m</td>
<td>27-160</td>
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<tr>
<td>Hardness</td>
<td>D785</td>
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<td><strong>Thermal</strong></td>
<td></td>
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<tr>
<td>Deflection T@ 264 Psi</td>
<td>D648</td>
<td>°F</td>
<td></td>
<td>°C</td>
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<td></td>
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<tr>
<td>Deflection T@ 66 Psi</td>
<td>D648</td>
<td>°F</td>
<td>150-200</td>
<td>°C</td>
<td>65-93</td>
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<tr>
<td>Vicat Softening Point</td>
<td>D1525</td>
<td>°F</td>
<td>248-266</td>
<td>°C</td>
<td>120-130</td>
<td></td>
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<tr>
<td>UL Temp Index</td>
<td>UL 746 B</td>
<td>°F</td>
<td></td>
<td>°C</td>
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<tr>
<td>UL Flammability Code Rating</td>
<td>UL 94</td>
<td>Linear Coefficient Thermal Expansion</td>
<td>D696</td>
<td>in/in/°F</td>
<td>60-110 Â· 10^-6</td>
<td></td>
</tr>
<tr>
<td>mm/mm/°C</td>
<td>108-198 Â· 10^-6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Environmental</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Water Absorption 24 Hour</td>
<td>D570</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>Clarity</td>
<td>D1003</td>
<td>%</td>
<td>Transmission</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>Outdoor Weathering</td>
<td>D1435</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>FDA Approval</td>
<td></td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>Chemical Resistance To:</td>
<td>Not attacked</td>
<td>Minimally attacked</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>-------------</td>
<td>---------------------------------------</td>
<td>--------------</td>
<td>--------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weak Acid</td>
<td>D543</td>
<td>Not attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong Acid</td>
<td>D543</td>
<td>Minimally attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weak Alkali</td>
<td>D543</td>
<td>Not attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong Alkali</td>
<td>D543</td>
<td>Not attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Molecular Weight</td>
<td>D543</td>
<td>Minimally attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvents</td>
<td>D543</td>
<td>Minimally attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>D543</td>
<td>Not attacked</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Electrical**

| 15.7-23.6 | Dielectric Strength                  | 400-600 V/mil |
| 2.2-3.0   | Dielectric Constant                 | 2.2-3.0 10(6) Hertz |
| 0.00005-0.003 | Power Factor | 0.00005-0.003 | 0.00005-0.003 |

**Other**

<table>
<thead>
<tr>
<th>Melting Point</th>
<th>D3418</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Transition Temp.</td>
<td>D3418</td>
<td>°F</td>
</tr>
</tbody>
</table>

**PROCESSING REQUIREMENTS**

Unfilled, unreinforced HDPE is not hygroscopic and normally does not require drying prior to processing. Filled HDPE will absorb small quantities of moisture and thus may require drying. If the HDPE is stored in outdoor silos, extreme temperature changes can cause moisture to condense on the pellets and thus necessitate drying. HDPE resins should be protected from contamination from dust, fibers, and other polymers as this type of contamination can affect both processing and end-use performance.

Normal processing temperatures for HDPE range from 350-600°F (177-316°C). The thermal stability of HDPE is usually good over the temperature range if the higher-temperature exposure times are kept relatively short; otherwise, the resin can degrade by cross-linking, chain scission, or both. It is normal for a slight change in melt index to occur during processing of HDPE.
Articles fabricated from HDPE can be ground and recycled. The recycled HDPE is normally blended with virgin HDPE before reuse, typically in amounts of 10% or less regrind. Above 10 percent, the physical properties of the fabricated product can be adversely affected. For best results, regrind must be protected from contamination from other polymers, dirt, paper, and so on.

PROCESSING-SENSITIVE END PROPERTIES

The impact strength, stiffness, and thermal stability of articles fabricated from HDPE are profoundly affected by processing conditions. For example, unidirectional orientation or overpacking a mold can greatly diminish the functional impact strength. If the processing temperatures are kept high and the process has a long resin residence time, the thermal stability of the finished article can be greatly reduced. The cooling rate will affect the stiffness and impact strength of the article: with a slower cooling rate, stiffness increases and impact strength decreases.

SHRINKAGE

Mold Shrinkage Characteristics

Mold Shrinkage Characteristics (in./in. or mm/mm)

*Material HDPE*

In the Direction of Flow

<table>
<thead>
<tr>
<th>Thickness</th>
<th>From</th>
<th>To</th>
<th>#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16</td>
<td>0.020</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>1/8</td>
<td>1/4</td>
<td>1/2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

Perpendicular to the Direction of Flow

*Note:* Mold shrinkage is approximate. It is affected by part design, mold temperature, thickness, injection pressure, packing time, cycle time, orientation, gate design, gate size, gate location, glass content, glass size, and filler content.

Polybutylene (PB)

STRUCTURE

The name polybutylene (PB) refers to commercial semicrystalline resins based on high-molecular-weight isotactic poly(l-butene) homopolymer and copolymer. The chemical structure of poly(l-butene) is represented by:
PB resins are thermoplastic. They are polyolefins and exhibit strength and toughness in both rigid and flexible end-product forms.

Isotactic poly(l-butene) was first synthesized by G. Natta in 1954. Chemische Werke Huels of West Germany started the first commercial production in 1969 and discontinued the operation in 1973. In 1975, Witco Chemical Corp. built a PB plant in Taft, La., which was acquired by Shell Chemical in 1977. Pipe was the first important application of polybutylene and remains to this day as the dominant end-use market for PB. Shell Chemical is the sole U.S. producer of polybutylene.

PB is produced via stereospecific Ziegler-Natta polymerization of 1-butene monomer. Commercial products are based on isotactic high-molecular-weight polymer.

PB resins retain their good mechanical properties at elevated temperatures. Recommended upper and lower use temperatures are approximately 230°F (110°C) and - 4°F (-20°C), respectively. Pipe resins, specifically, exhibit excellent flexibility and resistance to creep, environmental stress cracking, chemicals, and wet abrasion. Plumbing code approvals and listings have been received from most states and cities, as well as from major regulatory and standards-making bodies.

Film grades of PB provide good tear and puncture resistance as well as high impact and tensile strength. Glass reinforcement of polybutylene significantly increases its flexural modulus; it decreases its tensile strength and elongation. For a typical 40 wt% glass-filled pipe-grade PB, tensile properties at break are as follows: tensile strength, 1926 psi (13.3 MPa); elongation 14%; and flexural modulus (1% secant), 258,090
psi (1780 MPa).

APPLICATIONS

As earlier noted, the main commercial application for PB resins is in pipe. PB pipe has received hydrostatic design stress rating of 1000 psi (6.90 MPa) at 73°F (23°C) and 500 psi (3.45 MPa) at 180°F (82°C) from the Plastics Pipe Institute. Applications for small-diameter PB pipe include cold- and hot-water plumbing, the latter including residential and solar plumbing, and underfloor and hydronic heating. Other applications are in well piping, heat-pump piping, fire-sprinkler piping, and specialty hosing. Large-diameter PB pipe finds uses in the transportation of abrasive or corrosive materials at high temperatures in the mining, chemical, and power-generation industries.

Film applications of PB include heavy-duty shipping containers; food, meat and agricultural packaging; compression wraps; hot-fill containers; and industrial sheeting. Other applications include injection molding components, such as fittings for use in conjunction with PB pipe, and compression molding items, such as sheet for abrasion-resistant liner.

ADVANTAGES AND DISADVANTAGES

The advantages of PB in pipe end uses are its flexibility, toughness, and resistance to creep, environmental stress cracking, wet abrasion, and chemicals. PB films demonstrate high resistance to tear, puncture, and impact, and have high tensile strength.

The limitations of PB are a slower processing rate compared to other polyolefins in the heat state, a polymorphic transformation after melt processing, and low temperature brittleness.

PROCESSING TECHNIQUES

PB pipe can be fabricated via conventional single-screw extrusion technology using vacuum or pressure sizing for dimension control. After it exits from the die, the pipe should be cooled by water. The pipes can be joined via thermal fusion or mechanical fittings of several types.

The blown-film process is commonly used for producing PB film; PB film can also be cast on chill rolls. The films are heat-sealable. In addition, PB film can be coextruded or laminated with other films for specific applications. In-line embossing, with good pattern retention, is feasible without the application of heat.

Master Material Outline

Processability of Polybutylene

Process

A

B

C

Injection Molding

X

Extrusion

X
Thermoforming

Foam Molding

DIP. Slush Molding

Rotational Molding

Powder Fluidized Bed Coating

Reinforced Thermoset Molding

Compression/Transfer Molding

Reaction Injection Molding (RIM)

Mechanical Forming

Casting

Flame Spraying
RESIN FORMS
PB resins are produced in pellet form. In addition to pipe and film grades, homopolymer and copolymer
general-purpose grades are offered.

SPECIFICATION OF PROPERTIES
Five crystalline forms of poly(l-butene) have been reported. In conventional melt processing, crystallization
of the resins initially produces the metastable form II, which transforms to the stable form I over a period of 5
to 7 days at ambient temperature and pressure. During the transformation, density, crystallinity, hardness,
rigidity, stiffness, and tensile yield strength all increase to values characteristic of form I. After fabrication
and transformation to form I, these resins show crystallinity of 48 to 55% and density of 0.93 to 0.94 g/cm.

Master Outline of Material Properties
Material Polybutylene (Pipe grade, nominal MI - 0.4 g/10 min)

Property

Test Method

English Units

Value

Metric Units

Value

Mechanical

Density
D792
lb/ft3
58-59
58-59
58-59
58-59

Tensile Strength
D638
psi

0.93-0.94
4640-5075 MPa
32-35 Tensile Modulus
D638 psi
42,050-42,775 MPa
290-295 Flexural Modulus
D790 psi
54,375-55,100 MPa
375-380 Elongation To Break
D638 %
275-300 %
275-300 Notched Izod At Room Temp.
D256 ft-lb/in.
12-15 J/m
640-800
Hardness
D785
Shore D
60
Shore D
60

**Thermal**

Deflection T@ 264 Pa
D648
°F
129-140
°C
54-60

Deflection T@ 66 Pa
D648
°F
216-235
°C
102-113

Vicat Softening Point
D1525
°F
234-237
°C
112-114
UL Temp Index
UL746B
°F
°C

UL Flammability Code Rating
UL94
HB

HB

Linear Coefficient Thermal Expansion
D696
in./in.°F
0.003 073
mm/mm/°C
0.000 013

Environmental

Water Absorption 24 Hour
D570
%
[ 0.03
%
[ 0.03[/TD]

Clarity
D1003
%
Transmission
% Transmission

Outdoor Weathering

D1435

%

Black pigmented grades are weatherable

%

Black pigmented grades are weatherable

FDA Approval

Yes

Yes

Yes

**Chemical Resistance To:**

Weak Acid

D543

Not attacked

Not attacked

Strong Acid

D543

Minimal to badly attacked

Minimal to badly attacked

Weak Alkali

D543

Not attacked
Not attacked

Strong Alkali

D543

Not attacked

Not attacked

Low Molecular Weight Solvents

D543

Depends on solvent and temperature

Depends on solvent and temperature

Alcohols

D543

Not attacked

Not attacked

Electrical

Dielectric Strength

D149

V/mil

kV/mm

Dielectric Constant

D150

10(6)Hertz

2.2
After fabrication and transformation, the film-grade resins show 46 to 52% crystallinity and 0.90 to 0.92 g/cm³ density.

Typical properties of PB pipe resins are listed in the Master Outline of Materials Properties.

**PROCESSING REQUIREMENTS**

When PB is processed, the amount of regrind should not exceed 30% of the input.

Vacuum or pressure sizing is required for dimensional control in single-screw extrusion of pipe.

**PROCESSING-SENSITIVE END PROPERTIES**

Increasing pipe extrusion speed or drawdown reduces the tensile elongation to break, a key property for quality control of PB pipe. The effects of blown film processing parameters on mechanical properties can be found elsewhere.
**SHRINKAGE**

Mold Shrinkage Characteristics.

**Mold Shrinkage Characteristics (in./in. or mm/mm)**

**Material Polybutylene**

In the Direction of Flow

<table>
<thead>
<tr>
<th>Thickness</th>
<th>From</th>
<th>To</th>
<th>#</th>
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</thead>
<tbody>
<tr>
<td>mm: 1.5</td>
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<tr>
<td>in.: 1/16</td>
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<tr>
<td>Aged PB</td>
<td>0.013</td>
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<td></td>
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</table>

Perpendicular to the Direction of Flow

<table>
<thead>
<tr>
<th>Aged PB</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.004</td>
</tr>
</tbody>
</table>

*Note:* Mold shrinkage is approximate. It is affected by part design, mold temperature, thickness, injection pressure, packingtime, cycle time, orientation, gate design, gate size, gate location, glass content, glass size, and filler content.

**Fillers, Mica**

**CATEGORY**

Mica is a reinforcing filler. In some resin systems, it reduces resin costs by as much as a third, but imparts certain selected property improvements reported to surpass those of traditional reinforcements that cost three times as much.

To do this, mica must meet requirements pertaining to size, shape, and, to some degree, composition. There are two physically occuring categories of mica, "sheet" and "ground." Sheet mica is not used for composites. It is a relatively rare electrical grade, mined and sorted largely by hand. Ground mica, which is used as a reinforcing filler, is a processed flake of uniform size and thickness, generally recovered from pegmatite deposits.

**SOURCE**

Mica is part of the mineral class phyllosilicates, which is distinguished by a nearly complete basal cleavage between stacks of two-dimensional silicate crystals and a bond between negatively charged flakes linked
by positively charged alkali ions. The layers slide, and thus, mica is "slippery." In making further distinctions between these mica silicates, the various deposits might be classed as muscovite (primarily potassium aluminum silicate), phlogopite (generally magnesium potassium aluminum-ion silicate), biotite (similar to phlogopite but of weaker crystal structure), and rarer compositions that include lepidolite and zinwaidite. Typical function formulas of the more common micas are Muscovite, KAl2(Al Si3O10)(OH)2; Phlogopite, KMg3(Al Si3O10)(OH)2; and Biotite, K(MgFe)3(Al Si3O10)(OH)2.

Muscovite flake mica used in resin composites occurs very commonly in granitic rock deposits or metamorphosed schists, or gneisses, in North America. These deposits frequently occur concurrently with deposits of feldspar or spogamene in surface outcrop. Phlogopite mica occurs in metamorphosed sediments and is generally associated with pyroxenite. Suzorite mica is a phlogopite that is characterized as having little associated quartz or silica.

Such ore bodies can be mined and harvested by open-pit surface operations. They are shallow in depth: less than 500 ft (152 m). Since mica ore usually occurs with weak horizontal bonds, it lends itself to ripping or recovery by bulldozer or power shovel with minimal blasting.

After the ore has been quarried, it is crushed to a uniform size having individual lumps small enough to feed processing operations uniformly but large enough to minimize retained water from snow or rainfall.

Mica beneficiation is designed to eliminate gangue mineral, reduce particles to fractions of uniform size, and delaminate the flakes into flat, laminar, thin entities. The properties of mica are somewhat in conflict with processing and tend to make it difficult to meet beneficiation objectives.

Ground mica is either wet ground, dry ground, or fluid energy ground. In some cases two processes are employed.

Wet grinding is inefficient and is rarely used for resin composites because of its high cost, limited availability, and narrow range of diameters and aspect ratios.

Dry grinding consists of processes that crush, screen, delaminate, and separate by air or gravity the mica in various stages and sequences suited to the ore used and the desired finished product. The initial stage includes two or three crushing steps, incorporating jaw crushers and hammer mills. These are followed by a closed circuit system of air separators, screens, and mills. In the case of Suzorite mica, special delaminating mills and gangue removal flotation devices are employed.

**KEY PROPERTIES**

Muscovites and phlogopites are the only types of mica of importance in resin composites. These types have many similarities as well as some significant differences.

All micas are highly resistant to oxidation, acids or alkalies, fire or heat, electrical energy, water, or organic solvents. Table 1 gives properties in which phlogopites and muscovites are similar and dissimilar. There are differences that are often significant in plastics. Among these are the color, wide variation in decomposition temperature, water content, and stiffness. In general, the phlogopite micas have greater strength and high temperature resistance, however, the muscovites are slightly lighter in color. As a general rule, phlogopite composites tend to be tan or golden brown: muscovites are grey or beige.

Although there are several producers of mica in the United States, relatively few produce grades for plastics composite. They are listed in Table 2.

**PROCESSING CHARACTERISTICS**

*Processing Property*

*Phlogopite Mica at 40 wt%*

*Viscosity*
Increased Melt flow
Decreased Compounding
Easier to compound compared to glass fiber or calcium carbonate
Temperature Increased
Injection pressure Slightly higher
Flow in mold Difficult compared to virgin material
Mold shrinkage Decreased

APPLICATIONS
Depending on the individually varying cost/performance relationships, these benefits usually result from incorporating mica in composites:
Compared to all reinforcing fillers, mica provides
• Increased flexural strength, reduced gas permeability.
• Increased stiffness and reduced warp.

Properties of Phlogopites and Muscovites

Property
Phlogopite

Muscovite

Similar

Specific gravity
2.7-3.1

Hardness, mohs
2.5-3.0
2.5-3.0

Thermal conductivity perpendicular to cleavage, cal/cm

16 $\times$ 10(4)

16 $\times$ 10(4)

Modulus of elasticity, psi

25 $\times$ 10(6)

25 $\times$ 10(6)

(MPa)

(172,375)

(172,375)

Tensile strength, psi

38-42 $\times$ 10(3)

38-42 $\times$ 10(3)

(MPa)

(262-290)

(262-290)

Specific heat at 77°F (250°C)

0.20-0.21

0.20-0.21

Dissimilar

Refractive index

1.57-1.60

1.55-1.57

Maximum temperature with little decomposition °F (°C)

500 (932)

980 (1796)
Coefficient of thermal expansion perpendicular to cleavage, Å°C

1-2 10(-5)
11 10(-6)

Parallel to cleavage, Å°C

14 10(-6)
10 10(-6)

Water of constitution. %

1.0-3.2
4-5

Flexibility

More
Less

Transparency

Less
More

Compared to some reinforcing fillers, mica provides

• Increased heat-distortion temperature.
• Reduced cost and improved creep, and, where useful, such added benefits as improved ultraviolet and infrared resistance, microwave permeability, and heat shielding.

Mica provides little or no advantage over some lower cost fillers with respect to impact resistance, weld-line strength, and, sometimes, color. These drawbacks may be offset by combining mica with other fillers, modifying the resin, adding pigment, or using other additives.

Producers of Various Grades of Mica

Supplier

Trade Name

Type

Grades Available

J. M. Huber Corp.
Aspra Flex
Muscovite, dry/set ground
Unamin Corp.
Mica
Muscovite, dry ground

Franklin Mineral
Alsibrone
Muscovite, dry/set ground

M.I.C.A.
Mica
Muscovite, dry ground

Eagle Quality
Micaflex
Muscovite, dry

Suzorite Mica Products
Suzorite
Phlogopite, dry

(a) Formerly Martin Marietta Corp.

Physical Properties of Mica-reinforced Polypropylene Polymers
### Table 3
Physical Properties of Mica-reinforced Polypropylene Polymers

<table>
<thead>
<tr>
<th>Property</th>
<th>Unfilled (MPa)</th>
<th>25% 200S (MPa)</th>
<th>40% 200S (MPa)</th>
<th>40% Suzorite 60-S (MPa)</th>
<th>40% Suzorite 60-NP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, psi</td>
<td>3290 (23)</td>
<td>3,110 (22)</td>
<td>2,960 (20)</td>
<td>3,686 (25)</td>
<td>6,160 (65)</td>
</tr>
<tr>
<td>Flexural strength, psi</td>
<td>4,260 (29)</td>
<td>5,180 (36)</td>
<td>6,540 (45)</td>
<td>9,360 (65)</td>
<td></td>
</tr>
<tr>
<td>Flexural modulus, psi</td>
<td>133,00 (917)</td>
<td>317,000 (2,190)</td>
<td>518,000 (3,570)</td>
<td>1,040,000 (7,170)</td>
<td>1,200,000 (8,220)</td>
</tr>
<tr>
<td>Tangent flexural modulus, psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Izod unnotched, ft-lb/in.²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72°F (22°C)</td>
<td>5.3</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-18°F (0°C)</td>
<td>3.8</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Polypropylene copolymer (melt index 30).

**Physical Properties of Mica-reinforced High Density Polyethylene Polymers**

Unfilled(a)

Suzorite mica 10% Glass

Rein Forced(a) 10% 200 NP

Unfilled(b)

Suzorite mica 20% 200 NP

Rein forced(b) 40% 200 NP

Tensile strength, psi

3,400

3,790
<table>
<thead>
<tr>
<th>(MPa)</th>
<th>Flexural modulus, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>903</td>
<td>131,000</td>
</tr>
<tr>
<td>1,430</td>
<td>207,000</td>
</tr>
<tr>
<td>1,350</td>
<td>195,000</td>
</tr>
<tr>
<td>848</td>
<td>123,000</td>
</tr>
<tr>
<td>2,280</td>
<td>330,000</td>
</tr>
<tr>
<td>4,620</td>
<td>670,000</td>
</tr>
</tbody>
</table>

(MPa)

<table>
<thead>
<tr>
<th>(psi)</th>
<th>Flexural strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,835</td>
<td>2,070</td>
</tr>
<tr>
<td>3,180</td>
<td></td>
</tr>
<tr>
<td>4,290</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td></td>
</tr>
</tbody>
</table>
3,750
5,850
(MPa)

(14)
(26)
(40)
Izod unnotched 72°F (22°C) ft-lb/in.(2)

No break
13
6
(J/m)

(690)
(320)
-18°F (0°C) ft-lb/in.(2)

No break
11
5.4
(J/m)

(590)
(290)

(a) High molecular weight-high density polyethylene.
(b) High density polyethylene copolymer.

**Physical Properties of Mica-reinforced ABS and calcium Carbonate-filled PVC**
<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength, psi</th>
<th>Flexural Strength, psi</th>
<th>Flexural Modulus, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS + 5% Long Glass Fiber</td>
<td>7,930</td>
<td>10,300</td>
<td>437,000</td>
</tr>
<tr>
<td>ABS + 10% Suzoritea mica (92%, 44 Microns)</td>
<td>7,480</td>
<td>11,000</td>
<td>619,000</td>
</tr>
<tr>
<td>PVC + 10% CaCO(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC + 10% CaCO(3) + 33.3% Suzorex mica 200-PO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Notched Izod. ft-lb/in.

5.8

4.1

Coefficient of thermal expansionb

32-140°F, °F Å· 10(-5)

3.69

1.37

0-60°C, (°C Å· 10-5)

(6.65)

(2.47)

(a) Note the equivalent performance of both materials
(b) The coefficient of expansion of mica-reinforced PVC is the same as aluminum.
Mica has been developed to perform well with polyolefins (chiefly polypropylene, polyethylene, and copolymers), thermoplastic polyesters, nylon, and urethanes. It shows promise with styrenics, PVC, and thermosets.
POLYMERS FILLED

Physical Properties of Mica-reinforced Nylon 6, 6

Property

Unfilled

40% Suzorite mica 325-PO Reinforced

Tensile strength, psi

11,300

12,50

dry (MPa)

(78)

(86)

wet-16 h, 50Â°C psi

8,460

10,400
Flexural strength, psi
12,300
20,000
dry (MPa)
(85)
(138)
wet psi
14,700
101
(MPa)
Flexural modulus, psi
443,000
1,360,000
1,360,000
dry (MPa)
(3,060)
(9,380)
wet psi
126,000
840,000
869
(MPa)
Izod notched, ft-lb/in.
0.8
0.53
dry (J/m)
(43)
(28)
wet ft-lb/in.
0.93
(J/m)
(50)
Heat deflection, °F
153
401
264 psi (1.82 MPa)(°C)
(67)
(201)
COMMERCIAL GRADES

The average bulk density for the products given is between 11 and 18 lb/ft³. The aspect ratio varies between 46 and 85, depending on the grade. There are other grades for commodity uses. They are sometimes tried for composites but generally are not recommended because of the low-purity mica aspect ratio. In the case of Suzorite mica, these are identified as Z grades (for oil-well drilling) and 80SF (a joint cement grade). Other producers have similar identifying grade nomenclatures.

The use of mica as a reinforcing filler will generally provide a reduction in cost, compared to the unfilled resin, on both a weight and a volume basis. Further, this unit cost will frequently be lower than other reinforcements providing similar properties. This latter distinction is important. Use of mica reinforcement is only economically prudent when the properties sought favor the selection-in order words, for an "engineered" system, but not a general-purpose application.

Table 7
Properties of Polymethylpentene (TPX) Reinforced with Mica

<table>
<thead>
<tr>
<th>Property</th>
<th>Unfilled</th>
<th>200HK</th>
<th>200N</th>
<th>200PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, psi</td>
<td>3.85</td>
<td>3.870</td>
<td>3.870</td>
<td>3.860</td>
</tr>
<tr>
<td>(MPa)</td>
<td>(27)</td>
<td>(27)</td>
<td>(27)</td>
<td>(27)</td>
</tr>
<tr>
<td>Flexural strength, psi</td>
<td>3.82</td>
<td>4.540</td>
<td>5.100</td>
<td>4.860</td>
</tr>
<tr>
<td>(MPa)</td>
<td>(26)</td>
<td>(31)</td>
<td>(35)</td>
<td>(34)</td>
</tr>
</tbody>
</table>

(contd.)

Table 7 (contd.)

<table>
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<th>Unfilled</th>
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<td>(26)</td>
<td>(31)</td>
<td>(35)</td>
<td>(34)</td>
</tr>
</tbody>
</table>
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