

Polymer Processing

Modeling and Simulation

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CHAPTER 2

PROCESSING PROPERTIES

Did you ever consider viscoelasticity?

—Arthur Lodge

2.1 THERMAL PROPERTIES

The heat flow through a material can be defined by Fourier's law of heat conduction. Fourier's law can be expressed as

$$q_x = -k_x \frac{\partial T}{\partial x} \quad (2.1)$$

where q_x is the energy transport per unit area in the x direction, k_x the thermal conductivity and $\partial T/\partial x$ the temperature gradient. At the onset of heating, the polymer responds solely as a heat sink, and the amount of energy per unit volume, Q , stored in the material before reaching steady state conditions can be approximated by

$$Q = \rho C_p \Delta T \quad (2.2)$$

where ρ is the density of the material, C_p the specific heat, and ΔT the change in temperature. The material properties found in eqns. (2.1) and (2.2) are often written as one single property,

Table 2.1: Thermal Properties for Selected Polymeric Materials

Polymer	Specific gravity	Specific heat kJ/kg/K	Thermal conduc. W/m/K	Coeff. therm. expan. $\mu\text{m/m/K}$	Thermal diffusivity $(\text{m}^2/\text{s})10^{-7}$	Max temp. $^{\circ}\text{C}$
ABS	1.04	1.47	0.3	90	1.7	70
CA	1.28	1.50	0.15	100	1.04	60
EP	1.9	-	0.23	70	-	130
PA66	1.14	1.67	0.24	90	1.01	90
PA66-30% glass	1.38	1.26	0.52	30	1.33	100
PC	1.15	1.26	0.2	65	1.47	125
PE-HD	0.95	2.3	0.63	120	1.57	55
PE-LD	0.92	2.3	.33	200	1.17	50
PET	1.37	1.05	0.24	90	-	110
PF	1.4	1.3	0.35	22	1.92	185
PMMA	1.18	1.47	0.2	70	1.09	50
POM	1.42	1.47	0.2	80	0.7	85
coPOM ^a	1.41	1.47	0.2	95	0.72	90
PP	0.905	1.95	0.24	100	0.65	100
PPO ^b	1.06	-	0.22	60	-	120
PS	1.05	1.34	0.15	80	0.6	50
PTFE	2.1	1.0	0.25	140	0.7	50
uPVC ^c	1.4	1.0	0.16	70	1.16	50
pPVC ^d	1.31	1.67	0.14	140	0.7	50
SAN	1.08	1.38	0.17	70	0.81	60
UPE	1.20	1.2	0.2	100	-	200
Steel	7.854	0.434	60	-	14.1	800

^aPolyacetal copolymer; ^bPolyphenylene oxide copolymer; ^cUnplasticized PVC; ^dPlasticized PVC

namely the thermal diffusivity, α , which for an isotropic material is defined by

$$\alpha = \frac{k}{\rho C_p} \quad (2.3)$$

Typical values of thermal properties for selected polymers are shown in Table 6.1 [7, 17]. For comparison, the properties for stainless steel are also shown at the end of the list. It should be pointed out that the material properties of polymers are not constant and may vary with temperature, pressure or phase changes. This section will discuss each of these properties individually and present examples of some of the most widely used polymers and measurement techniques. For a more in-depth study of thermal properties of polymers the reader is encouraged to consult the literature [24, 46, 66].

2.1.1 Thermal Conductivity

When analyzing thermal processes, the thermal conductivity, k , is the most commonly used property that helps quantify the transport of heat through a material. By definition, energy is transported proportionally to the speed of sound. Accordingly, thermal conductivity

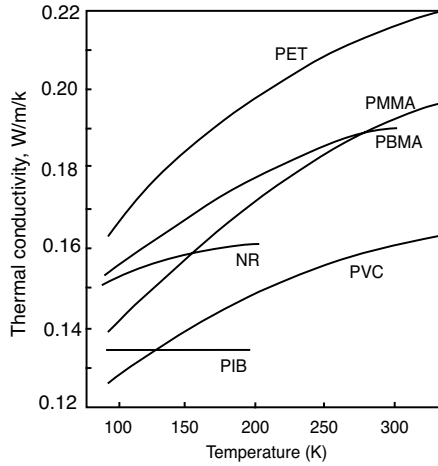


Figure 2.1: Thermal conductivity of various materials.

follows the relation

$$k \approx C_p \rho u l \quad (2.4)$$

where u is the speed of sound and l the molecular separation. Amorphous polymers show an increase in thermal conductivity with increasing temperature, up to the glass transition temperature, T_g . Above T_g , the thermal conductivity decreases with increasing temperature. Figure 2.1 [24] presents the thermal conductivity, below the glass transition temperature, for various amorphous thermoplastics as a function of temperature.

Due to the increase in density upon solidification of semi-crystalline thermoplastics, the thermal conductivity is higher in the solid state than in the melt. In the melt state, however, the thermal conductivity of semi-crystalline polymers reduces to that of amorphous polymers as can be seen in Fig. 2.2 [40].

Furthermore, it is not surprising that the thermal conductivity of melts increases with hydrostatic pressure. This effect is clearly shown in Fig. 2.3 [19]. As long as thermosets are unfilled, their thermal conductivity is very similar to amorphous thermoplastics. Anisotropy in thermoplastic polymers also plays a significant role in the thermal conductivity. Highly drawn semi-crystalline polymer samples can have a much higher thermal conductivity as a result of the orientation of the polymer chains in the direction of the draw.

For amorphous polymers, the increase in thermal conductivity in the direction of the draw is usually not higher than two. Figure 2.4 [24] presents the thermal conductivity in the directions parallel and perpendicular to the draw for high density polyethylene, polypropylene, and polymethyl methacrylate. A simple relation exists between the anisotropic and the isotropic thermal conductivity [39]. This relation is written as

$$\frac{1}{k_{\parallel}} + \frac{2}{k_{\perp}} = \frac{3}{k} \quad (2.5)$$

where the subscripts \parallel and \perp represent the directions parallel and perpendicular to the draw, respectively.

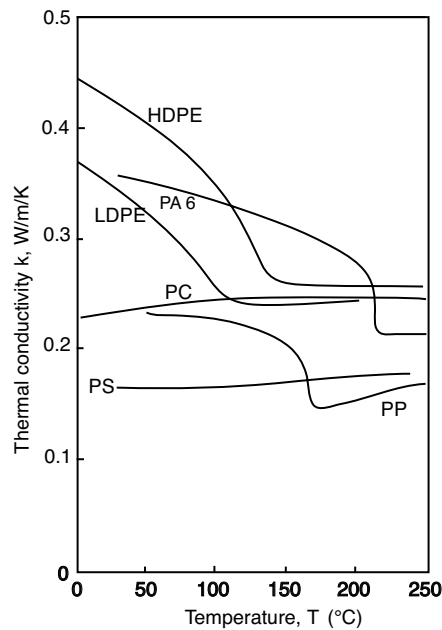


Figure 2.2: Thermal conductivity of various thermoplastics.

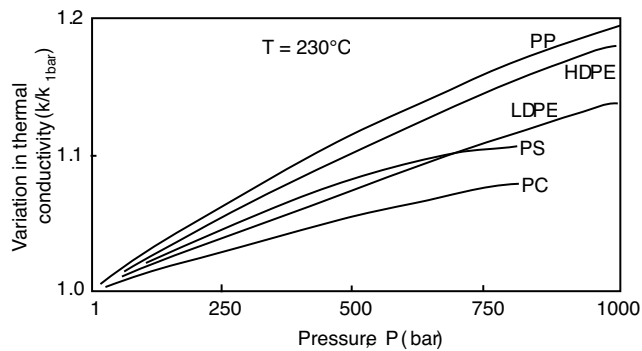


Figure 2.3: Influence of pressure on thermal conductivity of various thermoplastics.

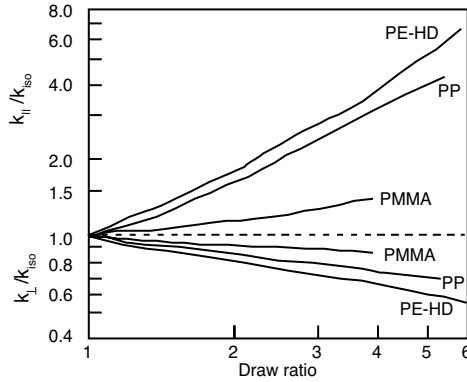


Figure 2.4: Thermal conductivity as a function of draw ratio in the directions perpendicular and parallel to the stretch for various oriented thermo-plastics.

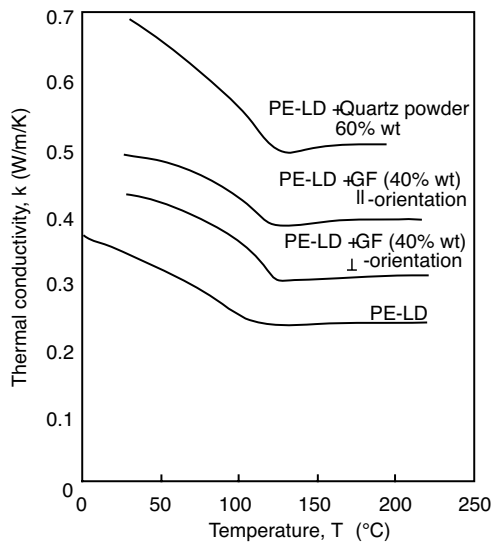


Figure 2.5: Influence of filler on the thermal conductivity of PE-LD.

The higher thermal conductivity of inorganic fillers increases the thermal conductivity of filled polymers. Nevertheless, a sharp decrease in thermal conductivity around the melting temperature of crystalline polymers can still be seen with filled materials. The effect of filler on thermal conductivity for PE-LD is shown in Fig. 2.5 [22]. This figure shows the effect of fiber orientation as well as the effect of quartz powder on the thermal conductivity of low density polyethylene.

Figure 2.6 demonstrates the influence of gas content on expanded or foamed polymers, and the influence of mineral content on filled polymers.

There are various models available to compute the thermal conductivity of foamed or filled plastics [39, 47, 51]. A rule of mixtures, suggested by Knappe [39], commonly used

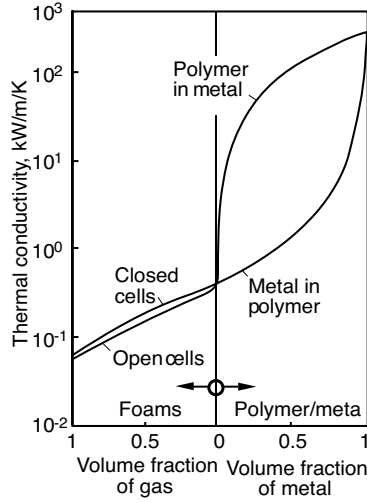


Figure 2.6: Thermal conductivity of plastics filled with glass or metal.

to compute thermal conductivity of composite materials is written as

$$k_c = \frac{2k_m + k_f - 2\phi_f(k_m - k_f)}{2k_m + k_f + \phi_f(k_m - k_f)} k_m \quad (2.6)$$

where, ϕ_f is the volume fraction of filler, and k_m , k_f and k_c are the thermal conductivity of the matrix, filler and composite, respectively.

Figure 2.7 compares eqn. (2.6) with experimental data [2] for an epoxy filled with copper particles of various diameters. The figure also compares the data to the classic model given by Maxwell [47] which is written as

$$k_c = \left(1 + 3\phi_f \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + 2} \right) k_m \quad (2.7)$$

In addition, a model derived by Meredith and Tobias [51] applies to a cubic array of spheres inside a matrix. Consequently, it cannot be used for volumetric concentration above 52% since the spheres will touch at that point. However, their model predicts the thermal conductivity very well up to 40% by volume of particle concentration. When mixing several materials the following variation of Knappe's model applies

$$k_c = \frac{1 - \sum_{i=1}^n 2\phi_i \frac{k_m - k_i}{2k_m + k_i}}{1 + \sum_{i=1}^n 2\phi_i \frac{k_m - k_i}{2k_m + k_i}} \quad (2.8)$$

where k_i is the thermal conductivity of the filler and ϕ_i its volume fraction. This relation is useful for glass fiber reinforced composites (FRC) with glass concentrations up to 50% by volume. This is also valid for FRC with unidirectional reinforcement. However, one must differentiate between the direction longitudinal to the fibers and that transverse to them.

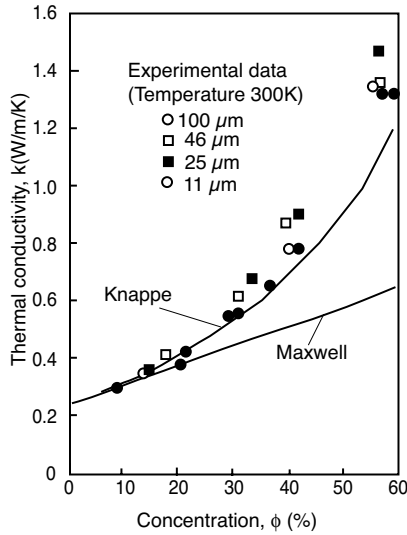


Figure 2.7: Thermal conductivity versus volume concentration of metallic particles of an epoxy resin. Solid lines represent predictions using Maxwell and Knappe models.

For high fiber content, one can approximate the thermal conductivity of the composite by the thermal conductivity of the fiber. The thermal conductivity can be measured using the standard tests ASTM C177 and DIN 52612. A new method currently being balloted (ASTM D20.30) is preferred by most people today.

2.1.2 Specific Heat

The specific heat, C , represents the energy required to change the temperature of a unit mass of material by one degree. It can be measured at either constant pressure, C_p , or constant volume, C_v . Since the specific heat at constant pressure includes the effect of volumetric change, it is larger than the specific heat at constant volume. However, the volume changes of a polymer with changing temperatures have a negligible effect on the specific heat. Hence, one can usually assume that the specific heat at constant volume or constant pressure are the same. It is usually true that specific heat only changes modestly in the range of practical processing and design temperatures of polymers. However, semi-crystalline thermoplastics display a discontinuity in the specific heat at the melting point of the crystallites. This jump or discontinuity in specific heat includes the heat that is required to melt the crystallites which is usually called the heat of fusion. Hence, specific heat is dependent on the degree of crystallinity. Values of heat of fusion for typical semi-crystalline polymers are shown in Table 2.2.

The chemical reaction that takes place during solidification of thermosets also leads to considerable thermal effects. In a hardened state, their thermal data are similar to the ones of amorphous thermoplastics. Figure 2.8 shows the specific heat graphs for the three polymer categories.

Table 2.2: Heat of Fusion of Various Thermoplastic Polymers [66]

Polymer	λ (kJ/kg)	$T_m(^{\circ}\text{C})$
Polyamide 6	193-208	223
Polyamide 66	205	265
Polyethylene	268-300	141
Polypropylene	209-259	183
Polyvinyl chloride	181	285

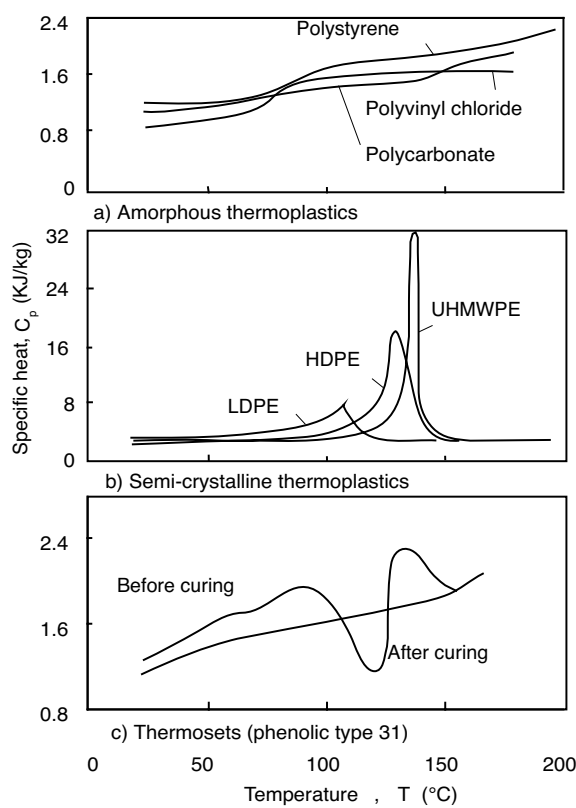


Figure 2.8: Specific heat curves for selected polymers of the three general polymer categories.

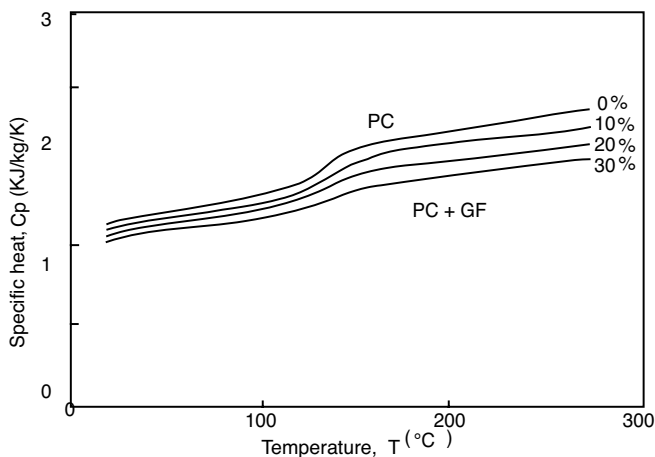


Figure 2.9: Generated specific heat curves for a filled and unfilled polycarbonate. Courtesy of Bayer AG, Germany.

For filled polymer systems with inorganic and powdery fillers, a rule of mixtures¹ can be written as

$$C_p(T) = (1 - \psi_f)C_{p_m}(T) + \psi_f C_{p_f}(T) \quad (2.9)$$

where ψ_f represents the weight fraction of the filler and C_{p_m} and C_{p_f} the specific heat of the polymer matrix and the filler, respectively. As an example of using eqn. (2.9), Fig. 2.9 shows a specific heat curve of an unfilled polycarbonate and its corresponding computed specific heat curves for 10%, 20%, and 30% glass fiber content. In most cases, temperature dependence of C_p on inorganic fillers is minimal and need not be taken into consideration. The specific heat of copolymers can be calculated using the mole fraction of the polymer components.

$$C_{p_{\text{copolymer}}} = \sigma_1 C_{p_1} + \sigma_2 C_{p_2} \quad (2.10)$$

where σ_1 and σ_2 are the mole fractions of the comonomer components and C_{p_1} and C_{p_2} the corresponding specific heats.

2.1.3 Density

The density or its reciprocal, the specific volume, is a commonly used property for polymeric materials. The specific volume is often plotted as a function of pressure and temperature in what is known as a pvT diagram. A typical pvT diagram for an unfilled and filled amorphous polymer is shown, using polycarbonate as an example, in Figs. 2.10 and 2.11. The two slopes in the curves represent the specific volume of the melt and of the glassy amorphous polycarbonate, separated by the glass transition temperature.

Figure 2.12 presents the pvT diagram for polyamide 66 as an example of a typical semi-crystalline polymer. Figure 2.13 shows the pvT diagram for polyamide 66 filled with 30%

¹Valid up to 65% filler content by volume.

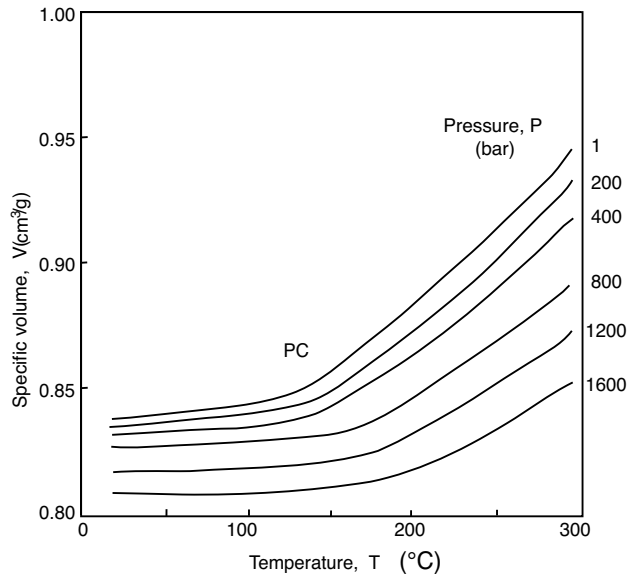


Figure 2.10: pvT diagram for a polycarbonate. Courtesy of Bayer AG, Germany.

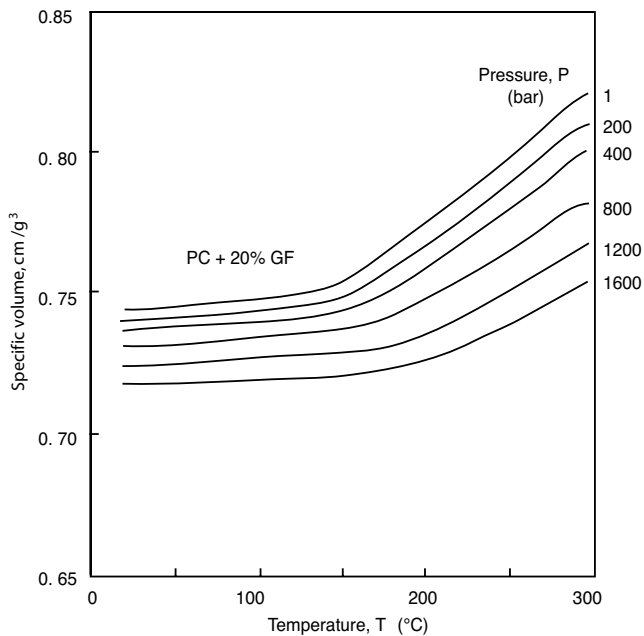


Figure 2.11: pvT diagram for a polycarbonate filled with 20% glass fiber. Courtesy of Bayer AG, Germany.

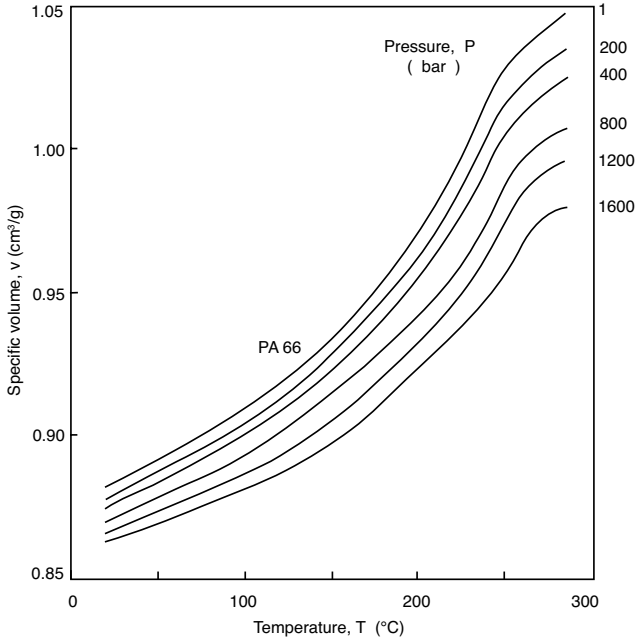


Figure 2.12: pvT diagram for a polyamide 66. Courtesy of Bayer AG, Germany.

glass fiber. The curves clearly show the melting temperature (i.e., $T_m \approx 250^\circ\text{C}$ for the unfilled PA66 cooled at 1 bar, which marks the beginning of crystallization as the material cools). It should also come as no surprise that the glass transition temperatures are the same for the filled and unfilled materials.

When carrying out die flow calculations, the temperature dependence of the specific volume must often be dealt with analytically. At constant pressures, the density of pure polymers can be approximated by

$$\rho(T) = \rho_0 \frac{1}{1 + \alpha_t(T - T_0)} \quad (2.11)$$

where ρ_0 is the density at reference temperature, T_0 , and α_t is the linear coefficient of thermal expansion. For amorphous polymers, eqn. (2.11) is valid only for the linear segments (i.e., below or above T_g), and for semi-crystalline polymers it is only valid for temperatures above T_m . The density of polymers filled with inorganic materials can be computed at any temperature using the following rule of mixtures

$$\rho_c(T) = \frac{\rho_m(T)\rho_f}{\psi\rho_m(T) + (1 - \psi)\rho_f} \quad (2.12)$$

where ρ_c , ρ_m and ρ_f are the densities of the composite, polymer and filler, respectively, and ψ is the weight fraction of filler.