

3.31 Degradation of Plastics and Polymers

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This article is a revision of the Third Edition article 18.6 by J. A. Brysdon, volume 2, pp 18:53–18:77, © 2010 Elsevier B.V.

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Glossary

Glass transition temperature The temperature at which polymer molecules cease being effectively locked into position and have sufficient rotational energy to be able to coil and uncoil.

Polymer resin A polymerized synthetic or chemically modified natural material, including thermoplastic materials such as polyvinyl chloride and thermosetting materials such as epoxy resins, which are used with other components such as fillers to form plastics.

Thermoplastic A polymeric material (e.g., nylon) which is capable of being repeatedly softened by increases in temperature and hardened by decreases in temperature.

Thermoset/thermosetting A polymeric material (e.g., an epoxy resin) which, upon curing, results in a three-dimensional structure and that decomposes rather than melts upon heating.

PTFE Polytetrafluoroethylene

PVC Polyvinyl chloride

PVdC Polyvinylidene chloride

PVdF Polyvinylidene fluoride

SBR Styrene butadiene rubber

SBS Styrene butadiene styrene triblock copolymer

Symbols

ΔG Change in Gibb's free energy

ΔH Change in enthalpy

L Latent heat of vaporisation

P Partial polarity

ΔS Change in entropy

T_g Glass transition temperature

T_m Melting temperature

Abbreviations

ABS Acrylonitrile butadiene styrene polymers

DSC Differential scanning calorimetry

FEP Fluorinated ethylene propylene resins

HIPS High impact polystyrene

MBS Methacrylate butadiene styrene polymers

PBT Polybutylene terephthalate

PEEK Polyetheretherketone

PES Polyether sulfone

PMMA Polymethylmethacrylate

PP Polypropylene

PPO Polyphenylene oxide

PPS Polyphenylene sulfide

PS Polystyrene

3.31.1 Introduction

From ancient times, organic materials, such as beeswax, have been used for surface protection of metallic and other artifacts. The nineteenth and especially the twentieth centuries saw huge advances^{1,2} in surface coatings for the protection of metals against corrosion. This development continues apace right up to the present day. Some of the drivers of these developments are not only the ever-present desire to improve protection, but also to find materials and systems which are less polluting and which conform with increasingly stringent environment protection legislation. The latter driver has, for example, led to much work on waterborne coatings³ to replace systems containing organic solvents, which were traditionally simply lost to the atmosphere. It is also the driving force behind the spectacular rise of polymeric materials which has led to the replacement of metals as the structural material in a vast range of manufactured

items. A glance around any room will reveal many plastic items which formerly would have been metallic.

In the past, corrosion control has involved, in the main, the use of metal alloys, protective coatings, inhibitors, etc. Corrosion problems may now often be circumvented by the use of organic polymers in the form of plastics or rubbers.¹ It must, however, be stressed that such polymeric materials are not totally inert to chemicals in their immediate environment, including, possibly, to metallic substrates or contacts.

3.31.2 Definition of 'Plastics'

In this section, both the terms 'polymer' and 'plastic' are encountered. The former is much easier to define than the latter. A polymer, or macromolecule, may be defined as a species with a molar mass much greater than that encountered in common organic substances such as alcohol, petrol, chloroform, etc., and which is comprised of smaller, repetitive molecular units. Although there is no specific definition that can universally define the polymeric (macromolecular) state, a molecular mass of at least several thousand is generally taken as indicating its start. Such polymer molecules may be linear, branched, have a network structure, etc. These different molecular geometries influence the properties of the given polymer very significantly.^{4,5}

It is difficult to provide a satisfactory definition of the term 'plastics'. Attempts at reasonably concise definitions tend to include certain materials such as rubbers, adhesives, fibers, glasses and surface coatings which are not usually considered as plastics, and to exclude a number of materials such as bituminous plastics, shellac and polytetrafluorethylene which usually are considered as plastics. In reality, the term becomes defined by common usage rather than by a physical/chemical description. However, in general, it may be said that plastics are usually high-molecular-weight polymers that at some stage in their existence are capable of flow, but may also be brought into a non-fluid form in which they have sufficient toughness and strength to be useful in self-supporting applications. Although they may be self-supporting, this does not exclude the possibility of reinforcing the plastics with fibers, or other fillers, or laminating them with other materials. Sometimes metals are coated with plastics, but usually at a greater thickness than is common with surface coatings such as paint films (which are, of course, also polymers).

The rapid rise of the plastics industry may be attributed to a number of factors. Foremost has been the fact that while many materials of construction

have been subjected to continual increase in their price, the development of the petrochemicals industry and economies of scale have, for most of the time, led to reductions in the prices of plastics materials. Thus, with the passage of time, more and more products constructed from traditional materials have become cheaper to produce from plastics. The trend of increased plastics usage seems bound to continue in the foreseeable future, now driven by our ever-increasing ability to make polymer molecules (plastics) with better controlled molecular architectures⁶ and by better processing technologies.⁷

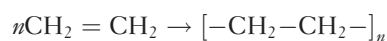
Such a growth also requires, of course, that plastics possess properties suitable for the end uses envisaged. It is now possible, by control of synthesis, by chemical modification, by careful control of the relevant processing technology (injection molding, extrusion, etc.) or by the selective use of additives such as fibers, nanofillers, etc., to make products varying widely in their properties. The following is a list of some of the salient properties expected of plastics materials.

1. Tenacity. While some plastics are rigid and others flexible, all commercial materials show a degree of strength and toughness when stressed rapidly, superior to simple crystals and common glass.
2. Low thermal conductivity.
3. Low electrical conductivity.
4. Low heat resistance compared with common metals. The vast majority of plastics will not withstand 100 °C for extended periods and only a very few highly specialized products will withstand temperatures of 400 °C and above.

3.31.3 The Chemical Nature of Plastics

3.31.3.1 Free-Radical Addition Polymerization of Monomers with Double Bonds

In this case, the reactive double bond in a small molecule, such as ethylene or propylene, allows it to join another similar molecule.⁵ These small molecules are known as monomer molecules. The chemical equation below shows this process for ethylene. The value of n in the equation can typically exceed 10 000 and can rise above 1 000 000.

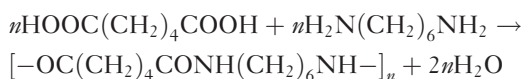


Such a molecule is referred to as a polymer, in this case polyethylene. Styrene, propylene, vinyl

chloride, vinyl acetate, and methyl methacrylate are other examples of monomers that can polymerize in this way. Sometimes, two monomers may be reacted together so that residues of both are to be found in the same chain. Such materials are known as copolymers and are exemplified by ethylene–vinyl acetate copolymers and styrene–acrylonitrile copolymers. If there are three such repeat units in a given polymer, it is termed a terpolymer.

3.31.3.2 Step-Growth Polymerization

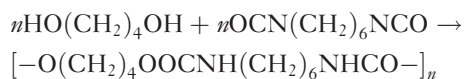
In this case, reaction between two functional groups occurs, which leads to the production of a polymer and also a small molecule. This is a condensation reaction. A good example of this type of chemistry is the reaction between adipic acid and hexamethylene diamine, which yields nylon-6,6 and water as the small molecule:



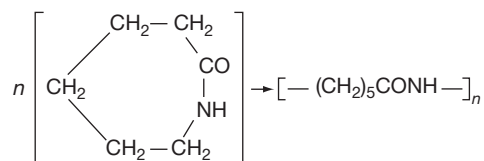
Most nylons, polyesters, phenolics and a number of other plastics are produced by this route.⁸

3.31.3.3 Rearrangement Polymerization

Here the mechanism resembles step-growth polymerization, but no small molecule is split at each individual reaction step. In the first example, 1,4-butane diol reacts with hexamethylene di-isocyanate to give polyurethane:



In the second, ϵ -caprolactam, a ring compound opens up to give nylon-6:



The polymerization of ϵ -caprolactam is commonly known as a ring-opening polymerization, a technique also used with other cyclic compounds such as ethylene oxide, propylene oxide and tetrahydrofuran.

3.31.3.4 Ionic Polymerization

In the case of ionic polymerization, the growing polymer molecules (commonly referred to as

polymer chains) are temporarily terminated by ionic groups, which may be anionic (anionic polymerization) or cationic (cationic polymerization). The major advantage of this type of polymerization is that it offers good control over the resulting molecular architecture.⁸

Polymers may also be obtained from biological sources.^{9,10} Cellulose, the principal constituent of cotton and a major constituent of wood, is such a polymer. So also are lignin, chitin from crustacean shells, natural rubber, gutta percha, and proteins. Sand (silica) may be considered as an inorganic polymer. While many of these are unmodified, some, like cellulose, cannot be considered as plastics in their natural state, but if chemically modified, useful plastics materials such as cellulose acetate, celluloid, and ethyl cellulose may be obtained. Natural rubber is clearly the basis of a huge worldwide industry.

3.31.4 The Physical Nature of Plastics

Many polymers, such as polystyrene, consist of long chain-like molecules of high molecular weight. A typical average molecular weight for a polystyrene sample is about 200 000 and since the molecular weight of the monomer is 104 this implies that there are around 2000 repeat units joined together in a typical molecule taken from that sample. It is the case in nearly all plastics that a given sample contains molecules covering a distribution of molecular weights. This distribution, in some cases, may be very wide.⁵ Since the backbone carbon–carbon bonds can rotate relatively freely, such molecules are most unlikely to be stretched out, but are more likely to be coiled up into what is referred to as a random-coil conformation.¹¹

In the case, for example, of polystyrene, the molecules at room temperature do not have enough rotational energy to twist around the backbone chemical bonds and so, in the mass, the polymer is rigid. On heating above a certain temperature, sufficient energy for such subchain movement is obtained and on application of a shearing stress in processing such as extrusion, the polymer molecules partly uncoil. Chain segments slip past each other and, in the mass, flow occurs. On cessation of stress, slippage ceases, the chains again coil up and, on cooling, the mass again hardens. If desired, the whole process of heating, shearing and cooling may be repeated. Materials that behave in this way are known as

thermoplastics.^{7,11} Two points should, however, be noted. Firstly, if cooling is faster than the chain recoiling process, then a frozen-in molecular orientation will result. This can grossly affect the polymer properties, in some cases adversely. Secondly, repeated heating and shearing may be accompanied by changes such as oxidation and polymer degradation, which will limit, in practice, the number of times heating and cooling can be applied on a particular polymer sample. In terms of tonnage, the bulk of plastics produced are thermoplastics, a group that includes the polyethylenes, polypropylene, polystyrene, polyvinyl chloride (PVC), the nylons, polycarbonates and cellulose acetate. There is, however, a second class of materials, the thermosetting plastics.^{7,11} They comprise long-chain molecules, similar to a typical thermoplastic molecule, however, as rather smaller molecules. They are formed, often in a mold, into the desired final shape and then subjected to chemical reaction, often by heating, in such a way such that the molecules link with one another to form a cross-linked network as shown in **Figure 1**. As the molecules are now interconnected, they can no longer slide extensively past one another and the material is said to have set, cured or cross-linked. Plastic materials behaving in this way are designated as thermosetting plastics, a term which is also used to include those materials that can be cross-linked with suitable catalysts at room temperature. Important thermosetting plastics include the phenolic resins, melamine-formaldehyde resins, the epoxy resins and unsaturated polyester resins used in glass-reinforced plastics.

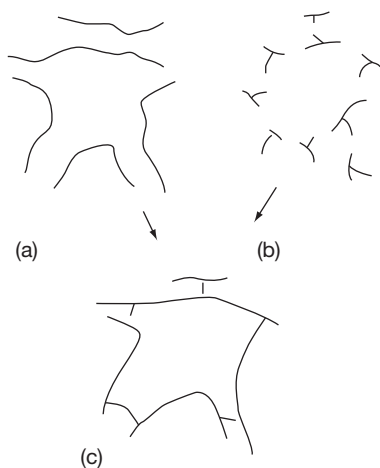


Figure 1 Joining up of (a) long-chain molecules or (b) branched molecules to produce (c) a cross-linked polymer.

3.31.4.1 Thermoplastics

Thermoplastics may be considered in four subclasses: (a) amorphous thermoplastics; (b) rubber-modified amorphous thermoplastics; (c) plasticized amorphous thermoplastics, and (d) crystalline thermoplastics.

3.31.4.1.1 Amorphous thermoplastics

These are made from polymers that have a sufficiently irregular molecular structure to prevent them from crystallizing. Examples of such materials include polystyrene and polymethyl methacrylate. The structural irregularity in these examples arises from the free-radical addition polymerization process used in their synthesis. This results in the repeat unit side groups being present in essentially random configurations,⁵ which is sufficient to prevent crystallization.

At very low temperatures, these materials are glass-like and rigid. On heating, a temperature is eventually reached where the material softens. If the polymer is of sufficiently high molecular weight, it becomes rubbery above this temperature. The temperature at which this occurs is known as the glass transition temperature (T_g),^{5,11} and is in effect the temperature at which the polymer molecules have sufficient rotational energy to be able to coil and uncoil. As the individual polymer molecules, in their random-coil conformations, interpenetrate each other, the resulting chain entanglements prevent flow. At higher temperatures there are two possibilities. Polymers of moderate molecular weight may achieve such energy that they can flow, while high molecular weight materials may decompose before the flow point is reached. This is shown schematically in **Figure 2**,

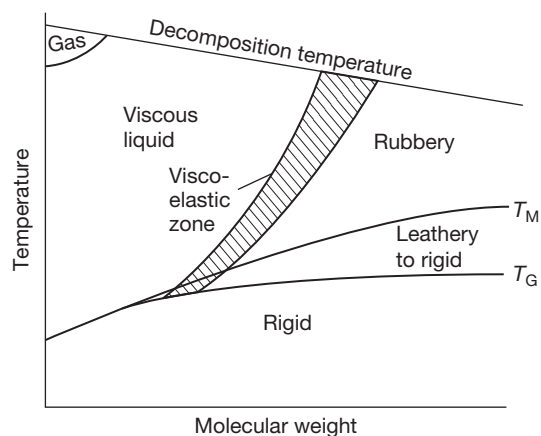


Figure 2 Temperature-molecular weight phase diagram for amorphous polymers.

which indicates the phases in which this type of polymer can occur. It should be stressed that the boundary lines will change position with change of polymer type.

It can be seen that up to a certain molecular weight a polymer may be processed either as a liquid (by injection molding, extrusion, etc.) or as a rubber (by vacuum forming, sheet blowing, hot pressing). In the case of a polymer of much higher molecular weight, it can be seen that it can only be shaped in the rubbery state, and if it is intended to be processed by, say, injection molding, then the molecular weight may first have to be reduced. An important illustration of this is with well-known acrylic materials such as Perspex (polymethyl methacrylate), which can have too high a molecular weight to be injection-molded.

It is possible to make some generalizations about the properties of amorphous thermoplastics.

1. The T_g will determine the maximum temperature of use of the material as a rigid thermoplastic. For amorphous rubbers, the T_g value will determine the minimum temperature of use.
2. Below T_g , most amorphous polymers show a more or less linear stress-strain curve with no yield point. The tensile strengths are typically around 50 MPa, elongation at failure usually less than 10%, and the elastic modulus typically around 2.5 GPa. Since the area under the curve provides a measure of the energy required to rupture the specimen, and since this area is small, such polymers will have a low impact strength (which is closely related to the energy to break) and will break with a brittle fracture.
3. They are generally more permeable to gases than crystalline polymers. This is more so above T_g than below.
4. They usually have a much wider range of solvents than crystalline polymers.

3.31.4.1.2 Rubber-modified amorphous polymers

The brittleness of amorphous polymers has been a hindrance in their commercial development. However, for reasons now substantially understood, the addition of rubbery polymers as dispersed droplets into the glassy polymer can often lead to substantial increases in impact strength,¹² albeit usually at some cost to tensile strength and, in many cases, to transparency.

The most important polymers of this important class are as follows.

1. High-impact polystyrene (a polystyrene modified with a styrene-butadiene rubber (SBR) or a polybutadiene rubber).
2. ABS, which is based on a copolymer of acrylonitrile, butadiene and styrene.
3. Methacrylate-butadiene-styrene polymers (MBS) and related materials, which are chemically similar to ABS but are often available in transparent form.
4. Rubber toughened epoxy resins.
5. High-impact PVC; in this case the impact modifiers are not always rubbers, but the mechanism of their action is probably similar.

3.31.4.1.3 Plasticized amorphous thermoplastics

Certain plastics may be mixed with high boiling temperature, low-volatility liquids to give products of lower T_g . The most important example of this class occurs with PVC, which is often mixed with liquids such as di-*iso*-octyl phthalate, tritolyl phosphate, or other diesters to bring the T_g below room temperature. These liquids work by increasing the free volume in the materials, thereby facilitating the segmental motions that constitute the glass transition process. If their volatility is a problem in a given case, it may be possible to use either a polymeric plasticizer¹³ or a chemically bound plasticizer.¹⁴ The resultant plasticized PVC is flexible and to some degree quite rubbery. Other commonly plasticized materials are cellulose acetate and cellulose nitrate.

It is essential to appreciate that such plasticizers may also considerably modify the chemical properties of the plastic material since the plasticizer may be readily extracted by certain chemicals and chemically attacked by others while the base polymer may be unaffected.

3.31.4.1.4 Crystalline thermoplastics

While polymers such as polyethylene and nylon-6,6 do not show any regular external form, which is characteristic of crystals, closer examination reveals that they have many properties common to crystalline materials. They exhibit distinct X-ray diffraction patterns⁵ and exhibit specific melting in differential scanning calorimetry (DSC).⁵ Although the exact nature of this crystallinity is not fully resolved in some cases, it would appear that polymer segments pass through zones in which molecular arrangement is highly ordered, that is, crystalline. In some ways these zones act like knots, or cross-links, holding the individual molecules of such materials together.

The effect of heating crystalline polymers from low temperatures is more complex than with amorphous polymers. Initially, the material is rigid and hard. As the temperature goes through the T_g , light crystalline materials soften slightly and become leather-like, but highly crystalline materials show relatively little change in properties. Further heating results in the crystals melting, often over quite a wide temperature range, and the polymer becomes rubbery. Whether or not it melts or decomposes first on further increase in temperature will depend on both the particular polymer and its molecular weight.

A typical phase diagram for such polymers is given in **Figure 3**. With such crystalline polymers, the melting point, T_m , replaces the T_g as the factor usually determining the maximum service temperature of thermoplastics and minimum service temperature of rubbers. However, it is more difficult to make generalizations about properties. The following remarks may, however, be pertinent for crystalline polymers.

1. Below T_g , tensile strengths are usually at least as high for crystalline polymers as for amorphous ones. Between T_m and T_g , the strength and rigidity will be very dependent on the degree of crystallinity and to some extent on the molecular weight. Tensile strengths commonly range from below 10 to around 90 MPa.
2. In most cases, crystal densities differ from those of amorphous polymers. This leads to differences in refractive index, which in turn cause scattering of light at boundaries between amorphous and crystalline zones. Such materials are opaque, except in certain instances where the crystal structure can be carefully oriented to prevent such scattering of light.

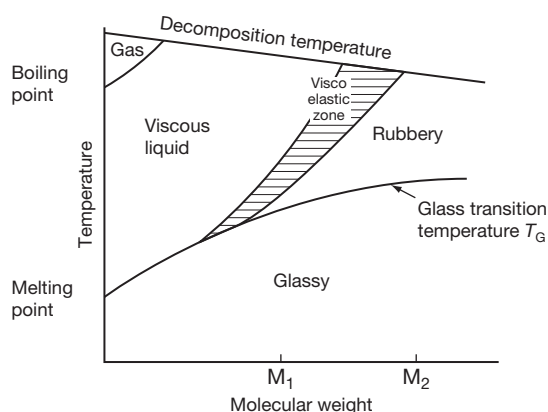


Figure 3 Temperature–molecular weight phase diagram for crystalline polymers.

3. The close molecular packing makes diffusion more difficult than with amorphous polymers compared under similar circumstances, that is, either below T_g , or above T_g but below T_m , of the crystalline polymer.
4. Thermodynamic considerations lead to considerable restriction in the range of solvents available for such polymers.^{5,11}

3.31.4.2 Thermosetting Plastics

If glycerol, a trihydric alcohol, reacts with phthalic anhydride, three ester links can be made from each glycerol unit. Continued reaction will eventually cause the molecules to link up in a three-dimensional network in which, theoretically at least, the whole polymer mass becomes one giant molecule.

For reasons of production feasibility, such cross-linked plastics are normally prepared in two stages. In the first stage, either a low-molecular-weight branched polymer or a higher-molecular-weight linear (unbranched) polymer is produced. Such materials are thermoplastic and in most cases soluble in some solvents. At a convenient (later) time, this intermediate is subjected to heat, electromagnetic radiation (such as ultraviolet), or chemical reactants, such that the branched molecules join together, or the linear polymers cross-link, thereby producing an infusible, insoluble material. Since, in the early days of the plastics industry, the cross-linking processes required heat, these materials became known as 'thermosetting plastics.' Today this term is commonly extended to materials which can cross-link at room temperature: for example, many organic coating systems (or paints).

Because thermosetting plastics have an irregular form, they are amorphous, and because of their network structure, they are invariably rigid. They do not dissolve without decomposition, but may swell in appropriate solvents, the amount of swelling decreasing with increasing cross-link density. Well-known thermosetting plastics include the phenolics, urea–formaldehyde and melamine–formaldehyde resins, unsaturated polyesters and epoxy resins.

3.31.4.3 Reinforced Plastics

The mechanical properties of plastic materials may often be considerably enhanced by embedding fibrous materials in the polymer matrix.¹⁵ While such techniques have been applied to thermoplastics, the greatest developments have taken place with the thermosetting plastics. The most common reinforcing materials are

glass and cotton fibres,¹⁶ but many other materials including paper, carbon fiber, inorganic whiskers, particulates including nanoscale particulates,¹⁵ are used. Reinforcing fibers normally have a modulus of elasticity that is substantially greater than the resin, so that under tensile stress much of the load is borne by the fibers. The modulus of the composite is, therefore, intermediate to that of the fiber and of the resin.

In addition to the nature of resin and fiber, the laminate properties also depend on the degree of bonding between the two main components and on the presence of other additives, including entrained air bubbles. Because of this, some parts, fabricated by simple hand build-up techniques, may exhibit strengths no better, or even worse, than unreinforced materials. This problem is often worst with glass fibers, which are, therefore, normally treated with special finishes to improve the resin–glass bond.

The highest mechanical strengths are usually obtained when the fiber is used in fine fabric form, but for many purposes the fibers may be used in mat form, particularly glass fiber. The chemical properties of such laminates are largely determined by the nature of the polymer, but capillary attraction along the fiber–resin interface can occur when some of these interfaces are exposed at a laminate surface. In such circumstances, the resistance of both the reinforcement and the matrix must be considered when assessing the suitability of a laminate for use in chemically demanding situations. For more information, the reader is referred to the article on polymer–matrix composites.

3.31.5 Polymer Orientation

It is not difficult to appreciate that if polymer molecules are aligned, as in **Figure 4(a)**, then a much higher tensile strength will be obtained if a test is carried out in the X–X direction as opposed to the Y–Y direction. It is also not difficult to understand

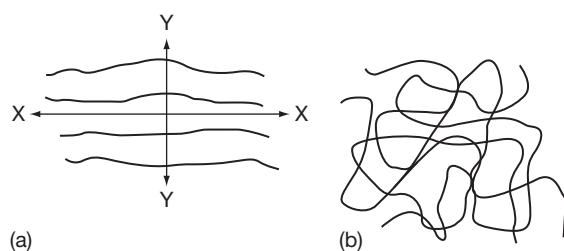


Figure 4 Polymer segment alignment: (a) parallel and (b) random.

why such a material has lower impact strength than a randomly coiled mass of molecules, **Figure 4(b)**, because of the ease of cleavage of the material parallel to the X–X direction.¹⁵

Similar remarks may also be made where crystal structures, or fiber reinforcements, are aligned rather than the individual molecules. For fibers and filaments such orientation is desirable, but for solid objects where impact strength is often more important than tensile strength such orientation is usually unwelcome. It can also have further unwanted effects. This arises from the fact that oriented molecules are thermodynamically unstable and will at the first opportunity try to achieve random-coil conformations. Thus, on heating samples up to temperatures near T_g , severe distortion can occur, leading to warped moldings.

Another serious effect, solvent stress cracking,¹⁷ occurs with liquids which are not in themselves solvents but which may wet the polymer surfaces. These facilitate relief of frozen-in stresses by surface cracking, which can be a severe problem in using many injections and blow moldings with specific chemicals. Examples of this are white spirit with polystyrene, carbon tetrachloride with polycarbonates and soaps and silicone oils with low-molecular-weight polyethylenes.

In addition to orientation in one direction (monoaxial orientation), biaxial orientation is possible. This is achieved when the sheet is stretched in two directions, resulting in layering of the molecules. This can increase the impact strength, tensile strength and solvent cracking resistance of polymers, and with crystalline plastics the polymer clarity may also be improved.

3.31.6 The Chemical Properties of Polymers

It is common practice to talk about the chemical resistance of polymers, unaware of the fact that this can mean different things. To avoid this it is probably wiser to differentiate between the following.

1. Resistance of a polymer to chemical attack resulting in breakdown of some covalent bonds and the formation of new ones. This could involve molecular breakdown initiated by heat or radiation, including ultraviolet light.
2. Resistance to dissolution by liquids.
3. Resistance to cracking in aggressive environments.
4. Permeability to gases and liquids.