

Towards an Understanding of the Heat Distortion Temperature of Thermoplastics

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A systematic understanding of the heat distortion temperature (HDT) of amorphous and semi-crystalline polymers is possible through a direct correlation with the modulus-temperature behavior. For amorphous polymers, the precipitous drop in modulus at the glass transition temperature makes the HDT a well-defined, reproducible and predictable property. Furthermore, the addition of reinforcing fillers has a negligible effect on the HDT of the amorphous polymer. For semi-crystalline polymers, however, the exact opposite may hold true. The modulus exhibits a "plateau" region between the glass transition and the melting transition. Hence the HDT often is difficult to predict, is sensitive to thermal history and may be greatly increased through the addition of fillers. More importantly, the HDT may *not* be an accurate measure of the upper use temperature for semi-crystalline polymers in load-bearing situations since considerable stiffness may still be retained even upon exceeding the HDT.

INTRODUCTION

The heat distortion temperature (HDT) is defined (ASTM D648-72) as the temperature at which a given specimen bar in a specified environment deflects 0.25 mm (10 mils) in flexure under a given external load. (The ASTM D648-72 test refers to the HDT as the "deflection temperature under flexural load." For this paper, we shall use the HDT designation.) Since this measured heat distortion temperature corresponds to a single point on the deflection-temperature curve (temperature is raised at 2°C per min), a great deal of potentially useful information is discarded when one merely reports the heat distortion temperature. Nonetheless, the heat distortion temperature has played an important role in the characterization of engineering thermoplastics. For this reason alone, it merits a better understanding.

In Fig. 1, we show how the HDT for some semi-crystalline polymers increases as a result of the addition of reinforcing fillers (1-3). We see that the HDT is very sensitive to the particular polymeric matrix chosen, the amount of filler loading, the type of filler incorporated and also the thermal history of the sample. The HDT of PBT (polybutylene terephthalate), for example, can be raised by as much as 150°C with the addition of glass fibers. Furthermore, at high filler loadings, there is a "saturation" effect and any additional filler does not increase the HDT. Annealing lowers the "saturation" point to a lower filler loading, as shown for the glass filled PBT.

If we now look at a representative sample of amorphous polymers, as shown in Fig. 2 (which is drawn to the same scale as Fig. 1 for comparison), we see that the HDT of amorphous polymers is insensitive to those

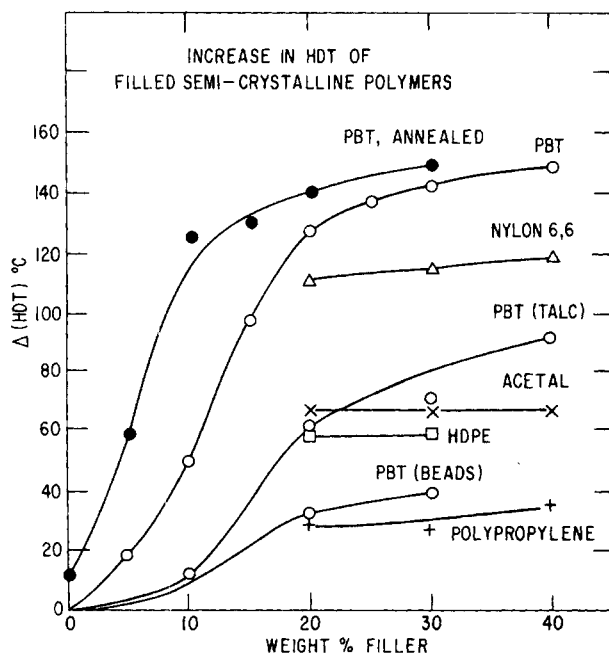


Fig. 1. Increase in HDT for some filled semi-crystalline polymers. (Filler is glass fiber, except where noted. Beads are glass beads.)

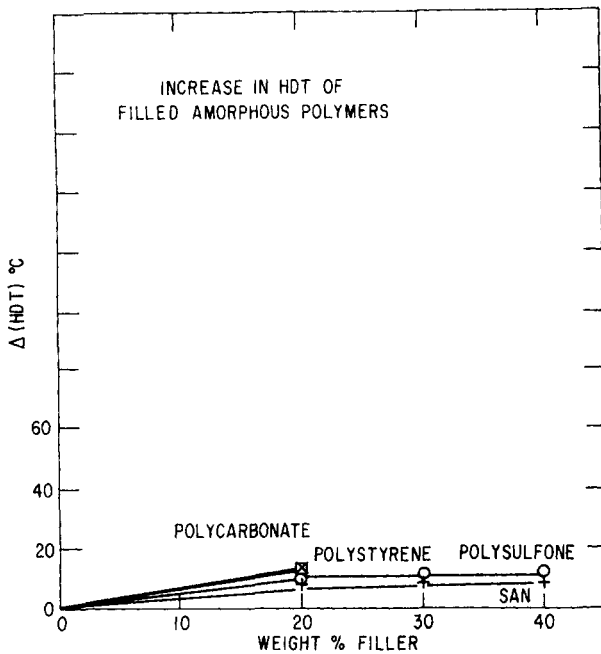


Fig. 2. Increase in HDT for some filled amorphous polymers. (Filler is glass fiber for all cases.)

material and processing parameters that strongly affect the HDT of semi-crystalline polymers (2, 4, 5). The addition of inert fillers increases the HDT of these amorphous polymers by at most 5 or 10°C.

In this paper, we will discuss the heat distortion temperature properties in terms of the modulus-temperature behavior (6) and show how this approach can explain the different HDT behavior of amorphous and semi-crystalline polymers.

THE HEAT DISTORTION TEMPERATURE

The heat distortion temperature (HDT) represents the temperature at which a specimen softens sufficiently to produce a 0.25 mm (10 mil) deflection under an external load. This softening of the specimen can be understood in terms of its modulus-temperature curve. To establish this relationship between modulus and HDT, we must examine the ASTM heat distortion test in detail.

Under flexural loading (three-point bending), the deflection of an ideal beam is given by (see Fig. 3)

$$\delta = \frac{FL^3}{48EI} = \frac{\sigma_{max}L^2}{6Ed} = \frac{\epsilon_{max}L^2}{6d} \quad (1)$$

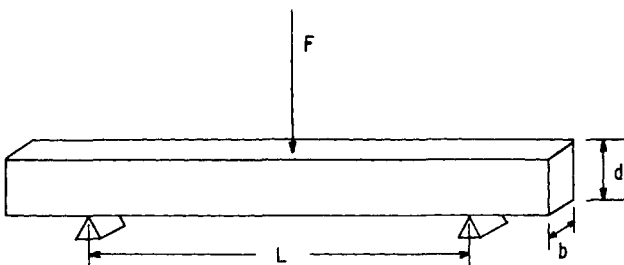


Fig. 3. ASTM D648-72 heat distortion specimen: $L = 100$ mm (4 in.), $d = 13$ mm ($\frac{1}{2}$ in.), $b = 3$ mm to 13 mm ($\frac{1}{8}$ to $\frac{1}{2}$ in.).

where δ = deflection, L = distance between supports, d = specimen width, F = applied load, I = areal moment of inertia of a beam, σ_{max} = maximum fiber stress, ϵ_{max} = maximum fiber strain, and E = modulus of sample. (The ASTM D648-72 test specifies a maximum fiber stress of 455 kPa (66 psi) or 1820 kPa (264 psi.) The higher stress is generally applied in testing engineering polymers.)

In an HDT test, there are several contributions to the total deflection which we must consider. First, we have the ideal small strain elastic deflection given by Eq 1. However, since the sample is initially loaded at $T_o = 23^\circ\text{C}$, there is an initial deflection $\delta(T_o)$ which must be subtracted to yield the net elastic deflection.

$$\delta_{elastic}(T) = \delta(T) - \delta(T_o) = \frac{FL^3}{48I} \left[\frac{1}{E(T)} - \frac{1}{E(T_o)} \right] \quad (2)$$

Secondly, we must consider the contribution due to creep, which is given by

$$\delta_{creep} = \epsilon_{creep} \Delta t \left(\frac{L^2}{6d} \right) \quad (3)$$

where $\epsilon_{creep} \Delta t$ is the strain due to creep during a time interval Δt (see Eq 1). Finally, the effect of thermal expansion, which results in a negative deflection since the bottom supports are rigidly fixed, is given by

$$\delta_{thermal} = -\alpha d \Delta T \quad (4)$$

where α = thermal expansion coefficient.

All of these contributions to deflection must be incorporated into the time-temperature profile of the HDT test, i.e., a heating rate of 2°C per min. The total deflection at temperature T is then given by:

$$\delta_{net}(T) = \int_0^t \{ \delta_{elastic}^i + \delta_{creep}^i + \delta_{thermal}^i \} dt' = \frac{FL^3}{48I} \left\{ \frac{1}{E(T)} - \frac{1}{E(T_o)} \right\} + \int_0^t \left(\frac{L^2}{6d} \right) \epsilon_{creep}^i dt' - \int_{T_o}^T \alpha_i dT \quad (5)$$

where t is the elapsed time when the system reaches temperature T .

In order to obtain a detailed understanding of the HDT of polymers, one must consider all of the above-mentioned contributions to the total deflection. However, the contributions due to creep and thermal expansion become significant only at high temperatures (and consequently long test times). Furthermore, these two contributions are of opposite signs and hence tend to cancel. Therefore, in order to simplify the problem, we have chosen to neglect the effects of creep and thermal expansion. As will be shown in this paper, a good qualitative understanding of the HDT properties is then possible in terms of the modulus-temperature properties.

If we now assume negligible creep and thermal expansion effects, Eq 5 becomes

$$\delta_{net}(T) = \frac{FL^3}{48I} \left\{ \frac{1}{E(T)} - \frac{1}{E(T_0)} \right\} \quad (6)$$

We can rewrite Eq 6 and solve for the tensile modulus E_{10} which will produce a net deflection of 0.25 mm (10 mils)

$$E_{10} = \frac{FL^3}{48I} \left\{ \frac{1}{0.25\text{mm} + \delta(T_0)} \right\} \quad (7)$$

where $\delta(T_0)$ is the initial deflection shown in Eq 2.

Typically, $\delta(T_0)$ is about 0.075 mm (3 mils) which corresponds to a modulus of 3.24 GPa at 23°C. Thus, using a standard ASTM HDT specimen bar at a maximum fiber stress of 1.82 MPa (264 psi), we have

$$E_{10} \approx 0.75 \text{ GPa} \quad (8)$$

and using $\nu = 1/3$ for Poisson's ratio, the corresponding shear modulus is

$$G_{10} \approx 0.28 \text{ GPa} \quad (9)$$

What this means is, assuming negligible creep and thermal expansion effects, the specimen will deflect 0.25 mm (10 mils) under the applied load F (which gives a maximum fiber stress of 1.82 MPa or 264 psi) when the shear modulus of the sample has fallen to G_{10} . The lowering of modulus occurs, of course, since the sample is being heated at 2°C per min during the test. The corresponding temperature is the heat distortion temperature (HDT). Figure 4 graphically illustrates the determination of the HDT from a modulus-temperature curve. It should be noted that there have been other attempts to define a softening temperature on the basis of modulus-temperature curves. For example, the flex temperature is taken arbitrarily as the temperature at

which the shear modulus of a sample in a Clash-Berg torsion test falls to 0.31 GPa (7, 8).

There are, assuredly, some glaring deficiencies in the use of modulus-temperature curves to determine the HDT of a sample, some of which are listed below:

- As mentioned earlier, the effects of creep and thermal expansion are neglected and they could become important for the high HDT plastics for which the total test period exceeds an hour and reaches high temperatures.

- Since the flex bar samples in the heat distortion test are thick, the temperature rise in the interior of the test bar may lag the rise in the temperature bath. Thus, the 0.25 mm (10 mil) deflection may occur at a slightly higher temperature than the modulus curve might predict.

- When shear modulus curves are used instead of tensile modulus curves, conversion from shear modulus values to tensile modulus values is usually accomplished with a constant value of Poisson's ratio. However, a temperature dependence in Poisson's ratio leads to inaccuracies (see Ref. 6 for example).

- The time scale of the dynamic mechanical experiment may be different from that of the heat distortion test. A time-temperature shift of the modulus curve may be necessary.

- Non-linearity in the constitutive equations and differences in the tensile and compressive moduli of the samples may lead to errors in the use of the ideal beam bending equations.

These are valid objections which must be considered in establishing a predictive capability using modulus-temperature curves. As will be shown in the remainder of this paper, however, these objections are inconsequential for the determination and understanding of the HDT behavior of amorphous polymers. For semi-crystalline polymers, it will be shown that, although our simplifying assumptions preclude a reliable quantitative determination of the HDT, a qualitative understanding of the multifaceted behavior of the HDT of semi-crystalline polymers is readily available.

AMORPHOUS POLYMERS

The HDT behavior of amorphous polymers can be easily explained in terms of the modulus-temperature curves. (Our discussion is limited to polymers whose glass transition temperature exceeds "room temperature.") Figure 5 shows shear modulus curves for polystyrene (9), polycarbonate (10) and polyvinyl chloride (11), which are representative of amorphous polymers. Typically, we observe that $G > 1 \text{ GPa}$ for $T < T_g$ and $G < 5 \text{ MPa}$ for $T > T_g$, where T_g is the glass transition temperature. This drop of nearly three orders of magnitude in G occurs over a narrow temperature span of less than 10 to 20°C. We can immediately make several observations concerning the HDT of amorphous polymers on the basis of this observed behavior of the modulus-temperature curve:

1. It was shown in the previous section that the HDT marks the temperature at which G falls to G_{10} , a value of roughly 0.28 GPa. For amorphous polymers, since G

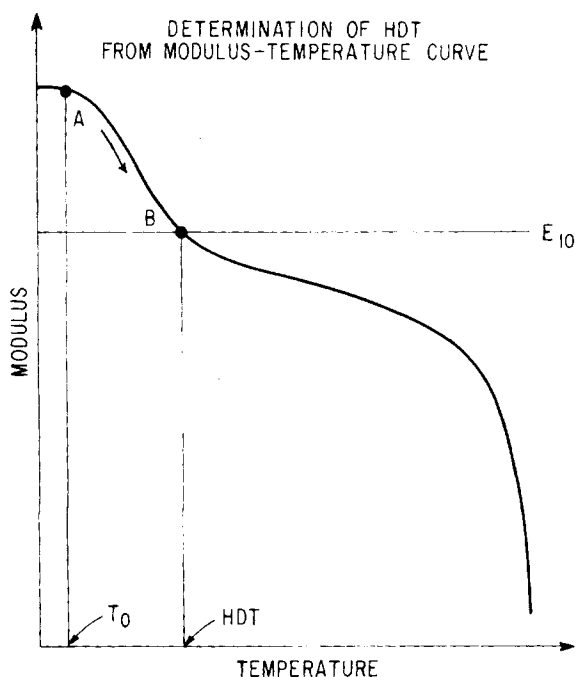


Fig. 4. Determination of HDT from a modulus-temperature curve. Point A represents initial loading of sample at T_0 and point B represents the 0.25 mm (10 mil) deflection point at the heat distortion temperature, HDT and modulus E_{10} .

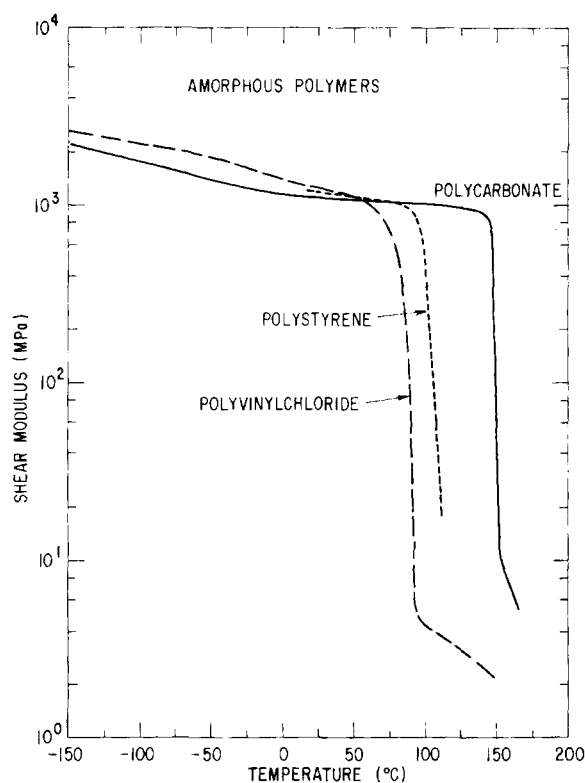


Fig. 5. Modulus-temperature curves for representative amorphous polymers: (a) polycarbonate (10), (b) polystyrene (9), and (c) polyvinyl chloride (11).

falls very rapidly through G_{10} in the transition region, the HDT is well defined. The predicted HDT is insensitive to the actual value of G_{10} chosen—a large change in G_{10} leads to a very small change in HDT. The modulus-temperature curve is thus an excellent tool for determining the HDT. (This method was employed by Witnauer and Palm (12) for various amorphous thermosets and thermoplastics for which they arbitrarily chose G_{10} to be 10^5 psi = 0.69 GPa.)

2. Since the modulus falls precipitously in the glass transition region, the measured HDT should be very close to T_g (13).

3. The addition of reinforcing fillers into amorphous thermoplastics leads to modulus enhancement, hence raising the modulus curves (see Fig. 6). However, as the temperature approaches the glass transition temperature, the matrix, which binds the reinforcing fillers, begins to soften. The modulus drops rapidly near T_g and thus T_g is the limiting heat distortion temperature for reinforced amorphous polymers. Consequently, the addition of a reinforcing filler, although stiffening the matrix, only leads to a minimal rise in the heat distortion temperature.

In summary, for amorphous polymers, the heat distortion temperature is a measure of the modulus relaxation which occurs at the glass transition temperature. For this reason, the addition of reinforcing fillers or the variation of processing conditions, although affecting other physical properties such as flex modulus, flex strength or impact strength, has negligible effect on the HDT for amorphous polymers. One could thus use

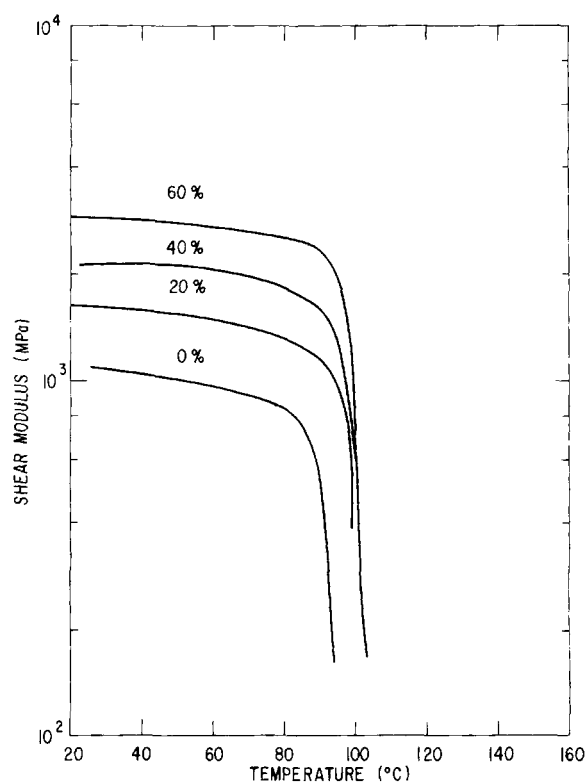


Fig. 6. Modulus temperature curves for asbestos-filled polystyrene (taken from Nielsen, Wall and Richmond (14)).

modulus curves to predict the HDT of amorphous polymers, but the predicted temperature will invariably be very close to the corresponding glass transition temperature.

SEMI-CRYSTALLINE POLYMERS

For semi-crystalline polymers, however, the modulus-temperature behavior is markedly different from that of amorphous polymers. In the glass transition region, for example, the shear modulus drops to a much lesser extent, falling from about 1.0 GPa to about 0.1 GPa. Furthermore, this drop in modulus usually occurs over a much broader temperature range. The modulus exhibits a "plateau" and drops slowly up to the melting temperature, whereupon it drops rapidly. Figure 7 shows this behavior for some representative semi-crystalline polymers, polypropylene (15), polyethylene terephthalate (16), and polyoxymethylene (17). We can make the following observations concerning the HDT of semi-crystalline polymers on the basis of their modulus behavior:

1. It is obvious to see that a determination of the HDT from a modulus curve will not, in general, yield a precise, reproducible value unless it lies close to the glass transition temperature or the melting temperature. The modulus curve drops very slowly from about 1 GPa to 0.01 GPa so that a small uncertainty in the modulus curve in this plateau region is magnified into a large uncertainty in the resultant HDT determination. This means that the modulus curve is not always an accurate tool for prediction of the HDT of semi-crystalline polymers. This also means, however, that the HDT is itself not necessarily an accurate measure of the

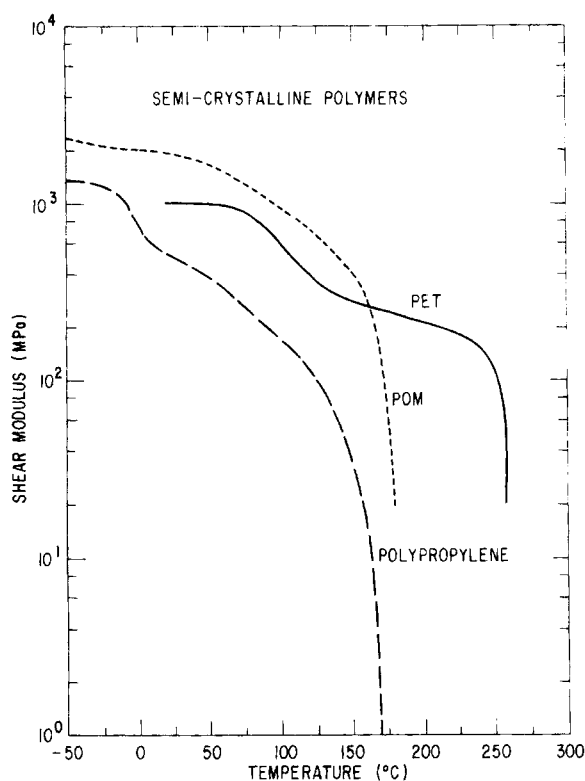


Fig. 7. Modulus-temperature curves for representative semi-crystalline polymers: (a) poly(ethylene terephthalate) (16), (b) polyoxymethylene (17), and (c) polypropylene (15).

upper use temperature for semi-crystalline polymers. The sample could still retain considerable stiffness at temperatures exceeding the measured HDT if the HDT lies in the plateau region and this plateau region is relatively flat.

2. Although the HDT of an amorphous polymer is limited to its glass transition temperature, the HDT of a semi-crystalline polymer can theoretically be raised above its glass transition temperature up to its melting temperature by raising the modulus in the plateau region between the glass transition and the melting transition above the critical modulus value, E_{10} or G_{10} , which would lead to the 0.25 mm (10 mil) deflection.

3. The behavior of the modulus curve in the plateau region may depend strongly upon the amount of crystallinity in the sample (see Fig. 8). We thus expect the following factors to be important in affecting the modulus curve and hence the HDT of the sample:

- Thermal history of polymer—processing conditions (such as mold temperature and injection speed and pressure), residual strains, annealing (15, 18, 19).
- Crystalline sizes—shorter blocks melt before large blocks, thus the presence of short blocks causes a greater relaxation at lower temperatures (20).
- Presence of impurities or other nucleating agents which could increase crystallinity during processing.
- A second mechanism which has an even greater effect in raising the HDT is that of modulus enhancement due to addition of a reinforcing filler to the poly-

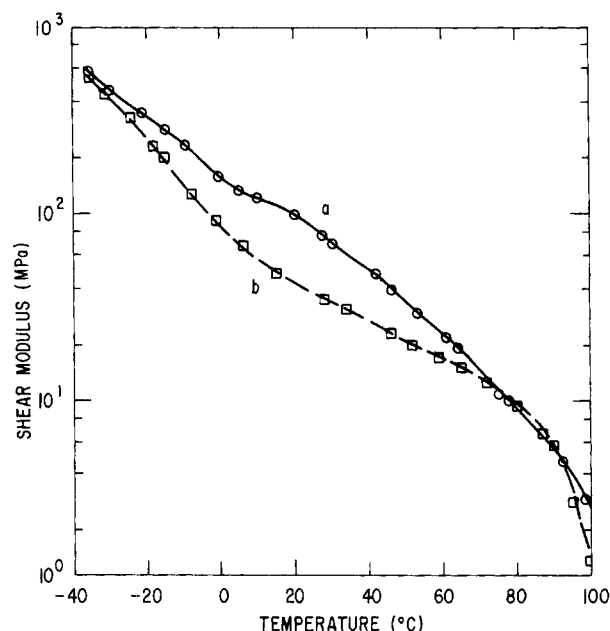


Fig. 8. Modulus-temperature curves for polyethylene. Effect of crystallinity: (a) slowly cooled from melt to 20°C and (b) quenched from melt into ice water (Taken from L. Nielsen (24)).

mer. The HDT can be raised very close to its theoretical maximum value, the melting temperature. The modulus enhancement due to fillers is of course highly dependent upon factors such as filler shape, aspect ratio, adhesion, sizing, orientation, homogeneity and filler size distribution (2, 21). However, the details of these contributions are not of immediate concern insofar as understanding the general features of the behavior of the HDT of thermoplastics and hence will not be discussed.

In summary, for semi-crystalline polymers, in the plateau region between the glass transition and the melting temperature, the modulus curve changes slowly with increasing temperature and is sensitive to changes in specimen thermal history, morphology, and molecular weight distribution. Consequently, HDT predictions based upon modulus curves are subject to wide uncertainties. Furthermore, unlike amorphous polymers, modulus enhancement through the addition of reinforcing fillers can lead to greatly increased HDT values.

CASE STUDY OF A SEMI-CRYSTALLINE POLYMER

McInerney and Hylton (22) have measured shear modulus curves for poly(butylene terephthalate) (PBT) and glass-fiber reinforced PBT. The samples chosen were 100 percent PBT, PBT with 10 weight percent of $\frac{1}{8}$ in. chopped strand glass fibers, PBT with 30 weight percent glass fibers, and a 30 percent glass fiber reinforced PBT sample annealed for one hour at 177°C. The shear modulus curves were obtained using a Rheometrics mechanical spectrometer. The results are presented in Fig. 9. Also presented in this figure are the HDT values taken by Mellinger and Olszewski (1) and the values of G_{10} corresponding to a deflection of 0.25 mm

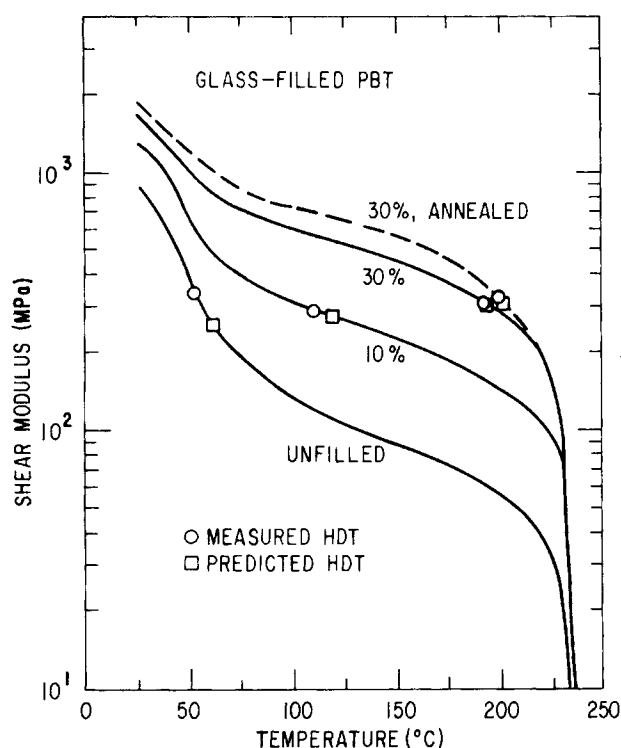


Fig. 9. Shear modulus vs temperature curves for PBT: (a) unfilled, (b) 10 wt percent glass, (c) 30 wt percent glass and (d) 30 wt percent glass, annealed (Taken from McInerney and Hylton (22)). Circles correspond to HDT values measured by Mellinger and Olszewski (1). The squares correspond to G_{10} values assuming a Poisson's ratio value of $1/3$.

(10 mils) using Eq 7 and a Poisson's ratio value of $1/3$. We observe the following:

- The HDT predicted by the shear modulus curves correspond very well with the measured HDT values.
- The addition of glass fibers leads to significant modulus enhancement and consequently increased values for the HDT.
- Annealing of the 30 percent glass fiber reinforced sample leads to further modulus enhancement and a slight increase in the HDT. The higher HDT for the annealed sample is partially due to an increase in the crystallinity of the surface layers of the sample (23).
- Maximum realizable heat distortion temperatures are attained with no more than 30 percent glass fiber reinforcement. Further addition of glass fibers does not increase the HDT significantly. This is the "saturation" effect illustrated in Fig. 1.

CONCLUSION

A systematic understanding of the behavior of the heat distortion temperature of amorphous and semi-crystalline polymers is possible through a direct correla-

tion with the modulus-temperature behavior of the sample. The strong dependence of the HDT of some semi-crystalline polymers on the filler loading, the filler type and thermal history can be readily understood. The "saturation" effect is also easily explained. The insensitivity of amorphous polymers to all these effects is equally evident. Finally, the inadequacy of the HDT to accurately specify an upper use temperature for semi-crystalline polymers is described.

ACKNOWLEDGMENT

The author gratefully acknowledges E. J. McInerney and D. C. Hylton for the use of their shear modulus curves and G. A. Mellinger and W. V. Olszewski for their heat distortion data.

REFERENCES

1. G. A. Mellinger and W. V. Olszewski, G.E. Research & Development Center, Schenectady, N.Y., private communication.
2. H. S. Loveless and D. E. McWilliams, *Polym. Eng. Sci.*, **10**, 139 (1970).
3. A. C. Bernardo, *SPE J.*, **26**, 39 (1970).
4. F. G. Krautz, *SPE J.*, **27**, 74 (1971).
5. J. G. Mohr, S. S. Oleesky, G. D. Shook, and L. S. Meyer, "SPI Handbook of Technology & Engineering of Reinforced Plastics/Composites," Nostrand, New York (1973).
6. L. E. Nielsen, *Trans. Soc. Rheol.*, **9**, 243 (1965).
7. R. F. Clash, Jr. and R. M. Berg, *Ind. Eng. Chem.*, **34**, 1218 (1942).
8. ASTM D1043-51.
9. S. Newman and W. P. Cox, *J. Polym. Sci.*, **46**, 29 (1960).
10. K. H. Illers and H. Breuer, *Kolloid Z.*, **176**, 110 (1961).
11. K. Schmieder and K. Wolf, *Kolloid Z.*, **134**, 149 (1953).
12. L. P. Witnauer and W. E. Palm, *J. Appl. Polym. Sci.*, **2**, 371 (1959).
13. A. T. Riga, *Polym. Eng. Sci.*, **14**, 764 (1974).
14. L. E. Nielsen, R. A. Wall, and P. G. Richmond, *SPE J.*, **11**, 22 (1955).
15. L. E. Nielsen, "Mechanical Properties of Polymers," Reinhold, New York (1962).
16. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York (1967).
17. J. M. McKelvey, "Polymer Processing," Wiley, New York (1962).
18. M. T. Watson, G. M. Armstrong, and W. D. Kennedy, *Mod. Plast.*, **34**, 169 (1956).
19. J. A. Melchore and H. F. Mark, *Mod. Plast.*, **31**, 141 (1953).
20. L. E. Nielsen, *J. Appl. Polym. Sci.*, **2**, 351 (1959).
21. N. G. McCrum, "A Review of the Science of Fibre Reinforced Plastics," H. M. Stationery Office, London (1971).
22. E. J. McInerney and D. C. Hylton, G.E. Major Appliance Lab., Louisville, Kentucky, private communication.
23. S. Y. Hobbs, G.E. Research and Development Center, Schenectady, N.Y., private communication.
24. L. E. Nielsen, *SPE J.*, **16**, 525 (1960).