

# Effect of Relative Humidity on the Mechanical Properties of Poly(1,4-Butylene Terephthalate)\*

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## Synopsis

Three grades of poly(1,4-butylene terephthalate) (PBT) were aged up to three years at 100, 75, 50, and 11% relative humidity and temperatures of 66–93°C. The decrease in mechanical properties, caused by hydrolysis, occurs rapidly at the higher temperatures and relative humidities and progressively slows as the temperature and/or humidity are decreased. Equations for making life-cycle predictions at any combination of temperature and humidity were derived from Arrhenius plots. If a 50% loss in tensile strength constitutes failure, then the PBT examined should be expected to last only three to four years at 50°C and 100% relative humidity. Reducing the humidity level to 50% extends the useful life at this temperature to 10–20 years. Predictions based on the tensile strength half-life should not be used where toughness or impact properties are important because PBT embrittles long before the tensile strength half-life is reached.

## INTRODUCTION

Injection molding grades of poly(1,4-butylene terephthalate) (PBT) have shown tremendous market growth in the last five years. They offer an excellent balance of mechanical and electrical properties along with fast processability. The UL temperature index\*\* is as high as 140°C. One questionable characteristic of PBT resins has been their long-term resistance to warm humidity. In an earlier study,<sup>1</sup> injection-molded samples were aged for 18 months at 0 and 100% relative humidity (RH). The dry samples showed little degradation. However, the results measured on specimens which were aged at 100% RH indicated that tensile strength would fall to half the initial value in four to 10 years at 45°C for the various grades examined. This result does not indicate the full measure of degradation however, because samples which are aged in humidity become embrittled long before the tensile half-life is reached. Thus we have a dichotomy. At 0% RH, the material exhibits excellent environmental resistance, but at 100% RH, it degrades at an appreciable rate. Actual use conditions are rarely at either extreme.

There have been few studies which evaluated the effect of RH on polymer degradation. Two studies measured hardness changes as a function of temperature and RH for several urethane potting compounds.<sup>2,3</sup> Gardner and Martin examined molded polycarbonate samples at two humidities.<sup>4</sup> McMahon et al. investigated the hydrolytic degradation of polyethylene terephthalate film and fiber at several humidity levels.<sup>5</sup> However, there is no firm basis for de-

\* Based on a paper presented at the Society of Plastics Engineers, 37th Annual Technical Conference, 1979.

\*\* The temperature index is an arbitrary continuous-use temperature limit for specific grades of commercial plastics. It is derived from long-term oven-aging test programs according to a standard Underwriters' Laboratories procedure.

TABLE I  
Relative Humidities Maintained by Saturated Aqueous Salt Solutions

Solution	Relative Humidity (%) at		
	66°C	82°C	93°C
Lithium chloride (LiCl)		11	11
Sodium bromide (NaBr)	50	50.9	
Sodium chloride (NaCl)	74.5	76.4	77

termining the performance of PBT at normal humidity conditions. To fill this gap we have evaluated the performance of three types of PBT at relative humidities between 0 and 100% RH.

### TEST PROCEDURE

Three grades of PBT were aged at 100, 75, 50, and 11% RH. The test period extended the three years at temperatures from 66 to 93°C. The three materials tested were: Valox 310-SEO, a flame-retardant PBT; Valox 420-SEO, a glass-fiber-reinforced flame-retardant PBT; and Tenite 6PROA, a non-flame-retardant unreinforced formulation. The first two products are supplied by General Electric; Tenite is a product of Eastman Chemical. In this test program, injection-molded tensile bars were suspended in sealed containers over saturated aqueous salt solutions to obtain the required humidity conditions (Table I). Salt selection was based on data from refs. 6-8. After exposure, the specimens were tested according to ASTM D638 to determine tensile properties. Glass content of the reinforced specimens was determined by ashing at 760°C.

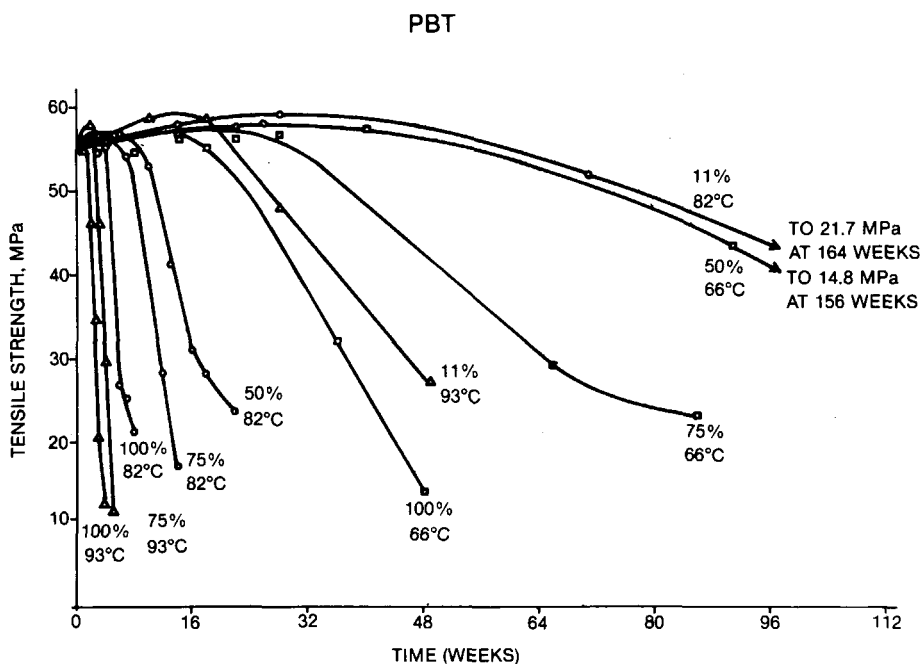


Fig. 1. Effect of aging conditions on the tensile strength of unfilled PBT [ $\Delta$ ) 93°C; (O) 82°C; (□) 66°C].

FLAME-RETARDANT PBT

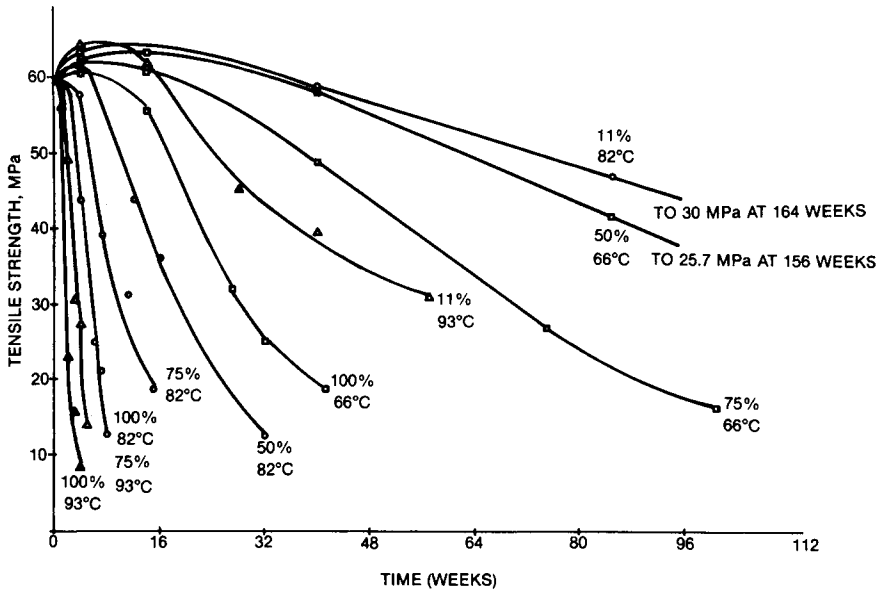


Fig. 2. Effect of aging conditions on the tensile strength of flame-retardant PBT (symbols as in Fig. 1).

EXPERIMENTAL RESULTS

Plots of tensile strength versus time for the three resins are included in Figures 1-3. Plots of elongation versus time are included in Figures 4-6. Examination of these plots indicates that both tensile strength and elongation follow the same pattern. Degradation occurs rapidly at the higher temperatures and relative humidities and progressively slows as temperature and humidity are decreased.

GLASS FILLED FLAME-RETARDANT PBT

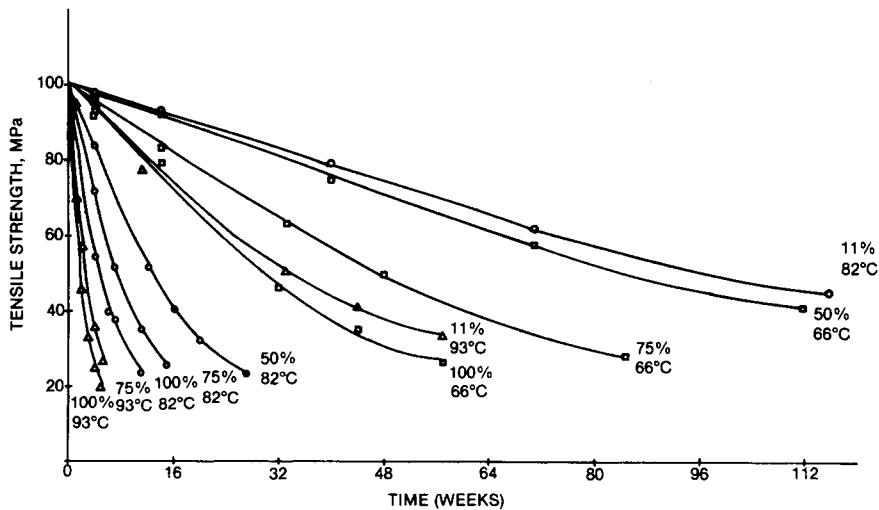


Fig. 3. Effect of aging conditions on the tensile strength of glass-fiber-reinforced flame-retardant PBT (symbols as in Fig. 1).

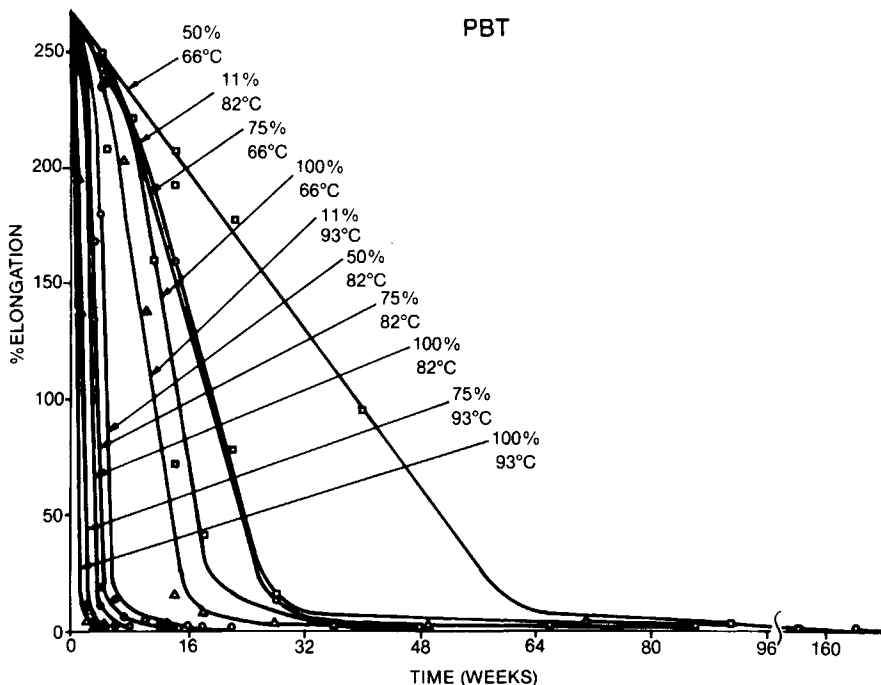


Fig. 4. Effect of aging conditions on the elongation of unfilled PBT (symbols as in Fig. 1).

Arrhenius plots based on the tensile strength half-life are included in Figures 7-9.

## DISCUSSION

Hydrolytic degradation of PBT occurs because chain scission at the ester linkage causes a progressive reduction in molecular weight. Previous studies have shown that the tensile strength and elongation of thermoplastics are insensitive to variations in molecular weight only above a limiting value.<sup>9</sup> Unpublished intrinsic viscosity data from the study reported in ref. 1 indicate that this grade of unfilled PBT is significantly above the tensile strength minimum molecular weight, while the flame-retardant PBT and glass-reinforced PBT are slightly higher than this minimum value. As a result, unfilled PBT shows little change in tensile strength during the initial portion of the humid aging.

PBT moldings are tough, strong products. Unfortunately, toughness is one of the first qualities that is lost during exposure to warm humidity. Elongation is a measure of this parameter so an estimate of toughness limits can be obtained from Figures 4-6. Predictions based on tensile strength half-life should not be used where toughness or impact properties are important because PBT embrittles long before the tensile strength half-life is reached. Depending on the application, one might consider a plot based on impact strength, elongation, or perhaps a smaller reduction in tensile strength. One cautionary note should be added: impact strength and elongation are dependent on morphology as well as molecular weight. As shown in ref. 1, elongation of unfilled PBT decreases

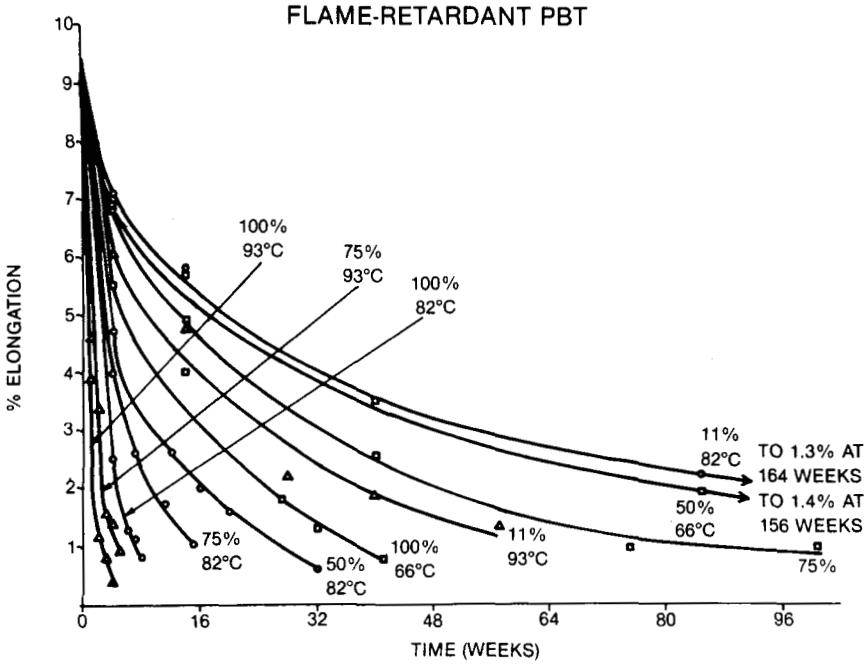


Fig. 5. Effect of aging conditions on the elongation of flame-retardant PBT (symbols as in Fig. 1).

with thermal aging even at 0% RH. Thus Arrhenius plots which are based on elongation measurements represent at least two different rate processes: structural rearrangements and molecular weight degradation. These may have different activation energies, so extrapolations are questionable. Comparisons of the present results with the earlier study show excellent agreement for flame-retardant PBT and unfilled PBT at 100% RH (Figs. 7 and 8). However,

GLASS FILLED FLAME-RETARDANT PBT

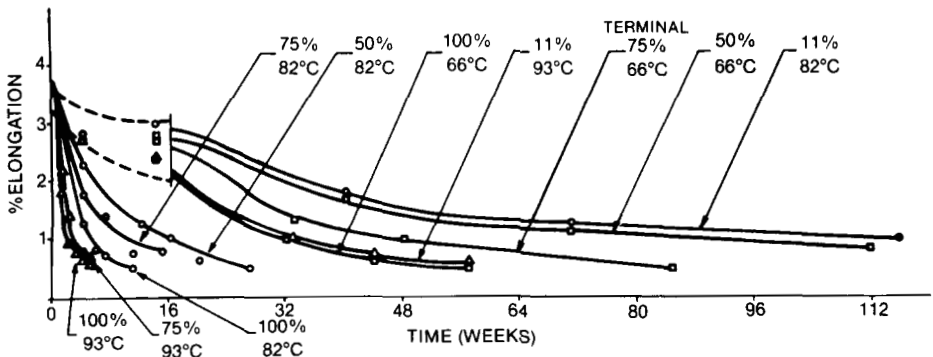


Fig. 6. Effect of aging conditions on the elongation of glass-fiber-reinforced flame-retardant PBT (symbols as in Fig. 1).

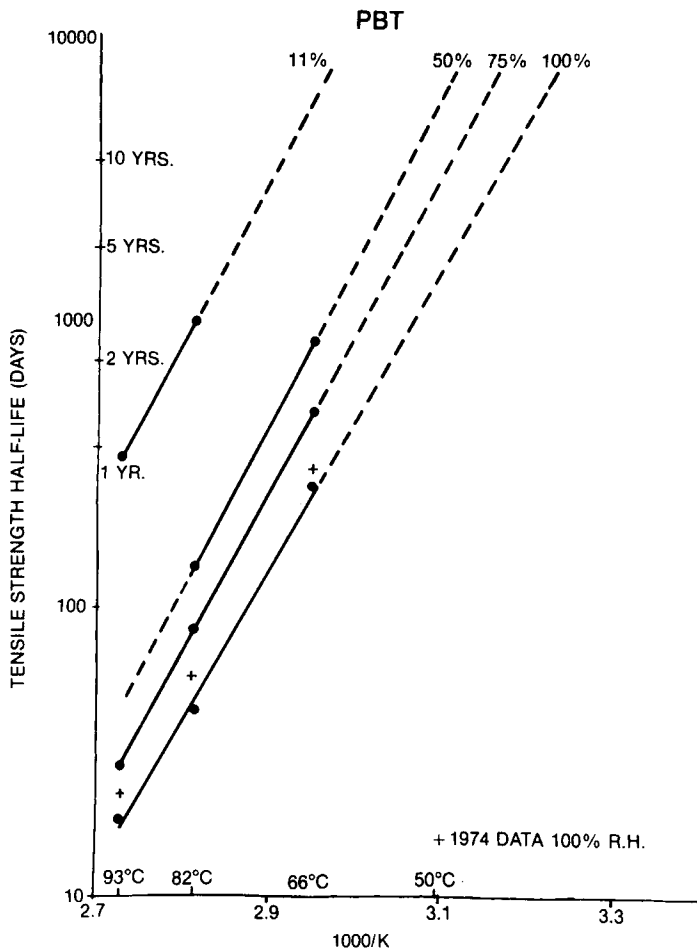


Fig. 7. Tensile strength half-life of unfilled PBT at 11, 50, 75, and 100% RH.

a substantial discrepancy appears in the glass-reinforced PBT data (Fig. 9). This difference was traced to a difference in glass content between the two batches. The material tested in ref. 1 had a glass content of 39.3%, while the material used in the present study had a fiberglass level of 26.5%.

Arrhenius plots, such as those included in Figures 7-9, are useful for making life cycle predictions. If a 50% loss in tensile strength constitutes failure, then PBT parts should be expected to last only three to four years at 50°C and 100% RH. Reducing the humidity level to 50% RH extends the useful life at this temperature to 10-20 years. Similar plots based on a 25% loss in tensile strength project life cycles of 1.5-2.5 and 6-12 years for these two conditions. Even the unfilled PBT produced brittle fractures at this level. Therefore, humidity conditions should be examined carefully in any PBT application where toughness is a functional requirement.

The combined effects of temperature and humidity on unfilled PBT can be expressed as

$$\ln t_{1/2} = 12,680/T - 1.36 \ln(R) - 31.73 \quad (1)$$

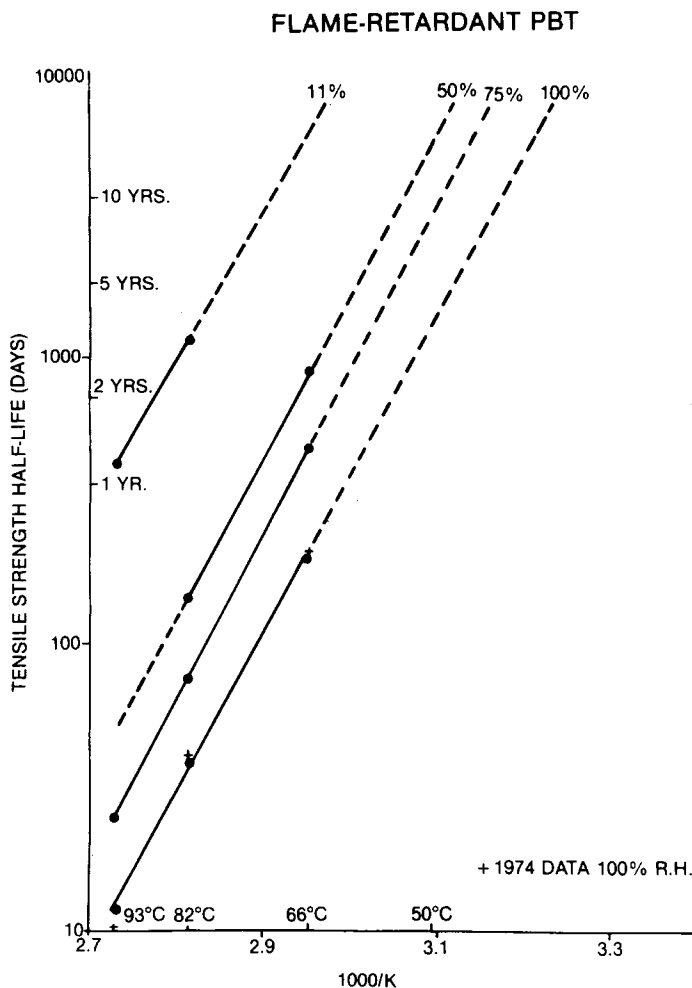


Fig. 8. Tensile strength half-life of flame-retardant PBT at 11, 50, 75, and 100% RH.

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 can be written for glass-reinforced PBT

$$\ln t_{1/2} = 13,134/T - 1.33 \ln(R) - 33.41 \quad (2)$$

At low RH other reactions such as esterification and oxidation become more prominent obscuring the true hydrolysis rate. Therefore, these equations may be less reliable at low relative humidities.

The experimental results on flame-retardant PBT can also be represented by an Arrhenius equation at any given relative humidity. However, the combined temperature and RH data are not well represented by an equation of the form used for the other two resins. At 100% RH, half-life is less than that observed in unfilled PBT. It is tempting to attribute this to differences in initial molecular weight. However, the two resins exhibit very similar responses at the other humidity conditions, so other factors, such as water absorption, flame retardants, or other additives, must also be considered.

## GLASS FILLED FLAME-RETARDANT PBT

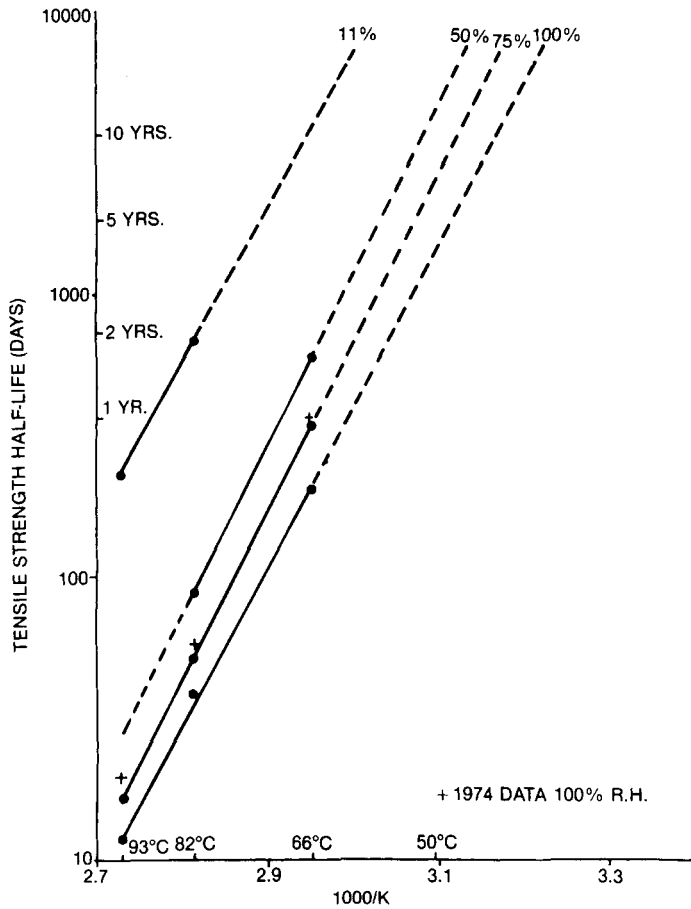


Fig. 9. Tensile strength half-life of glass-fiber-reinforced flame-retardant PBT at 11, 50, 75, and 100% RH.

From a fundamental point of view, Figures 7–9 and the equations cited above should be based on concentration of water in the specimens rather than relative humidity. There are several factors, however, which complicate this approach. The amount of water absorbed by semicrystalline polymers decreases with increasing crystallinity and orientation.<sup>10</sup> These two factors are affected by molding conditions, part geometry, and thermal history. The density of poly(ethylene terephthalate) (PET) increases as it undergoes hydrolysis.<sup>5</sup> This was attributed to increasing crystallinity in one study,<sup>5</sup> and to increasing molecular order without additional crystallization in another.<sup>11</sup> Since PET and PBT are very similar in structure, it is likely that the density of PBT also increases as it hydrolyzes. Ester hydrolysis creates hydrophilic carboxyl end groups in the polymer. Consequently, water absorption continues to increase as the material degrades. It would be difficult to represent all these variables in an equation. From a practical engineering point of view however, correlations in terms of relative humidity are more useful tools for predicting long-term performance.



## CONCLUSIONS

PBT products are sensitive to warm humidity. At 100% RH and 50°C, they lose half of their tensile strength in three to four years. However, if the relative humidity is lowered to 50%, the half-life increases to more than ten years. These lifetimes are applicable only for nonimpact applications. Where toughness is an important quality, the useful life is considerably shorter.

PBT additives appear to affect humidity resistance, probably through their influence on water absorption.

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Received January 25, 1980

Accepted March 4, 1980