ENVIRONENTAL DEGRADATION OF ADVANCED AND TRADITIONAL ENGINERING MATERIALS

Chapter 14. Forms of Polymer Degradation: Overview

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Forms of Polymer Degradation – Overview

Introduction

Usage of polymeric materials

Although polymers have existed naturally on earth since well before the dawn of humans, the ubiquitous role they play in today's society is much more recent. The modern plastics industry is often dated from the mid- nineteenth century, with John Hyatt's invention of celluloid (a synthetic modification of natural cellulose). The first wholly synthetic polymer was phenolic, invented by Leo Baekland by condensing phenol with formaldehyde in 1906. In the decades following 1930, industrial research by Wallace Carouthers and others produced a great outpouring of new polymers: nylon, polyethylene terephthalate, polystyrene, and many others. The bar graph in Figure 1 shows how polymers now rank alongside metals, ceramics, and natural materials in terms annual tonnage (a graph using volume rather than weight would show polymers even more prominently, due to their low density).
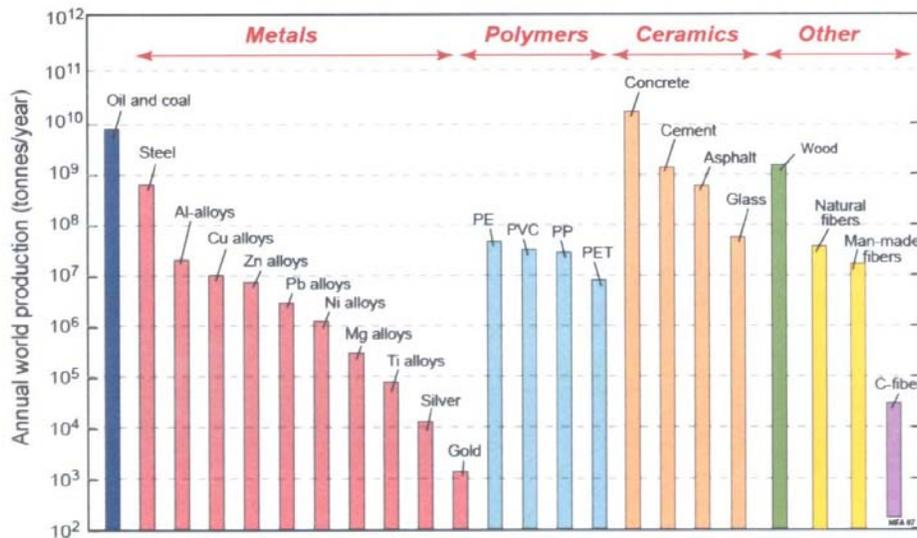

Figure 1. Graph of materials production ca 2008 (1).

Nature of polymeric materials

Most commercial polymers are long-chain hydrocarbon molecules, containing thousands of carbon atoms bonded covalently along the length of the chain. (Some important polymers –such as nylon - have noncarbon elements such as nitrogen or oxygen in the chain, and one – polydimethyl siloxane – has no carbons along the chain). Figure 2 shows the composition of polyethylene. The single covalent bonds in the chain are very strong and stable, accounting for polymers' well-known chemical stability. There is also easy molecular rotation around these bonds, leading to substantial flexibility in the chain.
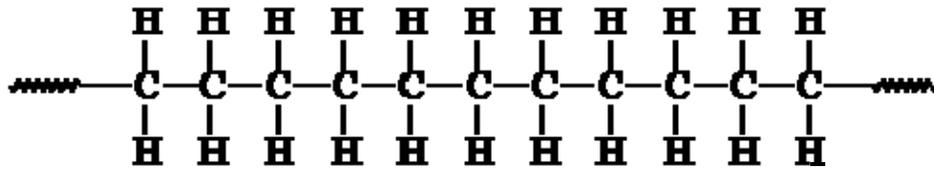
Figure 2. Representation of a portion of the polyethylene molecule (*from http://pslc.ws/macrog/kidsmac/images/pe02.gif*)

The high bond strength exists from carbon to carbon along the chain, but the lateral bonding to adjacent molecules or nearby portions of the same molecule is much weaker. Since mechanical loads applied to a bulk polymer act on both the weak and strong bonds, polymers are much weaker and more complaint than metals and ceramics that have strong bonds in all directions. But if the molecules in a polymer are oriented along a common direction as in a fiber, the material can exhibit very high strength and stiffness in that direction. (This is true in the polyaramid Kevlar®, for instance.) Such a material is much weaker in its transverse direction, however; i.e. such a material is *anisotropic.*

The combination of strong covalent bonds within an individual polymer molecule and weaker secondary bonds between neighboring molecules produces the useful ability in some polymers to be molded into complex shapes at relative low processing temperatures. *Amorphous* polymers are those that do not form ordered crystalline structures and they can be processed at temperatures above their so-called glass transition temperature (T_g). Above T_g individual amorphous polymer molecules are free to undergo large scale motion past one another, providing molecular mobility required for molding without scission of main chain bonds and resultant thermal degradation. Some polymers do form ordered crystallites, and these *crystalline* polymers must be heated above their crystalline melting point (T_m) for molding.

Classes of polymeric materials
Polymers exist in a wide variety of classifications and functions. There are some thirty major chemical classes of polymers, most with many subcategories of molecular weights, fillers, chemical modifications, and other features. They are classified by function (commodity, engineering, and specialty), industrial sectors (plastics, textiles, rubbers, adhesives), morphology (crystalline versus amorphous) or processability (thermoplastic versus thermoset). Polymers are *thermoplastics* in terms of processability if they can be melted and remolded repeatedly. Polymers may also be *thermosets* such as vulcanized rubber or cured epoxy – these materials can be set to a given shape only once; they cannot be recycled after that other than being ground and used as fillers in other materials.

Unlike metals, most polymers are not available as alloys, or solid solutions of one another. Most polymers are immiscible in each other, so they cannot be mixed (an alloy of polystyrene and polyphenylene oxide is an exception). Although classical alloys are uncommon, different monomers may be copolymerized in a single main chain molecule. Copolymers may be formed randomly or by alternating sequences of individual monomers. These are called block copolymers. Block copolymers will often form complex phase-segregated morphologies and may retain certain physical and mechanical properties characteristic of each separate starting polymer. Phase-separated polymer blends may also be used to tailor polymer properties. Polystyrene is a brittle plastic, but it can be toughened significantly by blending it with a well-chosen size distribution of rubber particles. Advanced composites can also be created by strengthening certain polymers (notably polyesters, phenolics and epoxies) with strong, stiff fibers (notably glass, aramid, or carbon).

Mechanisms of Environmental Degradation in Polymers

Depending upon the environment, polymers are generally more durable than metals because the covalent bonds of which polymer main chains are composed are inherently stable. Polymers do not rust, but they can exhibit environmental degradation through a variety of mechanisms. These include thermal and photolytic depolymerization, moisture absorption and hydrolysis, microbial degradation and flammability.

Thermal depolymerization
Although long-chain single-bonded polymer molecules are chemically stable, they can be depolymerized back to the low-molecular weight state if sufficient thermo-chemical driving energy is available. This degradation is usually negligible at ambient temperatures, but in some polymers it may be a problem during processing. One important example is a condensation polymer such as nylon 66. During polymerization nylon 66 converts two monomers – adipic acid and hexamethylene diamine – to three products: nylon polymer, water, and heat. At sufficiently high extents of reaction, as the concentration of product rises, the probability of back reaction to monomer increases, lowering the yield of polymer. This is handled industrially by removing water and keeping the temperature low during polymerization. But later, when the polymer is melted during extrusion or injection molding, especially if water is present, conditions will be right for depolymerization. This degradation mechanism – a consequence of Le Chatilier's principle – is avoided by making sure the polymer resin is dried before melt processing.

Photolytic oxidation
The photon energy in solar radiation is the most damaging component of the outdoor environment, serving to initiate a wide variety of chemical changes in polymeric materials (2). According to the Planck-Einstein law $E = h\nu = hc/\lambda$ (where E, h, ν . c and λ are energy, Planck's constant, frequency, and wavelength, respectively), the energy contained in a photon rises as the wavelength decreases. Although the sun emits radiation over a wide range of wavelengths extending from below 100 nm to over 3000 nm, the earth's atmosphere prevents radiation of wavelength less than approximately 290 nm from reaching the surface. Figure 3 shows the spectral distribution of surface sunlight in the ultraviolet range, and compares the solar spectrum with the energy received from an S-1 mercury sunlamp at a distance of 220 mm. The energy of ultraviolet photons is comparable with that of the dissociation energies of polymeric covalent bonds, which lie in the range of approximately 290-460 kJ/mole. Such photons have the capability of altering the polymer's chemical structure.
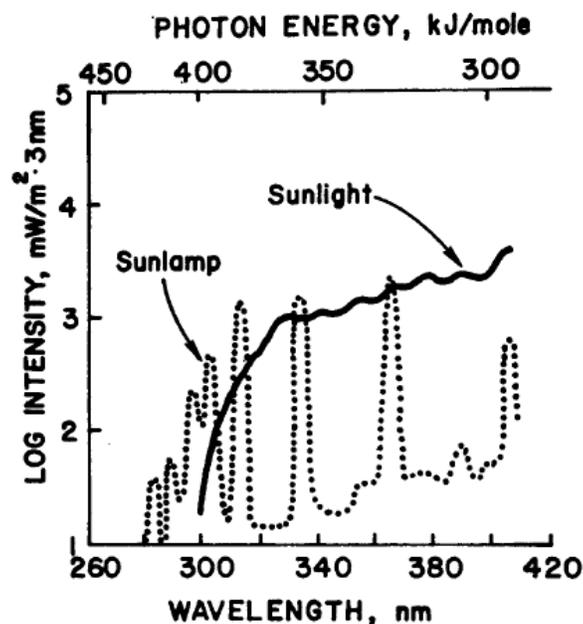
Figure 3. Typical spectrum of surface solar intensity and emission spectrum from S-1 mercury sunlamp (3).

In order to induce chemical change, the photon must first be absorbed by the material, and a material totally transparent in the UV range will not exhibit photoinitiated corrosion. Many chemical entities often found in polymers, however, have characteristic ultraviolet absorptions. The carbonyl group, for instance, has a broad absorption peak at approximately 300 nm due to the excitation of a nonbonding electron into the π^* molecular orbital. Such UV-absorbing groups may be present naturally in the polymer; or they may be introduced adventitiously by any of several means, such as oxidation during fabrication, polymerization anomalies, introduction of various additives, etc. The energy contained in photon-excited high-energy orbitals may be dissipated harmlessly in the form of heat, but a certain fraction of these excited states may relax by initiating chemical change. It is this latter process that produces deterioration.

The deterioration process is frequently some form of photoinitiated oxidation. Typically, the process is initiated when a sufficiently energetic photon strips away a labile proton from the polymer, leaving behind a free radical:

$$RH \xrightarrow{h\nu} R\bullet + H\bullet \tag{1}$$

The radical is highly unstable, and reacts easily with atmospheric oxygen to form a peroxy radical, which further reacts to form hydroperoxide:

$$R\bullet + O_2 \longrightarrow ROOH \tag{2}$$

The oxidation process may now be repeated, so that the initial abstraction by the photon serves to set up a chain reaction which may include thousands of steps. The hydroperoxides formed are generally felt to be the direct cause of degradation in polymer properties, as they decompose via mechanisms which cause polymer chain scission and/or crosslinking.

Scission and crosslinking may be regarded as competitive mechanisms, with one or the other

dominating in a particular situation. Crosslinking may also be deleterious, in that it reduces molecular mobility and leads to the sort of brittleness often seen in elastomers which have been exposed to sunlight.

Another deleterious result may be the production of chromophoric chemical species. Such groups may impart an unacceptable discoloration to the polymer if they absorb in the visible range of light, and an autocatalytic UV degradation may be established if UV-absorbing chromophores are produced, which in turn serve to capture more UV photons. These groups, however, may also serve as convenient means of monitoring the extent of the deterioration process, since they are often amenable to quantitative analysis by suitable spectroscopic techniques.

Moisture Absorption
Although polymers do not rust in the presence of environmental moisture, most polymers absorb some moisture through diffusion in high humidity environments. The extent of moisture absorption in a given polymer will be a function of its hydrophilicity or chemical compatibility with water.   Absorbed water is generally less damaging to polymeric materials than is sunlight, but its effects may be important in certain cases. Its role is usually to act as a plasticizer, decreasing the glass transition or softening temperature and yield strength of the polymer. This latter effect has caused concern for polymer matrix composites employed in advanced aircraft, where absorbed moisture may lower the resin matrix T_g to the point that the material is unable to withstand the severe aerothermal loadings encountered (4). Cases in which water causes permanent degradation by hydrolysis of chemical bonds are not common, and the plasticizing effects can generally be reversed upon drying the material. Rainfall, however, may act in concert with photo-initiated oxidation to produce erosion of the material, serving to wash away the embrittled surface layer so as to expose new material to direct sunlight.

Water is of special concern in the case of glass-fiber reinforced polymer matrix composites, since glass is known to be subject to permanent hydrolytic damage, especially when simultaneously exposed to stress. Water causes significant reductions in the strengths of fiberglass composites, and it has been common practice in the marine industry to design to "wet" rather than dry strength limits. The nature of the water-induced damage is not well understood, since its effect is often but not always reversible on drying (5). The difference between wet and dry values has been reduced by the development of surface treatments applied to the fibers before impregnation. These surface treatments are considered by many to stabilize fiber-matrix adhesion by forming chemical bonds between the glass fibers and organic resin, although others argue that the treatment acts primarily to shield locally defective regions of the fiber from the corrosive effects of the water.

Outmigration of diluents and unreacted monomers
Polymers can be filled and modified in a great may ways and this versatility is an important key to their commercial success. Fillers and additives used in polymer products include plasticizers and reactive diluents, antioxidants, UV stabilizers, colorants, flame retardants, mechanical reinforcements, and inert fillers to reduce costs. Plasticizers are important fillers, often used in polyvinyl chloride to impart flexibility to what is inherently a rigid plastic. The characteristic "plastic" odor often detected in children's' toy stores is due to the outmigration of the phthalate plasticizer from PVC. This outmigration is a degradation mechanism, as loss of plasticizer reduces the material's flexibility. Outmigration of diluents occurs by diffusion, the same mechanism which allows environmental moisture to migrate into the material, increasing its flexibility and decreasing its high temperature stability.

Most materials can pose certain safety problems, during their manufacture, use, or disposal. As

mentioned earlier, polymers are low-energy stable compounds, generally inert and unreactive. As such, they pose few dangers to human health or the environment. However, the monomers from which they are made are sometimes toxic, and not all of these chemicals are converted to the polymeric state after polymerization. These materials can migrate from the bulk of the material to the surface and into the environment. Most consumers are now aware that a constituent of polycarbonate, bisphenol-A, is thought to produce certain health problems, especially in infants. This worry has impacted consumer acceptance of what has long been considered a versatile plastic of extremely high quality.

Flammability
Polymers are synthesized from fossil fuels, so it is not surprising that they can burn. One measure of their flammability is the limiting oxygen index ("LOI"), the percentage of oxygen in the air needed to support combustion. LOI over 23 indicates a resistance to burning, and many polymers have LOI greater than this. For instance the LOI of PVC is near 30, although, when plasticized, its LOI drops to near 18. Even with a room temperature LOI above 23, however, polymers can contribute to fires when fed by nearby flame, for instance by burning wood. In addition, the LOI of a given polymer may be temperature dependent, and it may drop as the temperature rises during a fire.

As mentioned earlier, combustion products from burning polymers can be dangerous. Chlorine is released when PVC burns, for instance, and of course chlorine is toxic. However, polymer outgassing products probably aren't the main danger in fires. Most fires occur in conditions of limited oxygen, so that substantial carbon monoxide concentrations are developed. CO is such a major threat in fires that polymer products, while of concern, are not usually the main problem.

Even in the absence of unreacted monomers or additives, toxic chemicals can be released if the polymer degrades, for instance in a fire.

Physical aging and other mechanical effects
Physical aging occurs in polymers due to a variety of processes. Over long periods of time, small scale rearrangement of short segments of the polymer main chain and side chains may lead to changes in the physical properties of the material such as increasing density or changes in dimensions under stress. In some polymers, under stresses applied during use these molecular rearrangements can lead to other more pronounced changes such as *crazing*. Crazing (6) is a degradation mechanism prevalent in amorphous plastics such as polystyrene and polycarbonate. Crazes look like cracks, but are actually internal debond regions in which a void is spanned by fibrils of polymer connecting the uncrazed material on either side of the material. Figures 4 and 5 show the appearance and morphology of crazes.
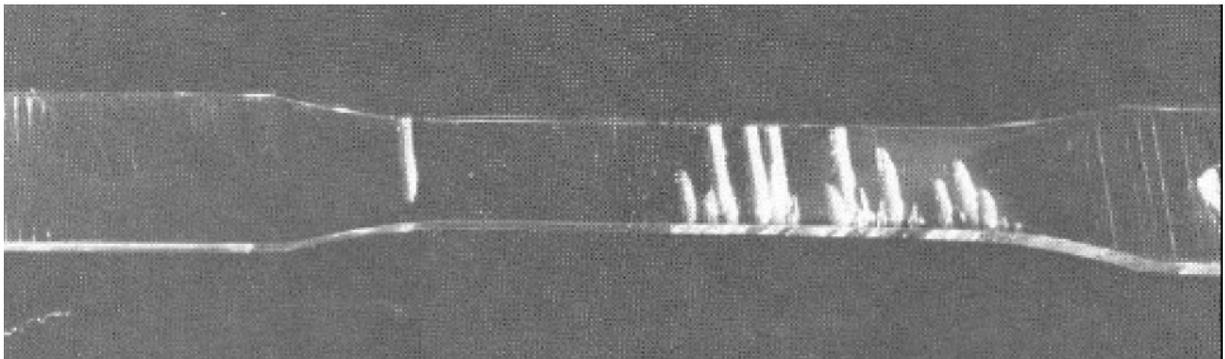

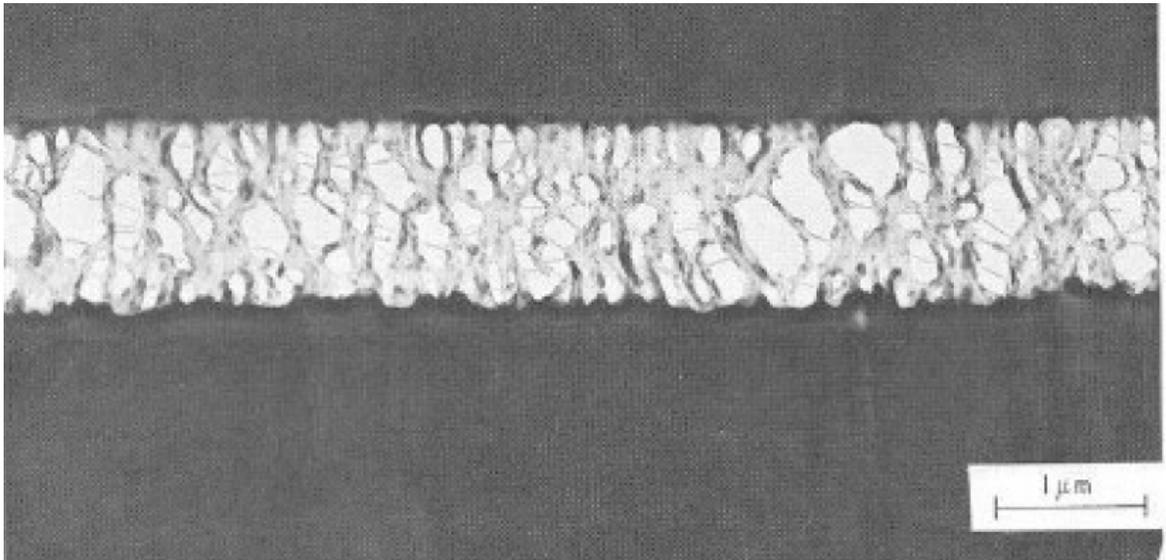Figure 4. Crazes in a tensile specimen (6)

Figure 5. Micrograph of a craze, showing the fibrils spanning the void region within the craze
(6)

These crazes grow under the influence of tensile stresses, and are facilitated by factors such as
absorbed diluents that increase molecular mobility. Diluents most effective in promoting crazing are
those whose solubility parameters are close to that of the polymer itself; acetone in polystyrene or
polycarbonate is a dramatic example.

Crazes differ from true cracks in that the fibrils are capable of supporting mechanical stress, and a
crazed specimen may exhibit a substantial fraction of the failure stress of the uncrazed polymer.
However, as the load in maintained or increased, the fibrils may rupture, so that crazing can be a
precursor to brittle fracture. A phenomenon known as *environmental stress cracking* ("ESC") is related
to craze breakdown. When a compatible environmental agent diffuses along an internal crack by
capillary action, it can plasticize the material in the high-stress region at the tip of the crack. This
facilitates crazing at the crack tip, which under continued stress experiences fibril rupture and crack
extension. Eventually the crack extends through the entire specimen, leading to a brittle-appearing
fracture. Both stress and environment are thus involved in this process, which accounts for a large
fraction of failures in polymeric articles.

Creep and creep rupture are other mechanical processes that occur in polymers during use. These time
dependant degradation and failure processes reflect the underlying molecular mobility of the materials,
and may be exacerbated by elevated temperature and humidity.   Like all the other mechanisms of
polymer degradation discussed above, they are thermally activated processes.

Kinetics of degradation
As described above, there are very many distinct mechanisms of material degradation and a kinetic
scheme could conceivably be developed for each of them. But as a simple general approach,
degradation may be seen as a kinetic process in which the chemical bonds providing the material's
strength are gradually consumed, or a second material diffuses in or out of the bulk of the material.

As an example that contains a reasonable overall picture of such a process, we might propose a first-
order mechanism for main chain bond scission in which the number of unbroken bonds decreases at a
rate proportional to the number of unbroken bonds remaining:

$$\frac{dn}{dt} = -Kn \rightarrow \frac{dn}{n} = -K\,dt \rightarrow n = n_0 e^{-Kt} \qquad (3)$$

Here n is the fraction of unbroken bonds remaining and K is a rate constant for the process. In such a process the number of unbroken bonds falls to zero only at $t \rightarrow \infty$, and clearly total failure will occur well before that. Perhaps a reasonable scaling law would take the lifetime-to-failure t_f to scale with the *average* time $\langle t \rangle$ for a bond scission, which can be computed as

$$t_f \approx \langle t \rangle = \frac{\int n \cdot t\,dt}{\int n\,dt} = \frac{1}{K} \qquad (4)$$

Treating the process as thermally-activated and stress-aided, we can write the rate constant K as an Arrhenius-Eyring expression:

$$K = K_0 \exp \frac{-\left(E^* - \psi V^*\right)}{kT} \qquad (5)$$

Here E^* and V^* are an activation energy and volume, and ψ is the mechanical stress on the bond. Determining ψ is nontrivial, as ψ obviously varies over the distribution of bonds and is dependent on the material's microstructure. But as another approximation, we might take the atomic stress to scale with the externally applied stress, giving

$$\psi \approx \sigma \rightarrow t_f = t_0 \exp \frac{\left(E^* - \sigma V^*\right)}{kT} \qquad (6)$$

Where $t_0 = 1/K_0$. A relation similar to this was proposed by S.N. Zhurkov (7), who conducted a large number of important and innovative studies of the physics of thermomechanical degradation. He argued that mechanical fracture is in fact a thermal degradation process, in which an applied stress acts to lower the energy barrier to thermofluctuational bond dissociation Figure 6 shows this relation to describe the time to failure in a wide variety of materials, including ceramics, metals and polymers.
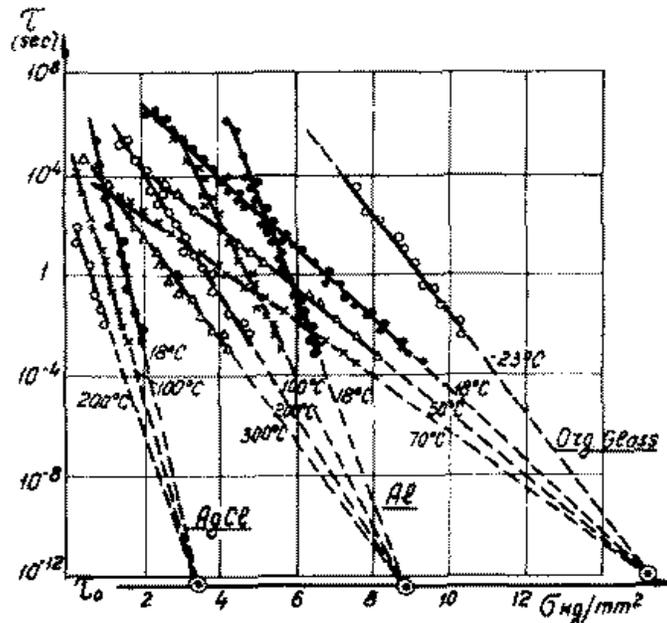
Figure 6 - Time and temperature dependence of the creep-rupture lifetime of solids (7). Org. Glass is PMMA.

Bacterial and fungal degradation
Attack by microorganisms is another possible mechanism of environmental degradation in polymers. Microbial attack is most problematic in high humidity environments, since growth of microbial species on a polymeric material requires the presence of environmental moisture. Bacterial and fungal growth has been observed on some solid polymers, but it is most commonly observed in textiles. Microbial attack can degrade the properties of a range of textile materials such as fibers, fabrics and webbings. Even in relatively dry environments, if the material is buried underground or worn as part of a garment, sufficient environmental moisture may be present to facilitate microbial attack.

Protection against Environmental Degradation in Polymers

Physical or chemical stabilization against environmental degradation in polymers may be achieved by blocking any of the steps in the deterioration process. Since the effects of UV radiation are the most serious threat to environmental durability, a number of techniques have been developed to counter them. UV radiation may be excluded by various coatings or paints. Fillers such as carbon black may also be used as screening agents, or the radiation may be absorbed harmlessly by chemical agents which dissipate the photon energy without chemical change. Radical scavengers may be employed to terminate chain radicals and halt the propagation steps, and various deactivators are available that serve to stabilize the hydroperoxide groups formed during photolytic oxidation (see equations 1 and 2). The reader is referred elsewhere (e.g., Reference 4) for a more complete treatment of stabilization.

Paints and Coatings
Organic paints and other coatings have been used successfully to protect polymeric materials from UV radiation, but these conventional surface treatments cannot exclude diffusion of environmental moisture into the bulk of the polymer. Since absorption of moisture into the material does not result in main chain bond scission, this rarely causes degradation leading to failure. However moisture absorption can have serious consequences in the use of polymer matrix composites in high performance

applications such as aircraft structures. Strength and stiffness values used to design aircraft structures from these materials must be measure under "hot wet" conditions to account for the decreased properties the materials will exhibit if those conditions are encountered in flight (8).

Novel surface treatments
Novel surface treatments are being developed to provide greatly enhanced hydrophobicity and /or oleophobicity to the surface of polymer films or fabrics (9,10). Such surfaces could provide some level of protection against moisture sorption and subsequent diffusion, protection against microbial attack, and even the potential for self-cleaning. These treatments are based on the behavior of some naturally occurring surfaces such as that of the lotus leaf.   Observing these natural surfaces provides clues to creating superhydrophobic / superoleophobic surfaces, i.e. surfaces which have water and oil contact angles greater than 150°. Since the wettability of a solid surface is determined by two parameters, surface energy (γ) and geometrical roughness, the combination of these two parameters can be used for the development of superhydrophobic and superoleophobic surfaces. Development of these technologies is still at an early stage, and the durability of the surface treatments is often insufficient for commercial use. Great strides have been made in this area in the last 5-10 years, however, and this type of surface treatment may be used more extensively in the future.

There are also a range of antimicrobial surface treatments which have been used to prevent the growth of bacterial and fungal organisms on both naturally occurring and synthetic polymers. These include formulations based upon cationic silver or copper (11,12), and quarternary ammonium compounds or QACs (13). In contrast to the action of antibiotics which kill microbial species by interruption of metabolic pathways within the cell, these treatments appear to work primarily by disruption of the cellular membrane, although some effects on cell metabolism may occur.

Another novel approach to providing antimicrobial properties to polymers is the incorporation or attachment of antimicrobial peptides (AMPs) to polymeric surfaces (14,15). AMPs are small peptides containing anywhere from 2 to 50 amino acids and are found in the immune systems of all classes of life. They are potent naturally occurring antibiotics. Significant effort is focused currently on investigation of the mechanism of antimicrobial activity in AMPs and their potential use in antimicrobial surface treatments.

Summary

Materials engineers usually want to eliminate or slow degradation, since that leads to longer lifetimes and increased safety in their designed products. Polymers are attractive materials candidates in this regard, since they do not exhibit the rusting so troublesome in ferrous materials. On the other hand, environmental activists often criticize plastic products exactly because they are so stable, which contributes to litter that is very slow to disappear. We have outlined in the above discussion how polymers, while free of rusting, exhibit their own degradation mechanisms, perhaps the most pervasive being photolytic bond scission leading to discoloration and loss of mechanical strength and stiffness. Polymeric materials, especially in the form of textiles, are also subject to microbial attack which is not present in metals. The materials engineer and systems designer must be aware of these features affecting the durability of polymers, considering them appropriately in product design and taking steps to stabilize the material against these mechanisms.

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