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How Time and Heat Affect Properties of Plastics

A number of plastics can withstand short-term service at 300 to 400 F with little serious effect. But change "short term" to "continuous," and the number of suitable materials drops appreciably. Here are new data on the plastics that maintain useful strength, even after hundreds of hours of high-temperature service.

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DEGRADATION, crosslinking, and oxidation are the primary mechanisms that change the mechanical properties of a polymer exposed to high temperatures.

- Degradation is caused by pyrolytic or by chemically enhanced scission of the chain molecules. Pyrolysis, if occurring alone, leads to a progressive reduction of molecular weight, and with it, to a loss in strength, elongation, and toughness, followed by a decrease in softening temperature and in lower creep resistance. In general, the rate of polymer degradation is doubled with each 10° C increase in temperature.
- Crosslinking consists of the formation of bonds between individual polymer chains as a result of preceding degradation. Crosslinking ties the molecules into a rigid network and produces a hard, brittle structure which cannot be melted or dissolved.
- Oxidation, which is often catalyzed by water, promotes fragmentation to a brittle, lower molecular weight structure.

In most cases, all three mechanisms occur simultaneously. Their effects may balance each other for a while, creating the impression that no changes are taking place. Eventually, one of the reactions prevails, leading either to drastic softening or drastic embrittlement of the polymer.

Heat-aging affects the tensile impact strength of a resin more rapidly than any other property. For this reason, the temperature index assigned to a compound (UL Method 746, for continuous-use temperature rating) is generally based on tensile impact strength. But if a material is to be used in applications where impact strength is not critical, a rating based on that property may be unnecessarily conservative. Basing the ratings on tensile strength, for example, rather than on tensile impact strength would be more practical for use in designing for such applications. Data generated in the study reported here are based on tensile strength.

Thermal Aging Tests

The molded samples were thermally aged at 400 and 500 F—temperatures that exceed those normally used in UL thermal aging programs for indexing glass-reinforced and unreinforced thermoplastic resins. As a consequence, some apparently anomalous behavior was observed.

Tests at 400 F: Best performers, after 1,500 hr at 400 F, were the reinforced thermoplastic polyimide, FEP, and ETFE composites and the polyarylsulfone and poly-p-oxybenzoate resins. These materials suffered little or no loss in tensile strength, as shown in Table 1. The polyamide-imide resin lost only 18% of its initial tensile strength. Next best were the reinforced polyphenylene sulfide (30% decrease) and the reinforced polyethersulfone (50% drop).

Lower in the scale of strength retention after 1,500 hr at 400 F are glass-reinforced nylon 6/6 (61% loss) and glass-reinforced polyester (77% decrease). The reinforced polysulfone resin exhibited a 50% loss in tensile strength after only 250 hr at 400 F; yet this material has the highest UL thermal index listing for a thermoplastic resin. This apparent anomaly is a consequence of using a test temperature, in this study, that exceeds the

Table 1—Tensile Strength of Plastics After Thermal Aging at 400 F

Base Resin and Glass Content (% by wt)	Tensile Strength (psi)						
	Initial	After Aging at 400 F (hr)					
		100	250	500	750	1,000	1,500
Polyimide (30)	13,000	13,800	13,800	13,800	13,800	13,400	13,000
Ethylene-tetrafluoro-ethylene (ETFE) (20)	11,300	11,700	11,500	11,400	11,300	11,300	11,200
Fluorinated ethylene propylene (FEP) (20)	5,000	5,100	4,700	4,700	4,700	4,700	4,700
Polyphenylene sulfide (40)	23,200	23,700	23,000	22,900	20,400	18,600	16,500
Polyethersulfone (40)	22,700	23,000	19,400	15,200	12,800	12,100	11,300
Nylon 6/6 (50)	31,000	24,200	19,500	18,600	17,200	15,600	12,000
Polyester (40)	22,100	20,000	18,200	14,800	9,500	7,000	5,000
Polysulfone (40)	20,300	15,000	10,000	7,800	4,300	—	—
Polyarylsulfone* (0)	13,100	13,200	13,400	13,000	12,950	12,900	12,750
Poly-p-oxybenzoate† (0)	13,900	14,200	14,000	13,900	13,850	13,850	13,750
Polyamide-imide§ (0)	27,400	27,200	27,000	26,500	24,500	23,800	22,500

*Astrel 360 (3M) †Ekkcel I-2000 (Carborundum) §Torlon 4203 (Amoco)

Table 2—Tensile Strength of Plastics After Thermal Aging at 500 F

Base Resin and Glass Content (% by wt)	Tensile Strength (psi)						
	Initial	After Aging at 500 F (hr)					
		100	250	500	750	1,000	1,500
Polyimide (30)	13,000	15,000	14,300	13,400	12,800	12,000	11,200
Ethylene-tetrafluoro-ethylene (ETFE) (20)	11,300	11,500	10,000	7,000	5,000	3,800	2,300
Polyphenylene sulfide (40)	23,200	16,400	16,000	15,500	15,000	14,500	13,800
Fluorinated ethylene propylene (FEP) (20)	5,000	5,100	4,800	4,700	4,700	4,600	4,500
Polyethersulfone (40)	22,700	15,600	14,800	14,300	13,700	14,200	10,500
Nylon 6/6 (50)	31,000	17,600	10,300	9,400	—	—	—
Polyester (40)	22,100	Melted	—	—	—	—	—
Polysulfone (40)	20,300	Melted	—	—	—	—	—
Polyarylsulfone (0)	13,100	11,500	10,500	10,000	9,500	8,400	7,600
Poly-p-oxybenzoate (0)	13,900	10,800	10,200	10,000	9,700	9,500	9,000
Polyamide-imide (0)	27,400	27,200	26,600	26,000	24,500	23,500	22,000

glass-transition temperature (374 F) of polysulfone resin.

Tests at 500 F: Among the resins tested, the reinforced polyimide retained the largest percentage of its initial tensile strength (86%) after 1,500 hr, as shown in Table 2. Tensile strength of reinforced polyphenylene sulfide and polyethersulfone dropped 40% and 54% respectively—outstanding, considering their rather ordinary performance in the 400 F tests. Despite the large percentage losses, both of these materials maintained strengths above 10,000 psi after 1,500 hr at 500 F.

In the same test, the reinforced ETFE lost 80% of its initial tensile strength. The reinforced polyester (PBT) and polysulfone resins distorted severely early in the test program.

Be Cautious

From the data generated by these heat-aging tests, it becomes apparent that the thermal rating of a reinforced resin, determined by UL Method 746, is higher when the material is tested at higher aging temperatures. For example, from the data of tests conducted in the range of 500 F, glass-reinforced polyphenylene sulfide would yield a UL continuous-use temperature of 180 C (356 F), while data based on tests in the 400 F range would result in a 150 C (302 F) thermal rating. Similarly, the glass-reinforced polyethersulfone has a 175 C (347 F) continuous-use temperature based on the 500 F area, while the 400 F aging data yield a 150 C (302 F) rating.

In other tests, to determine the continuous-use temperature of reinforced nylon 6/6, similar results were observed. For test temperatures of 140 and 150 C, a thermal rating for 50% glass-reinforced nylon 6/6 was calculated at 115 C. The same procedure, but at test temperatures of 205 and 255 C, yielded a continuous-use temperature of 140 C (see Box).

Thus, caution must be exercised in interpreting results of long-term aging tests. Two hypotheses may explain the apparent anomaly:

1. At higher test temperatures, the predominance of crosslinking over chain-scission reactions results in increased tensile strength.
2. The formation of a dense, crosslinked skin decreases the oxygen penetration, which results in a higher tensile strength than might be expected for a given test period.

How Temperature Ratings Are Determined

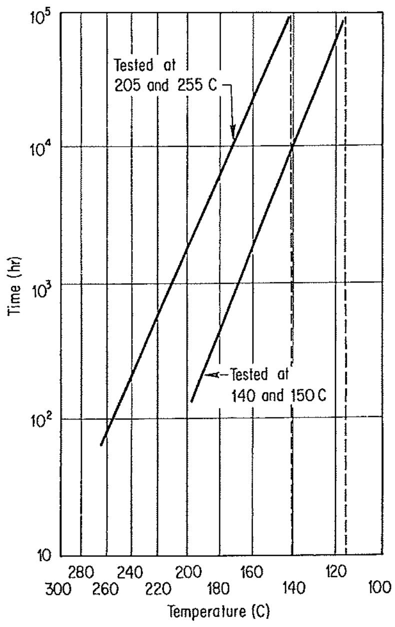
The most widely accepted means of establishing thermal endurance of a polymer is that used by Underwriters' Laboratories to determine the temperature index (continuous-use temperature rating). This test procedure (UL Method 746) is based on the logarithmic time-temperature relationship that exists for the aging of a thermoplastic polymer; that is, thermal degradation obeys what is known as the Arrhenius reaction-rate equation.

The UL test procedure for glass-fortified thermoplastics consists of these steps:

1. A polymer is aged at two or more different test temperatures.
2. Reduction of properties caused by thermal degradation is monitored periodically to generate property-degradation curves.
3. The time required, at each test temperature, to reduce a physical property to 50% of its original value is then plotted, and an Arrhenius curve is fitted to the data points by regression analysis.

A control material with a known index is run concurrently with the new polymer being indexed to eliminate effects of test variability. The control material used for glass-reinforced composites is normally the base resin.

The curve generated by this procedure is used to predict the property half-life of the polymer at any temperature. The UL temperature index, or continuous-use temperature, is determined by the interrelationship of the curves for the control and for the composite being indexed. Generally, the continuous-use temperature is determined by dropping a vertical line from the intersection of the 100,000-hour line and the Arrhenius curve, as shown in the figure.



Arrhenius curves for tensile strength of 50%-glass-reinforced nylon 6/6, tested at different temperatures.

Continuous-Use Temperature of Plastics

(UL Method 746)

Base Resin and Glass Content (% by wt)	Continuous-Use Temperature (C)	(F)
Nylon 6/6 (50)	140	284
Polyester (40)	130	266
Polysulfone (40)	150	302
Polyethersulfone (40)	175	347
Ethylene-tetrafluoroethylene (ETFE) (20)	175	347
Polyphenylene sulfide (40)	180	356
Fluorinated ethylene propylene (FEP) (20)	210	410
Polyimide (30)	200	392
Polyamide-imide (0)	210	410
Polyarylsulfone (0)	185	365
Poly-p-oxybenzoate (0)	200	392
Polytetrafluoroethylene (PTFE) (25)	260	500

These data are based on retention of tensile strength.

Since most products are designed with a safety factor of two (on life), a part molded from an indexed compound will meet minimum requirements of the application after 100,000 hr of exposure at the rated temperature.