

8 Polyolefins, Polyvinyls, and Acrylics

This chapter focuses on polymers made from monomers that contain a carbon–carbon double bond through which the polymer is made by addition polymerization as discussed in Section 1.1.1. An alkene, also called an olefin, is a chemical compound made of only carbon and hydrogen atoms 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 alkene of this series is ethylene. 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. There are many other vinyl monomers that substitute different functional groups onto the carbon–carbon double bond. Vinyl alcohol is a particularly important one. Acrylic polymers are also polymerized through the carbon–carbon double bond. Methyl methacrylate is the monomer used to make poly(methyl methacrylate).

8.1 Polyolefins

The structures of some of the monomers used to make polyolefins are shown in Figure 8.1. Structures of the polymers may be found in the appropriate sections containing the data for those materials.

8.1.1 Polyethylene

Polyethylene (PE) can be made in a number of ways. The method by which 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 to the ASTM D1248—12 Standard Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable, are as follows:

- Ultra low-density polyethylene (ULDPE), polymers with densities ranging from 0.890 to 0.905 g/cm³, contains comonomer.

- Very low-density polyethylene (VLDPE), polymers with densities ranging from 0.905 to 0.915 g/cm³, contains comonomer.
- Linear low-density polyethylene (LLDPE), polymers with densities ranging from 0.915 to 0.935 g/cm³, contains comonomer.
- Low-density polyethylene (LDPE), polymers with densities ranging from about 0.915 to 0.935 g/cm³.
- Medium-density polyethylene (MDPE), polymers with densities ranging from 0.926 to 0.940 g/cm³, may or may not contain comonomer.
- High-density polyethylene (HDPE), polymers with densities ranging from 0.940 to 0.970 g/cm³, may or may not contain comonomer.

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

Figure 8.2 shows the differences graphically. The differences in the branches in terms of number and length affect the density and melting points of some of the types.

Branching affects the crystallinity. A diagram of a representation of the crystal structure of PE is

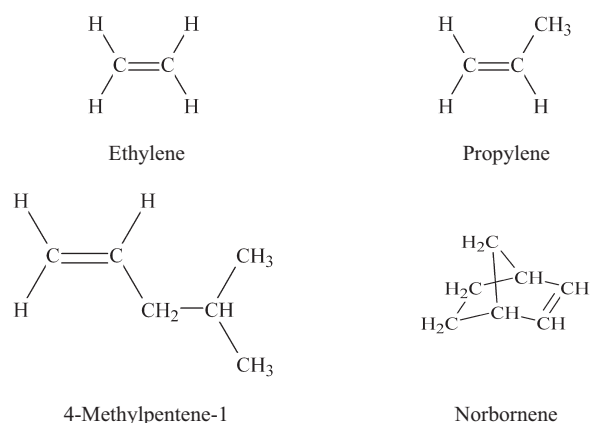


Figure 8.1 Chemical structures of some monomers used to make polyolefins.

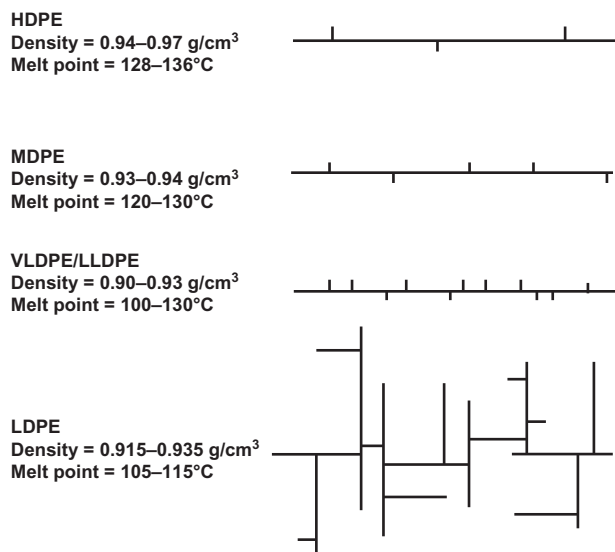


Figure 8.2 Graphical depictions of PE types.

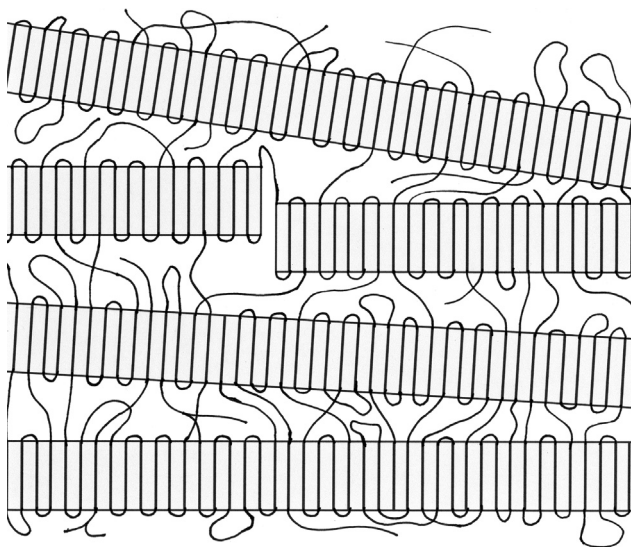


Figure 8.3 Graphical diagram of PE crystal structure.

shown in Figure 8.3. 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 8.3. A high degree of branching would reduce the size of the crystalline regions, which leads to lower crystallinity.

Thermooxidative degradation:

Random scission is the primary initial degradation pathway in PE. As shown in Figure 8.4, the scission produces a pair of radicals. The radicals

can rearrange, transfer, and react to produce preferentially propene and 1-hexene, although other hydrocarbons may be produced in smaller quantities. As shown in Figure 8.4, the radical tends to locate on the fifth carbon because of the geometrically favorable chain arrangement that has a transitional six-member ring. Oxygen can react with the radicals to produce peroxides and hydroperoxides. Polymer branching may also occur.

Stabilization:

- **Acid scavenger:** such as hydrotalcite.
- **Phenolic antioxidant:** such as 2,6-di-*tert*-butyl-4-(4,6-bis(octylthio)-1,3,5-triazine-2-ylamino) phenol.
- **Phosphite:** such as bis-(2,4-di-*t*-butylphenol) pentaerythritol diphosphite.
- **Thiosynergist:** such as didodecyl-3,30-thiodipropionate.
- **Quencher:** such as (2,20-thiobis(4-*tert*-octylphenolato))-*N*-butylamine-nickel(II).
- **Optical brightener:** such as 2,20-(2,5-thiophenediyl) bis(5-*tert*-butylbenzoxazole).

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

Applications and uses: Packaging including films, bottles, water pipes, hip and knee replacements, toys.

Data for PE plastics are shown in Figures 8.5–8.7.

8.1.2 Polypropylene

The three main types of polypropylene (PP) generally available are as follows:

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.

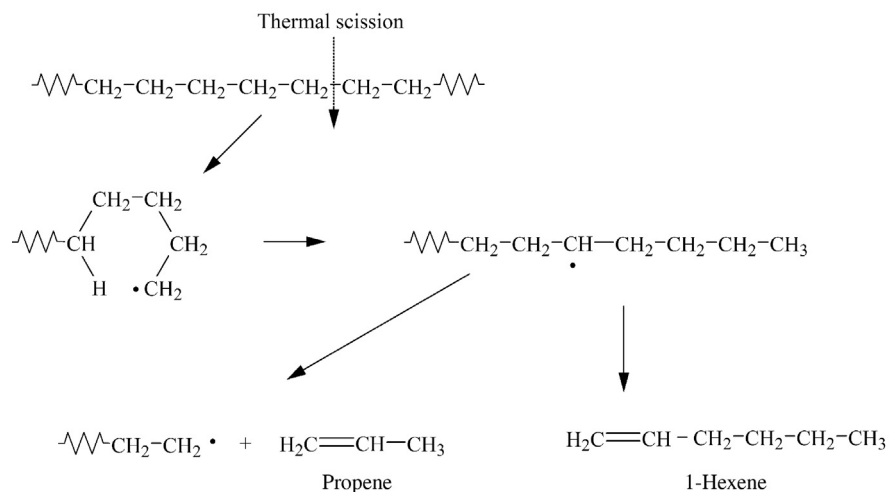


Figure 8.4 Degradation pathways of PE that produce propene and 1-hexene.

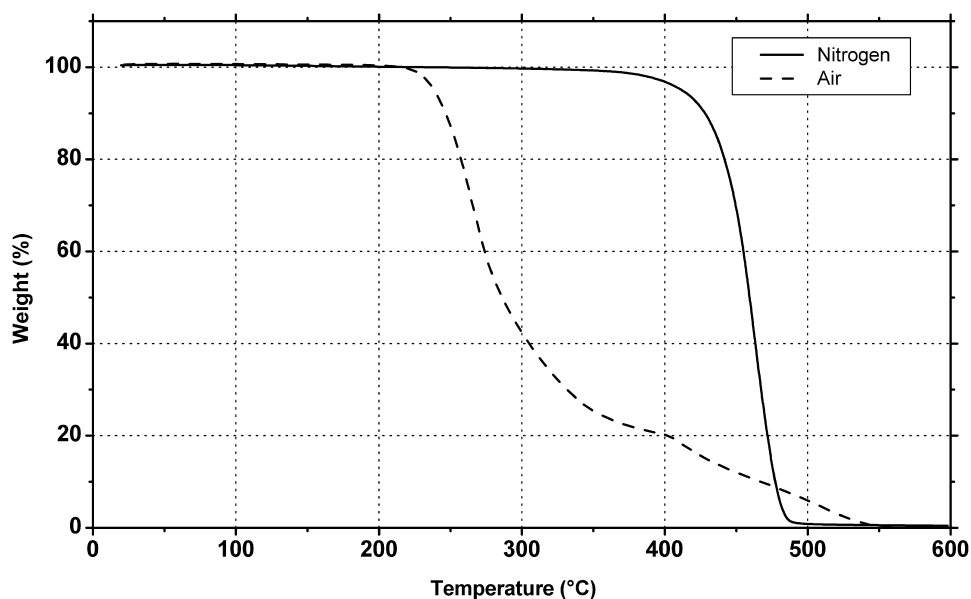


Figure 8.5 Thermogravimetric analysis (TGA) of PE in air and nitrogen [1].

2. *Random copolymers* (homophasic copolymer) 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 copolymer), 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 at 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.

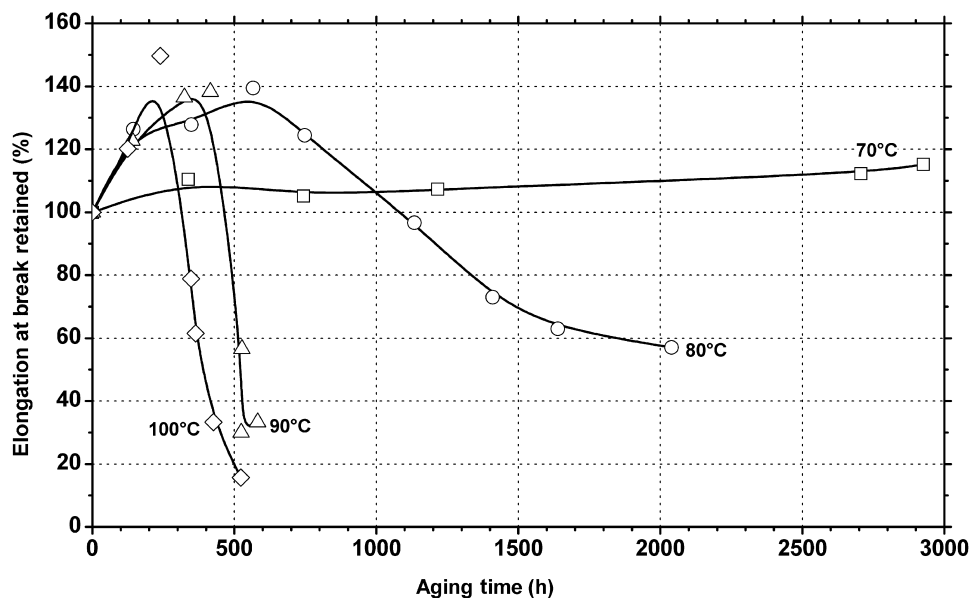


Figure 8.6 Elongation at break retained versus aging time in air at various temperatures of LDPE [2].

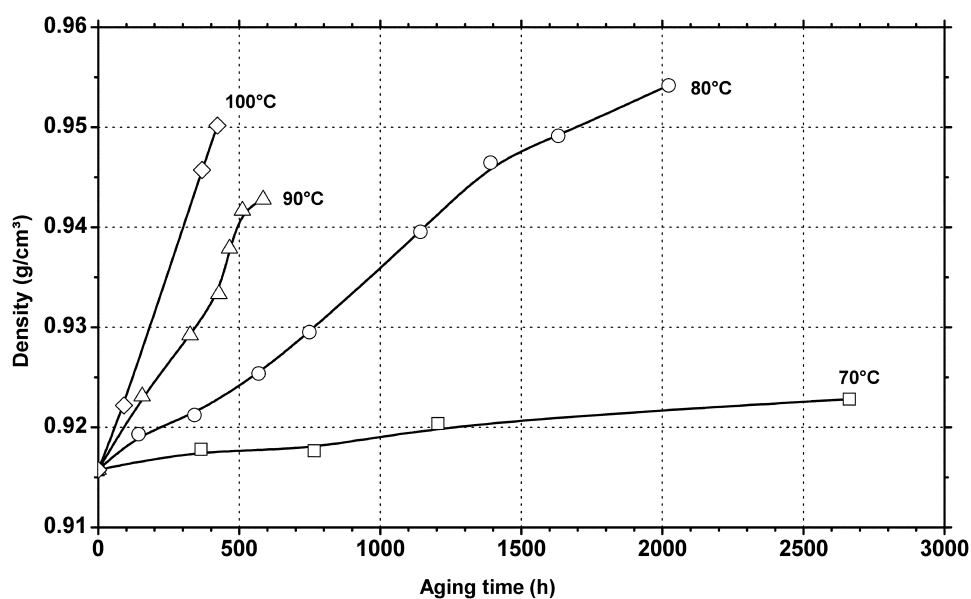


Figure 8.7 Density versus aging time in air at various temperatures of LDPE [2].

Oriented and multilayered films of PP are also common.

Thermooxidative degradation:

Random scission is the primary initial degradation pathway in PP. As shown in Figure 8.8, the scission produces a pair of radicals. The radicals can rearrange, transfer, and react to produce preferentially pentane, 2-methyl-1-pentene and 2,4-dimethyl-

1-heptene although other hydrocarbons may be produced in smaller quantities. Oxygen can react with the radicals to produce peroxides and hydroperoxides. Polymer branching does not occur in PP.

Stabilization:

- **Phenolic antioxidant:** such as 2,6-di-*tert*-butyl-4-(4,6-bis(octylthio)-1,3,5-triazine-2-ylamino) phenol.

- **Phosphites:** such as bis-(2,4-di-*t*-butylphenol) pentaerythritol diphosphite.
- **Thiosynergist:** such as didodecyl-3,3 thiodipropionate.
- **Quencher:** such as (2,2'-thiobis(4-*tert*-octylphenolato))-*N*-butylamine-nickel(II).
- **Optical brightener:** such as 2,2'-(2,5-thiophenediyl) bis(5-*tert*-butylbenzoxazole).

Manufacturers and trade names: Ineos polypropylene, LlyondellBasell Adflex™, Mophen, ExxonMobil™ Bior™, OPPalyte, Dow Chemical, Flint Hill Resources.

Applications and uses: 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 8.9 and 8.10.

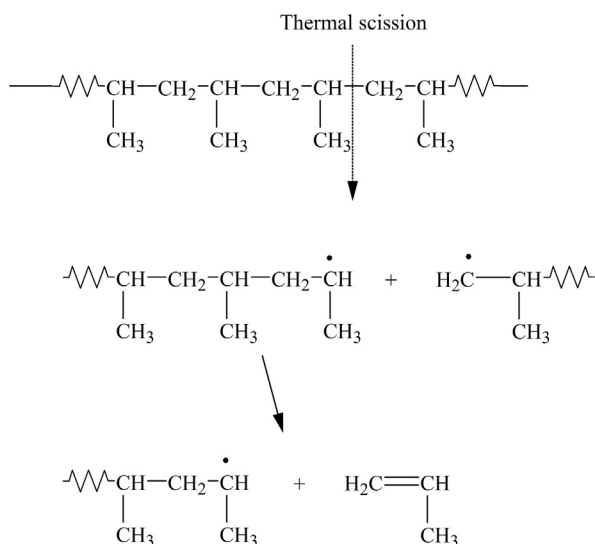


Figure 8.8 Degradation pathways of PP.

8.2 Benzocyclobutene Polymer

Benzocyclobutene (BCB) polymer was developed at Dow in the late 1980s. It is based on BCB (also known as bicyclo[4.2.0]octa-1,3,5-triene or 1,2-dihydrobenzocyclobutene). The monomer and polymer structures are shown in Figure 8.11. It is used in microelectronic applications.

Manufacturers and trade names: Dow Cyclotene™.

Data for BCB-based plastics are shown in Figures 8.12 and 8.13.

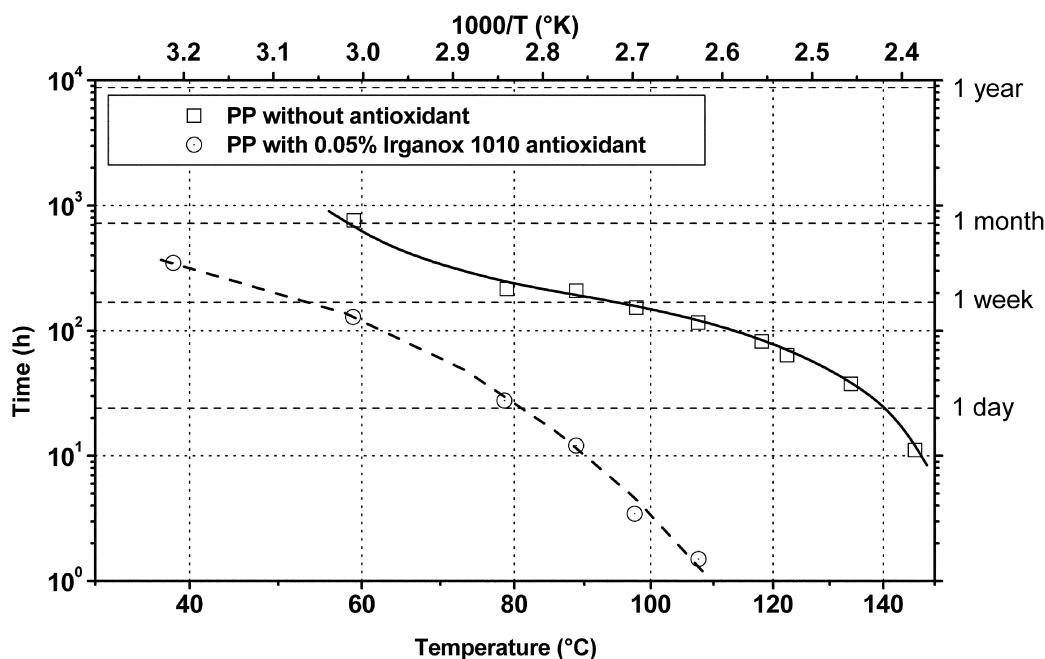


Figure 8.9 Thermal stability of PP measured by embrittlement time versus temperature [3].

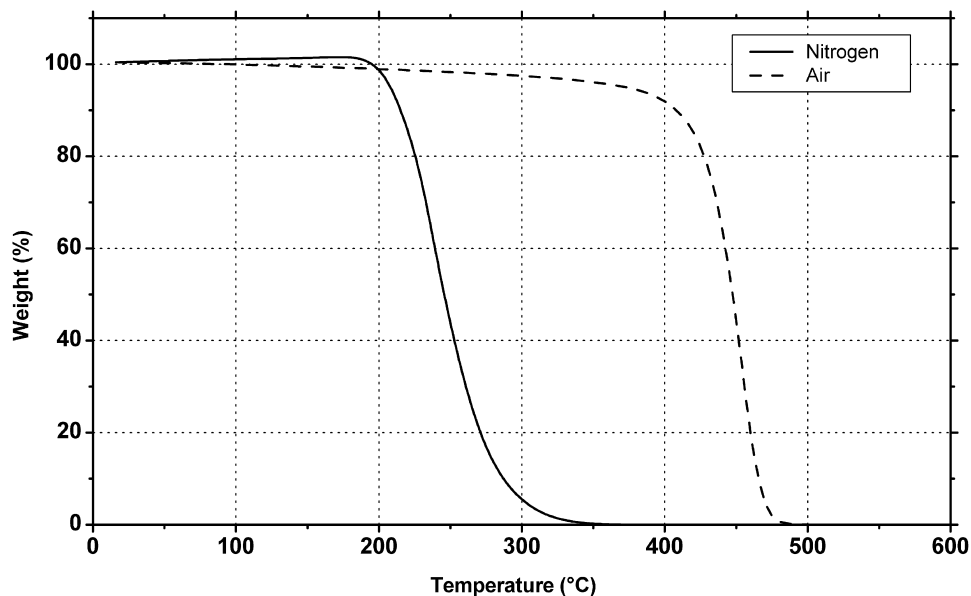


Figure 8.10 Thermogravimetric analysis (TGA) of PP in air and nitrogen [1].

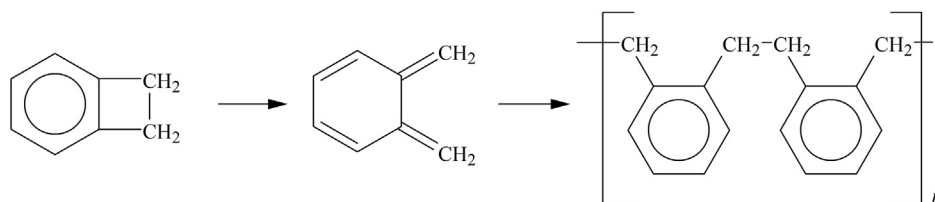


Figure 8.11 Structure of BCB and corresponding polymer made from it.

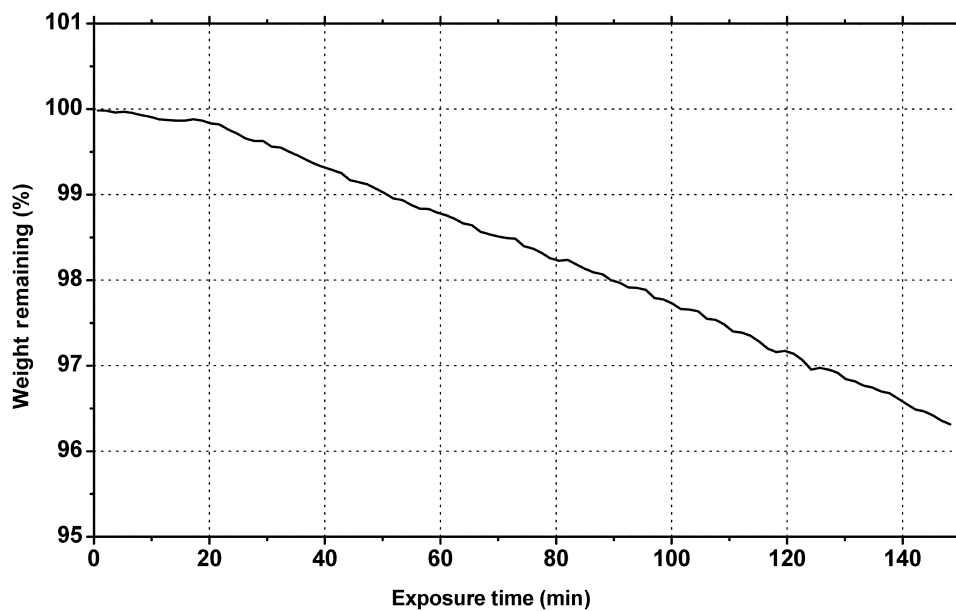


Figure 8.12 Isothermogravimetric analysis under nitrogen at 350°C of Dow Cyclotene™ 4026 polybenzocyclobutene polymer [4].

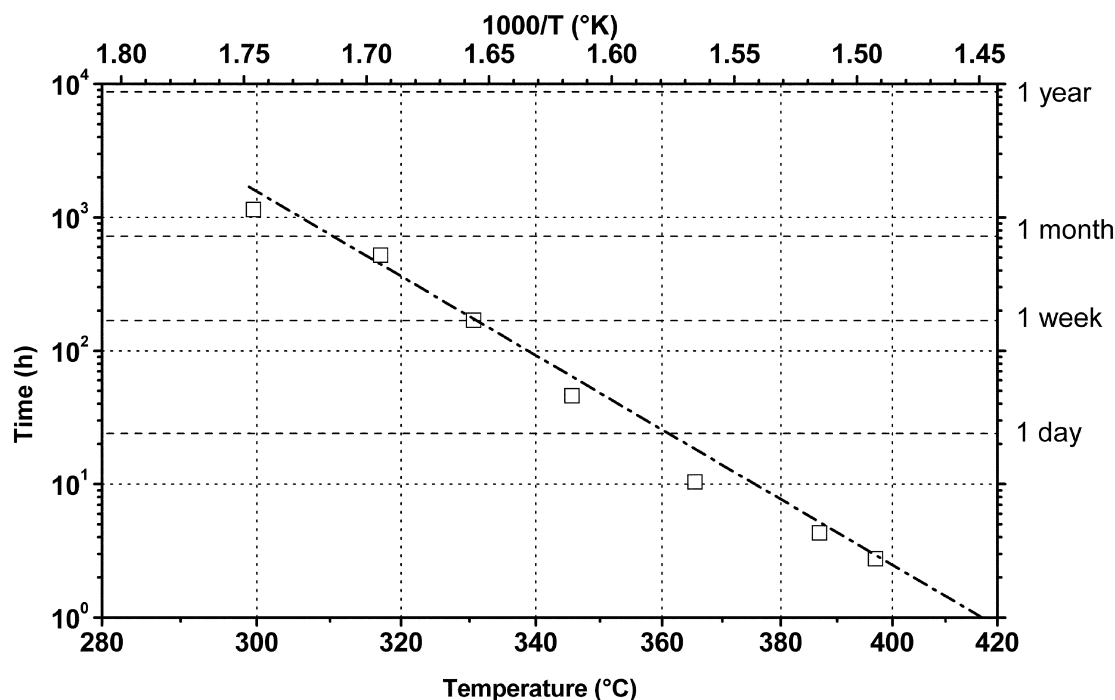


Figure 8.13 Thermal stability as measured by time to 1% weight loss versus temperature of polybenzocyclobutene polymer [4].

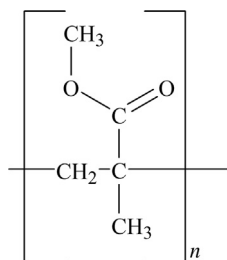


Figure 8.14 Structure of PMMA.

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

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 found in [Table 8.1](#).

8.3 Polyacrylics

While a large number of acrylic polymers are manufactured, polymethyl methacrylate (PMMA) is by far the most common. The structure of PMMA is shown in [Figure 8.14](#). 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. It is also highly weather resistant. PMMA has a CAS number of 9011-14-7.

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

8.4 Polyvinyl Chloride

Polyvinyl chloride (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.

Table 8.1 Heat Aging of Cyro XT Acrylic Polymer Compounds for Medical Packaging [5]

	Tensile Strength (MPa)	Elongation at Break^a (%)	Tensile Modulus^a (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Izod Impact Resistance fppi at 23°C	Deflection Temperature (°C)
XT 375TE							
Initial	56700	11	2751000	87600	2551000	2.05	78
3 weeks	57200	11	2868000	91400	2468000	2.03	85
6 weeks	55800	12	2868000	90000	2606000	2.08	85
12 weeks	55000	10	2689000	86200	2427000	2.13	83
XT 375							
Initial	57300	11	2710000	87800	2461000	2.03	80
3 weeks	57400	7	2827000	92400	2675000	2.00	84
6 weeks	54700	8	2820000	92300	2579000	2.04	86
12 weeks	55800	11	2675000	87700	2544000	2.05	84
XT X800RG							
Initial	49700	6	2310000	64100	2434000	2.21	80
3 weeks	50000	7	2537000	77400	2275000	2.20	86
6 weeks	49000	9	2386000	79300	2193000	2.29	86
12 weeks	49200	8	2365000	76500	2372000	2.35	85
PETG 6763							
Initial	52400	104	2062000	77200	1875000	0.55	70
3 weeks	61400	33	2137000	90000	1931000	0.51	79
6 weeks	63700	21	2089000	92000	1999000	0.55	80
12 weeks	66900	5	2261000	91100	1986000	0.54	79

^aASTM D 638 Heat aging correlation* to real-time (storage at 22°C): * Aging rate = Q10.

Note: ASTM D 3045 "Standard Practice for Heat Aging of Plastics Without Load" Conditions: Temperature = 50°C.

There are three broad classifications for rigid PVC compounds: Type I, Type II, and CPVC. 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.

Thermal degradation of PVC:

Every PVC article undergoes a certain amount of thermal degradation on the way to becoming a finished product. The amount of thermal degradation depends on the total heat history of the resin, from manufacture to formulation in the extruder. PVC heat stabilizers are typically added. Tin mercaptide heat stabilizers are commonly used for PVC building products. The mercaptide portion of the stabilizer is detrimental to long-term weathering of vinyl compounds. Therefore, while it is important to have enough stabilizers present to prevent the thermal decomposition of the PVC resin, an excess should be avoided so that the weathering of the finished product is not affected by an excess of sulfur.

Chemical structure of PVC includes three bonds: C—H, C—Cl, and C—C. Heat can lead to dehydrochlorination which can lead to the formation of single and conjugated double bonds of various lengths which depend on conditions (length and severity of processing). This reaction is shown in Figure 8.15. Presence of oxygen during processing contributes to further damage because it may oxidize double bonds, create radicals (Figure 8.16), and then carbonyl groups. On top of that, thermal stabilizers are

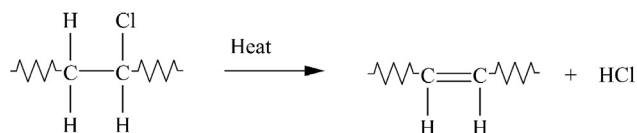


Figure 8.15 Dehydrochlorination of PVC by heat.

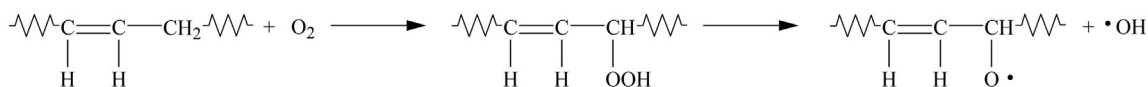


Figure 8.16 Radical generation in PVC.

added to minimize thermal decomposition and these can become photosensitizers.

Typical results of photodegradation include changes in molecular weight, yellowing, loss of mechanical properties, and gel formation.

Stabilization:

- **Acid scavenger:** hydrotalcite.
- **Phenolic antioxidants:** ethylene-bis(oxyethylene)-bis(3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)-propionate).
- **Phosphite:** trinonylphenol phosphite.
- **Thiosynergist:** 2,2'-thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate].
- **Optical brightener:** 2,2'-(2,5-thiophenediyl) bis(5-*tert*-butylbenzoxazole); 2,2'-(1,2-ethylenediyl-di-4,1-phenylene)bisbenzoxazole.

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 8.17–8.20.

8.5 Ethylene–Vinyl Acetate Copolymer

Ethylene–vinyl acetate (EVA) copolymer is a copolymer of ethylene and vinyl acetate as shown in Figure 8.21. Its CAS number is 24937-78-8.

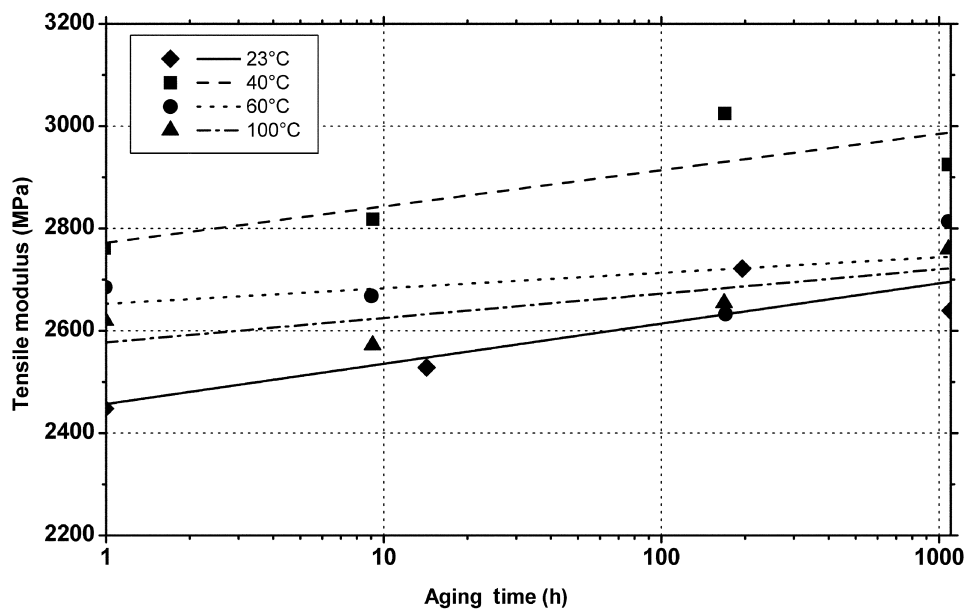


Figure 8.17 Tensile modulus versus aging time at several temperatures of PVC [6].

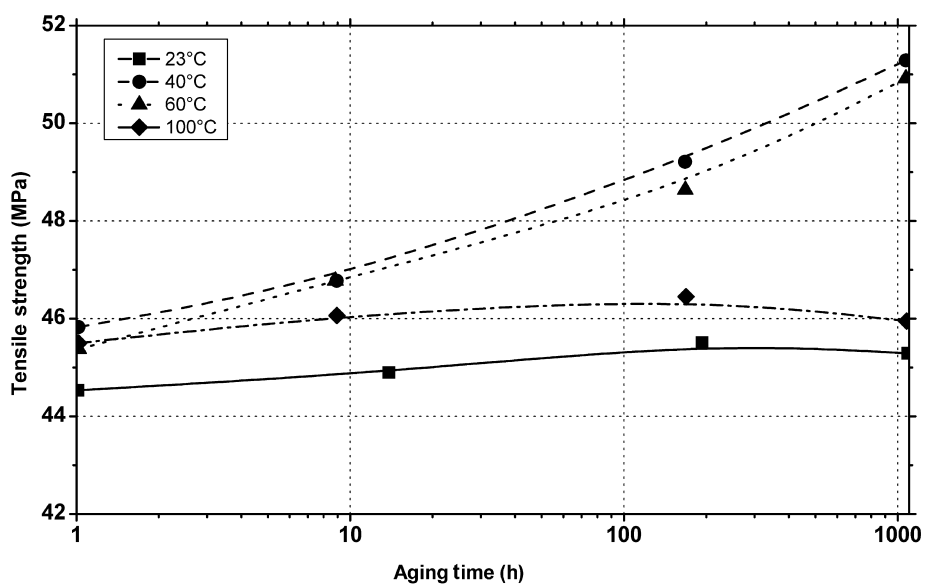


Figure 8.18 Tensile strength versus aging time at several temperatures of PVC [6].

Commercial resins range in vinyl acetate content from 7.5 to 33 wt%. Some grades are available with antiblock and slip additives. DuPont™ Elvax® grades vary by vinyl acetate content.

EVA properties vary depending on vinyl acetate content.

Higher vinyl acetate content:

- Increased gas permeability
- Increased impact strength—toughness
- Improved optical qualities—clarity
- Increased flex—crack resistance
- Increased cling
- Increased solubility

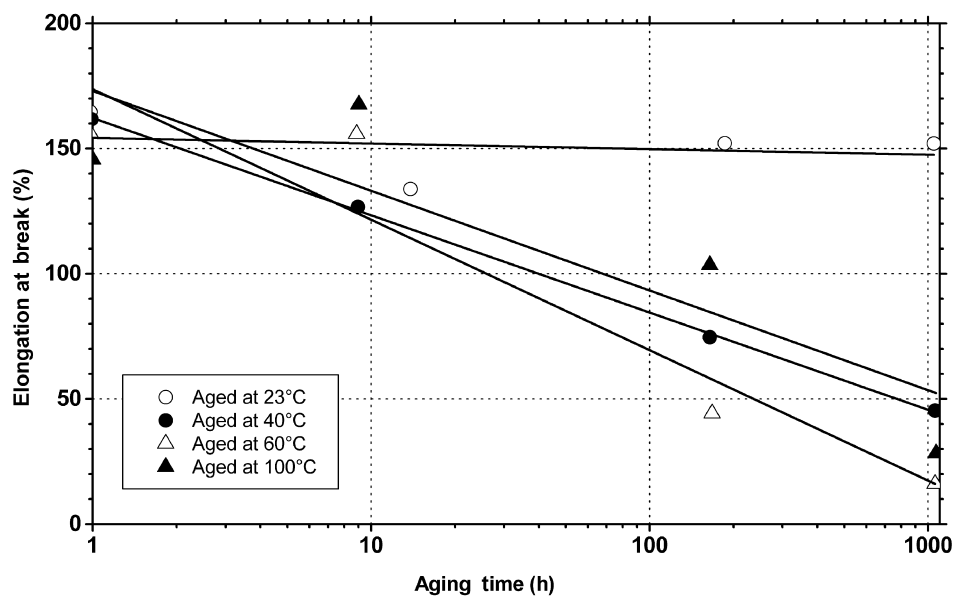


Figure 8.19 Elongation at break versus aging time at several temperatures of PVC [6].

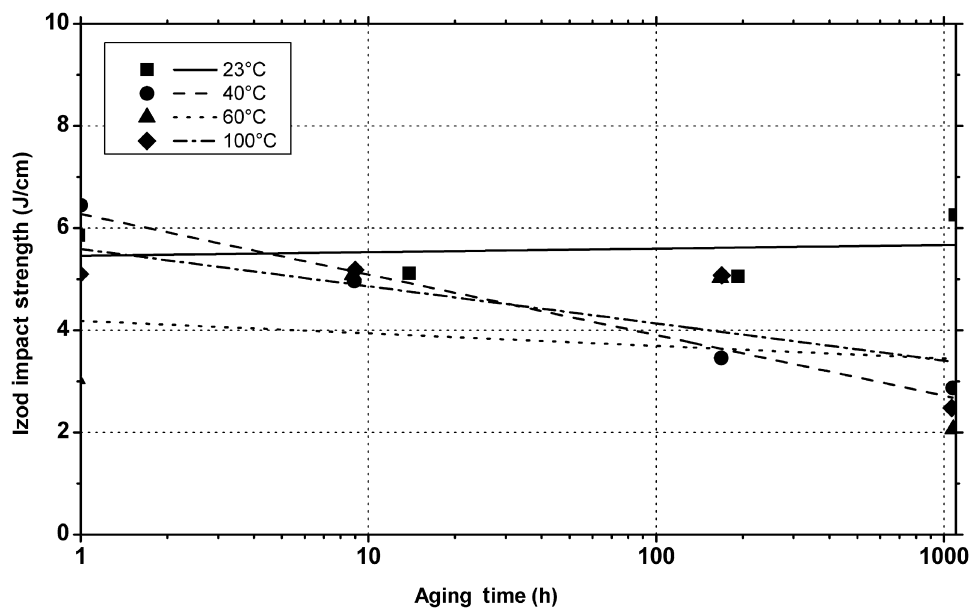


Figure 8.20 Izod impact strength versus aging time at several temperatures of PVC [6].

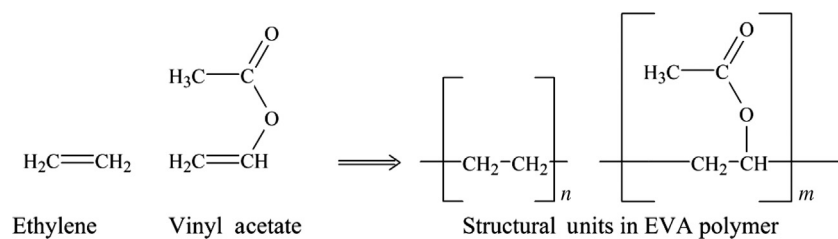


Figure 8.21 Structure of EVA polymers.

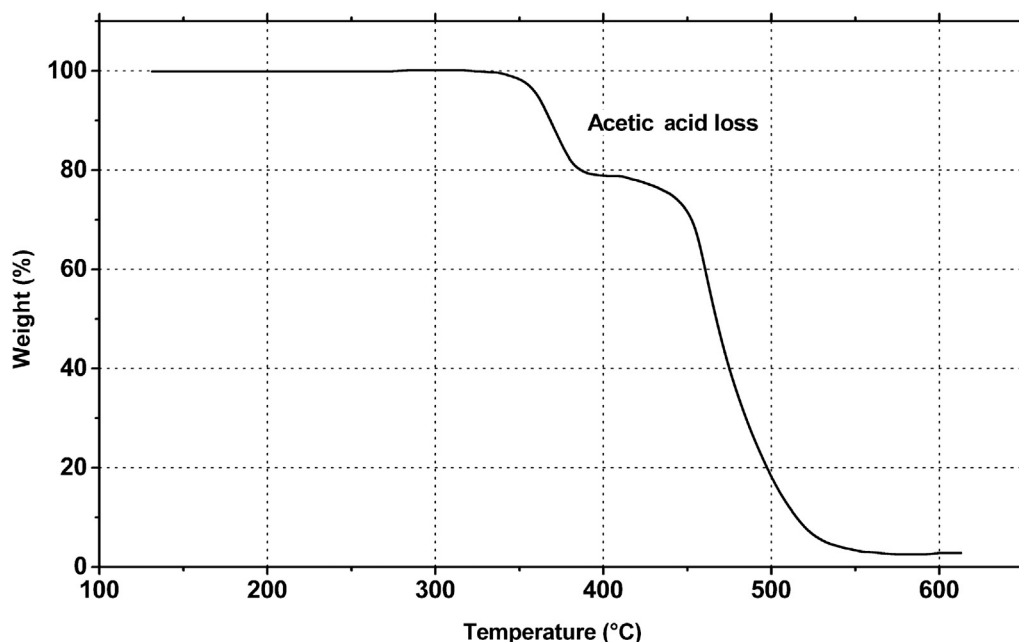


Figure 8.22 Thermogravimetric analysis (TGA) of EVA copolymer in nitrogen [7].

- Increased coefficient of friction
- Decreased sealing temperature—softening point
- Increased crystallinity
- Reduced stiffness
- Reduced surface hardness.

Manufacturers and trade names: DuPont™ Appeel® and Elvax®, Celanese EVA Performance Polymers Ateva®, Lanxess Levapren®, Baymond® L and Levamelt®, Arkema Evatane®. Data for EVA is given in Figure 8.22.

References

- [1] Peterson JD, Vyazovkin S, Wight CA. Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene). *Macromol Chem Phys* 2001;202:775–84.
- [2] Budrugaec P, Segal E. Changes in the mechanical properties and thermal behaviour of LDPE in response to accelerated aging. *J Therm Anal* 1998;53:801–8.
- [3] Zweifel H, editor. *Plastics additive handbook*. fifth ed. München: Hanser-Verlag; 2000.
- [4] <<http://www.dow.com/cyclotene/solution/stability.htm>>.
- [5] *Acrylic Polymers for the Medical Industry*, Cyro Industries, 2005.
- [6] Rabinovitch EB, Summers JW. The effect of physical aging on properties of rigid polyvinyl chloride. *J Vinyl Addit Technol* 1992;14: 126–30.
- [7] Chiu J. Applications of Thermogravimetry to the Study of High Polymers. *Appl Polym Symp* 1966;2:25.