Moisture-Related Failure

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PLASTIC MATERIALS and the composites made from them are frequently preferred to metals for use in structural applications because of favorable economic factors, weight reduction, or corrosion resistance. This article describes one aspect of corrosion resistance, namely, the adverse effects of moisture on the capability of a plastic to perform its task in a structural application. Because of space limitations, it is not possible to give numerous examples of the behavior of an extremely large number of plastics, so principles are emphasized wherever possible, and literature references are given for further reading. The more general aspect of chemical resistance is described in the article "Organic Chemical Related Failure" in this Volume.

Plastics are often regarded as being much more corrosion resistant than are metals. However, this view has pitfalls, and it is valuable to consider at this point how these two materials differ in their resistance to chemical attack. Generally, metals are attacked at their interfaces by electrochemical processes. Either they are dissolved (in aqueous solutions) or surface deposits build up, which may or may not limit the corrosive process. In either case, structural performance is adversely affected. Corrosion by diffusion of attacking species into metal is rare, although a well-known example that is directly related to failure mechanisms is hydrogen embrittlement of steel.

On the other hand, diffusion of species into plastics is common. The amount of such diffusion and its effect on properties range from none to catastrophic, such as the complete dissolution of certain plastics in appropriate solvents. The amount of diffusant absorbed may not be directly correlated to its effect on properties, especially in comparisons of different plastics. Adverse effects arising from penetrants are not necessarily chemical in nature; that is, no chemical bonds need be altered for deleterious effects to occur. This type of damage has been called physical corrosion (Ref 1, 2). Furthermore, this type of behavior characterizes most aspects of the interaction of water with structural plastics.

Chemical reactions that may occur in plastics cannot be studied electrochemically because they are generally nonconducting. Such reactions may encompass the range of organic reactions into which the polymer backbone and the various attacking species may enter. While attack by aqueous solutions of acids, alkalies, or oxidants is common, chemical attack of structural plastics by water itself is somewhat rare. Well-known exceptions are the hot-water degradation of polycarbonate (PC) and the thermosetting polyesters.

It is significant that in cases involving no attack of a plastic by an active ion, the presence of dissolved ion actually may act to diminish the amount (and the effect) of water absorption. Water absorption may be viewed as an osmotic phenomenon; that is, the amount of water absorption is governed by the thermodynamic activity of water either in solution or in the vapor phase (Ref 1-3). Examples of this behavior are given in Fig. 1, which compares the effect of water absorption in vinyl ester-styrene copolymers in distilled water and in saturated sodium chloride (NaCl) solution. This figure also compares the effect of a decreased polarity of the polymer, in this case by varying the amount of styrene coreactant.

Organic polymeric materials generally absorb moisture to some measurable degree when immersed directly in water or when exposed to atmospheric moisture. The amount of moisture absorbed depends on the chemical nature of the material, whereas the rate of absorption of water by plastics often follows well-developed mathematical models. This absorption can have both reversible and irreversible effects on properties and performance. Sorbed moisture has been shown to act as a plasticizer, reducing the glass transition temperature, T_g, and the strength properties of a plastic. This effect on properties has been shown to be essentially reversible. However, as already indicated, sorbed water can also induce physical corrosion, or irreversible mechanical damage, by means of microcracking or crazing, as well as irreversible chemical degradation of the polymer structure.

Table 1 lists the water absorption values for selected plastics as determined by ASTM D 570 after a 24 h immersion at 25 °C (77 °F). Generally, the more polar the nature of the plastic, the greater its affinity for water. As Table 1 shows, materials of low polarity, such as polyethylene (PE) and polypropylene (PP), absorb less than 0.01 wt% water. PC, polysulfone (PSU), and cellulose acetate, which have increasingly greater polarities that are greater than those of polyolefins, display increasing affinities for water. Equilibrium value for water absorption will be significantly higher for many plastics, as will water absorption values obtained at elevated temperatures. No simple correlation between the number of polar groups and the solubility of water in a plastic exists because of such factors as the accessibility of the polar groups, the relative strength of the water-water versus the water-plastic bonds, and the degree of crystallinity (Ref 4).

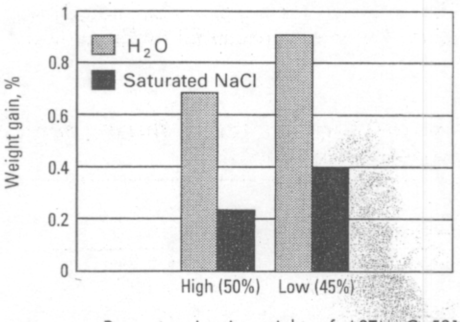


Fig. 1 Percent gains in weight of ASTM C 581 laminates of a high and low styrene containing vinyl ester exposed at 66 °C (150 °F) to a distilled and saturated sodium chloride solution for 120 days

Table 1 Water absorption values for selected polymers

Plastic	Water absorption, wt %
PTFE	0.00
PE, high density	<0.01
PP	<0.01
PVC	0.03
PS	0.05
PC	0.15
PSU	0.22
POM	0.25
Nylon 11	0.25
Polyvinyl butyral	1.0
Nylon 6	1.3
Cellulose acetate	1.7

PVC, polyvinyl chloride; POM, polyoxymethylene

Mechanisms of Moisture-Induced Damage

Bulk effects, such as a loss of stiffness, a lowering of the T_g, and an increase in creep and stress relaxation, are the most commonly observed problems that can lead to premature failure. These essentially stem from the same cause, which is related to the penetration of moisture into the bulk of the polymer, thereby plasticizing it, and inducing the undesirable effects. In general, the magnitude of the plasticization effects depends on the polarity of the polymer; these effects do not appreciably occur in nonpolar polymers, but rather, depend on the nature of the individual polymer. Because plastics differ widely in their susceptibility to these effects, the characteristics of important structural plastics are discussed below. The effects of moisture on modulus, creep, and stress relaxation cannot be discussed without noting the very important aggravating role played by temperature and stress.

The Effect of Moisture on T_g. Lowering the T_g is probably the most widely studied phenomenon related to failure of plastics, but it is not itself a true failure mechanism. For a structural plastic, the T_g is, simply put, an approximate upper limit of its useful temperature range. The plastic, which is hard and glassy below this temperature, becomes rubbery above it. However, the T_g is also a measure of the onset of long-range molecular movement in the plastic. Because the transition from glass to rubber is not a thermodynamic transition, but a manifestation of viscoelasticity, the exact value of the T_g depends on the method used to measure it, and the rate at which the temperature is changed during the measurement. For this reason, these parameters must be specified when reporting T_g measurements and when comparing data of different plastics. Semicrystalline plastics, in some cases, are exempt from the concern of exceeding the T_g because their crystalline melting point, always above their T_g, represents their temperature limit.

The effect of absorbed moisture on the T_g is invariably to lower it. This is consistent with the role of water as a plasticizer. As a rule of thumb, the more water absorbed, the lower the T_g. For this reason, a nonpolar plastic such as polystyrene (PS) is less affected than, for example, polymethyl methacrylate (PMMA). The lowering of T_g is sometimes quantitatively discussed in terms of several mixing formulas (Ref 5, 6). Currently, the most often used expression is:

$$T_g = \frac{X_1 C_{p1} T_{g1} + X_2 C_{p2} T_{g2}}{X_1 C_{p1} + X_{p2} C_{p2}} \qquad \text{(Eq 1)}$$

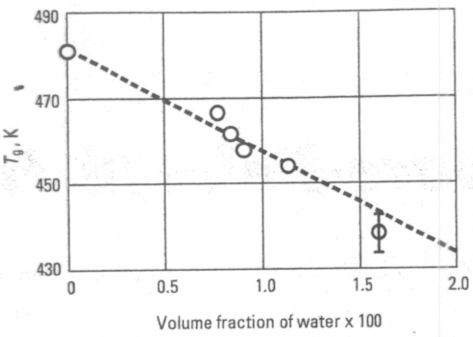


Fig. 2 Glass transition depression data (calculated). Curve as predicted by Eq 1. Source: Ref 10

In this expression, T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the polymer mixture, polymer 1, and diluent 2, respectively. The expressions C_{p1} and C_{p2} are the discontinuities in the heat capacities at the glass transitions of the components. This expression was first derived by Gordon (Ref 7) for polymer blends and was based on the Gibbs-DiMarzio entropy theory (Ref 8). Couchman provided an alternative derivation, based on a purely thermodynamic exposition (Ref 9). The extension of the Couchman approach to plastic-diluent systems, especially epoxy-water systems, has been carried out by Karasz *et al.* (Ref 10-12). Couchman's derivation (but not the result) has recently been criticized by Goldstein (Ref 13). The discussion is important to an understanding of the glassy state.

These relationships can be quite useful for predicting the loss of properties due to moisture. Such a relationship is shown in Fig. 2. Because the modulus falls precipitously at the glass transition, this type of data gives an absolute upper temperature limit. Most conservative design requires all application temperatures to be remote from the glass transition region. The relationship between T_g and the amount of absorbed water can be affected by many factors, such as additives, thermal pretreatments, presence or absence of fillers or reinforcements, and, in thermosets, amount and type of curative, degree of cure, and so forth.

Measuring the T_gs of moisture-containing resins is not accomplished without a good deal of care, because water is often lost during the measurement. This can be especially serious for high-T_g polymers, such as those used in high-technology applications. Examples of this are given in Table 2, with water loss being measured by thermogravimetric analysis (TGA). Essentially all the absorbed water may be lost unless proper precautions are taken. Measurements of T_g are often carried out by differential scanning calorimetry (DSC) (as was done by Karasz); DSC techniques are particularly adaptable to preventing loss of moisture during T_g measurements.

A method that satisfactorily measures the T_g in water-saturated thermoplastics and thermosets that do not have an excessively high cross-link density is to seal the plastic and a small amount of water in a high-pressure DSC pan and then measure in a normal manner (Ref 14). The pan contains three phases (liquid and gaseous forms of water, and polymer) and thus has but one degree of freedom by Gibb's phase rule, namely temperature, because this is necessarily the independent variable in a measurement of T_g. Results of using this method are given in Table 3, where they are contrasted with measurements in standard DSC analysis. The plastic, in principle, remains fully saturated with moisture during the run. A T_g measured by this technique is thus a "worst case" value of a plastic that is fully moisture saturated. A major drawback is that no values of T_g of intermediate saturations can be obtained. Other DSC techniques seem to be satisfactory as well. Simply sealing a moisture-containing plastic into a DSC high-pressure pan may be adequate, especially if the plastic sample is large, in comparison to the vapor space. A drawback of the DSC method is that it generally fails to give measurable T_gs for resins having a very high cross-link density, in particular, some of the aerospace epoxy resins.

Perhaps the most popular method of T_g measurement is dynamic mechanical analysis (DMA). Not only is the glass transition clearly distinguished, but other relaxations as well, and the shear or tensile complex moduli are measured and have a clear connection to the moduli of interest for engineering design. In Fig. 3, representative dynamic mechanical data are given, with some of the commonly used measures of T_g pointed out. To date, it is not possible to run experiments in an autoclave to prevent loss of moisture. Nonetheless, there is much to recommend this technique as a routine screening method for the T_g of moisture-containing plastics and composites.

Table 2 Water losses during temperature scans (thermogravimetric tests)

Resin/curing agent or plastic	Beginning water content, wt%	Water loss, wt%
EPON Resin 826/diamino-diphenyl sulfone	2.28	−0.91 at 40 °C/min (70 °F/min) −2.02 at 10 °C/min (18 °F/min)
PC	0.32	−0.2 at 40 °C/min (70 °F/min) −0.39 at 10 °C/min (18 °F/min)
PSU	0.57	−0.25 at 40 °C/min (70 °F/min) −0.52 at 10 °C/min (18 °F/min)

Table 3 Differential scanning calorimetry comparison of T_g results from sealed and unsealed pans

Resin/curing agent or plastic	T_g, unsealed pan, Dry, °C	T_g, unsealed pan, Dry, °F	T_g, unsealed pan, Wet, °C	T_g, unsealed pan, Wet, °F	T_g, sealed pan, resin and water, °C	T_g, sealed pan, resin and water, °F
EPON Resin 826(a)/EPON curing agent Y(b)	167	33	134 (1st scan)	275	125	257
EPON Resin 826/methylenedianiline	165	330	...	...	122	252
EPON Resin 826/Jeffamine D-230(b)	92	200	88	190	62	145
EPON Resin 826/Jeffamine D-400(b)	50	120	...	...	30	85
PC	148	300	139	280	132	270
PSU	184	365	184	365	158	315

(a) Tradename of Shell Chemical Company. (b) Tradename of Texaco Chemical Company

In one common mode of operation, the temperature is increased in jumps of 5 to 10 °C (9 to 18 °F) and held for 2 min, after which the dynamic mechanical parameters are measured. This technique tends to give conservative values for the T_g of dry plastics, but is not a good technique to use when determining the T_g for moisture-containing ones, particularly if the T_g is above 100 °C (212 °F). In many instances, the plastic specimen is completely dried out by this technique. A better technique is to ramp the temperature, as in the DSC and DMA techniques, at 10 °C/min (18 °F/min), for example. A further improvement (Ref 15) is to enclose the specimen in a polytetrafluoroethylene (PTFE) bag containing oil saturated with water. Thermomechanical analysis (TMA) is also a recognized method for measuring T_g (Ref 16).

Another method of assessing T_g of composite materials by modulus measurement is used in the aerospace industry. A number of specimens of a size suitable for measuring flexural modulus are placed in a humidity chamber until they reach saturation. Then the flexural modulus is determined for individual specimens at increasing temperatures in oil baths. The modulus versus temperature curve is plotted, and the T_g is identified by a rapid drop of modulus on the curve. Although rather tedious and time-consuming, this method has proved to be very satisfactory for advanced composite structures, for which performance is critical. Shear modulus (G_{12}) also can be determined, using ±45° tension tests.

It is likely that more work has been done on the effect of moisture on the T_g of epoxy resin systems than on any other plastic system. Of particular interest is the system based on tetraglycidyl methylenedianiline (TGMDA)/diamino-diphenyl sulfone (DDS). The chemical structures of these materials, which are the principal epoxy matrix resin systems currently used in advanced composite aircraft/aerospace applications, are given in Fig. 4. As can be seen from Table 4, the TGMDA/DDS can absorb as much as 6.5 wt% water. This absorbed water results in a dramatic drop in T_g (Ref 17-19). The reduction of the T_g resulting from the absorbed moisture is also given in Table 4 and corresponds with the 13 to 15 °C/wt% (25 to 30 °F/wt%) water content, as predicted by Ellis and Karasz. Also, the amount and rate of moisture absorption of a typical TGMDA/DDS laminate were found to increase with periodic exposure to thermal spikes (Ref 20), such as those experienced on a supersonic aircraft. The absorptivity coefficient of a graphite-epoxy laminate was shown to double with such an exposure.

Not all epoxy resin systems absorb as much water as the TGMDA/DDS system because the amount of water absorbed by an epoxy resin depends on the polarity of the epoxy resin system. Figure 5 gives the equilibrium water uptake values obtained by Morel, Bellenger, and Verdu (Ref 21) for two epoxy resins of different polarities, with three different curing agents also having varying degrees of polarity. The values are of the expected order because the TGMDA has more polarity than the diglycidyl ether of bisphenol A (DGEBA), and the polarity of the curing agents follows the order SO_2 is greater than CH_2, which is greater than O (Ref 21). The effect of moisture on the T_g depends on the amount of moisture absorbed, which in turn depends on the chemical structure of the cured resin.

Effect of Moisture on Creep and Stress Relaxation. Creep and stress relaxation are more important considerations in plastic materials than they are in metals. Unlike the T_g, these can be true failure mechanisms. For a plastic used above its T_g, these phenomena can be quite important, particularly in amorphous plastics with no microcrystalline phase and therefore no microcrystallites to act as "anchors." Most plastics used for structural applications are used at temperatures below their T_gs. However, creep and stress relaxation can still represent significant factors that a designer must consider.

Creep is the name for the increase in deformation that occurs under a constant load, in addition to the initial elastic deformation, and stress relaxation is the decrease in stress with time after stressing to a constant deformation. A designer considering the use of a plastic composite leaf spring in the rear suspension of an automobile would want to know how much the rear of the car would sag after a given period of time. This sag is an example of creep. When designing a plastic oil pan in which the bolts are tightened to a certain stress, a designer must ensure that the bolts will not become loose in service. The loosening of the bolts would be an example of stress relaxation. In this case, the bolts are tightened against an initial modulus of the oil pan, and the plastic is deflected a definite, though unmeasured, amount.

The cause of both creep and stress relaxation is the relaxation of molecular seg-

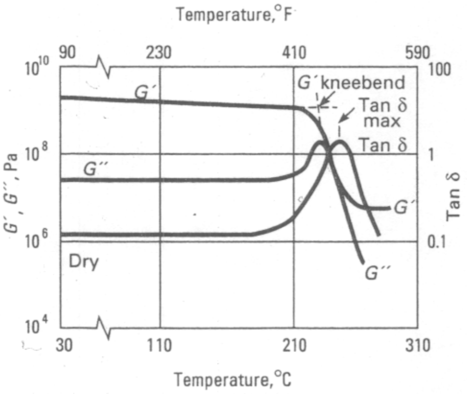
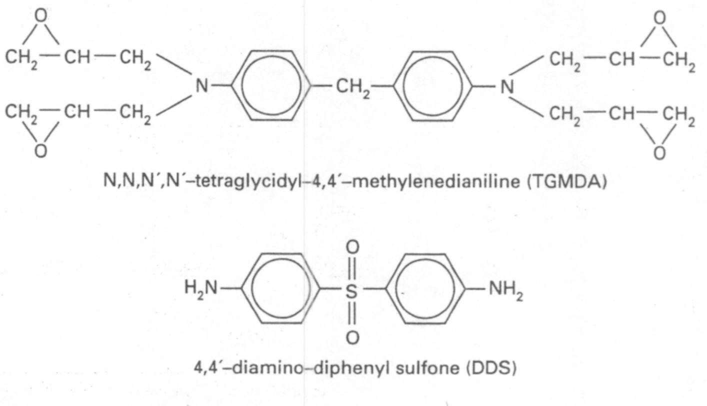


Fig. 3 Typical dynamic mechanical spectrum of high-temperature epoxy resin system



N,N,N′,N′-tetraglycidyl-4,4′-methylenedianiline (TGMDA)

4,4′-diamino-diphenyl sulfone (DDS)

Fig. 4 Chemical structures of TGMDA and DDS

Table 4 Effect of water on the T_g of TGMDA/DDS systems

	System I(a)	System II(b)	System III(c)
Moisture gain, wt%	6.5(d)	5.5(d)	5.0(e)
Glass transition temperature			
Dry, °C (°F)	246 (475)	175 (350)	200 (390)
Wet, °C (°F)	144 (290)	112 (235)	140 (285)
°C/wt% water absorbed	15.7	11.5	12.0

(a) NARMCO 5208 (Ref 20). (b) TGMDA/32 phr DDS/$BF_3 \cdot H_2NCH_3$ (Ref 18). (c) TGMDA/50 phr DDS (Ref 17). (d) Immersion in water at 71 °C (160 °F). (e) Immersion in water at 60 °C (140 °F)

ments under stress on a time scale greater than that of loading. Higher temperatures accelerate the relaxational processes, of course, making creep and stress relaxation more important. An excellent and practical review of creep and stress relaxation is found in Ref 22 and 23. A fundamental approach is given in Ref 24. Creep and stress relaxation are not only important in a practical sense as possible failure mechanisms, but they are also used in laboratory studies of the viscoelastic nature of plastics.

It is very useful to know that, in many cases, the creep and stress relaxation curves at several temperatures can be laid side by side and shifted horizontally to form a single curve (see Fig. 6). If one curve is not shifted and the other curves are shifted to the left and right of it, the temperature of the unshifted curve is called the reference temperature. Any one of the available curves may be chosen to represent the reference temperature. The superposed curve resulting from the shifting is called a master curve, on which the horizontal scaling of the reference curve (usually logarithmic) is simply extended to the left and right. The amount that each curve is shifted, identified as a_T, is measured and recorded.

The construction of the master curve makes it possible to predict the creep or stress relaxation at the reference temperature (or other temperatures) for very long periods of time, even years, using experimental measurements that extend only over hours, weeks, or months. This remarkable property, called the time-temperature equivalency, occurs in most of the commonly encountered plastics. Examples of creep and stress relaxation curves are shown in Fig. 6, 7, and 8. Figure 7 is a master curve of the tensile creep of a commercial grade of PC (Ref 22), while Fig. 6 is previously unpublished data on the flexural creep of a composite material. The constituents of the composite are an aromatic amine cured epoxy resin and uniaxial 67 wt% glass roving reinforcement. In the creep tests, the reinforcement was parallel to the long axis of the specimens.

There are precautions for using time-temperature superposition for the prediction of long-term behavior. The time-temperature superposition is valid, strictly speaking, only if linear viscoelastic equations are applicable; this is called Boltzmann linearity. Thus, in practice, the application should be limited to regions in which an increase in stress from *S* to k*S* produces a change (increase) in deformation from *x*(*t*) to k*x*(*t*). For instance, in the case of the epoxy composite mentioned above, stress levels up to at least 345 MPa (50 ksi) were tolerated at temperatures below 93 °C (200 °F). However, above this temperature, only lower stresses gave linear behavior. Although a 345 MPa stress level translates to approximately 20 MPa (3 ksi) stress in the resin (which is a high load for viscoelastic behavior, even for a glassy polymer), linearity is apparently maintained because deflection is limited by the reinforcement. Another possible pitfall is that a new failure mechanism that has not been taken into account may appear after a long period. Chemical degradation could be one such mechanism, and the effect of water, which will be discussed, is yet another.

Relaxation processes are usually accelerated by moisture; as noted above, the severity of this effect depends on the nature of

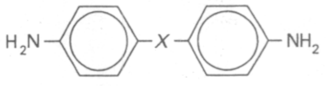
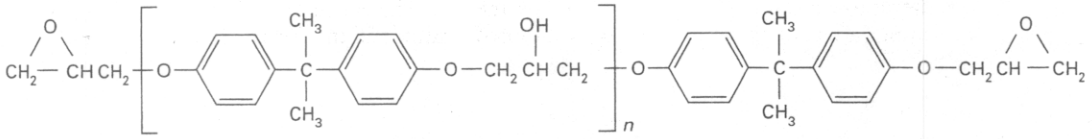
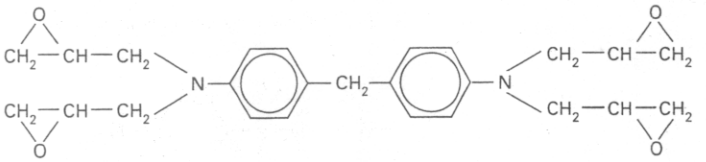
Resin structure			
	X = —O—	X = —CH_2—	X = —SO_2—
 Bisphenol A epoxy resin molecule	1.9	2.1	2.8
 TGMDA	2.8	4.3	5.1

Fig. 5 Comparison of water absorption of epoxy resin systems of differing polarities

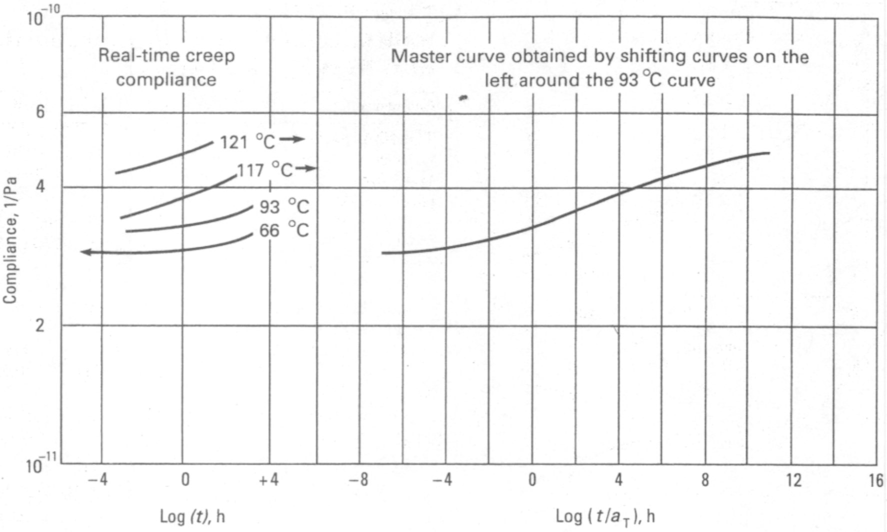


Fig. 6 Flexural creep compliance of parallel glass fiber reinforced aromatic amine cured epoxy resin (EPON Resin 826)

the plastic, the amount of water absorbed, the temperature, and the severity of the loading to which the part is subjected. In the case of the flexural creep of the epoxy resin composite discussed above, the behavior of specimens soaked for long times in water at 66 °C (151 °F) and then tested for creep, also at 66 °C (151 °F), was essentially the same as for the dry specimens tested similarly; thus, no additional shift need be applied to the creep curves. However, in experiments that were similar but were conducted at 93 °C (200 °F), a shift factor due to water ($-\log a_w$) equal to 3.94 had to be applied to the curve for the water-soaked specimen to bring it into reasonable agreement with the master curve. This demonstrated that a wet composite will creep at 93 °C (200 °F) to the same extent as a dry one at about 113 °C (235 °F). Furthermore, nonlinearity in the Boltzmann sense was introduced at lower stress because of the increase in compliance. In addition, other failure mechanisms peculiar to the effect of moisture on composites were sometimes observed. A very careful and detailed study of the effect of moisture and temperature on the creep of polyester resins was conducted by Maksimon *et al.* (Ref 26). It was found that the effect of moisture and temperature on the shift of the data was not independent, but interactive.

Moisture-Induced Fatigue Failure. Resistance to fatigue failure is an important criterion in the design of many plastic parts, and it is fair to say that many plastic parts actually fail by this mechanism. However, the effect of moisture on fatigue of plastics has not been widely studied. In the few studies reported, the effect of absorbed moisture is not uniformly bad, but in fact sometimes acts to improve performance. Manson and Hertzberg (Ref 27) found that fatigue crack propagation in PC was slower above a certain stress level than in dry nitrogen, but the converse was true below this stress level. More complete studies have since been made on plastic materials having an important application as marine ropes. In these studies, polyester materials were affected very little by water or seawater; nylon 6/6 was more affected. The presence of ions, either in seawater or added to solution, did not promote stress cracking in these fibers and ropes (Ref 28-30).

Moisture-Induced Failure in Composites. This review would not be complete without a discussion of moisture-induced failure mechanisms in composite materials. The discussion will focus mainly on reinforcing glass and carbon fibers, and will be limited, for clarity, to composites reinforced with continuous, uniaxially oriented fibers. Damage mechanisms may take several forms. The plastic matrix is subject not only to the damage mechanisms discussed above, but also to interfacial and stress-cracking mechanisms. An example of interfacial failure is the much-discussed loss of compressive strength in carbon fiber reinforced epoxy composites under hot, wet conditions. Fiber buckling may occur in this type of failure, allowed by the creep of the more compliant matrix. Another type of moisture-induced damage often seen in composite materials is delamination, which also may contribute to the compressive failure described above. These damage mechanisms are seen in shear and compression, but not in tensile loadings. Stress cracking, however, is a tensile failure, and is more commonly associated with glass fibers than with carbon. Water alone is known to cause this effect, but the situation

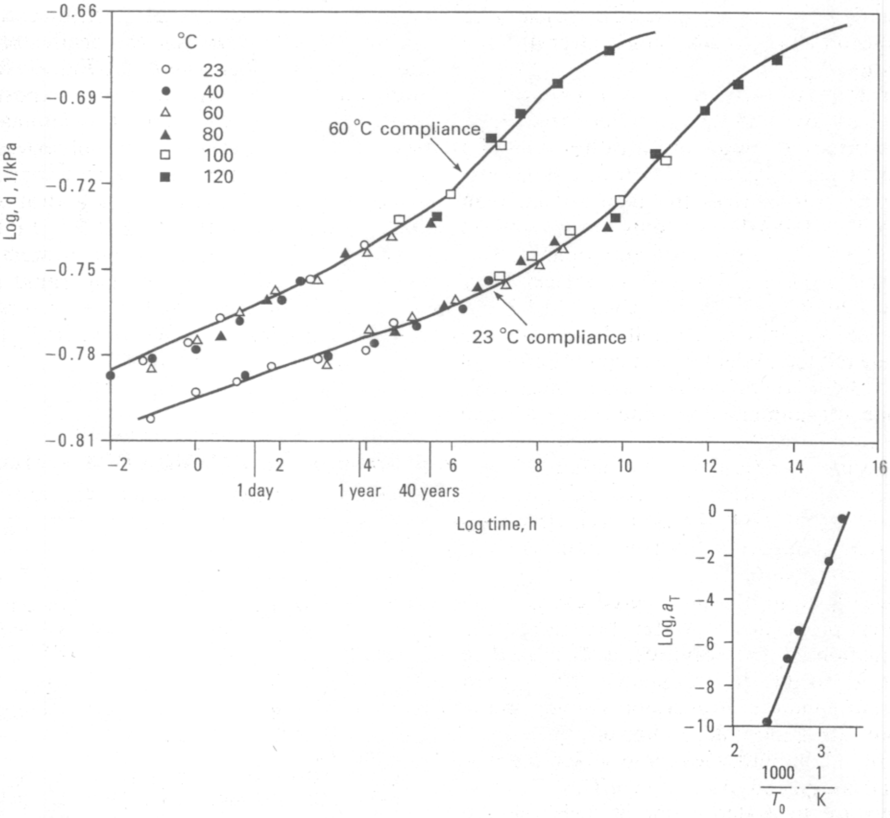


Fig. 7 Polycarbonate creep compliance at 23 °C (73.4 °F) and 60 °C (140 °F) with Arrhenius plot of shift factor. Source: Ref 22

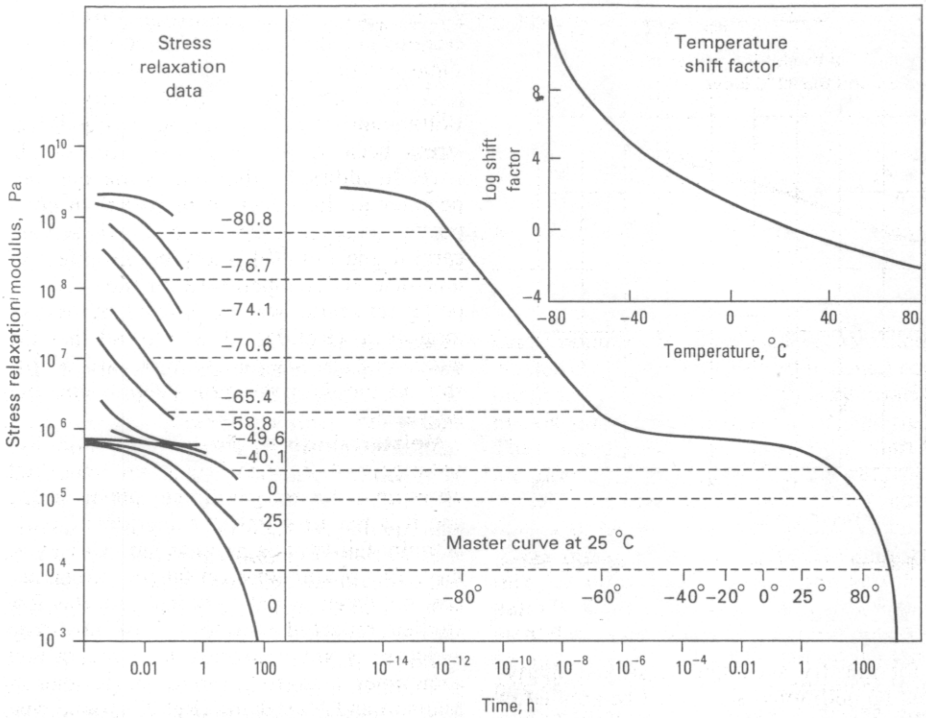


Fig. 8 Time-temperature superposition principle illustrated with polyisobutylene data. Reference temperature of the master curve is 25 °C (77 °F). Insert graph shows the amount of curve shifting required at different temperatures. Source: Ref 25

is greatly aggravated in fibers exposed to aqueous solutions of acids (Ref 31, 32). These failures, when they occur, may be sudden, and in critical applications can be catastrophic.

Blistering is a delamination failure that occurs in some composites when exposed to moisture. According to Ref 3, this phenomenon is promoted by osmotic pressures that build up when diffusing water increasingly dilutes ionic species at the fiber-matrix interface. This damage mechanism is fairly common in polyester composites, as well as in vinyl ester resins.

Effect of Moisture on Mechanical Properties

Thermoset resins, specifically epoxy and polyester, are described below.

Epoxy Resins. Absorbed water not only results in a depression of the T_g of plastic materials, but also causes a loss in other performance properties. For example, Apicella and Nicolais (Ref 33) have shown that the epoxy resin system based on the DGEBA cured with tetraethylenetriamine (TETA), and conditioned in water at 20 and 50 °C (68 and 120 °F), absorbed 2.96 and 3.22 wt% water, respectively, resulting in a decrease of their elastic moduli by 5.9 and 6.6 MPa (60 and 67 kgf/cm^2) (Ref 33). Brewis and his coworkers noticed the same behavior in an epoxy resin adhesive based on DGEBA cured with di(1-aminopropyl-3-ethoxy) ether (Ref 34). After a 24 h immersion in water, the adhesive became highly ductile, resulting in reduced yield strength, tensile strength, and modulus.

The TGMDA/DDS epoxy resin system, used for over 15 years, suffers from high moisture absorption and a rather dramatic loss of performance in hot/wet conditions. Table 5 summarizes the data obtained on two TGMDA/DDS systems cured with 54 and 100% of the stoichiometric quantities of curing agent (Ref 35). As can be seen from the table, the two systems absorbed 4.7 and 5.8 wt% water, which resulted in a decrease of the moduli under hot/wet conditions of 19 and 36%, respectively, when measured while still immersed in water at 93 °C (200 °F) after 2 weeks of immersion in water at this same temperature. The effect of high levels of moisture on the performance above 93 °C (200 °F) of a TGMDA/DDS system is apparent from the data summarized in Table 6.

Degradation of amine cured epoxy resin matrix properties by water, because of the formation of microcavities, is discussed in Ref 36 to 38. It was shown that sorbed moisture induces irreversible damage in the resin, the amount depending on the temperature and humidity levels to which the material is exposed. As shown in Table 7, upon exposure to water vapor at 65% relative humidity, the failure mode of the epoxy resin system being studied by Brewis and his coworkers changed from ductile to brittle. They propose that this loss of properties is associated with the formation of microcavities after long-term exposure of the epoxy resin to high humidity. Fedors has shown that water-soluble inclusions, such as undissolved salts, in a glassy epoxy resin matrix can nucleate crack formation when the resin is immersed in water (Ref 39).

Table 5 Effect of absorbed moisture on the physical properties of a TGMDA/DDS system

Components	A	B
TGMDA, parts	100	100
BPA epoxy novolac(a), pph	8.2	8.2
DDS, pph	28	51.9
Glass transition temperature		
Dry, °C (°F)	242 (470)	262 (505)
Wet, °C (°F)	174 (345)	170 (340)
Flexural properties, RT/dry		
Strength, MPa (ksi)	117 (17)	131 (19)
Modulus, GPa (10^6 psi)	4.0 (0.580)	3.8 (0.548)
Flexural properties, wet(b)		
Strength, MPa (ksi)	83 (12)	76 (11)
Modulus, GPa (10^6 psi)	3.2 (0.471)	2.4 (0.352)
Modulus, wet/dry(c) % retention	81	64
Moisture gain, %	4.7	5.8

(a) EPI-REZ SU-8 (Interez, Inc.). (b) Tested in water at 93 °C (200 °F) after 2 weeks immersion at 93 °C (200 °F). (c) Tested in water at 25 °C (77 °F) after 2 weeks immersion at 25 °C (77 °F)

Polyester Resins. The most widely used class of thermoset resins for fiber-reinforced applications is the polyester-base resins. The structures of the three most common types—the orthophthalic esters, the isophthalic esters, and the bisphenol A/fumarate resins—are given in Fig. 9. The effect on mechanical properties of exposure to 100 °C (212 °F) water on glass laminates based on these three types of polyesters is given in Fig. 10. Despite the fact that the orthophthalic polyester shows a dramatic loss of properties at 100 °C (212 °F), it is the most widely used matrix resin system in fiberglass-reinforced boats. The rapid decline in properties results from exposure to water at temperatures well above its T_g and

Table 6 Hot/wet neat resin properties of a TGMDA/DDS system

System: 90 parts TGMDA, 10 parts EPI-REZ SU-8

Flexural properties	Dry	Wet
Moisture content, %	...	3.6(a)
At 25 °C (77 °F)		
Strength, MPa (ksi)	140 (20)	90 (13)
Modulus, GPa (10^6 psi)	3.8 (0.550)	3.5 (0.500)
Elongation, %	3.9	2.5
At 150 °C (300 °F)		
Strength, MPa (ksi)	76 (11)	40 (6)
Modulus, GPa (10^6 psi)	2.6 (0.370)	1.5 (0.215)
Elongation, %	3.2	3.5
At 175 °C (350 °F)		
Strength, MPa (ksi)	83 (12)	35 (5)
Modulus, GPa (10^6 psi)	2.3 (0.330)	1.1 (0.155)
Elongation, %	4.2	4.0

(a) After 48 h immersion in boiling water

Table 7 Effect of moisture on an epoxy resin adhesive system

Mechanical properties	Dry	24 h immersion at 100 °C (212 °F)	Dried 48 h after 65 °C (150 °F)(a)	3 months at 65% RH at 25 °C (77 °F)
Yield strength, MPa (ksi)	48 (7.0)	24 (3.5)	58 (8.4)	...
Tensile strength, MPa (ksi)	41 (5.9)	24 (3.5)	52 (7.5)	54 (7.8)
Elongation, %	7.1	37	6.8	5.1
Modulus, GPa (10^6 psi)	1.70 (0.25)	1.02 (0.15)	1.56 (0.25)	1.77 (0.26)
Failure mode	Ductile	Ductile	Ductile	Brittle

(a) Dried 24 h in a vacuum oven at 65 °C (150 °F) after 24 h immersion at 100 °C (212 °F)

well above general-use temperatures. Martin and Gardner report that glass-reinforced orthophthalate ester was untestable after 10 months of exposure at 100% relative humidity at 93 °C (200 °F), and significantly deteriorated at 82 °C (180 °F) (Ref 40). A glass-reinforced isophthalate polyester test specimen was relatively unaffected under the same conditions. Unfortunately, no tests were carried out at lower temperatures.

The mechanism of the moisture-induced failure of polyesters is quite complex. For example, Apicella and his coworkers have shown that the action of water on polyesters is a combination of the result of leaching of low molecular weight components initially present in the resin, chemical attack on the ester linkages, and plasticization by the sorbed water (Ref 41). Also, Pritchard and his coworkers have concluded that in neat polyester resin, degradation begins with water uptake, swelling, and leaching of non-bound substances (Ref 42). However, these workers have found that hydrolysis is the principal irreversible process, accelerated by osmotic-induced cracking. This osmotic process was ascribed to traces of water-soluble, phase-separated materials, particularly glycols.

It was reported in Ref 3 that interfacial bonding between polyester and clean glass fibers was rapidly destroyed by diffused water, with the initiating mechanism being dependent on the glass composition. Bond fracture with E-glass and C-glass reinforcing fibers was shown to be due to osmotic pressure generated at the interface by water-soluble materials leached from the glass fibers. However, when coupling agents were used, debonding was important only with hot water immersion. What effect this moisture-induced disbonding had on the mechanical properties of the glass-reinforced systems was, however, not examined. A method for predicting laminate properties of isophthalate esters after long-term immersion in water has been developed by Pritchard and Speake (Ref 43). These expressions were used to predict tensile property changes at 15 °C (60 °F) over a period of 15 years. Similar methods were used to predict property changes at 30 °C (85 °F), and were experimentally confirmed for absorption times of nearly 3 years.

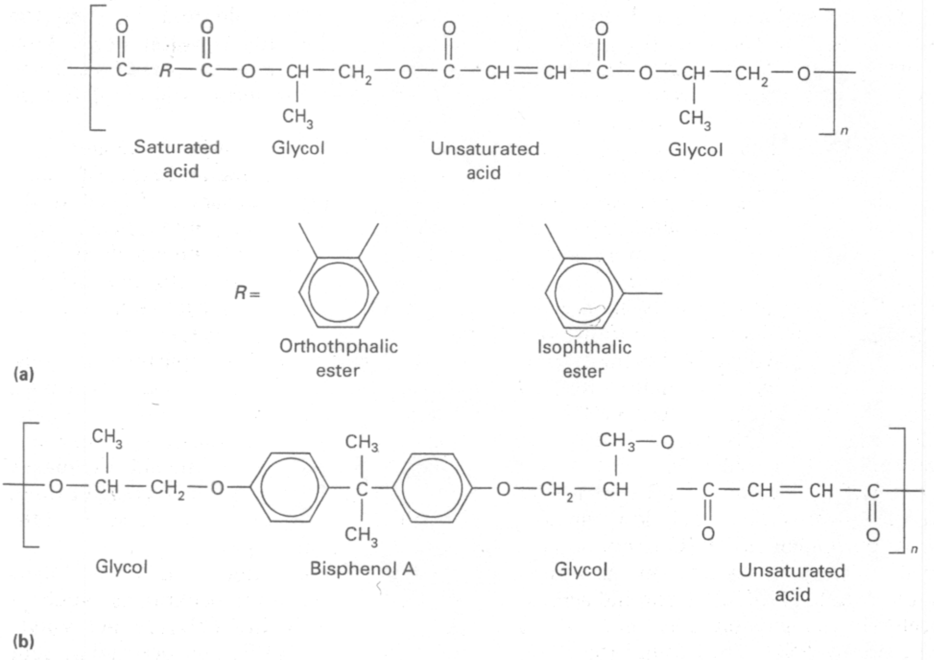


Fig. 9 Structure of unsaturated polyester resins. (a) Phthalate esters. (b) Bisphenol A/fumarate resins

Thermoplastics described below include polyester, PA, PC, PSU, polyoxymethylene (POM), and polyolefin.

Polyester. In an early, long-term aging study at 0% and 100% relative humidity on poly(1,4-butylene terephthalate) (PBT), Martin found that the dry samples aged 18 months showed little degradation (Ref 44). However, the results indicated that those aged at 100% relative humidity at 45 °C (115 °F) would lose up to half the initial value of mechanical properties in 4 to 10 years. In a more detailed study, Gardner and Martin (Ref 45) aged three grades of PBT up to 3 years at 100, 75, 50, and 11% relative humidity and temperatures of 66 to 93 °C (150 to 200 °F). They found the decrease in mechanical properties caused by hydrolysis occurs rapidly at higher temperatures and relative humidities. The hydrolytic degradation of polyesters results from the scission of the polymer chain at the ester linkage, which leads to a progressive reduction of molecular weight. Loss of tensile properties occurs rapidly after aging at higher temperatures and relative humidities. Elongation shows similar trends, although the loss of elongation is even more rapid. For example, the elongation of the material under almost all aging conditions fell essentially to zero in less than 32 weeks, whereas, at 32 weeks, greater than 50% retention of tensile strength was noted under several different aging conditions. Thus, toughness, or impact strength, is lost long before tensile strength half-life is reached.

Gardner and Martin have derived equations from Arrhenius plots for making life-cycle predictions at any temperature and humidity combination for both unfilled and filled PBT. The combined effect of temperature and humidity on unfilled PBT is written:

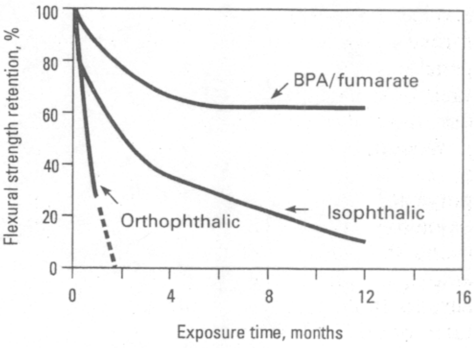


Fig. 10 Degradation of glass laminates in water at 100 °C (212 °F) for different polyester resin matrices

$$\ln_{t_{1/2}} = \frac{12\,680}{T} - 1.36\ \ln(R) - 31.73 \qquad \text{(Eq 2)}$$

where $t_{1/2}$ is the tensile strength half-life (days), T is the temperature (K), and R is the (fractional) relative humidity. A similar equation for glass-reinforced PBT is written:

$$\ln_{t_{1/2}} = \frac{13\,134}{T} - 1.33\ \ln(R) - 33.41 \qquad \text{(Eq 3)}$$

Gardner and Martin point out, however, that these equations may be less reliable at low relative humidity, because other reactions, such as esterification and oxidation, become more important than hydrolysis at low relative humidities. The authors did not study other polyesters, but similar trends could be expected in polyethylene terephthalate (PET), which would be expected to undergo the same hydrolysis, oxidation, and esterification reactions as PBT.

Polyamide. The effects of water on both unfilled and filled nylon 6, nylon 6/6, and nylon 6/10 have been studied by Woodham and Pinkston (Ref 46). The water absorption values after immersion at 23 °C (73 °F) for 160 days for unfilled samples of these three nylons were found to be about 10.2, 9.2, and 3.0 wt%. This would be expected, based on their polarity. Glass reinforcement reduces the rate of moisture pickup, with the most significant reduction being in nylon 6. For example, after 160 days under the above conditions, the moisture absorption of nylon 6 containing 40% glass reinforcement is only about 4.6 wt%, and that of nylon 6/10, containing the same amount of glass reinforcement, is about 2.0 wt%.

Woodham and Pinkston found that absorbed moisture affected the various physical properties differently. It plasticized the nylons; increasing amounts of absorbed water in unfilled nylons resulted in increasing Izod impact strengths. These increases in impact strength were particularly dramatic for nylon 6 and nylon 6/6. The glass-reinforced systems showed only slight increases in impact strength at increasing levels of moisture. Tensile and flexural strength of both the unfilled and filled nylons were found to decrease steadily with increasing levels of moisture. However, glass-reinforced systems at all moisture levels were generally found to maintain a higher level of their properties at saturation than were the dry, unreinforced systems.

Woodham and Pinkston's study was done at 23 °C (73 °F). However, nylon, like polyester, is susceptible to hydrolysis and oxidation. Gardner and Martin (Ref 47) found that unreinforced nylon 6/6, for example, is not suitable for long-term exposure to 100% relative humidity at temperatures of 66 °C (151 °F) or above. However, the strength of unreinforced nylon 6/6 was substantially reduced by long-term aging at 93 °C (200 °F), even at 0% relative humidity, indicating oxidative degradation of the plastic. Adding glass and stabilizers substantially improves the performance of nylons in hot/humid environments. Also, nylons that absorb less moisture retain their properties longer under hot/humid conditions. Nylon 12 loses about one-third of its strength because of absorbed water; however, further decreases, even at 66 °C (151 °F), were found to be quite small. At 93 °C (200 °F) glass-reinforced nylon 12 should be serviceable after 10 months at 100% relative humidity.

Polycarbonate. When aged under hot/humid conditions, PCs were found to have a rapid drop in weight-average molecular weight (Ref 48). For example, the weight-average molecular weight of a commercial-grade PC dropped to approximately 65% of its initial value after 40 weeks at 100% relative humidity and 65 °C (149 °F), and to 12% of its initial value at 93 °C (200 °F) and 100% relative humidity after the same length of time. Because the rate of hydrolysis is a function of both the temperature and the concentration of water in the plastic, the increased degradation at 93 °C (200 °F) is a result of both the increased temperature and increased water concentration. Water concentration at 65 °C (149 °F) and 100% relative humidity was found to be 0.416% in this study, and 0.470% at 93 °C (200 °F) and the same humidity level. At 75% relative humidity, the corresponding values were 0.337 and 0.365%. Thus, at constant temperature, the degradation rate over most of the temperature range is approximately halved when the relative humidity is reduced from 100 to 75%.

As indicated in the discussion on thermoplastic polyesters, the hydrolytic degradation leads to a progressive reduction in molecular weight and eventually to a loss of mechanical properties. In the study, the tensile strength was found to drop rapidly below a critical weight-average molecular weight of 33 800, and a transition from ductile to brittle failure was also observed at this point. Thus, brittle fracture occurred even in low-speed tensile tests of an injection molding grade of PC after exposure to 100% relative humidity for more than 12 days at 93 °C (200 °F). Extrapolations of Arrhenius plots based on 18 month tests indicate that the ductile-brittle transition at 38 °C (102 °F) would be reached after 5 years at 100% relative humidity. Reducing the relative humidity from 100 to 75% would reduce the hydrolysis rate by half at 82 °C (180 °F) and 93 °C (200 °F).

Polysulfone. As seen in Table 1, PSU, like PC, absorbs a relatively low amount of water, but unlike PC, PSU is not susceptible to hydrolytic degradation. Martin and Gardner (Ref 40) found that humid aging did accelerate an annealing effect in a commercial grade of PSU. They found the elongation after just a few months of humidity aging dropped from 90% to 6 to 7% elongation. No further change occurred after that time. Elongation in dry specimens, aged at 93 °C (200 °F), also dropped to the same level, but only after 18 months. During the 18 months of both dry and humid aging, all specimens had an increase of tensile strength of 6 to 16%; however, the effect appeared to occur faster in the humidity-aged specimens.

Polyoxymethylene. Unreinforced commercial grades of both acetal homopolymer and copolymer were found to be unaffected after 18 months of dry aging at 83 °C (181 °F) or at 66 °C (151 °F) and 100% relative humidity (Ref 40). In fact, the homopolymer showed only about a 6% drop in tensile strength after 1 month at 99 °C (210 °F) and 100% relative humidity, and a 3% drop at 82 °C (180 °F) and 100% relative humidity after 19 weeks. However, the tensile strength had dropped to such a point after 10 months at 82 °C (180 °F) and 100% relative humidity that the material was untestable. Under the same conditions, the tensile strength of the copolymer was unchanged. After a total of 18 months exposure at these conditions, the copolymer had lost about half of its original strength.

Because a strong odor of formaldehyde was observed in every 100% relative humidity test jar containing the acetal test specimens, the authors suggested that under hot/humid conditions these acetal polymers degraded by an unzipping mechanism.

Polyolefin. Because polyolefins such as PE, PP, and polybutylene absorb relatively little water (see Table 1) and contain no chemical bonds that are easily hydrolyzable, they are essentially unaffected by aging in water. Martin and Gardner (Ref 40) found, in a commercial 30% glass-reinforced PP, for example, that the long-term influence of humidity is rather small. After an initial drop in both tensile strength and elongation, the properties stabilized and did not change further.

Polyolefins are, however, rapidly oxidized at elevated temperatures, particularly those containing a tertiary hydrogen on the backbone, as in PP and polybutylene. These materials are protected with stabilizer packages containing antioxidants and ultraviolet-light stabilizers. Lusk (Ref 49) has shown that hot-water deterioration of polyolefin consists of two separate reactions: antioxidant depletion by water (through leaching or hydrolysis) and polymer oxidation. Thus, the service life of a polyolefin in hot water is a function of the specific plastic and stabilizer package, the temperature, and the humidity (or water pressure, in the case of hot-water pipe).

The effect of water on other polymers with all-carbon atom backbones, such as polystyrene, polyvinyl chloride, polyvinylidene chloride, PTFE, and polyisobutylene would be expected to behave somewhat similarly.

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