7 Polyolefins and Acrylics

In organic chemistry, an alkene, also called an olefin, is a chemical compound containing at least one carbon-to-carbon double bond. The simplest alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n}. The two simplest alkenes of this series are ethylene and propylene. When these are polymerized, they form polyethylene (PE) and polypropylene (PP), which are two types of the plastics discussed in this chapter. A slightly more complex alkene is 4-methylpentene-1, the basis of polymethylpentene, known under the trade name of TPX™. If one of the hydrogens on the ethylene molecule is changed to chlorine, the molecule is called vinyl chloride, the basis of polyvinyl chloride, commonly called PVC. Acrylic polymers are also polymerized through the carbon–carbon double bond. Methyl methacrylate is the monomer used to make polymethyl methacrylate (PMMA).

The structures of these monomers are shown in Figure 7.1 with polymer structures shown in Figure 7.2.

7.1 Polyethylene (PE)

PE can be made in a number of ways. The way it is produced can affect its physical properties. It can also have very small amounts of comonomers, which will alter its structure and properties.

The basic types or classifications of PE, according the ASTM D1248-12 Standard Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable, are:

- Ultra low density polyethylene (ULDPE)—Polymers with densities ranging from 0.890 to 0.905 g/cm^3, contain comonomer
- Very low density polyethylene (VLDPE)—Polymers with densities ranging from 0.905 to 0.915 g/cm^3, contain comonomer
- Linear low density polyethylene (LLDPE)—Polymers with densities ranging from 0.915 to 0.935 g/cm^3, contain comonomer (often a copolymer with butane (C4), hexane (C6), or octane (C8), when made with a metallocene catalyst designated as mLLDPE)
- Low density polyethylene (LDPE)—Polymers with densities ranging from about 0.915 to 0.935 g/cm^3
- Medium-density polyethylene (MDPE)—Polymers with densities ranging from 0.926 to 0.940 g/cm^3, may or may not contain comonomer
- High density polyethylene (HDPE)—Polymers with densities ranging from 0.940 to 0.970 g/cm^3, may or may not contain comonomer.

Additionally ultra high molecular weight polyethylene (UHMWPE) typically has a molecular weight 10 times that of HDPE.

Figure 7.3 shows the differences graphically. The differences in the branches in terms of number and length affect the density and melting points of some types.

Branching affects the crystallinity. A diagram of a representation of the crystal structure of PE is shown in Figure 7.3. One can imagine how branching in the polymer chain can disrupt the crystalline regions. The crystalline regions are the highly ordered areas in the shaded rectangles of Figure 7.4. A high degree of branching would reduce the size of the crystalline regions, which leads to lower crystallinity.

Manufacturers and trade names: Dow Chemical Dowlex®; Exopack Sclairfilm®; DuPont Tyvek®; LyondellBasell Alathon®, Petrothene®; ExxonMobil Paxon™, Pax-Plus™, Exceed™; Chevron Philips Marlex®; NOVA Chemicals Sclair®.

Uses and applications: packaging including films, bottles, water pipes, hip and knee replacements, toys.

Data for PE plastics are shown in Figures 7.5–7.23.

McKeen: The Effect of Temperature and other Factors on Plastics and Elastomers.
DOI: http://dx.doi.org/10.1016/B978-0-323-31016-1.00007-6

7.2 Polypropylene (PP)

The three main types of PP generally available are:

1. *Homopolymers* are made in a single reactor with propylene and catalyst. It is the stiffest of the three propylene types and has the highest tensile strength at yield. In the natural state (no colorant added) it is translucent and has excellent see through or contact clarity with liquids. In comparison to the other two types it has less impact resistance, especially below 0°C.
2. *Random copolymers* (homophasic copolymers) are made in a single reactor with a small amount of ethylene (<5%) added which disrupts the crystallinity of the polymer allowing this type to be the clearest. It is also the most flexible with the lowest tensile strength of the three. It has better room temperature impact than homopolymer but shares the same relatively poor impact resistance at low temperatures.
3. *Impact copolymers* (heterophasic copolymers), also known as block copolymers, are made in a two reactor system where the homopolymer matrix is made in the first reactor and then transferred to the second reactor where ethylene and propylene are polymerized to create ethylene propylene rubber (EPR) in the form of microscopic nodules dispersed in the homopolymer matrix phase. These nodules impart impact resistance both at ambient and cold temperatures to the compound. This type has intermediate stiffness and tensile strength and is quite cloudy. In general, the more ethylene monomer added, the greater the impact resistance with correspondingly lower stiffness and tensile strength.

Oriented and multilayered films of PP are also common.

Manufacturers and trade names: INEOS polypropylene; LyondellBasell Adflex™; Mophen; ExxonMobil Bicor™, OPPalyte™; Dow Chemical; Flint Hill Resources.

Uses and applications: plastic hinges, RF capacitors, food containers, plastic pails, car batteries, wastebaskets, pharmacy prescription bottles, cooler containers, dishes and pitchers, carpets, rugs and mats, ropes.

Data for PP plastics are shown in Figures 7.24–7.40.

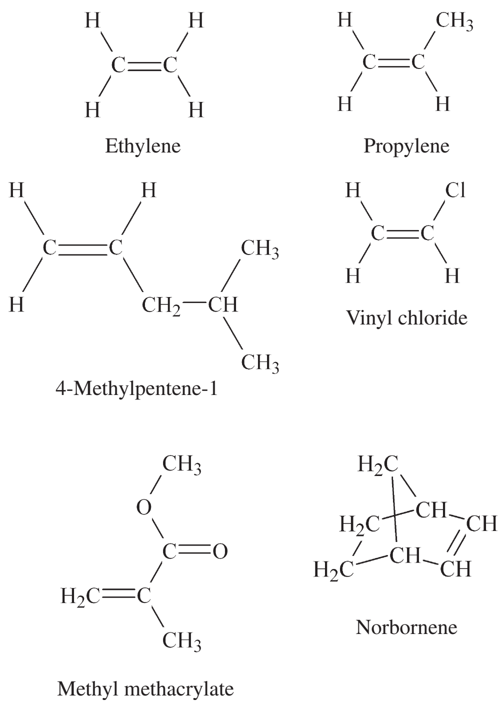

Figure 7.1 Chemical structures of monomers used to make polyolefins.

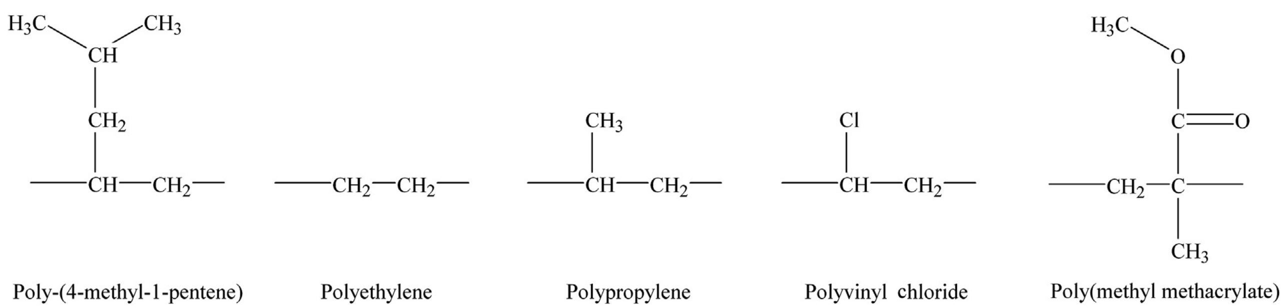

Figure 7.2 Structures of polyolefin polymers.

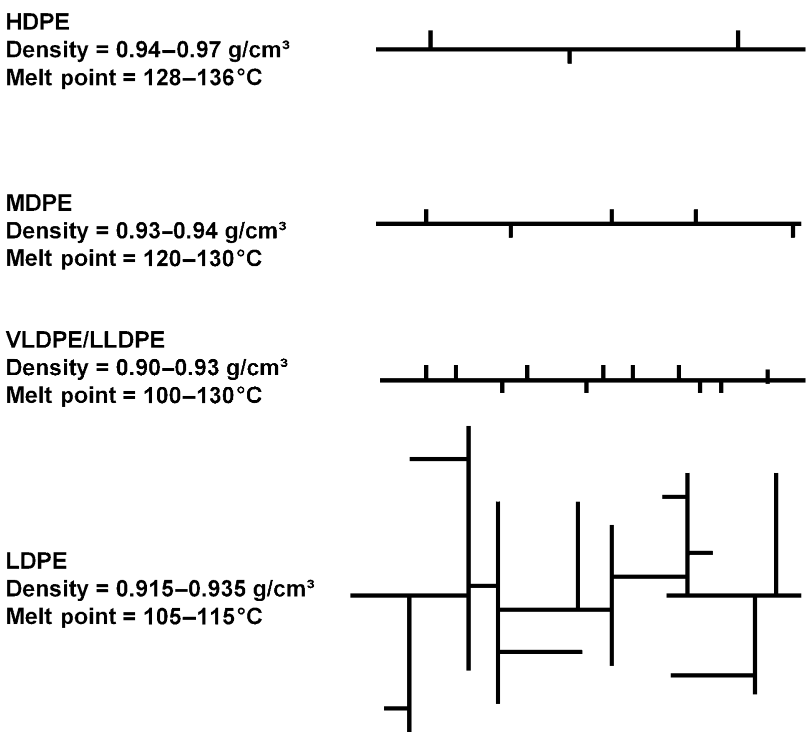

Figure 7.3 Graphical depictions of PE types.

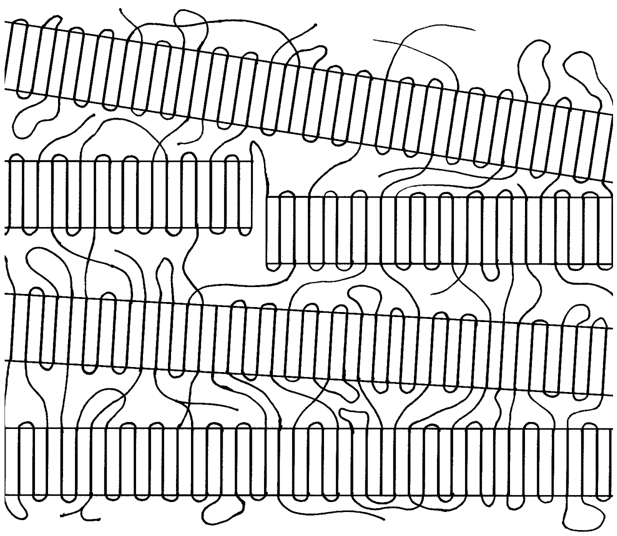

Figure 7.4 Graphical diagram of PE crystal structure.

7.3 Polymethylpentene (PMP)

4-Methylpentene-1 based polyolefin is a light-weight, functional polymer that displays a unique combination of physical properties and characteristics due to its distinctive molecular structure, which includes a bulky side chain as shown in Figure 7.41. Its CAS number is 89-25-8.

PMP is a crystalline polyolefin. PMP possesses many characteristics inherent in traditional polyolefins, such as excellent electrical insulating properties and strong hydrolysis resistance. Moreover:

- PMP has high heat resistance with a melting point of 220–240°C.
- PMP has excellent transparency; its transmittance of visible light is more than 90%. PMP has an especially high transmittance of ultraviolet light (300–400 nm).
- PMP has excellent chemical and oil resistance.
- PMP has good heat aging and steam (boiling water) resistance.
- PMP has low density, the lightest of all common plastics, so it is useful for weight alleviation.
- PMP has high electric insulation and a low dielectric constant.
- Since the surface tension of PMP is 24 dyne/cm, it has excellent nonstick character.

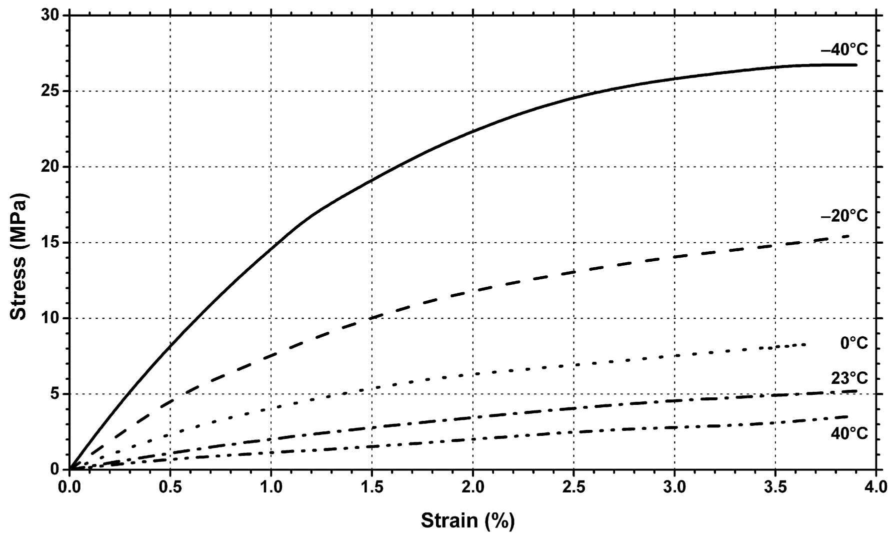

Figure 7.5 Stress vs. strain at various temperatures for Basell Polyolefins Lupolen® 1810H—low density (0.918 g/cm^3), MFR 1.5 g/10 min PE resin.

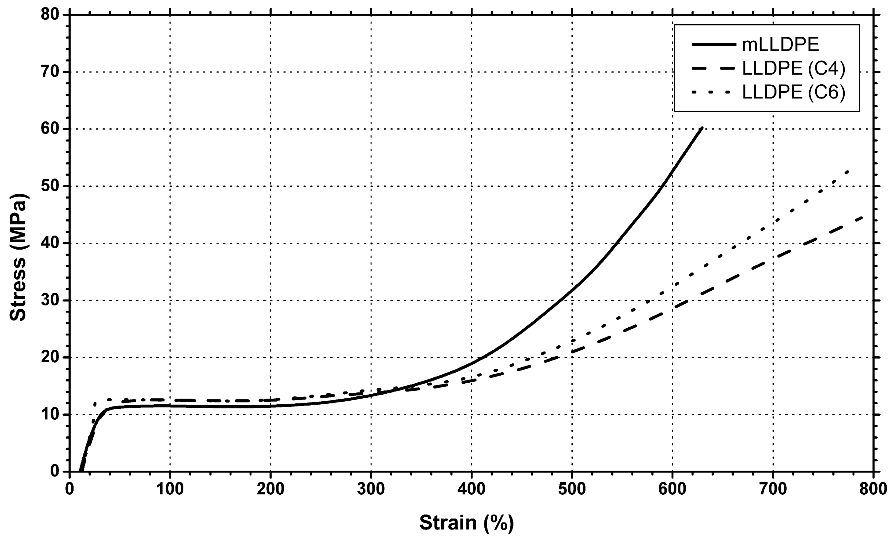

Figure 7.6 Tensile stress vs. strain for various LLDPEs.

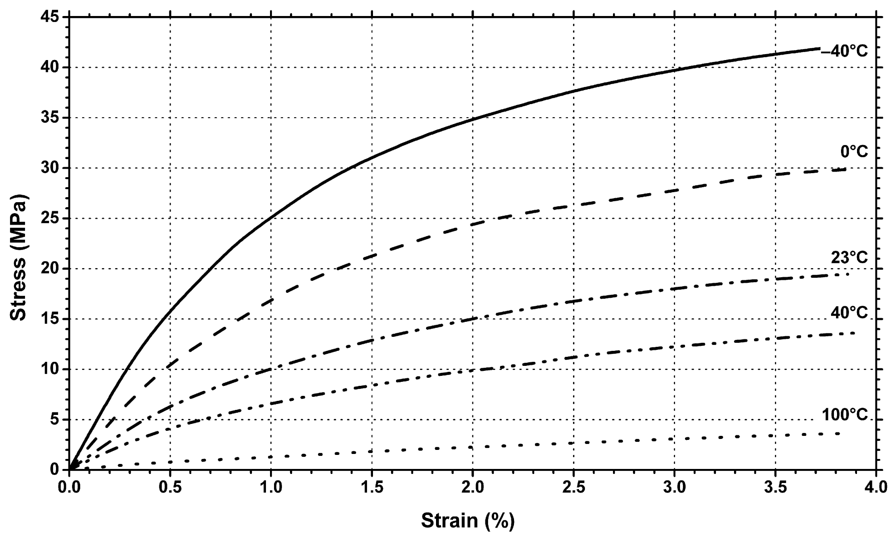

Figure 7.7 Stress vs. strain at various temperatures for Basell Polyolefins Lupolen® 5031L—high density (0.950 g/cm^3), MFR 6.5 g/10 min, stabilized PE resin.

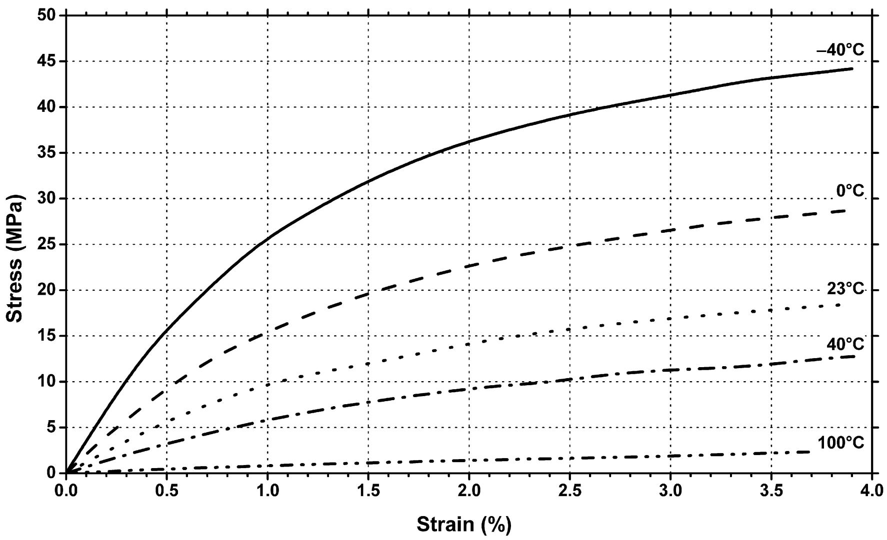

Figure 7.8 Stress vs. strain at various temperatures for Basell Polyolefins Lupolen® 5041H—high density (0.950 g/cm^3), MFR 1.5 g/10 min, stabilized PE resin.

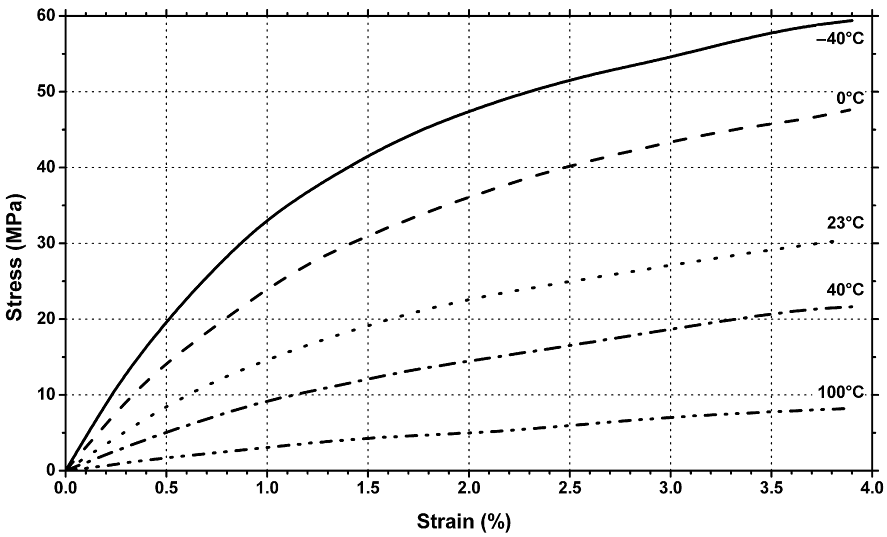

Figure 7.9 Stress vs. strain at various temperatures for Basell Polyolefins Lupolen® 5261Z—high density (0.952 g/cm^3), MFR 2 g/10 min, stabilized PE resin.

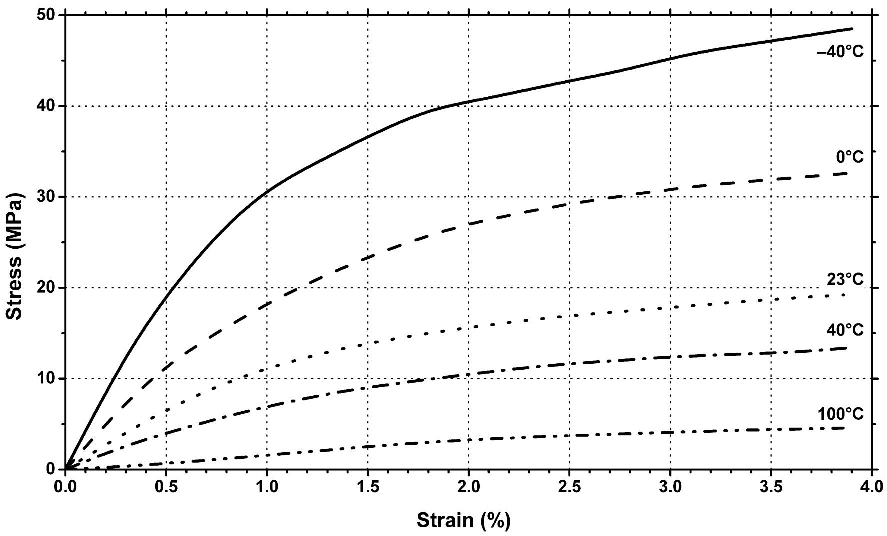

Figure 7.10 Stress vs. strain at various temperatures for Basell Polyolefins Lupolen® 6031M—high density (0.960 g/cm^3), MFR 8 g/10 min, stabilized PE resin.

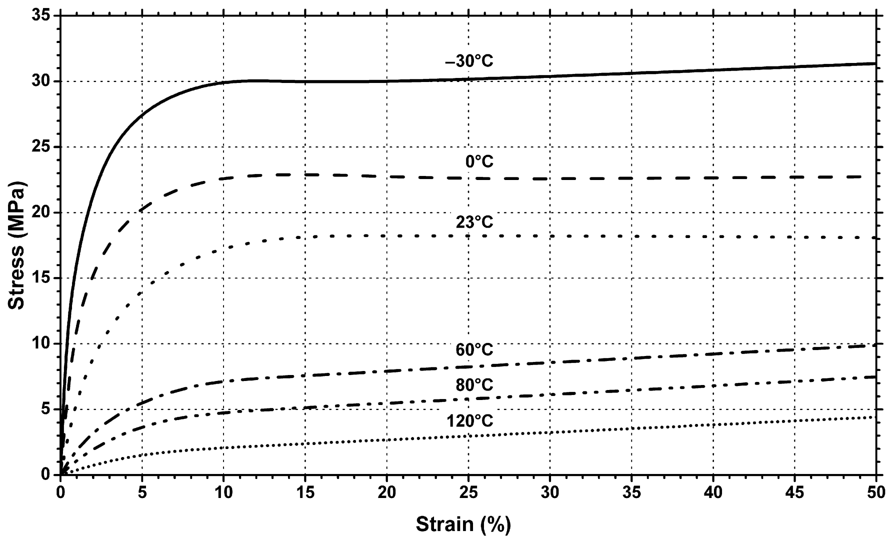

Figure 7.11 Stress–strain curves for Celanese GUR® 4120 UHMWPE measured at different temperatures [1].

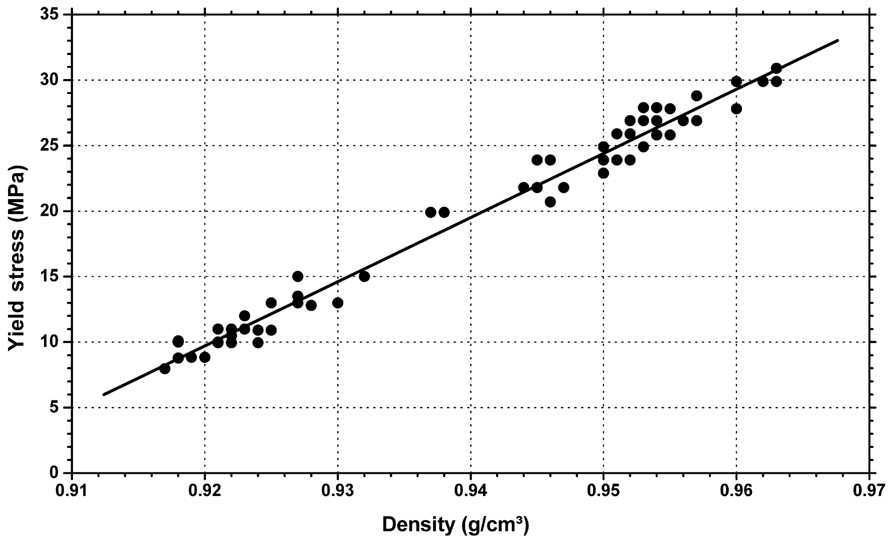

Figure 7.12 Yield stress vs. density for Basell Polyolefins PE resins [2].

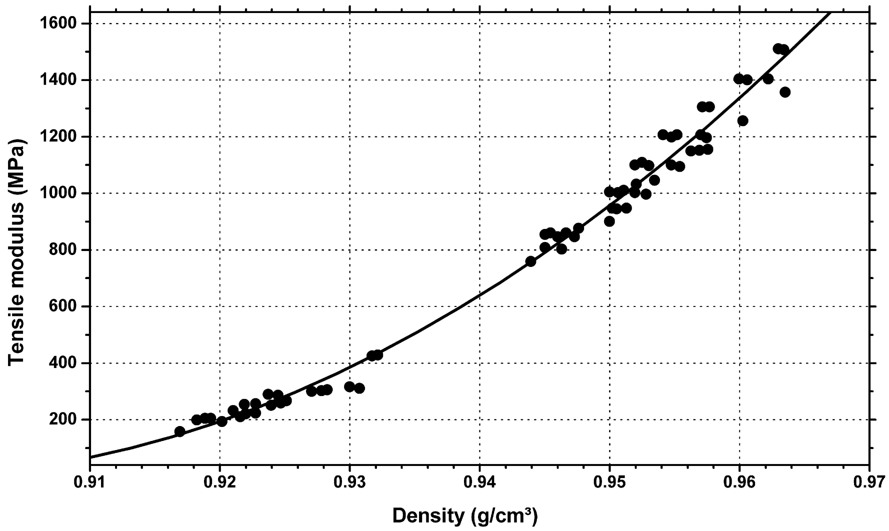

Figure 7.13 Tensile modulus vs. density for Basell Polyolefins PE resins [2].

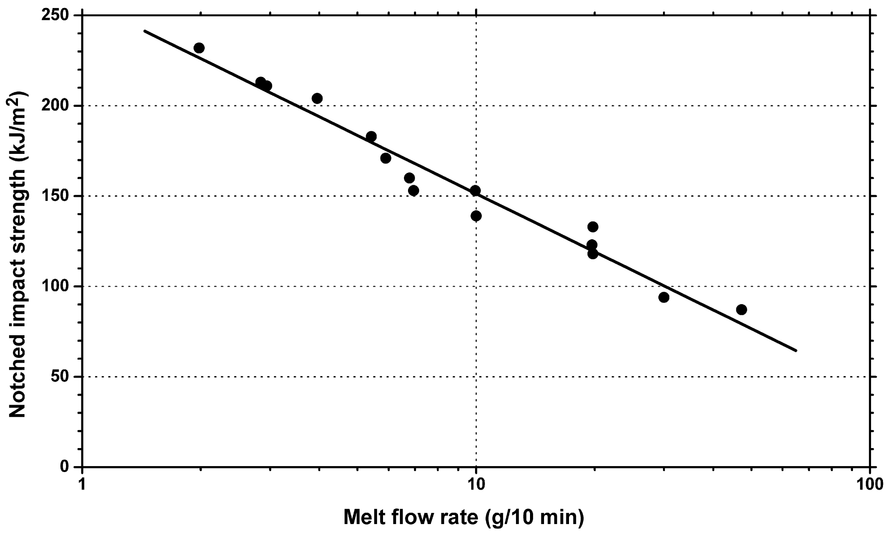

Figure 7.14 Notched tensile impact strength vs. melt flow rate (MFR) for Basell Polyolefins PE resins [2].

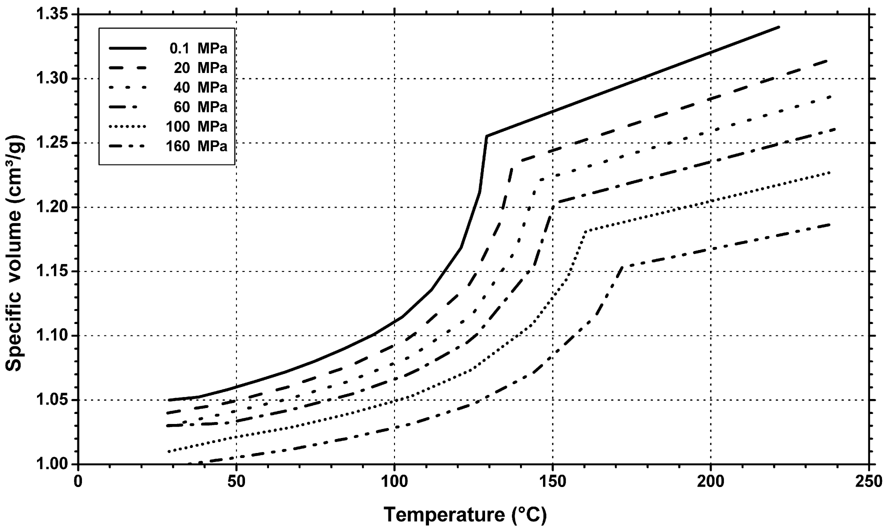

Figure 7.15 Specific volume vs. temperature and pressure (PVT) for Basell Polyolefins PE resins [2].

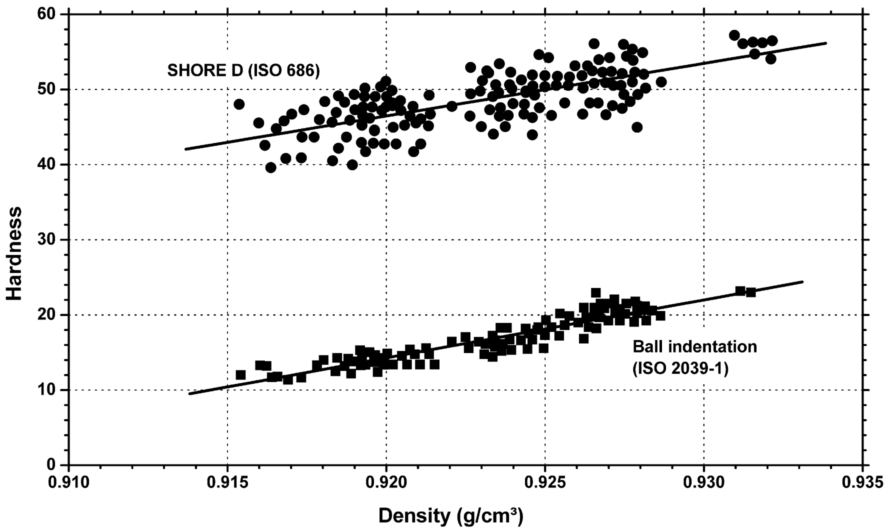

Figure 7.16 Hardness vs. density for Basell Polyolefins PE resins [2].

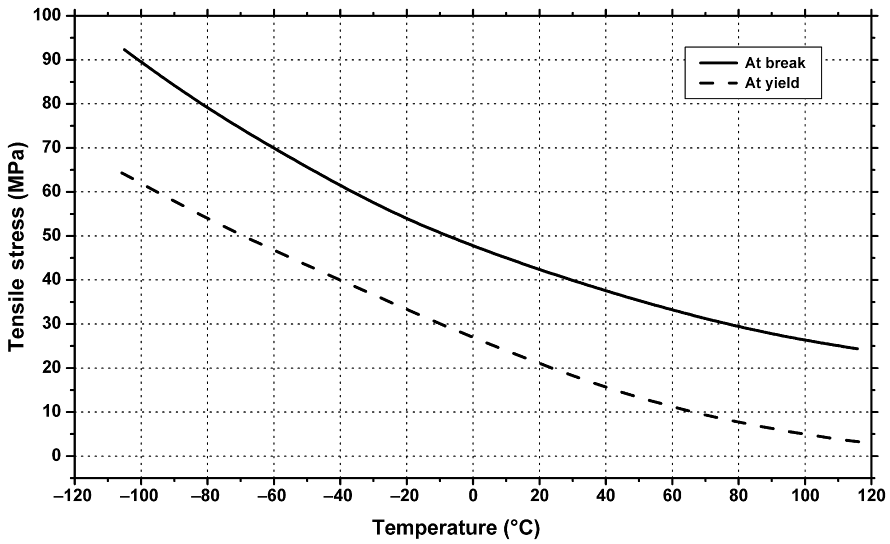

Figure 7.17 Tensile strength vs. temperature for Ticona ultra high molecular weight PE resin [1].

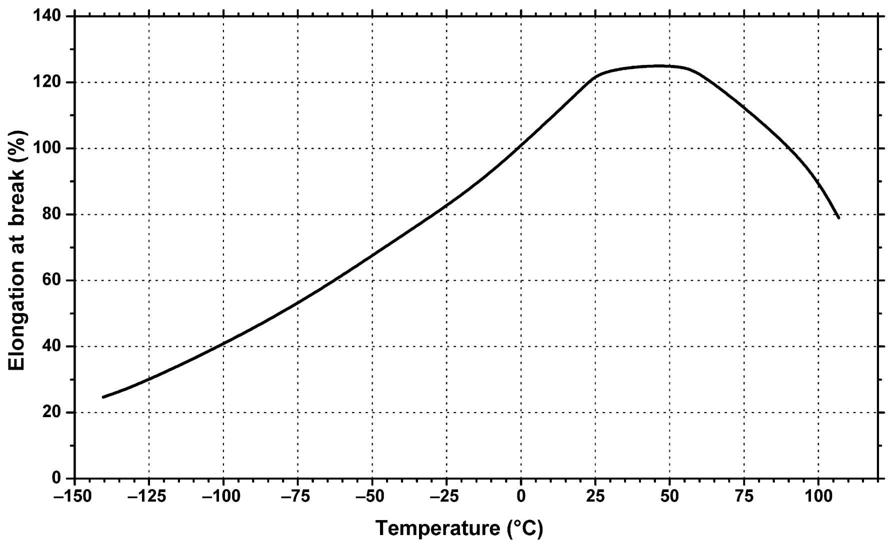

Figure 7.18 Elongation at break vs. temperature for Ticona ultra high molecular weight PE resin [1].

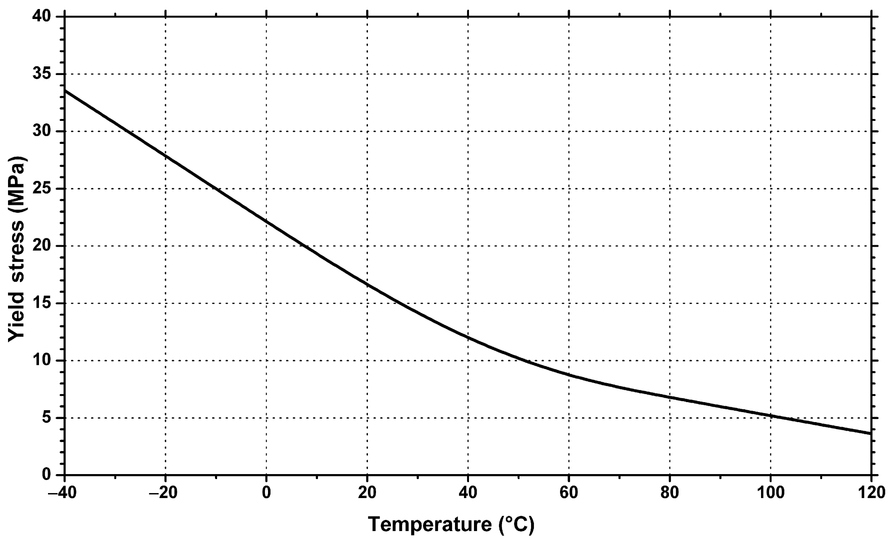

Figure 7.19 Yield stress vs. temperature for Ticona GUR® 4120—high bulk density, corrosion stabilized ultra high molecular weight PE resin [1].

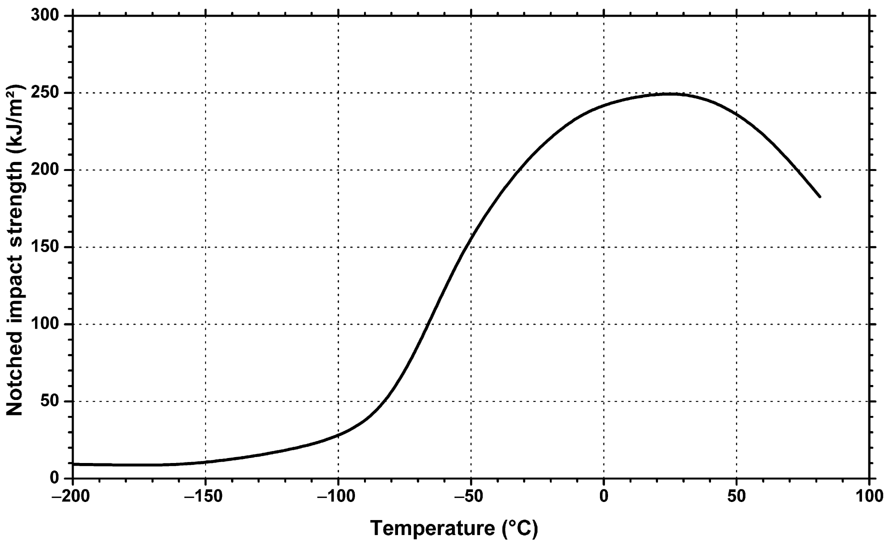

Figure 7.20 Notched Charpy impact strength vs. temperature for Ticona GUR® 4120—high bulk density, corrosion stabilized ultra high molecular weight PE resin [1].

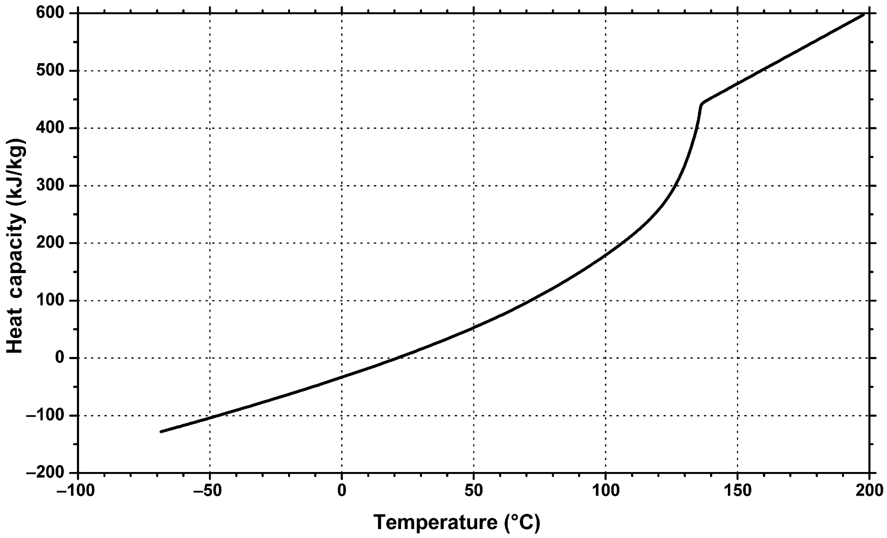

Figure 7.21 Heat capacity (enthalpy) vs. temperature for Ticona GUR® ultra high molecular weight PE resin [1].

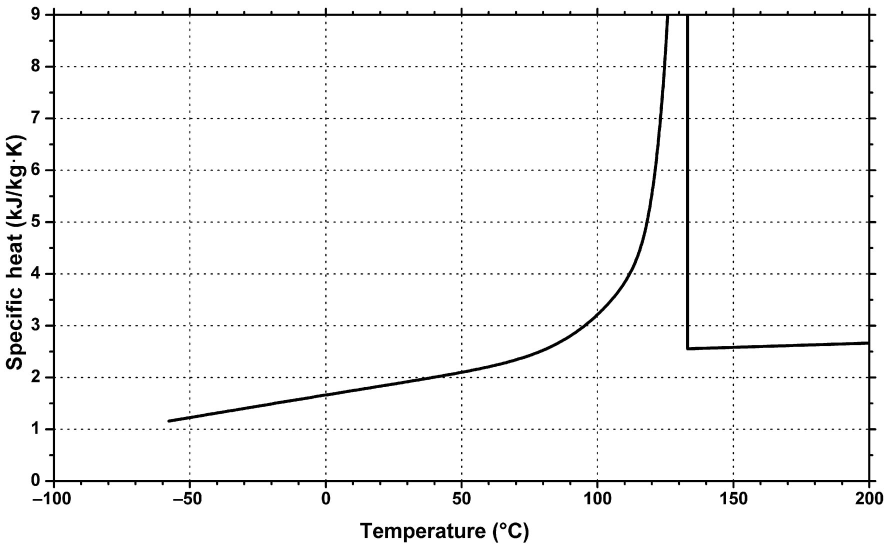

Figure 7.22 Specific heat vs. temperature for Ticona GUR® ultra high molecular weight PE resin [1].

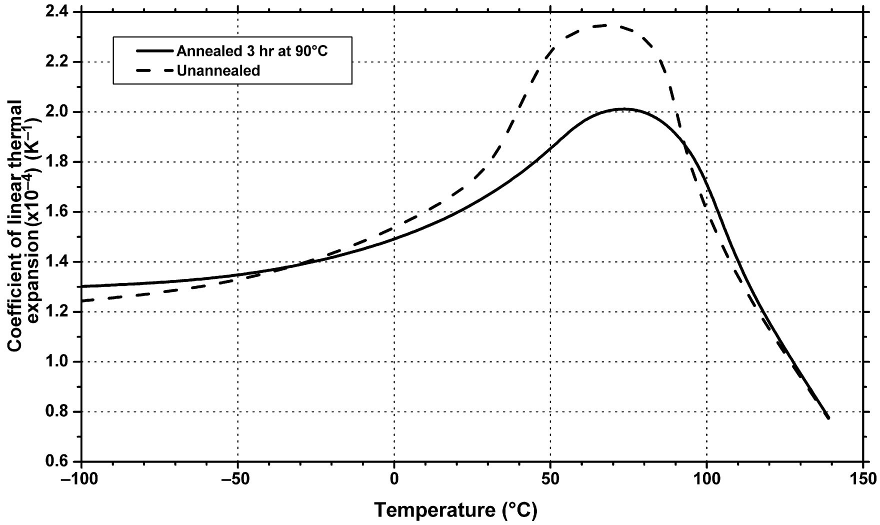

Figure 7.23 Coefficient of linear thermal expansion vs. temperature for Ticona GUR® 4120—high bulk density, corrosion stabilized ultra high molecular weight PE resin [1].

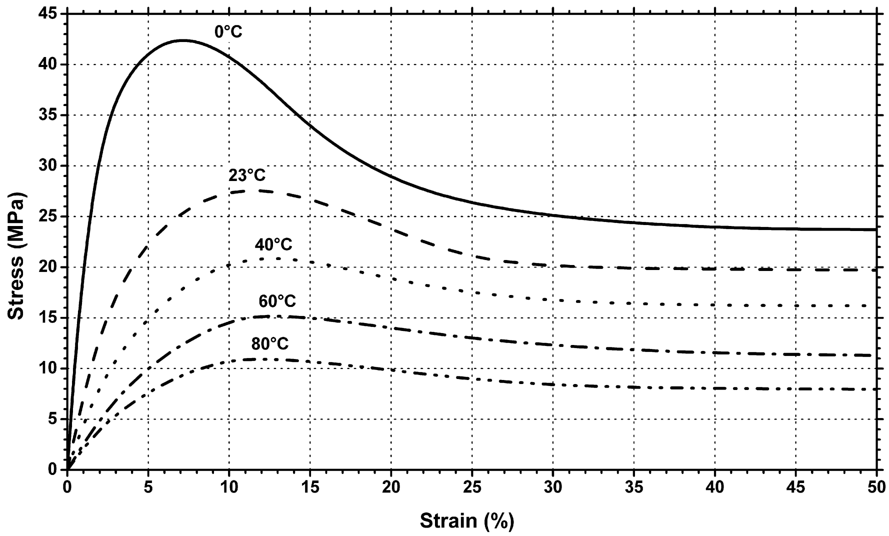

Figure 7.24 Stress vs. strain at various temperatures for Basell Polyolefins Hostalen® H1022—easy flow, high impact PP resin [3].

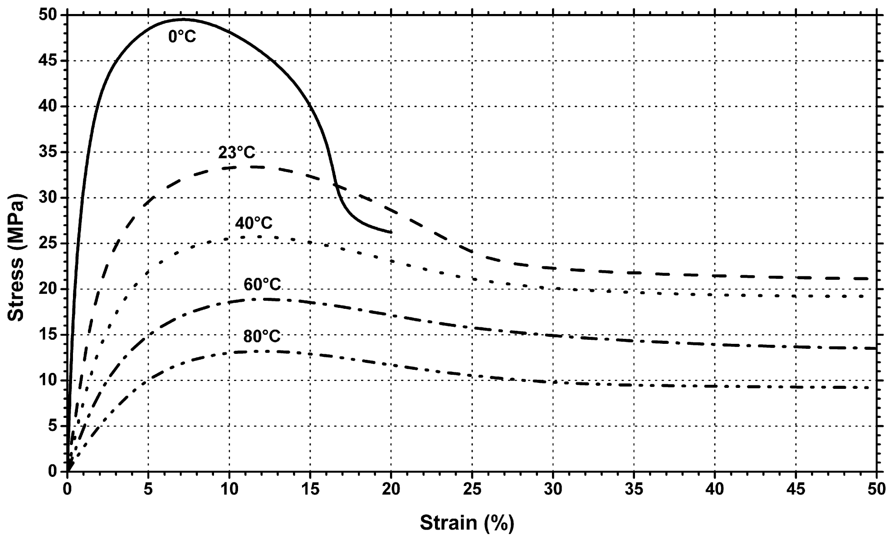

Figure 7.25 Stress vs. strain at various temperatures for Basell Polyolefins Hostalen® H2250—easy flow, high heat PP resin [3].

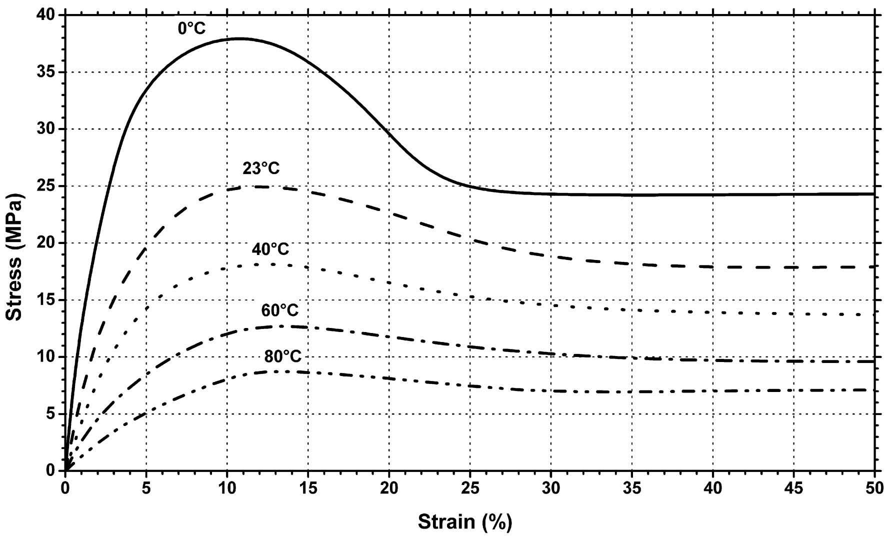

Figure 7.26 Stress vs. strain at various temperatures for Basell Polyolefins Hostalen® H5216—easy flow, random copolymer PP resin [3].

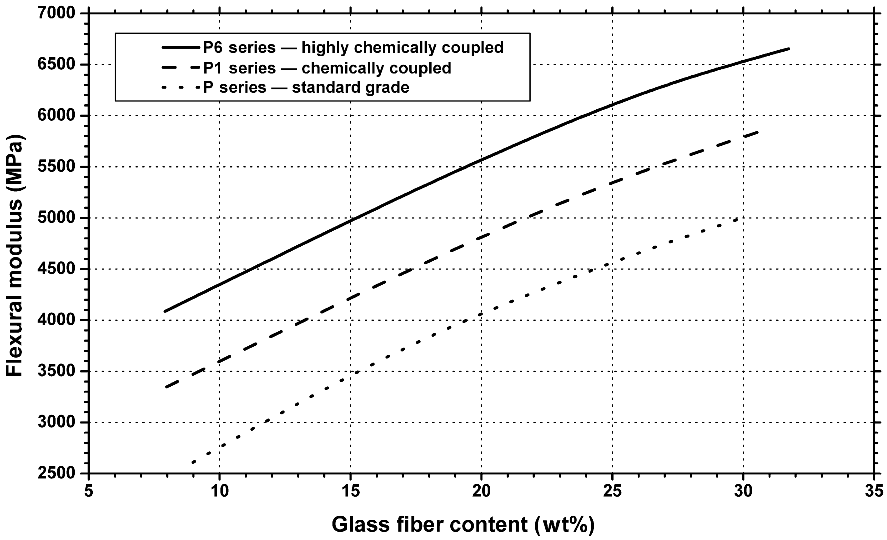

Figure 7.27 Flexural modulus at 23°C vs. glass fiber content for Asahi Kasei Thermylene® PP resins.

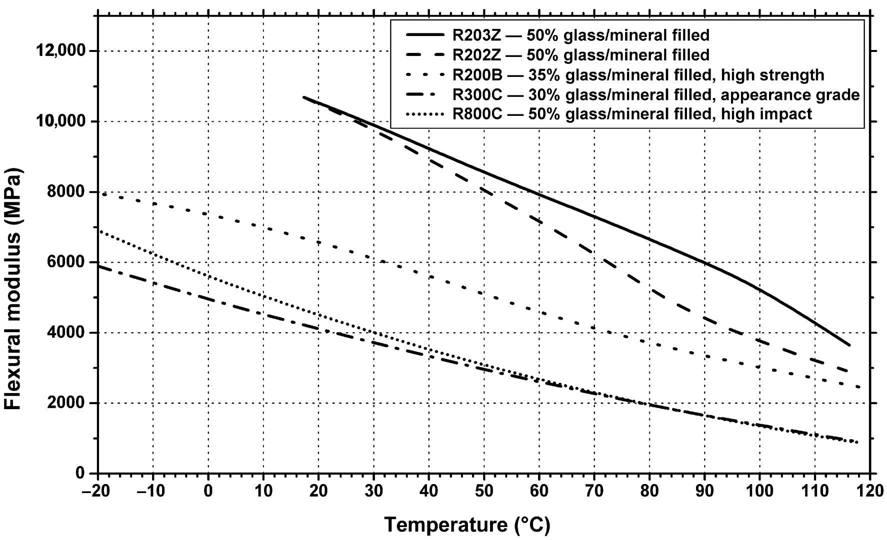

Figure 7.28 Flexural modulus vs. temperature for Chisso America Olehard® glass and mineral-filled PP resins.

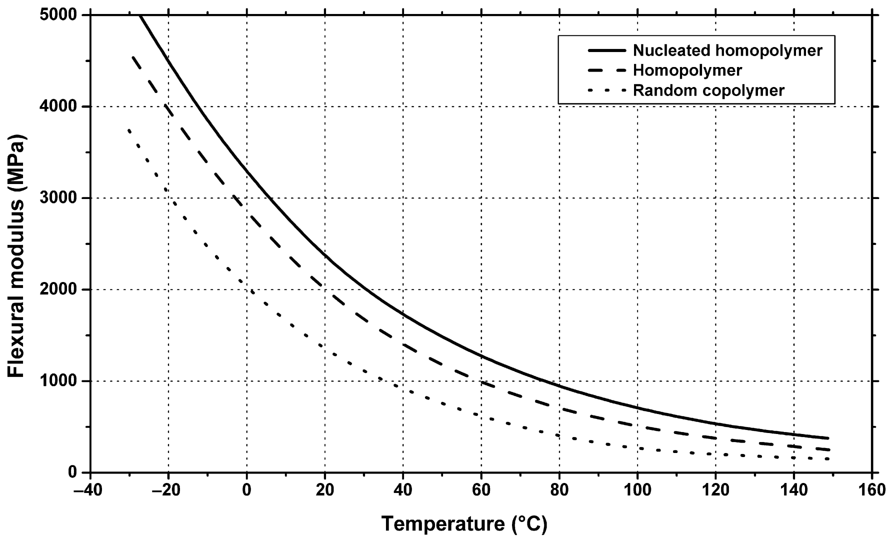

Figure 7.29 Flexural modulus vs. temperature for Chevron Phillips Chemical Marlex® PP resins.

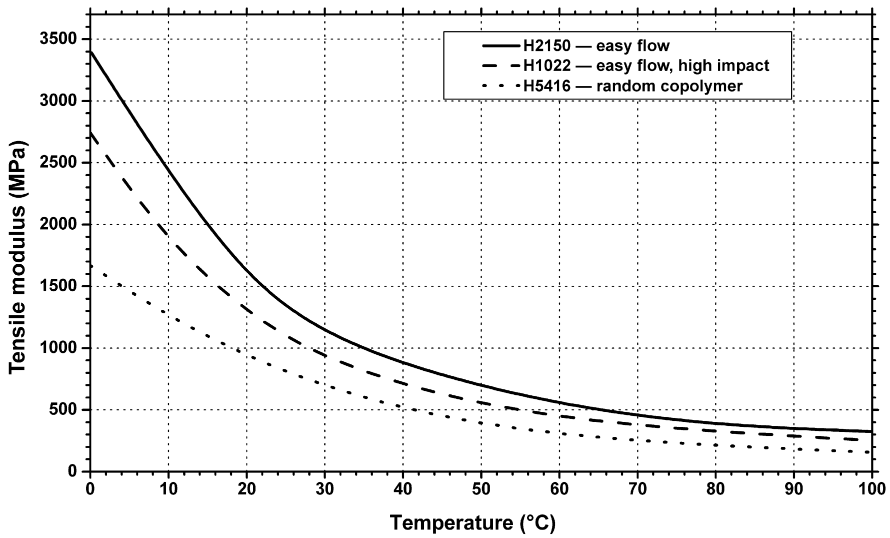

Figure 7.30 Tensile modulus vs. temperature for Basell Polyolefins Hostalen® PP resins [3].

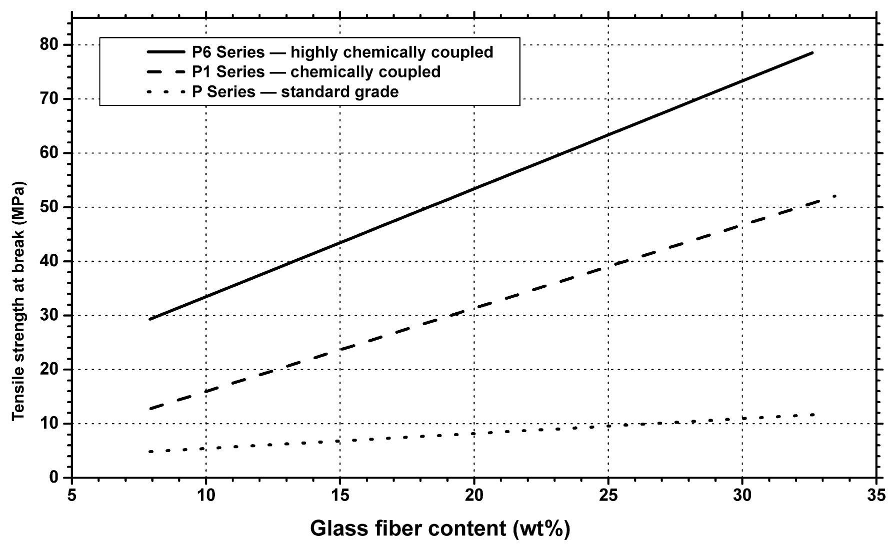

Figure 7.31 Tensile strength at break vs. glass fiber content at 23°C for Asahi Kasei Thermylene® PP resins.

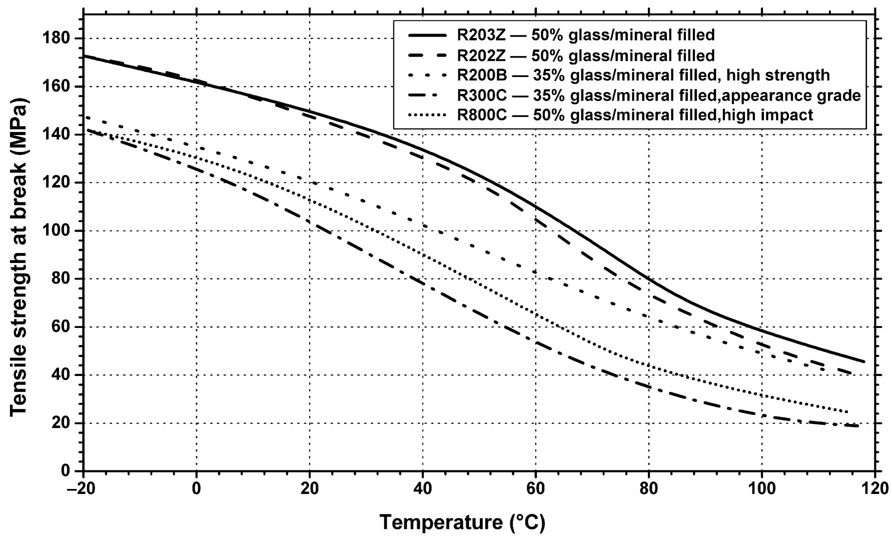

Figure 7.32 Tensile strength at break vs. temperature for Chisso America Olehard® glass and mineral-filled PP resins.

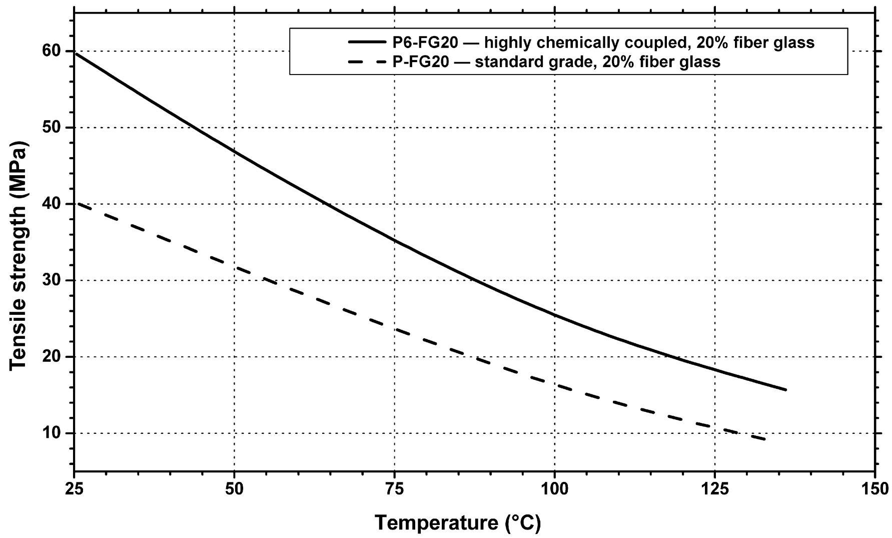

Figure 7.33 Tensile strength vs. temperature for Asahi Kasei Thermylene® PP resins.

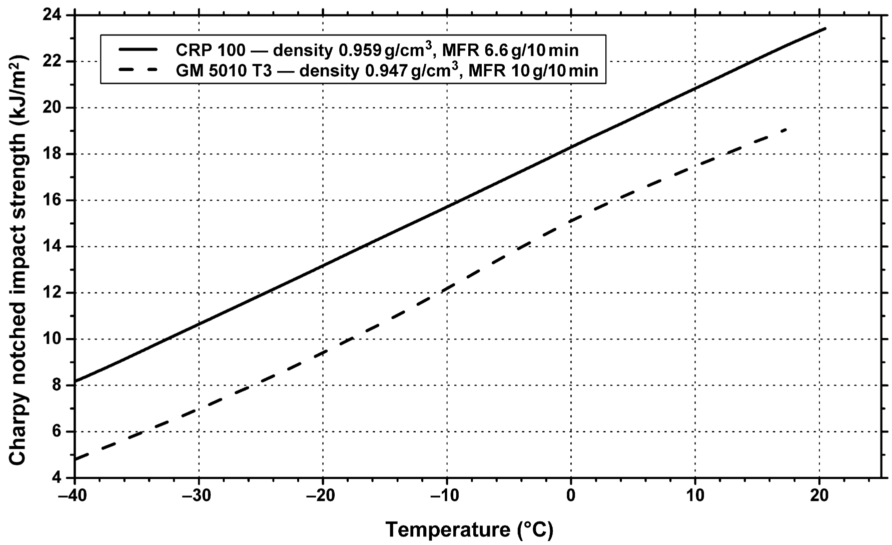

Figure 7.34 Notched Charpy impact strength vs. temperature for Basell Polyolefins Hostalen® PP resins [3].

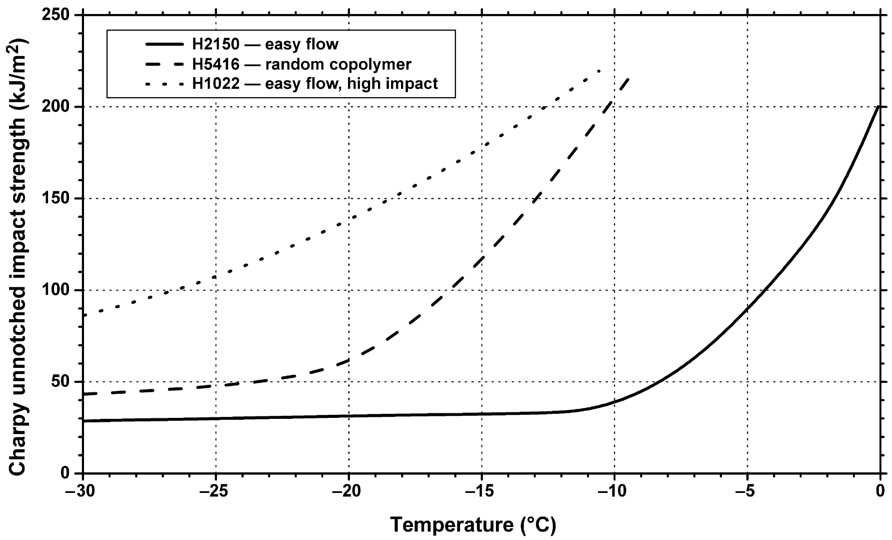

Figure 7.35 Notched Charpy impact strength vs. temperature for Basell Polyolefins Hostalen® PP resins [3].

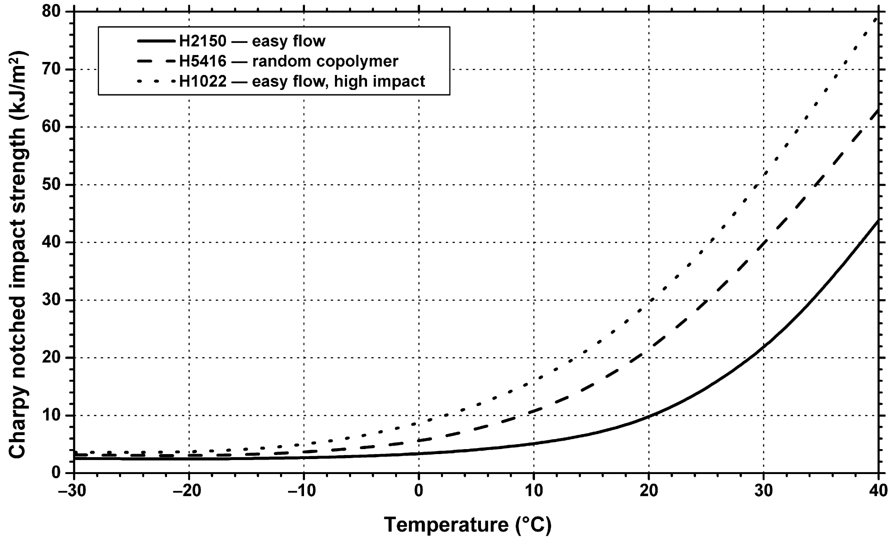

Figure 7.36 Notched Charpy impact strength vs. temperature for Basell Polyolefins Hostalen® PP resins [3].

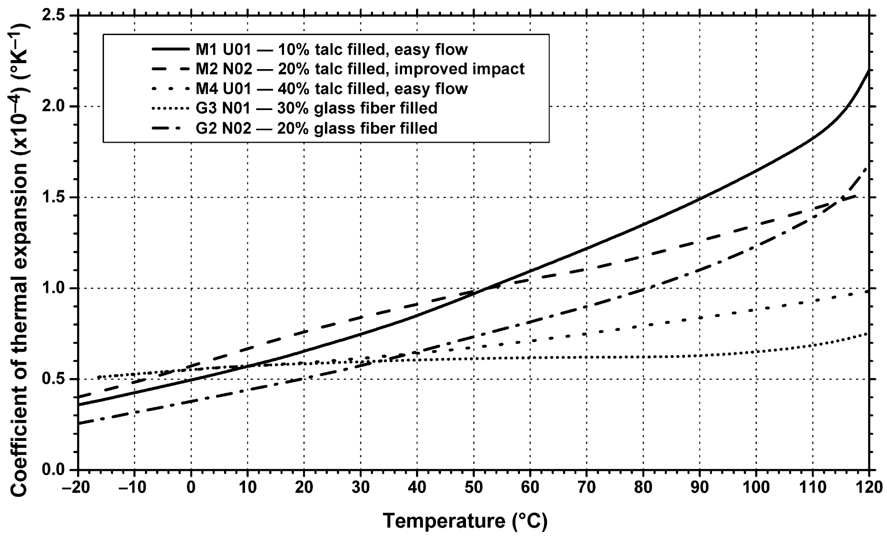

Figure 7.37 Coefficient of thermal expansion (in flow direction) vs. temperature for Basell Polyolefins Hostalen® PP resins.

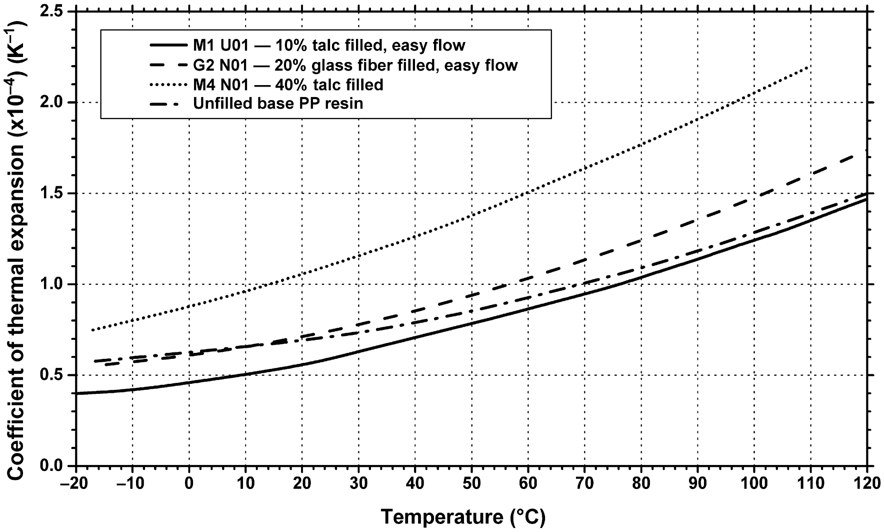

Figure 7.38 Coefficient of thermal expansion (in flow direction) vs. temperature for Basell Polyolefins Hostalen® PP resins.

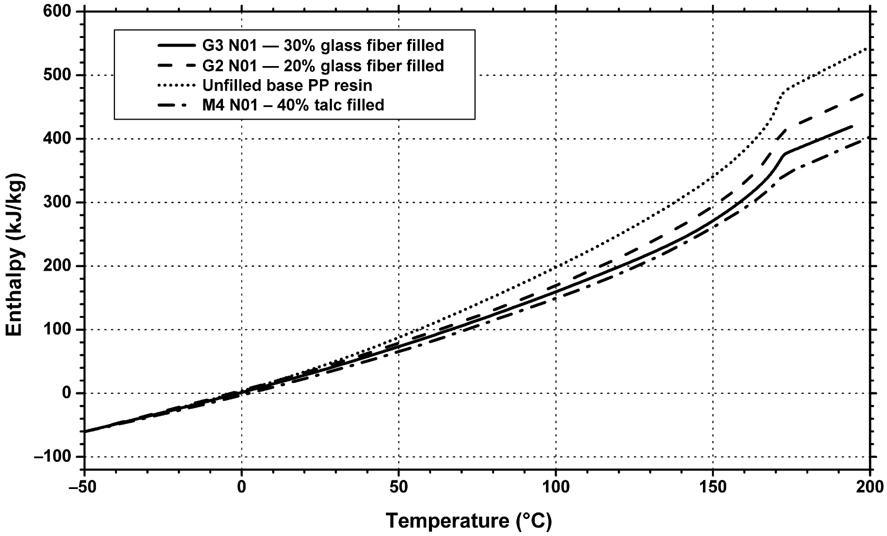

Figure 7.39 Enthalpy vs. temperature for Basell Polyolefins Hostalen® PP resins.

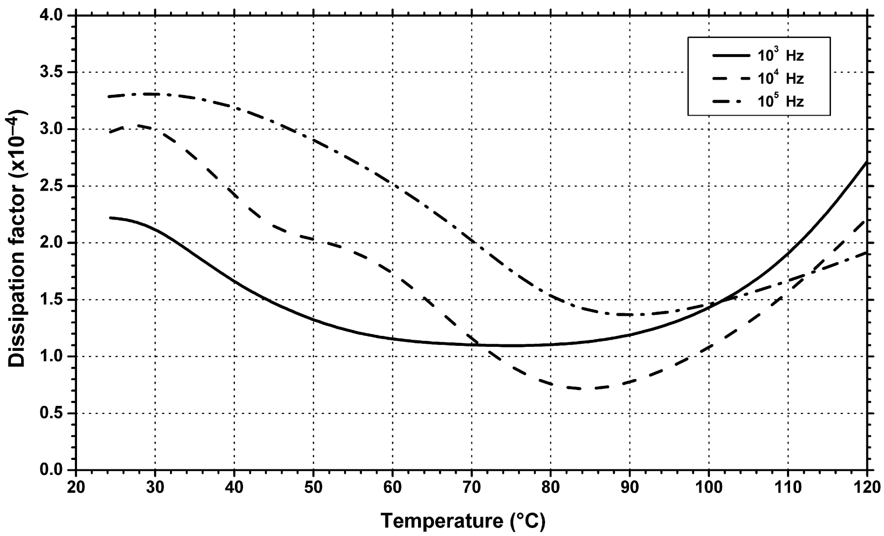

Figure 7.40 Dissipation factor vs. temperature and frequency for Basell Polyolefins Hostalen® PPN 1060 F PP resin.

Manufacturers and trade names: Mitsui Chemicals TPX™, Opulent™, Honeywell PMP; Chevron Philips Crystalor—discontinued.

Applications and uses: films, particularly release films, chemical tubing, cosmetic caps, and tubes.

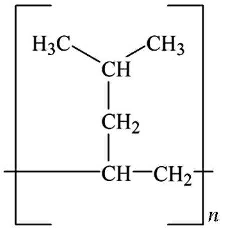

Figure 7.41 Structure of PMP.

Data for PMP plastics are shown in Figures 7.42–7.51.

7.4 Rigid Polyvinyl Chloride (PVC)

PVC is a flexible or rigid material that is chemically nonreactive. Rigid PVC is easily machined, heat formed, welded, and even solvent cemented. PVC can also be machined using standard metal working tools and finished to close tolerances and finishes without great difficulty. PVC resins are normally mixed with other additives such as impact modifiers and stabilizers, providing hundreds of PVC-based materials with a variety of engineering properties.

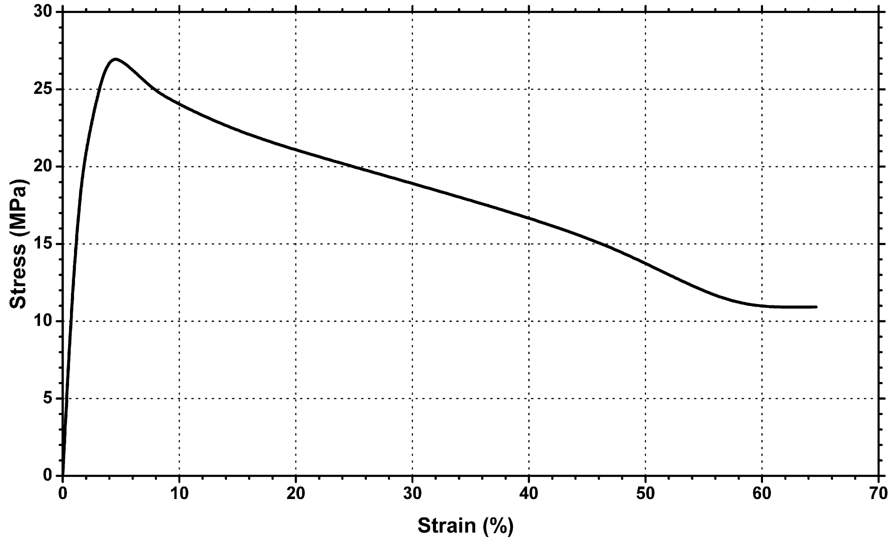

Figure 7.42 Stress vs. strain at room temperature for Ensinger Tecafine PMP [4].

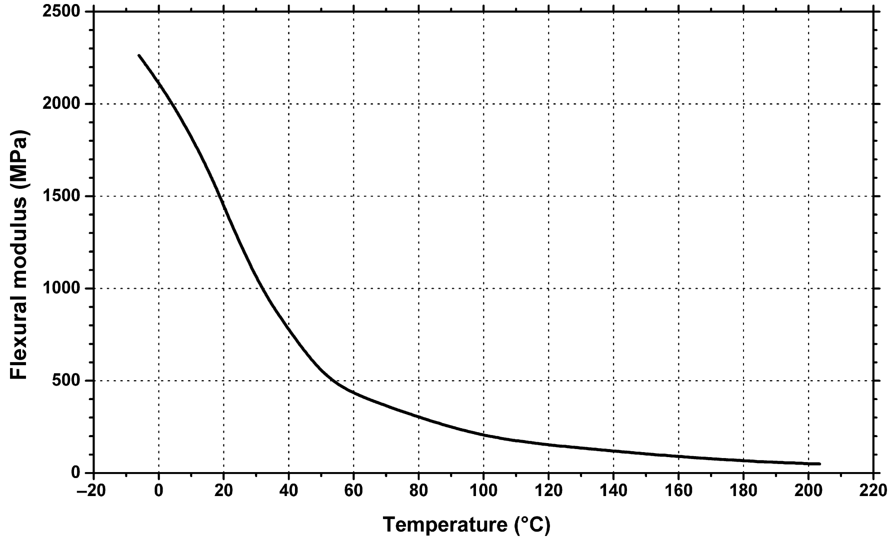

Figure 7.43 Flexural modulus vs. temperature for Mitsui Chemicals TPX™ RT18—general-purpose, unfilled PMP resin.

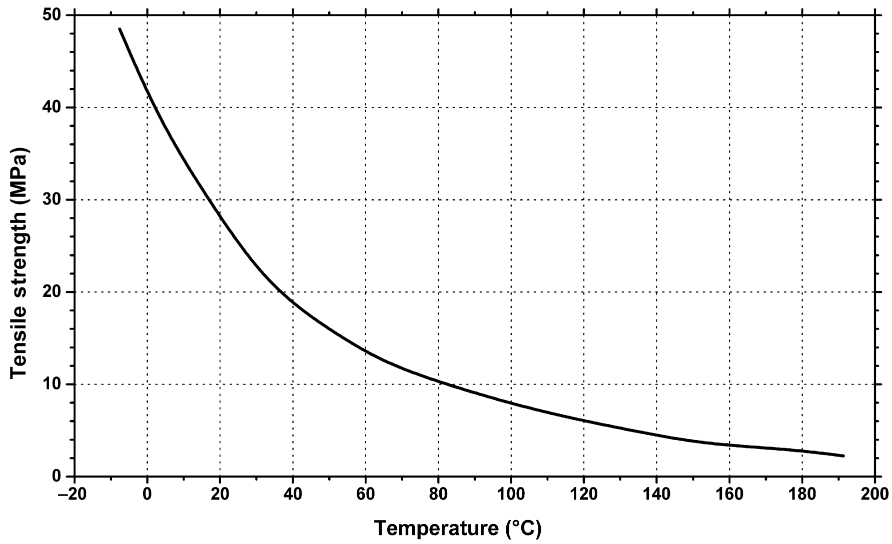

Figure 7.44 Tensile strength vs. temperature for Mitsui Chemicals TPX™ RT18—general-purpose, unfilled PMP resin [5].

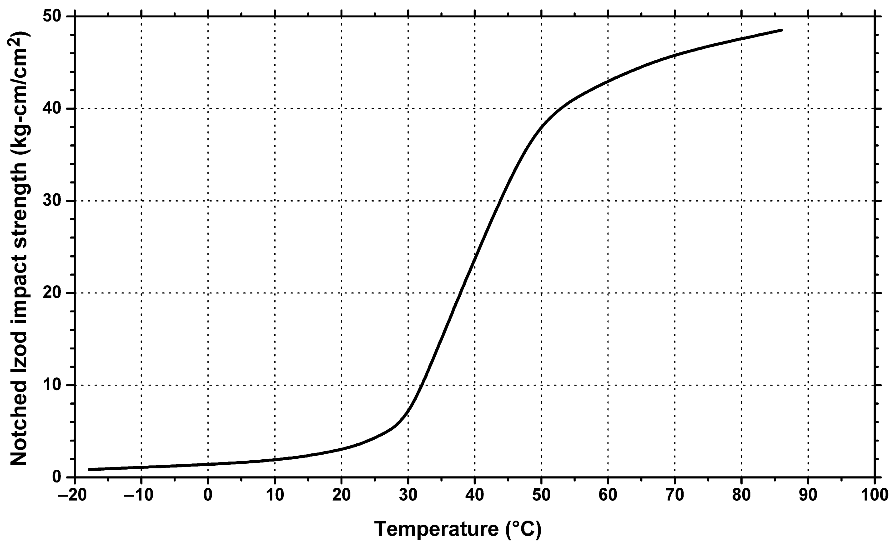

Figure 7.45 Notched Izod impact strength vs. temperature for Mitsui Chemicals TPX™ RT18—general-purpose, unfilled PMP resin.

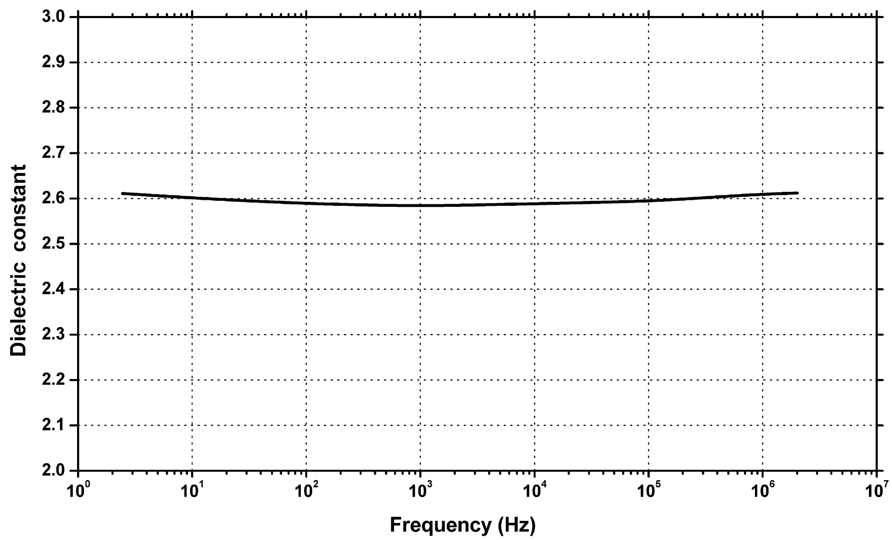

Figure 7.46 Dielectric constant vs. frequency at 20°C for Mitsui Chemicals FR-TPX™ T130—30% chopped glass filled PMP resin.

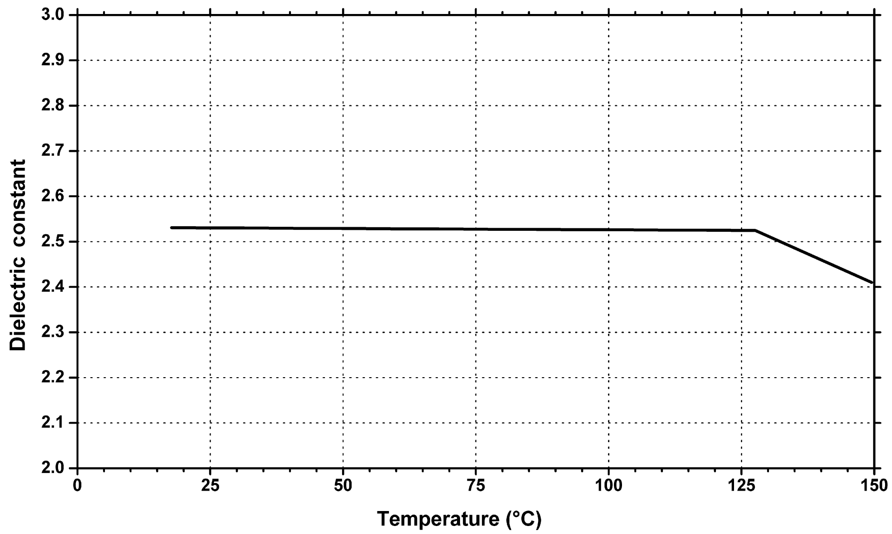

Figure 7.47 Dielectric constant at 1 MHz vs. temperature for Mitsui Chemicals FR-TPX™ T130—30% chopped glass filled PMP resin.

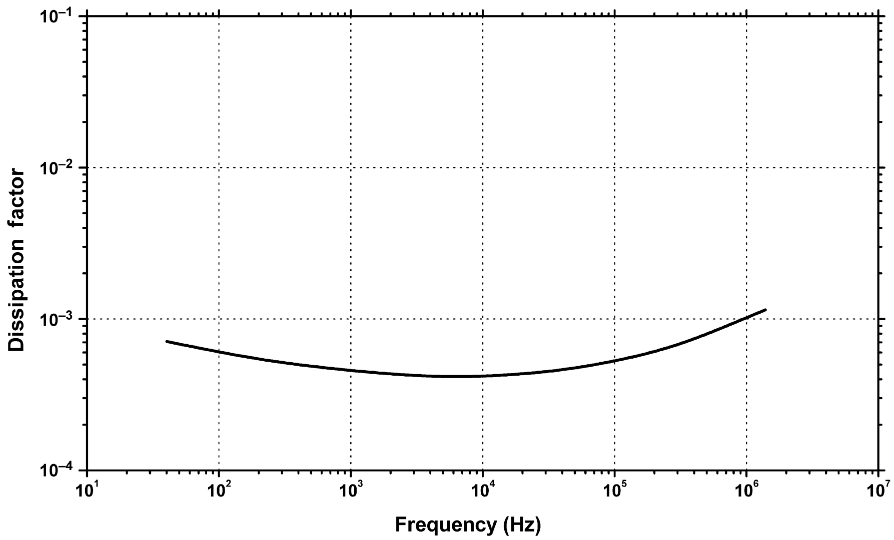

Figure 7.48 Dissipation factor vs. frequency at 20°C for Mitsui Chemicals FR-TPX™ T130—30% chopped glass filled PMP resin.

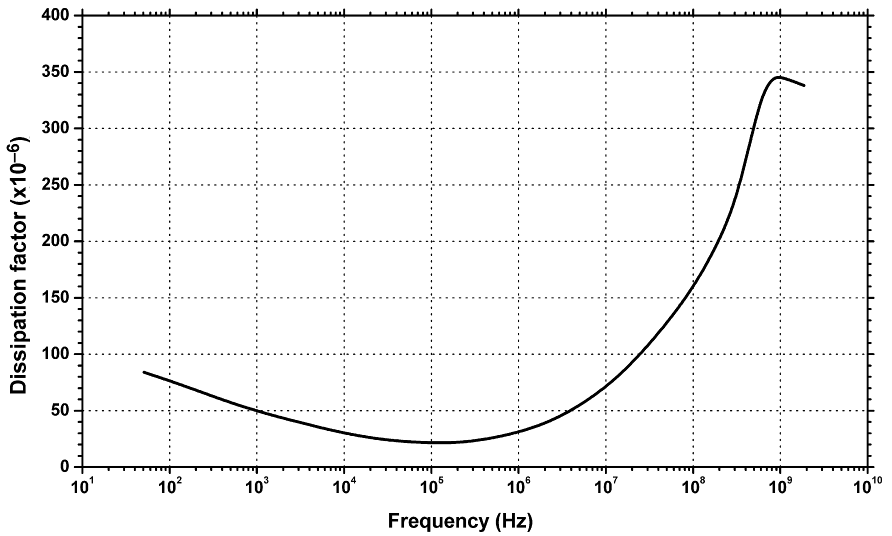

Figure 7.49 Dissipation factor vs. frequency for Mitsui Chemicals TPX™ RT18—general-purpose, unfilled PMP resin.

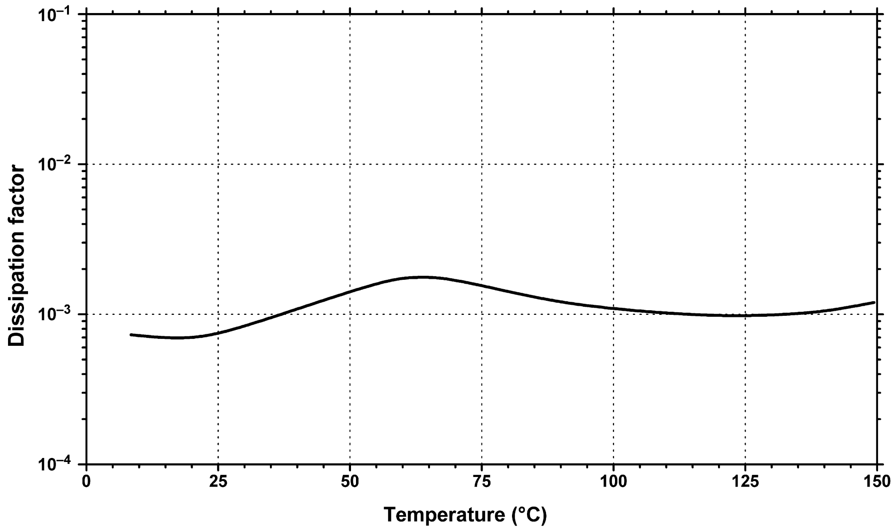

Figure 7.50 Dissipation factor vs. temperature at 1 MHz for Mitsui Chemicals FR-TPX™ T130—30% chopped glass filled PMP resin.

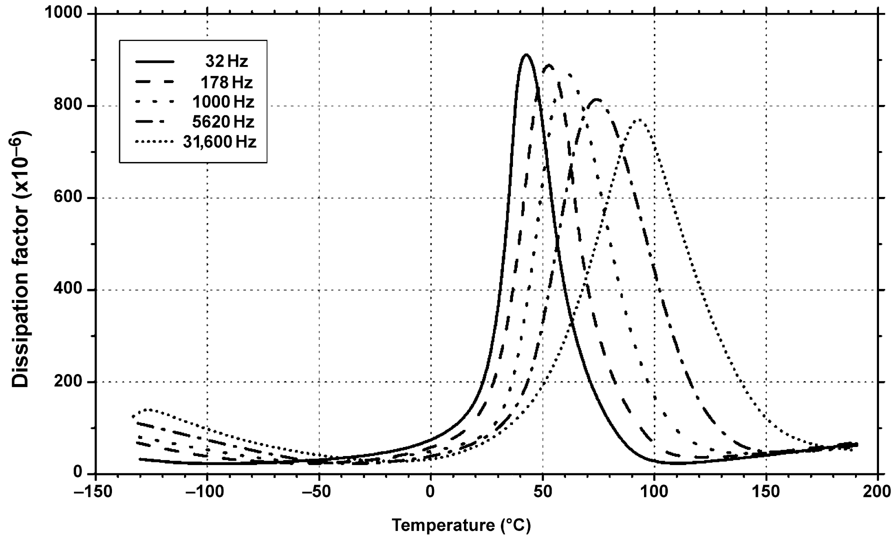

Figure 7.51 Dissipation factor vs. temperature and frequency for Mitsui Chemicals TPX™ RT18—general-purpose, unfilled PMP resin.

There are three broad classifications for rigid PVC compounds: Type II, chlorinated polyvinyl chloride (CPVC), and Type I. Type II differs from Type I due to greater impact values, but lower chemical resistance. CPVC has greater high temperature resistance. These materials are considered "unplasticized," because they are less flexible than the plasticized formulations. PVC has a broad range of applications from high volume construction related products to simple electric wire insulation and coatings. CAS numbers are 9002-86-2, 8063-94-3, 51248-43-2, and 93050-82-9.

Manufacturing and trade names: PolyOne Geon™, Fiberloc™; VPI LLC Mirrex®.

Applications and uses: Building siding, fence, and packaging are major markets for PVC. Rigid grades are blown into bottles and made into sheets for thermoforming boxes and blister packs. Flexible PVC compounds are used in food packaging applications because of their strength, transparency, processability, and low raw material cost. PVC film can be used in marine/boat windows, recreational vehicle windows, tents and awning windows, industrial curtains/enclosures, spray booths, rack covers, weld screens and partitions, clean rooms, golf cart covers, binder covers, tags and sign holders, menus, apparel and clothing, packaging, bags.

Data for PVC plastics are shown in Figures 7.52–7.59.

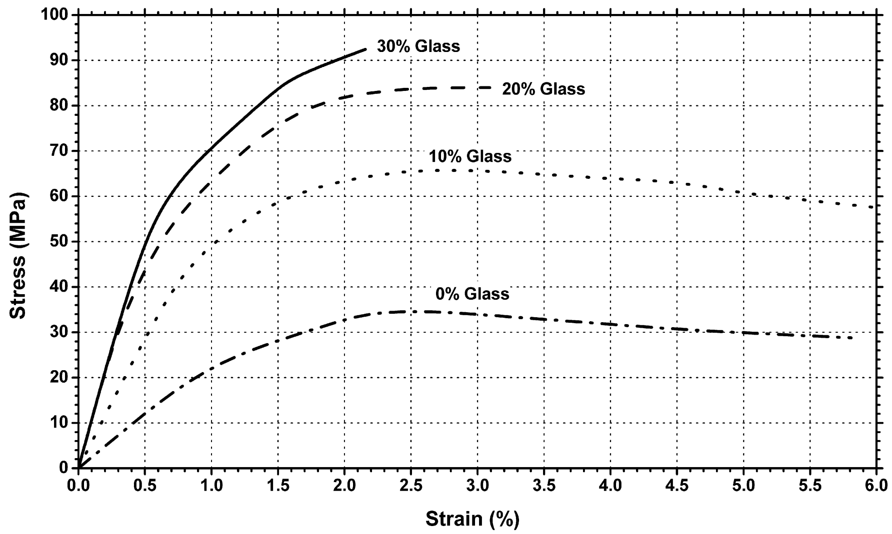

Figure 7.52 Stress vs. strain at 23°C for PolyOne Fiberloc™ rigid PVC resins with different amounts of glass fiber reinforcement.

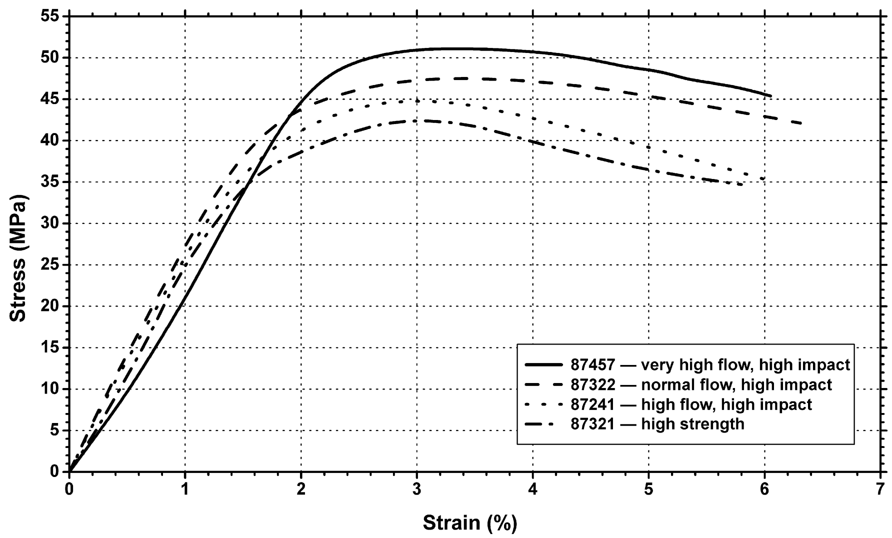

Figure 7.53 Stress vs. strain at 23°C for various PolyOne Geon™ rigid PVC resins.

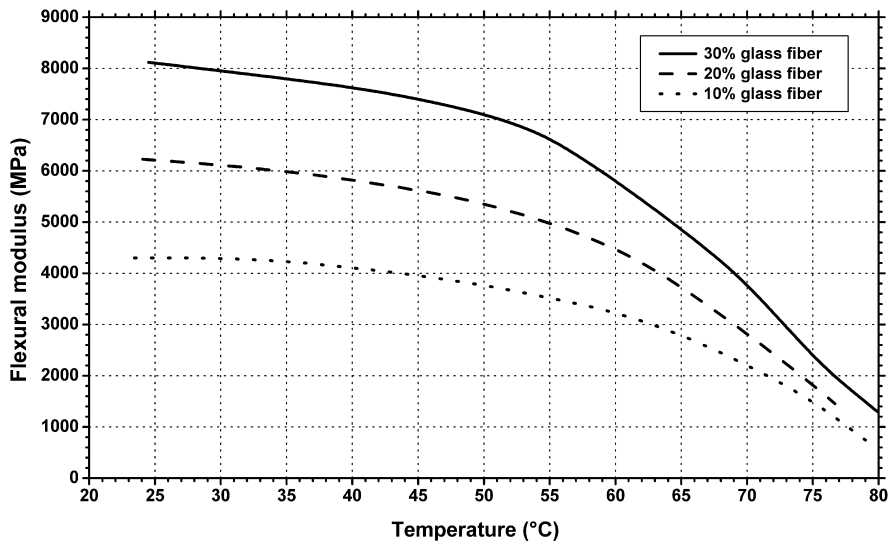

Figure 7.54 Flexural modulus vs. temperature for PolyOne Fiberloc™ rigid PVC resins with different amounts of glass fiber reinforcement.

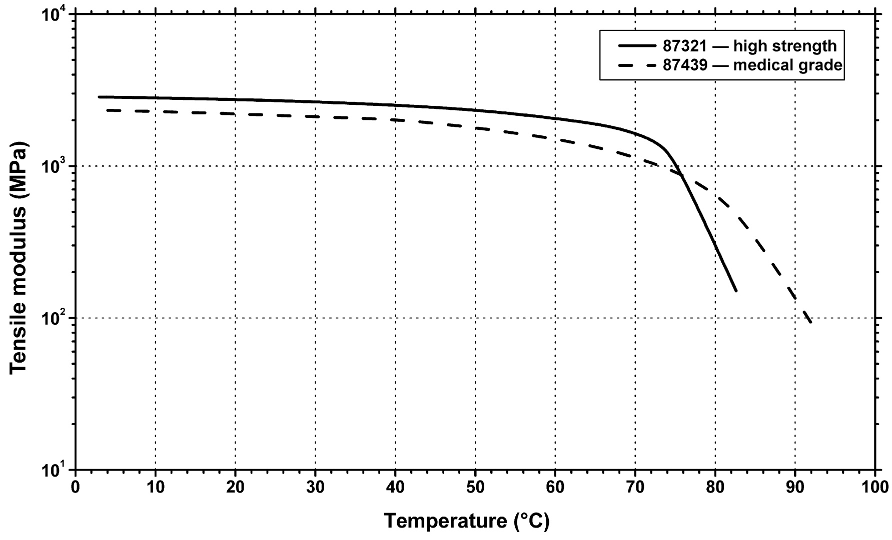

Figure 7.55 Tensile modulus vs. temperature for two PolyOne Geon™ rigid PVC resins.

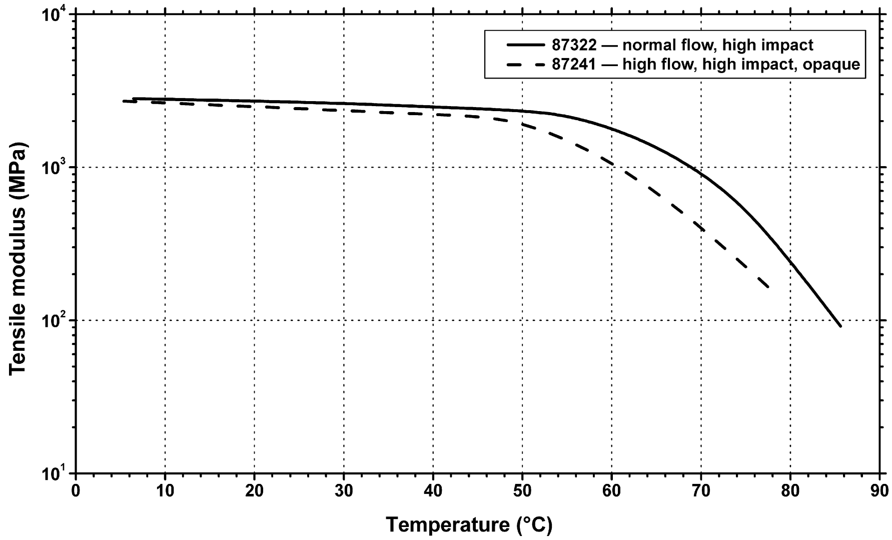

Figure 7.56 Tensile modulus vs. temperature for two PolyOne Geon™ rigid PVC resins.

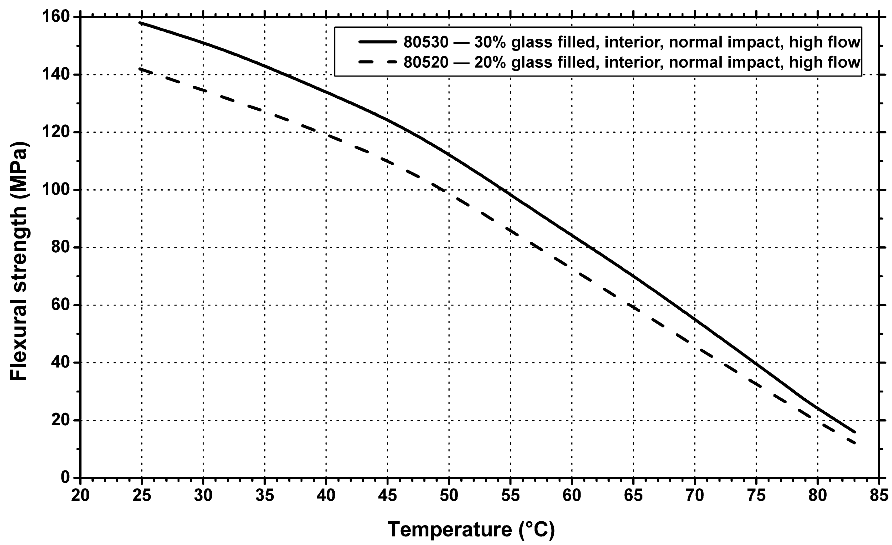

Figure 7.57 Flexural strength vs. temperature for PolyOne Fiberloc™ rigid PVC resins with different amounts of glass fiber reinforcement.

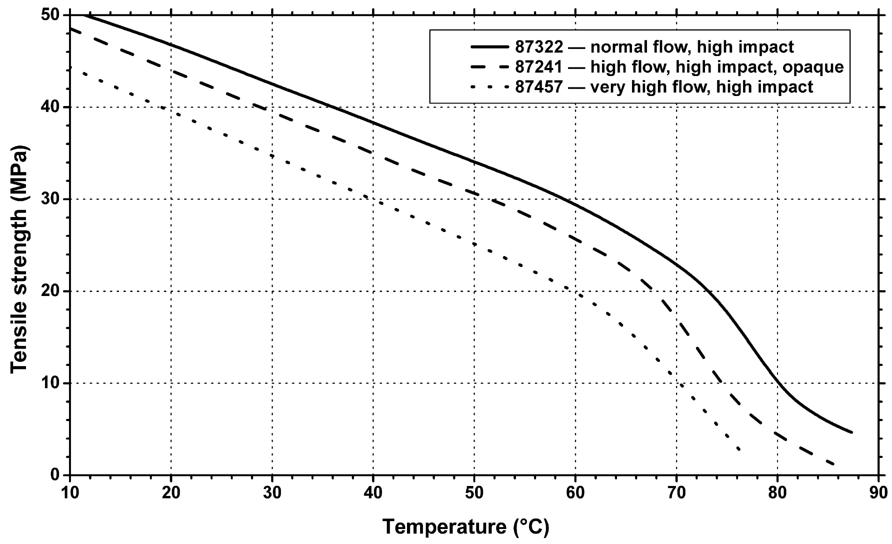

Figure 7.58 Tensile strength vs. temperature for PolyOne Geon™ rigid PVC resins.

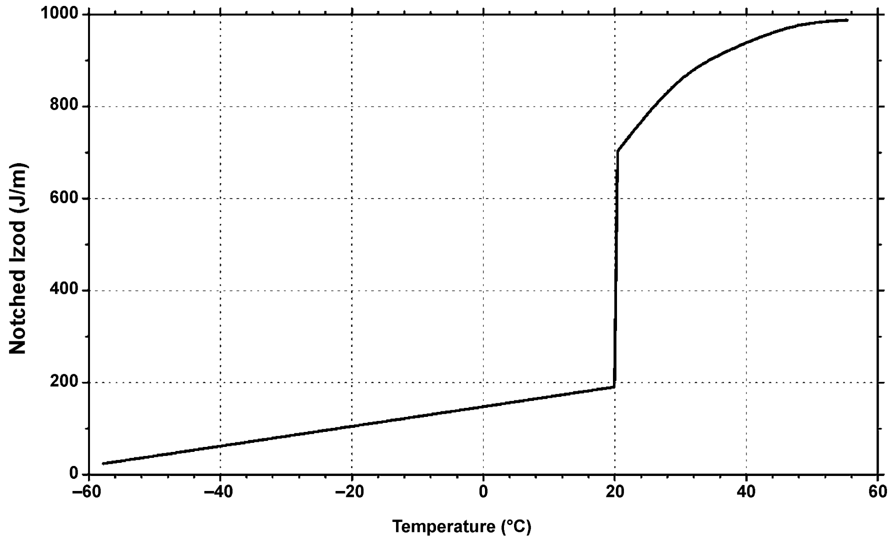

Figure 7.59 Notched Izod strength vs. temperature for PolyOne Geon™ 87241—high flow, high impact, opaque rigid PVC resin.

7.5 Cyclic Olefin Copolymer (COC)

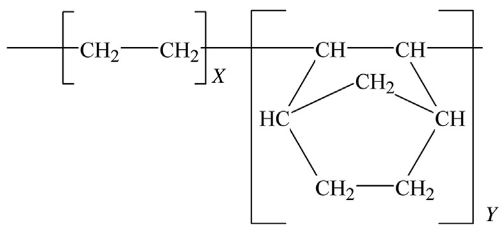

Figure 7.60 Chemical structure of COCs.

Cyclic olefin copolymer (COC) is an amorphous polyolefin made by reaction of ethylene and norbornene in varying ratios. Its structure is shown in Figure 7.60. The properties can be customized by changing the ratio of the monomers found in the polymer. Being amorphous it is transparent. Other performance benefits include:

- Low density
- Extremely low water absorption
- Excellent water vapor barrier properties
- High rigidity, strength, and hardness
- Variable heat deflection temperature up to 170°C
- Very good resistance to acids and alkalis

COC is often blended with other polyolefins.

Manufacturers and trade names: Topas Advanced Polymers Topas®.

Applications and uses: Transparent moldings such as lenses, sensors, primary packaging of pharmaceuticals, medical devices, and diagnostic disposables.

Data for COC plastics are shown in Figures 7.61–7.67.

7.6 Polyacrylics

While a large number of acrylic polymers are manufactured, PMMA is by far the most common. The structure of PMMA is shown in Figure 7.68. Nearly everyone has heard of Plexiglas®. PMMA has two very distinct properties that set the products apart from others. First it is optically clear and colorless. It has a light transmission of 92%. The 4% reflection loss at each surface is unavoidable. Second its surface is extremely hard. They are also highly weather resistant. PMMA has a CAS number of 9011-14-7.

Acrylic resins are available as homopolymer (primarily PMMA), copolymer, and terpolymer.

Manufacturers and trade names: Lucite International Lucite® Diakon® and Perspex®; Evonik Industries Plexiglas®, Acrylite®, Europlex®, and Rohaglas®; Arkema Oroglas®; Rowland Technologies, Inc. SolaTuf®; Mitsubishi Rayon Co., Ltd. Shinkolite®; Altuglas International Plexiglas®; Novacor.

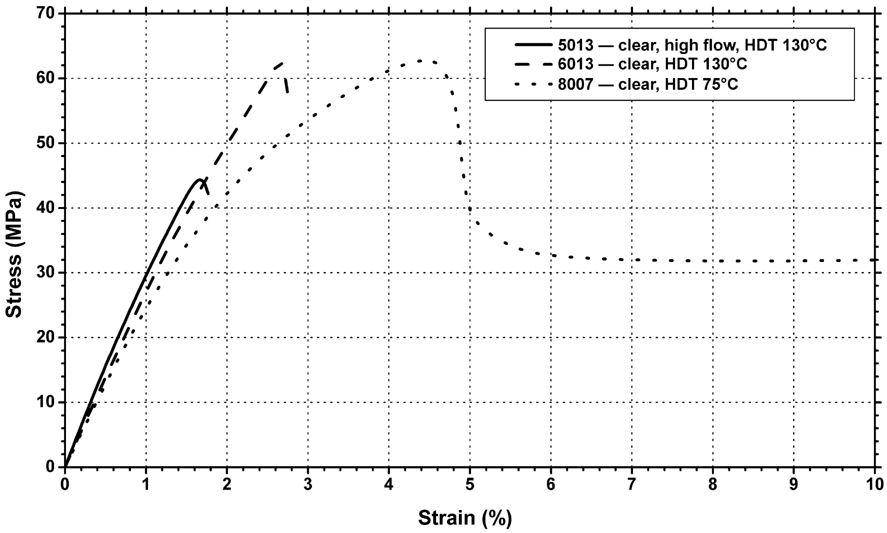

Figure 7.61 Stress vs. strain at 23°C for several Topas Advanced Polymers Topas® COC resins [6].

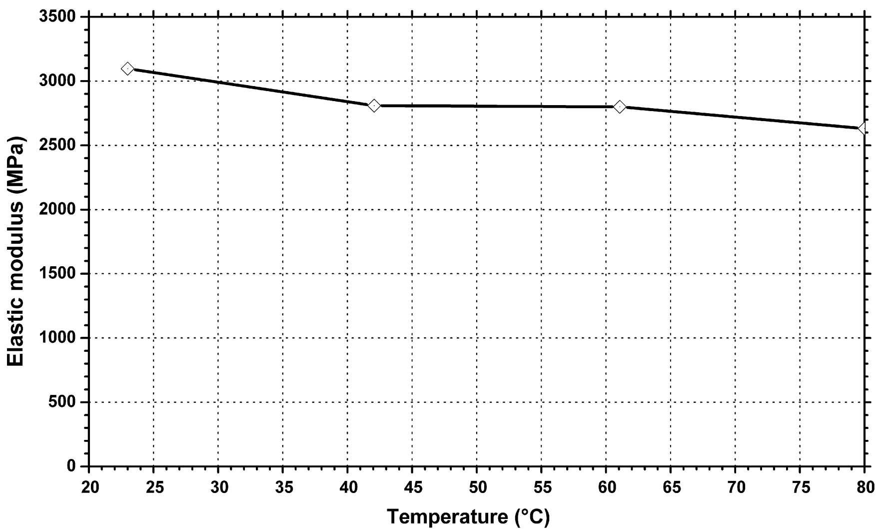

Figure 7.62 Elastic modulus vs. temperature for Topas Advanced Polymers Topas® 5013, 6013, 6015, and 6017 COC resins [6].

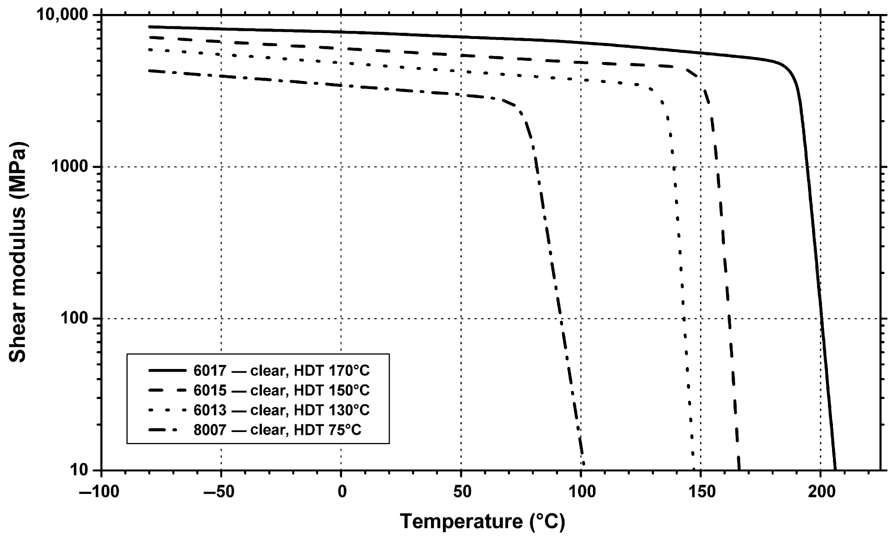

Figure 7.63 Shear modulus vs. temperature for Topas Advanced Polymers Topas® COC resins [6].

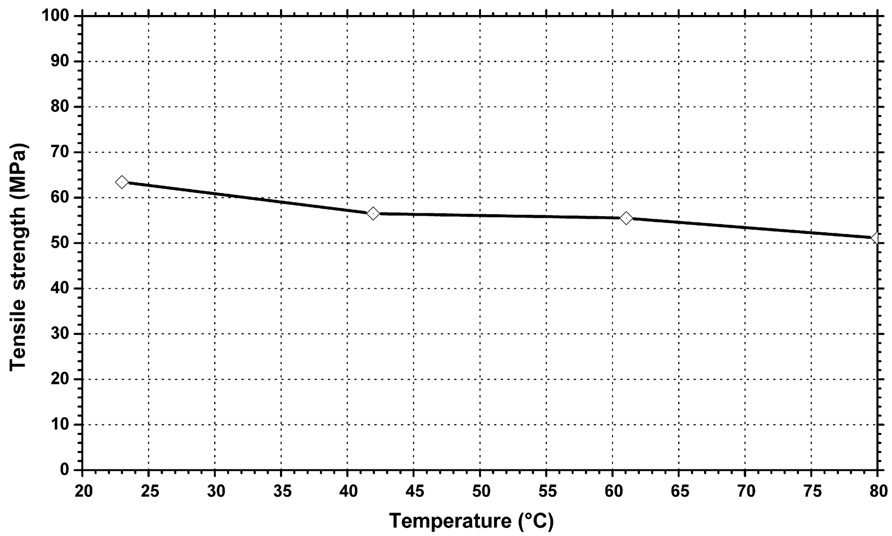

Figure 7.64 Tensile strength vs. temperature for Topas Advanced Polymers Topas® 5013, 6013, 6015, and 6017 COC resins [6].

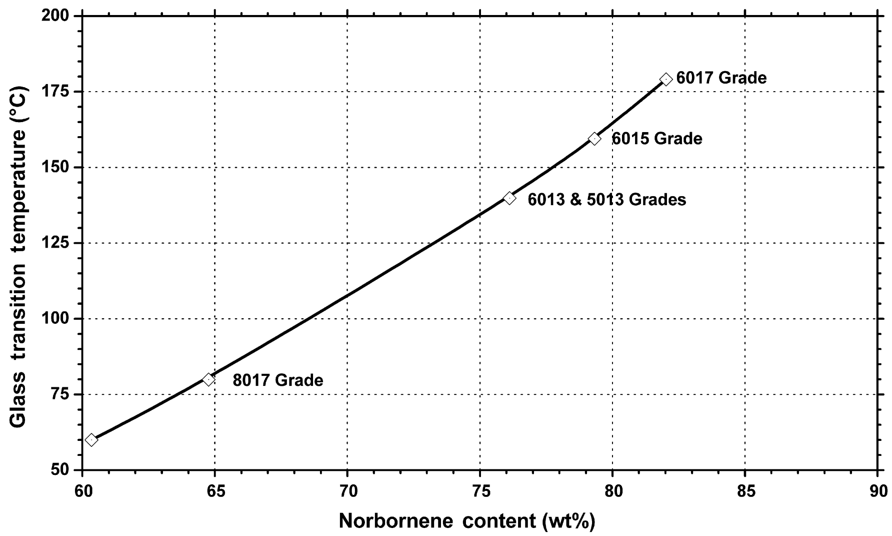

Figure 7.65 Glass transition temperature vs. norbornene content for Topas Advanced Polymers Topas® COC resins [6].

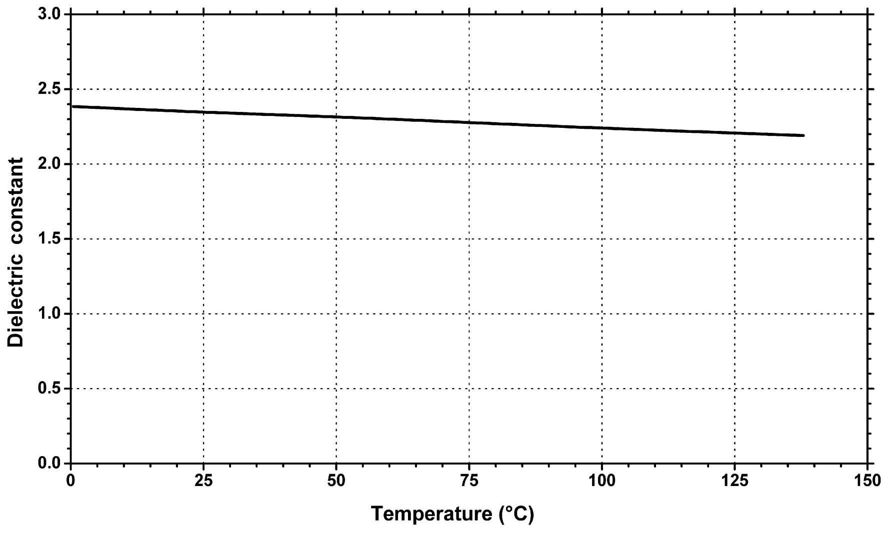

Figure 7.66 Dielectric content vs. temperature for Topas Advanced Polymers Topas® 6015—clear, HDT 150°C COC resin.

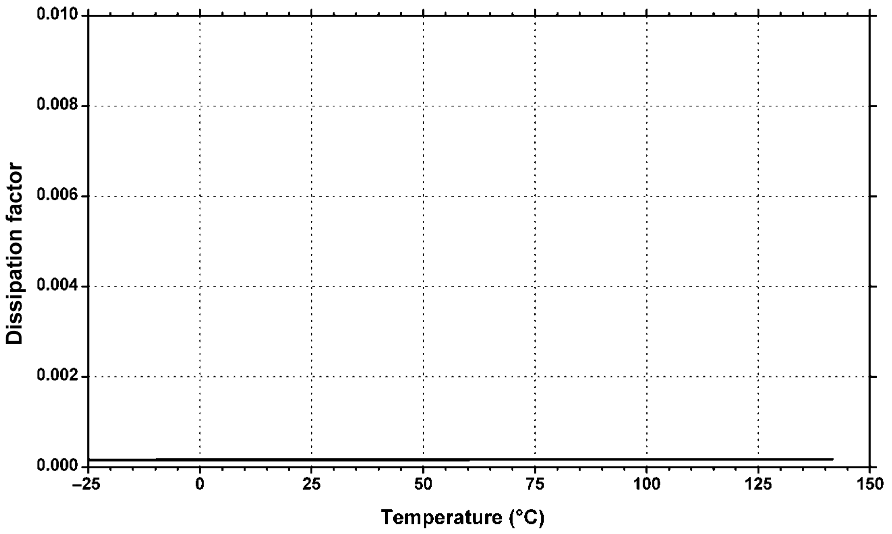

Figure 7.67 Dissipation factor vs. temperature for Topas Advanced Polymers Topas® 6015—clear, HDT 150°C COC resin [6].

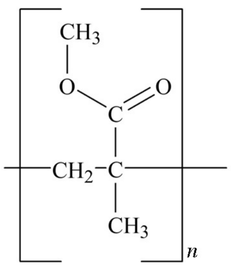

Figure 7.68 Structure of PMMA.

Applications and uses: optical parts, display items, tube and profile extrusion, automotive rear lights and dashboard lenses, extruded sheet, copying equipment and lighting diffusers, UV protective films for exterior laminates.

Data for acrylic plastics are shown in Figures 7.69–7.82.

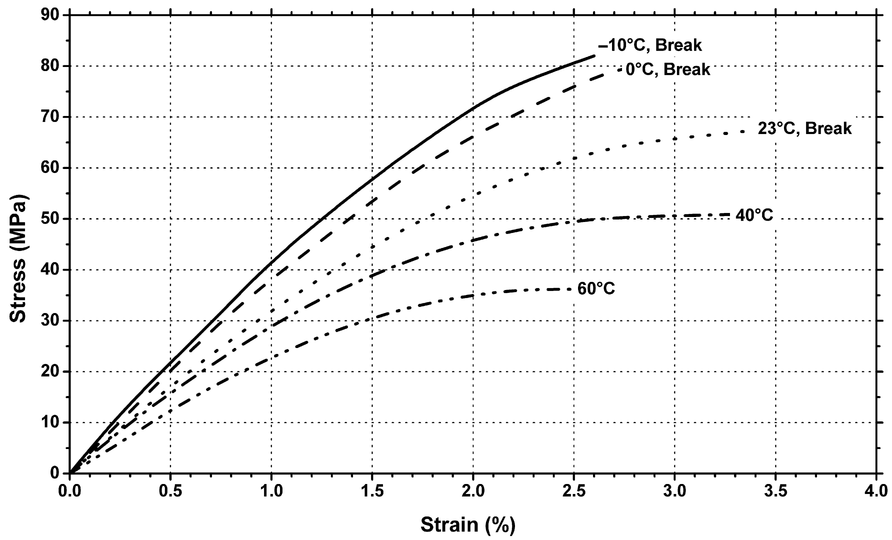

Figure 7.69 Stress vs. strain at various temperatures for Evonik Industries Plexiglas® 6N—standard grade acrylic resin.

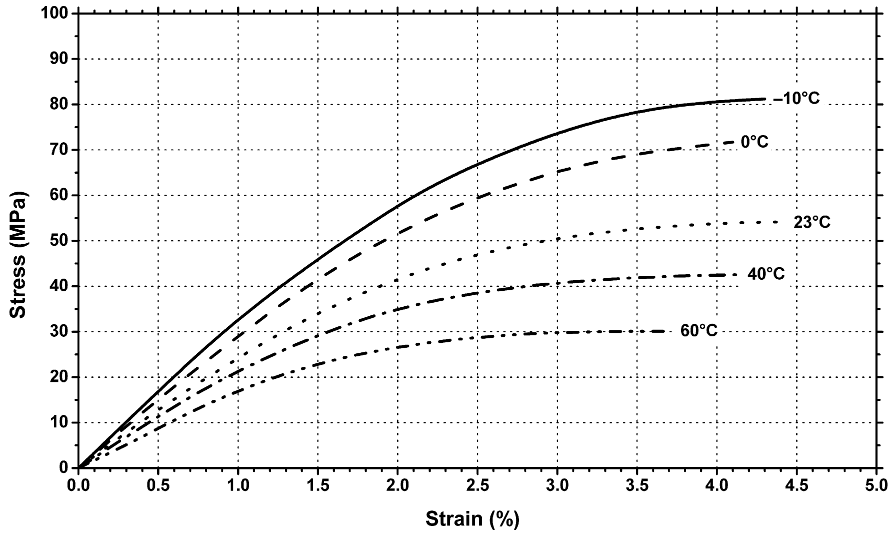

Figure 7.70 Stress vs. strain at various temperatures for Evonik Industries Plexiglas® zk20—high impact grade acrylic resin.

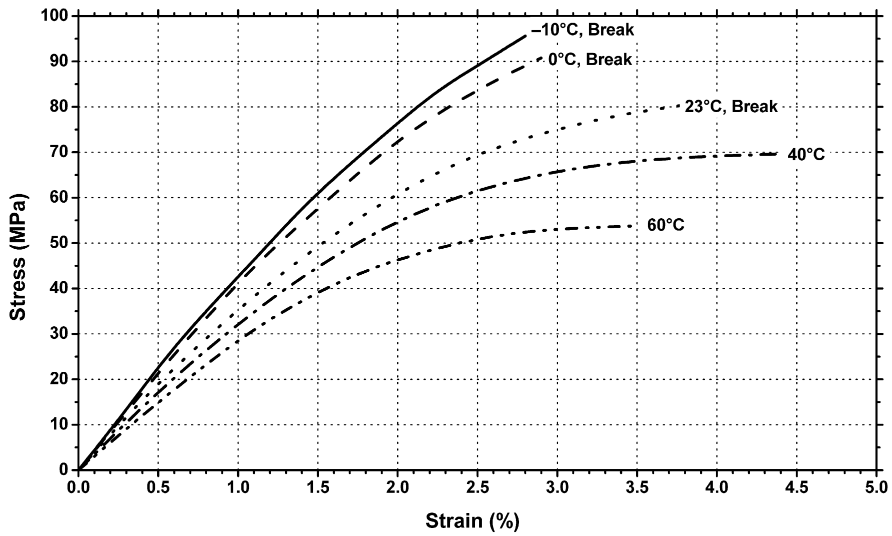

Figure 7.71 Stress vs. strain at various temperatures for Evonik Industries Plexiglas® hw55—heat resistant grade acrylic resin.

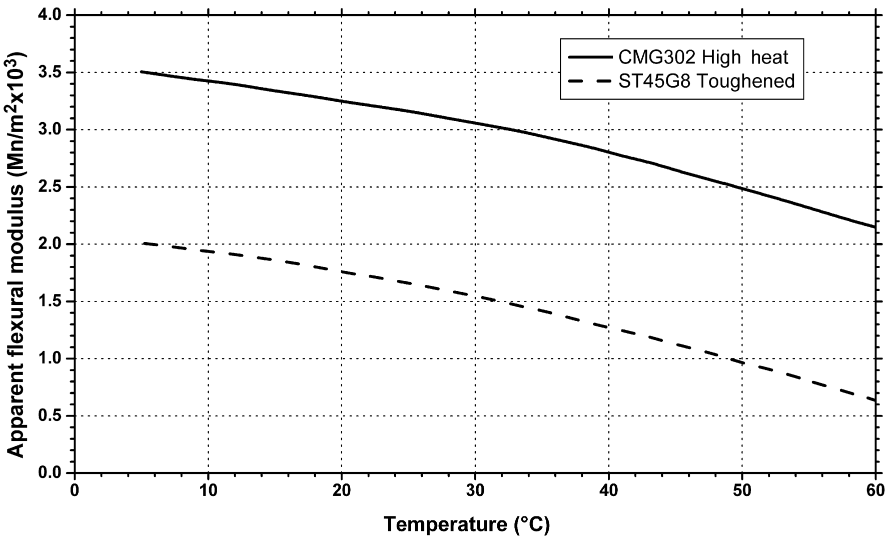

Figure 7.72 100-s apparent flexural modulus vs. temperature for Lucite International Diakon® acrylic resins [7].

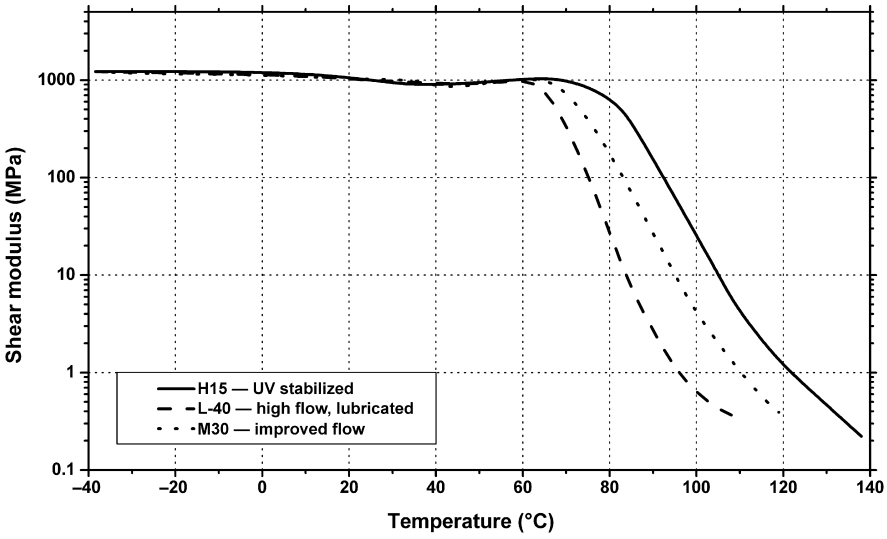

Figure 7.73 Shear modulus vs. temperature for Cyro Industries Acrylite® acrylic resins.

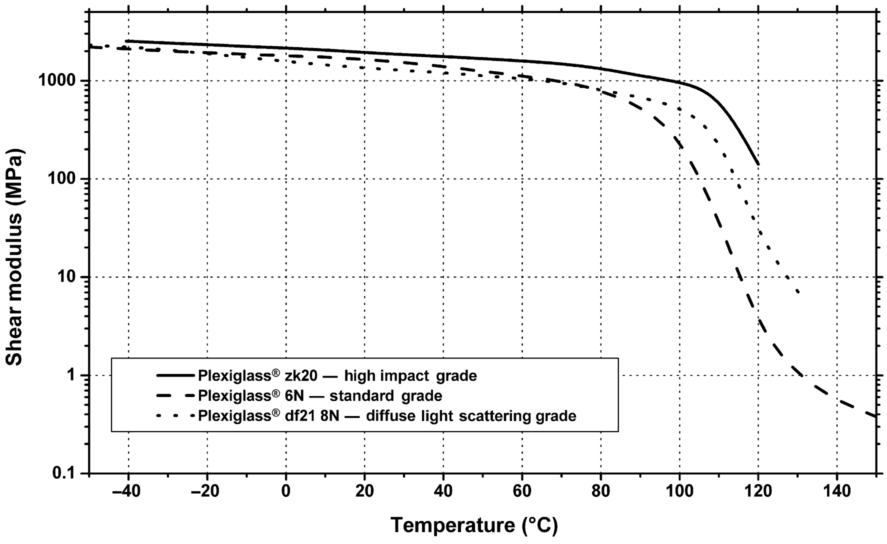

Figure 7.74 Shear modulus vs. temperature for Evonik Industries Plexiglas® acrylic resins.

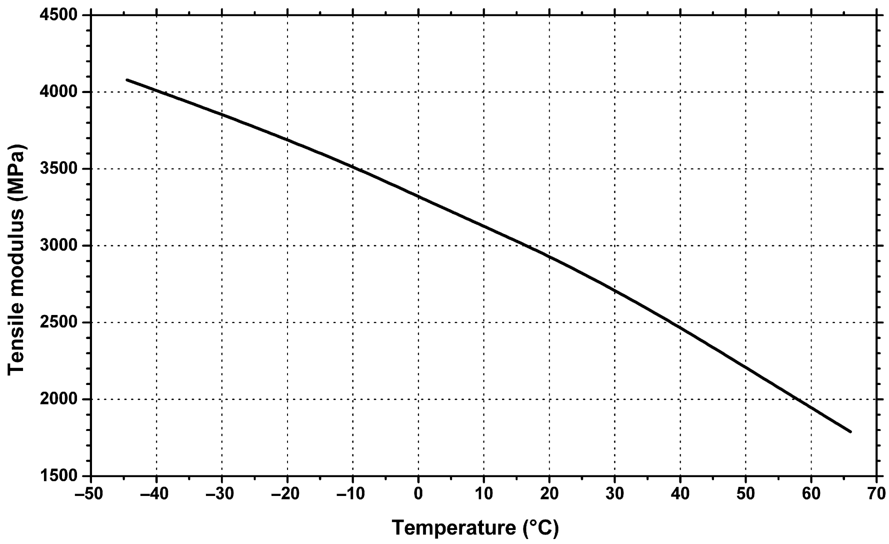

Figure 7.75 Tensile modulus vs. temperature for general-purpose acrylic resin.

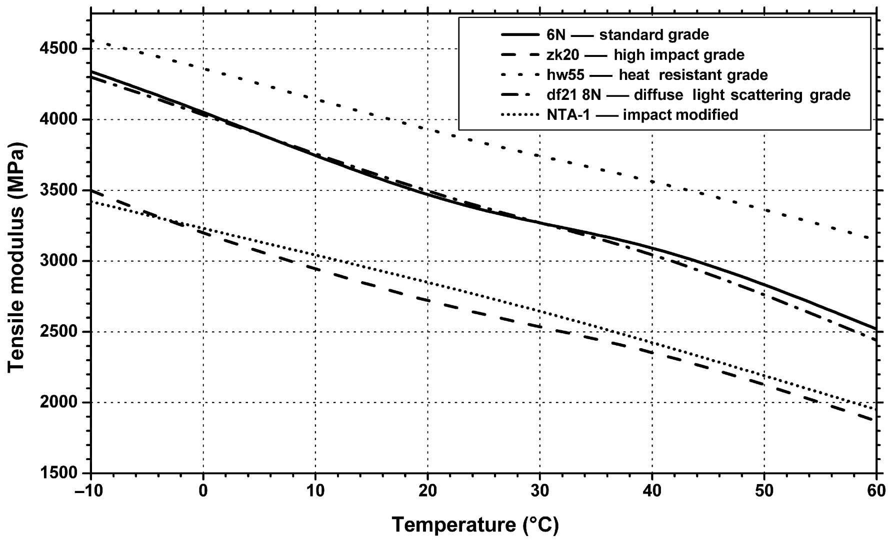

Figure 7.76 Tensile modulus vs. temperature for Evonik Industries Plexiglas® acrylic resins.

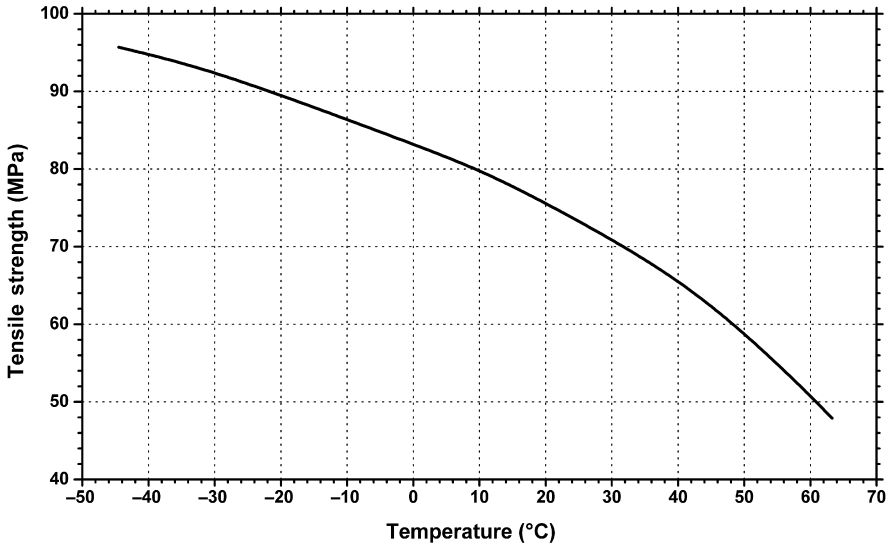

Figure 7.77 Tensile strength vs. temperature for general-purpose acrylic resin.

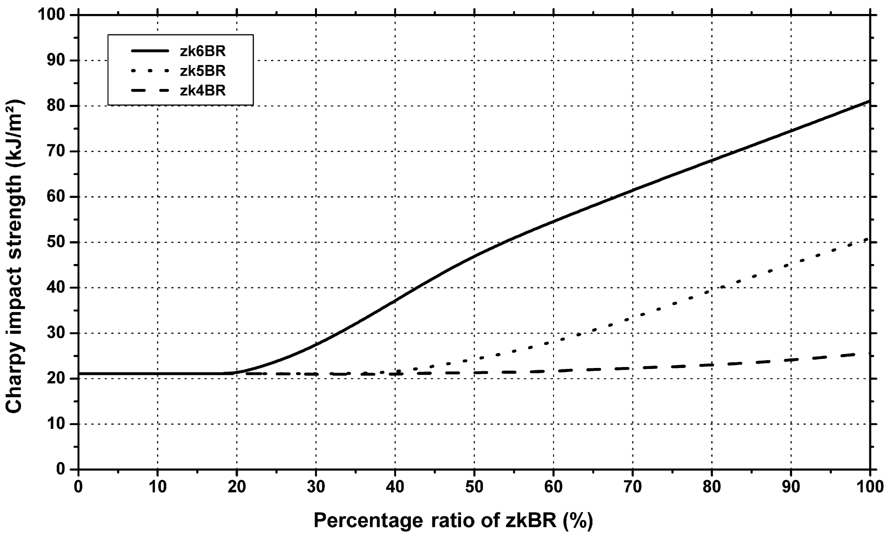

Figure 7.78 Charpy impact strength of Evonik Industries Plexiglas® 7N—general-purpose extrusion grade acrylic resin vs. percentage of Plexiglas® zkBR additives.

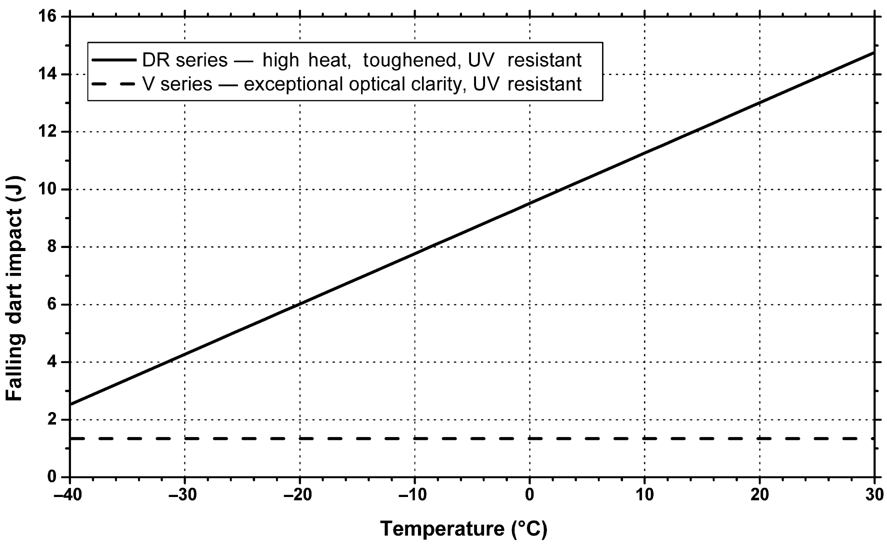

Figure 7.79 Impact strength vs. temperature for Evonik Industries Plexiglas® acrylic resins [8]. *Note*: sample size: 152 mm × 152 mm × 3.2 mm.

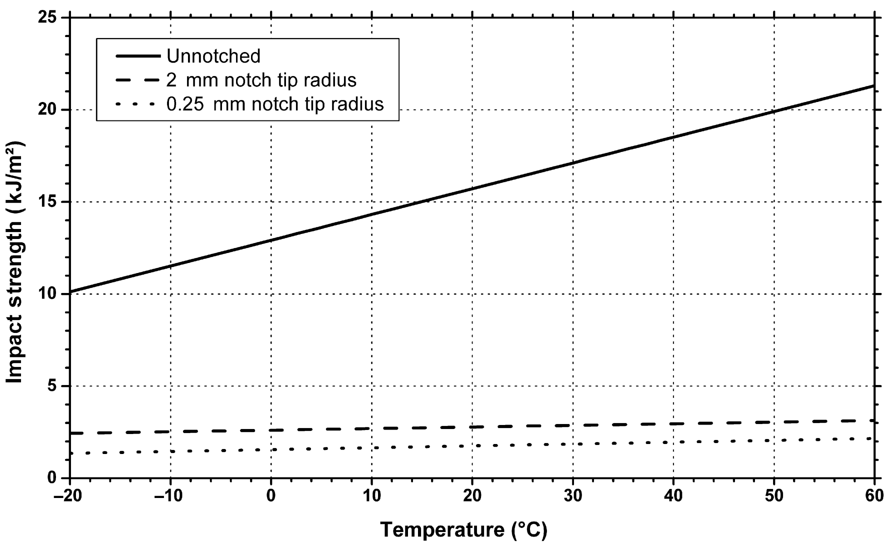

Figure 7.80 Charpy impact strength vs. temperature for Lucite International Diakon® CMG302 general-purpose high heat acrylic resin [7].

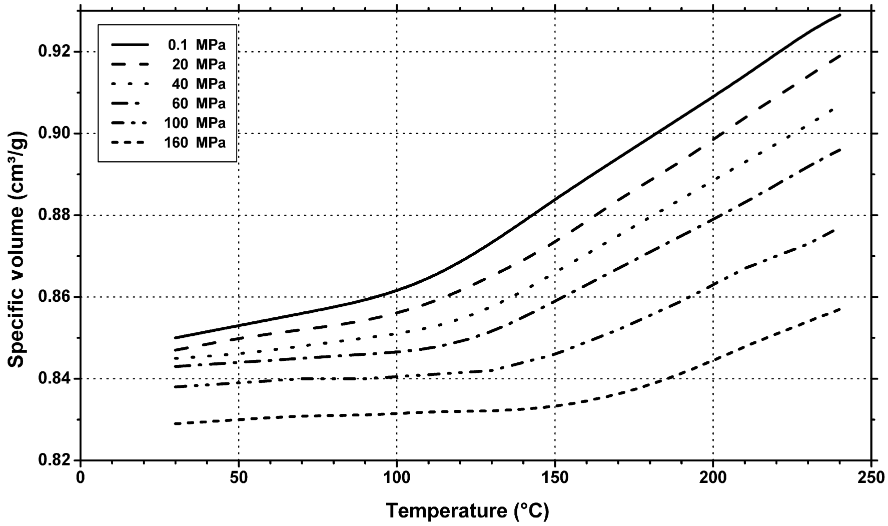

Figure 7.81 Specific volume as a function of temperature and pressure (PVT) for Evonik Industries Plexiglas® 7N—general-purpose extrusion grade acrylic resin.

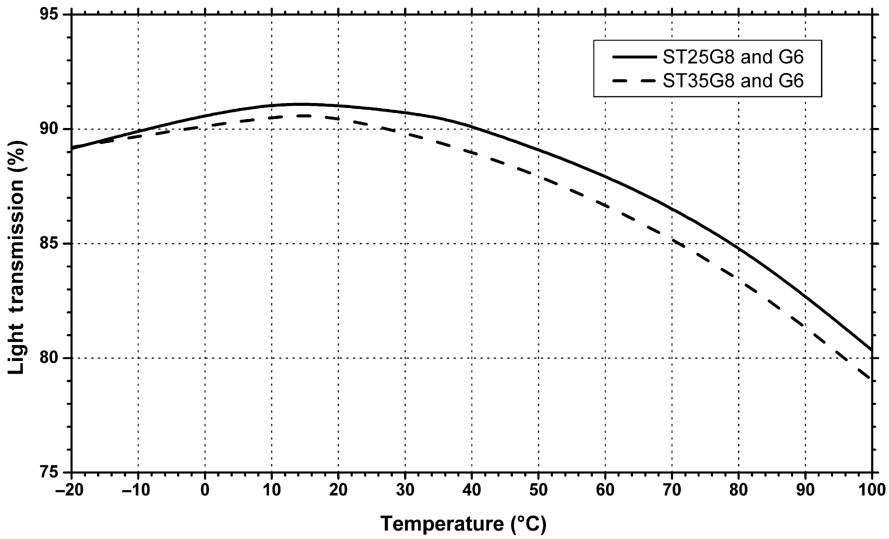

Figure 7.82 Light transmission vs. temperature for Lucite® Diakon® ST grades toughened acrylic polymers [7].

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