formability of the crystalline polymer, even though the temperature of the amorphous polymer may be substantially higher than its normal forming temperature. The thin barrier layer film will stretch when the crystalline polymer is at its forming temperature.

11.5 Foamed Plastics

Thermoplastic foams are produced by adding an appropriate foaming agent to the polymer during the extrusion process. There are three general classes of thermoplastic foams. High-density foams typically are more than about 70% of the density of their respective unfoamed polymers. About 20% (wt) of all thermoplastic foams are considered high-density foams. Medium-density foams have densities in the range of 20 to 70% of those of the unfoamed polymers. About 5% (wt) of all thermoplastic foams are considered medium-density foams. Low-density foams typically are less than about 20% of the density of their respective unfoamed polymers. About 75% (wt) of all thermoplastic foams are considered low-density foams [37].

11.5.1 High-Density Foams

Foaming agents

High-density and medium-density foam sheet are usually produced by adding a chemical foaming agent to the extruder hopper. Chemical foaming agents are pure chemicals that are thermally unstable above a very specific temperature range. There are two general classes of chemical foaming agents. *Exothermic foaming agents* generate heat when they decompose. Azodicarbonamide (AZ) is the most widely used exothermic foaming agent. It decomposes around 400 °F (205 °C) to produce about 220 cm^3 (STP)[26] of gas per gram of agent. The primary liberated gas is nitrogen.

Endothermic foaming agents require heat to decompose. Sodium bicarbonate (baking soda or $NaHCO_3$) is the most widely used endothermic foaming agent. It decomposes around 250 °F (120 °C) to produce about 135 cm^3 (STP) of gas per gram of agent. The primary liberated gases are carbon dioxide and water vapor. Endothermics are often required when the thermoformed foam product is used in contact with food or medical products.

Gauge control

Endothermics and exothermics are often combined with total concentrations of 0.5% (wt) to 2.0% (wt) to produce foam sheet having densities of about 70% of those of the unfoamed polymers. Foamed impact modified polystyrene (HIPS), ABS, polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polycarbonate (PC) are commercially available as sheet and other polymers can be custom foamed by several extrusion houses. Conventional flat extrusion dies and roll stacks are often used to produce high-density foam sheet. The greatest concern during extrusion is gauge control as the hot sheet may continue to expand for some distance after leaving the extrusion die. High-density foam sheet often does not have a quality surface. As a result, the foamed product may be cap-sheeted on one or both sides for appearance applications.

[26] STP = Standard Temperature and Pressure, usually 77°F (25°C) and 1 atmosphere (0.1 MPa).

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Typically, high-density foam sheet thermoforms in a manner similar to the unfoamed polymer. However, care must be taken to prevent overheating the sheet as excessive heat causes the cell gas to expand and in the extreme, to catastrophically collapse. Care must also be taken when pressing the heated sheet against the mold surface. Excessive pressure will cause cell collapse, resulting in an increase in local part density and reduction in local part thickness. This is particularly true in two- and three-dimensional corners. Chamfered corners are always preferred over radiused corners when thermoforming foam of any density.

High-density foam products are often called *structural* products, meaning that they are usually permanent products designed to carry loads. Very frequently, one of the primary design criteria is stiffness. Stiffness, S, is the product of the material modulus, E, and I, the moment of inertia or geometry of the structure. It is written as:

Structural products

$$S = E\,I \tag{11.1}$$

Stiffness

The moment of inertia is a function of the product design. For many structures, the moment of inertia is approximated by that for a flat panel:

$$I = G\,t^3 \tag{11.2}$$

Moment of inertia

Where G is a geometric parameter and t is the panel thickness. When the polymer is foamed, its modulus decreases in proportion to the square of the density:

$$E_f = E_o \left(\frac{\rho_f}{\rho_o}\right)^2 \tag{11.3}$$

Modulus

Where E_f is the modulus of the foam, E_o is the modulus of the unfoamed polymer, ρ_f is the density of the foam and ρ_o is the density of the unfoamed polymer.

There are two general reasons for producing high-density foam products. If the product weight is reduced at the same product thickness, the foamed product stiffness is:

$$S_f = E_f\,I \tag{11.4}$$

Stiffness of foamed product

Where S_f is the stiffness of the foamed product. This stiffness is related to the unfoamed stiffness as:

$$S_f = E_o \left(\frac{\rho_f}{\rho_o}\right)^2 I = S_o \left(\frac{\rho_f}{\rho_o}\right)^2 \tag{11.5}$$

The stiffness reduces in proportion to the square of the foam density. As an example, if the foam density is 70% of that of the unfoamed polymer, the foamed product stiffness is 49% of that of the unfoamed product.

If the product weight is to remain the same, the product thickness increases in proportion to the decrease in density. The foamed product stiffness is:

$$S_f = E_f\,I_f \tag{11.6}$$

Where I_f is the moment of inertia of the foamed product. The moment of inertia of the foam is given as:

$$I_f = I_o \left(\frac{\rho_o}{\rho_f}\right)^3 \tag{11.7}$$

The stiffness is related to the unfoamed stiffness as:

$$S_f = E_o \left(\frac{\rho_f}{\rho_o}\right)^2 I_o \left(\frac{\rho_o}{\rho_f}\right)^3 = S_o \left(\frac{\rho_o}{\rho_f}\right) \tag{11.8}$$

The stiffness increases in inverse proportion to the decrease in foam density. As an example, if the foam density is 70% of that of the unfoamed product, the foamed product stiffness is 143% of that of the unfoamed product.

11.5.2 Low-Density Foams

Low-density foam materials

Thermoformed low-density foam products are used primarily as thermal insulators such as pizza boxes and as shock mitigators such as egg cartons. Polystyrene (PS) and modified polystyrene (HIPS) dominate low-density foam thermoforming. Polyethylene (PE), crosslinked polyethylene (XLPE), polypropylene (PP), and polyethylene terephthalate (PET) foams are also thermoformed. Low-density foams are characterized by densities from 2 lb/ft^3 (30 kg/m^3) to at least 10 lb/ft^3 (160 kg/m^3). Although these foams can be extruded using modified extrusion equipment using flat dies, most commercial foams are produced on highly specialized extruders, annular dies, and shaping and take-off equipment [38]. These extrusion units are described in more detail in Chapter 12.

Foaming agents

Physical foaming agents are used to produce low-density foams. Aliphatic hydrocarbons such as butanes and pentanes, hydrochloroflorocarbon (HCFC) refrigerant gases such as chlorodifluoroethane (R-142b), and hydrofluorocarbon (HFC) refrigerant gases such as tetrafluoroethane (R-134a), are volatile liquids that vaporize to produce cell gases[27]. Carbon dioxide is the primary atmospheric gas used to produce foams. Argon and nitrogen are atmospheric gases that find limited use. Chemical foaming agents, as described earlier, are often added to the extruder. Although they also produce gas, they act primarily as nucleating agents for bubble production.

Closed-cell foams

Throughout the extrusion process, the gases generated either from decomposition of chemical foaming agents or volatilization of physical agents, or as atmospheric gases that have been dissolved in the polymer, are held in solution in the polymer melt by high melt temperature and pressure. Foam is produced as the gas-laden melt issues from an appropriately shaped extrusion die. Individual foam cells are formed by dissolution of the gas from the polymer melt and cell walls are created by biaxial stretching of the polymer. As a result, low-density thermoplastic foams are nearly always closed-cell foams.

[27] The Montreal Protocol restricts the use of chlorofluorocarbons (R-11 and R-12) and by 2030 the use of hydrochlorofluorocarbons (such as R-142b) in foams. The Kyoto Protocol may eventually restrict hydrofluorocarbons (such as R-134a).

Aging

Once the foam is produced, it is usually aged. Aging allows air to diffuse into the cells while a portion of the blowing gases diffuses out. This gas interchange is important in thermoforming. As the foam sheet is heated prior to forming, the internal cell gas pressure increases and the polymer softens. This causes the foam thickness to increase in the oven by 50% to as much as 100%. This secondary expansion allows the extruder to produce a higher-density and potentially a more stable foam. It also allows for increased stiffness in the final product.

Thermoforming challenges

Low-density foamed polymers are far more difficult to form than their unfoamed equivalents. Because the foam cell walls retain a portion of the blowing gas, amorphous polymer glass transition temperatures and crystalline polymer melting temperatures are depressed. As shown in Fig. 11.10, polystyrene (PS) glass transition temperature is depressed as much as 14 °F (8 °C) per 1% (wt) foaming gas. As a result, foams soften at temperatures below the polymer transition temperatures. As the foam is heated prior to forming, the polymer softens and the internal cell gas pressure increases. The effect is biaxial stretching of the cell membranes. Excessive temperature results in membrane rupture and catastrophic cell collapse. As a result, thermoplastic foams are heated quite slowly and only until secondary expansion is nearly complete. Because the foams are quite stiff at this temperature, they are nearly always formed between matched metal molds.

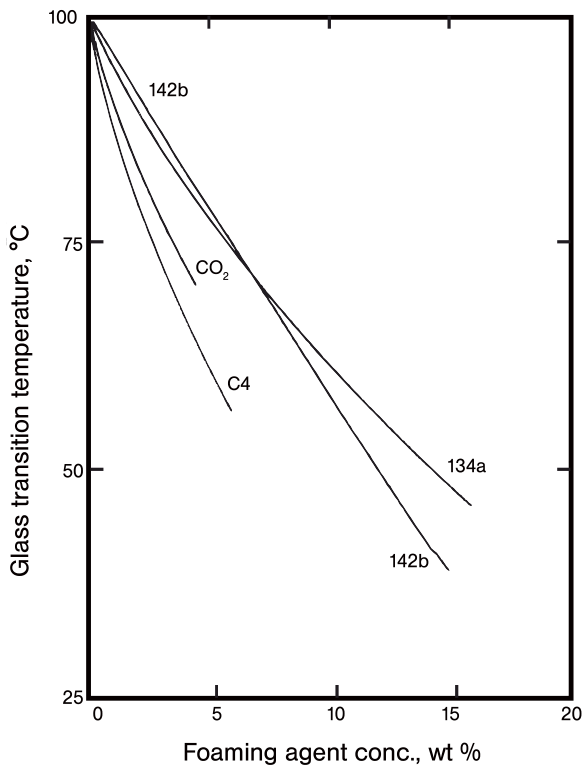

Figure 11.10: The effect of small gas molecule concentration on the glass transition temperature of polystyrene (PS)

Relatively deep draws are achieved by compressing the foam cells between the two halves of the mold rather than by biaxial stretching as is the case with unfoamed polymers.

The surfaces of low-density foams usually consist of a thin layer of higher-density, compressed cells. The surfaces are usually quite matte. To improve surface quality for graphical appearance or cut resistance, foams are laminated with unfoamed sheet stock typically 0.005 in (0.125 mm) in thickness.

11.6 Thermal Properties

When compared with metals and ceramics, polymers are thermal insulators. Thermoformers need to efficiently heat plastic sheet to a formable temperature. Thermoformers need to cool the formed part to a temperature at which the part retains the shape of the mold. Designers of thermoformed parts need to know how those parts expand and contract with temperature. Five thermal properties are important to thermoformers:

Thermal properties important to thermoformers

- Enthalpy or heat capacity, its derivative
- Thermal conductivity
- Temperature-dependent density
- Thermal diffusivity, being a function of heat capacity, thermal conductivity, and density
- Thermal coefficient of expansion or COE

Table 11.6 gives representative values of four of these properties for several thermoformable polymers.

Table 11.6: Physical Properties of Thermoformable Polymers

Polymer	Density lb/ft^3 (kg/m^3)	Thermal conductivity Btu/ft h °F (× 10^{-3} cal/cm s °C)	Heat capacity Btu/lb °F or cal/g °C	Thermal expansion coeff. × 10^{-6} °F^{-1} (× 10^{-6} °C^{-1})
PS	65.5 (1050)	0.105 (0.18)	0.54	40 (70)
ABS	65.5 (1050)	0.070 (0.12)	0.40	50 (90)
PC	74.9 (1200)	0.121 (0.207)	0.49	40 (70)
RPVC	84.2 (1350)	0.100 (0.171)	0.365	45 (80)
LDPE	57.4 (920)	0.23 (0.39)	0.95	140 (250)
HDPE	59.9 (960)	0.29 (0.50)	1.05	110 (200)
HomoPP	56.2 (900)	0.11 (0.19)	0.83	85 (150)
PET	85.5 (1370)	0.138 (0.236)	0.44	40 (70)
Low-density PS foam	4.0 (64)	0.016 (0.027)	0.5	110 (200)

11.6.1 Heat Capacity

Specific heat

Heat capacity, sometimes called specific heat, is a measure of the amount of energy needed to raise the temperature of the polymer by a specific amount. The field of study that focuses on energy uptake of materials is called thermodynamics. Enthalpy is the fundamental measure of energy uptake. The enthalpy of a material increases with increasing temperature. When a material passes through a primary transition such as melting, the shape of the temperature-dependent enthalpic curve changes dramatically. When a material passes through a secondary transition such as the glass-to-rubber transition, the shape of the temperature-dependent enthalpic curve changes subtly, if at all.

Temperature-dependent enthalpic curves for several thermoformable polymers were shown in Fig. 8.5. As expected, far more energy is required to heat a crystalline polymer from room temperature, say, to a temperature above its melting temperature, than is required to heat an amorphous polymer over the same temperature range. For example, it takes about twice as much energy to heat polyethylene (PE) from room temperature of 77 °F (25 °C) to 356 °F (180 °C) than it does to heat polystyrene (PS) over the same temperature span. Furthermore, because the thermoformed shape must be cooled, twice as much energy must be removed to cool PE to a given temperature than to cool PS to that same temperature.

Enthalpy-temperature curve

As seen in Table 11.3, specific heat or heat capacity for a given polymer is usually given as a single value. This value is the slope of the enthalpy-temperature curve and is determined by dividing the enthalpy difference by the appropriate temperature difference. This method is usually acceptable for amorphous polymers but should be used with caution for crystalline polymers. As is apparent with any crystalline polymer, the slope of its temperature-dependent enthalpy curve – and therefore its specific heat – changes dramatically in the polymer melting temperature range.

11.6.2 Thermal Conductivity

Plastics are thermal insulators

Thermal conductivity is the measure of steady-state energy transmission through a material. Thermal conductivity values for organic chemicals, including plastics, are in general orders of magnitude lower than those for metals, for examples. In other words, plastics are thermal insulators. As an example, the thermal conductivity of aluminum, the common thermoforming mold material, is nearly one thousand times greater than that for polystyrene (PS).

Even though thermal conductivity values for polymers are low, there are differences in values among polymers. For example, the thermal conductivity of high density polyethylene (HDPE) is about three times larger than that of polystyrene (PS) or ABS. The rate at which energy is conducted through a material is important when heating heavy-gauge sheet and cooling heavy-gauge formed parts. For very thick sheets, the rate of energy transfer into the sheet and out of the formed part into the mold and environment often controls the total cycle time. Although thermal conductivity values typically decrease slightly with increasing temperature, the values can be considered constant for most processing purposes.

11.6.3 Polymer Density

Specific volume

Although density is not truly a thermal property, its role is quite important during the thermoforming process. For most materials, space between molecules increases when they heat. The result is manifest as an increase in specific volume – the volume per unit mass. Density, the reciprocal of specific volume, decreases with increasing temperature. Near the polymer glass transition temperature, the slope of the temperature-dependent specific volume curve changes perceptively. Near the crystalline polymer melting temperature, the slope changes dramatically. Typically, the density of an amorphous polymer at its forming temperature may be 10 to 15% less than that at room temperature. The density of a crystalline polymer at its forming temperature may be as much as 25% less than that at room temperature. Obviously, as a formed polymer shape cools from its forming temperature, its density increases and its volume decreases. As a result, final part dimensions decrease and the part exhibits thermal shrinkage.

11.6.4 Thermal Diffusivity

Thermal diffusivity is a measure of time-dependent energy transmission through materials. It is the ratio of thermal conductivity to the product of density and specific heat, as shown:

$$\alpha = \frac{k}{\rho\, c_p} \tag{11.9}$$

Where α is thermal diffusivity, k is thermal conductivity, ρ is density, and c_p is specific heat. Because of the unique bundling of temperature-dependent characteristics of these polymer properties, thermal diffusivity is nearly temperature-independent for any given polymer.

11.6.5 Thermal Coefficient of Expansion

Linear and volumetric COE

Thermal coefficient of expansion (COE) is a measure of the dimensional change of a material with temperature. There are two types of COEs – linear COE and volumetric COE. Linear COE is usually used to determine the temperature-dependent change in a specific solid product dimension. If the product is isotropic, meaning that the product properties are the same in all principal directions, the linear coefficient of expansion is approximately one-third the volumetric coefficient of expansion. Typically, polymers have greater COEs than metals. For example, the linear COE for high density polyethylene (HDPE) is 200 mm/m °C (200×10^{-6} °C^{-1}) compared with 23×10^{-6} °C^{-1} for aluminum and about 12×10^{-6} °C^{-1} for steel. Crystalline polymers tend to have higher COEs than amorphous polymers. For example, the linear COE for polystyrene (PS) is 70×10^{-6} °C^{-1}, compared with 200×10^{-6} °C^{-1} for HDPE.

Keep in mind that COE is a parameter that designers must consider only after all product dimensional changes owing to effects such as recrystallization and stress relaxation have been accounted for.

11.6.6 Thermal Properties of Multilayer Structures, and Filled and Reinforced Polymers

Dominant layer determines properties

The thermal properties of multilayer structures depend strongly on the characteristics of the dominant layer and on the quality of the adhesion between layers. If the surface layer has a high thermal diffusivity value and the substrate has a low value, the surface layer may heat far faster than the substrate. If the value of COE of the surface layer is greater than that of the substrate, interfacial delamination may occur.

In general, for filled and reinforced polymers, the polymer density increases nearly linearly with increasing mineral loading. Thermal conductivity tends to increase with increasing mineral loading. Heat capacity usually remains constant or increases slowly. In general, thermal diffusivity, as defined as a ratio of these properties, usually does not change with the level of mineral loading. On the other hand, the COE value usually decreases rapidly with small levels of mineral loading. As the loading level increases, the decrease in value is not as rapid.

Fiber orientation important

Keep in mind that for most filled polymers, particle distribution is rather uniform throughout the polymer sheet, meaning that filled polymers can be considered as isotropic. This is usually not the case for fiber-reinforced polymers. Thermal properties can differ quite dramatically in the three principal directions, depending on the fiber orientation in the polymer. Thermal properties in the machine direction or the dominant fiber direction may differ greatly from those in the cross-machine direction and the through-thickness direction. This implies that the heating and cooling characteristics of filled sheet may differ substantially across and down the sheet.

Keep in mind that a filled, reinforced, or even heavily pigmented sheet may appear to radiantly heat faster than that sheet having no such additives. Minerals on the sheet surface block and absorb a portion of the radiant energy that would otherwise be absorbed by the polymer within the first few microns of the sheet surface. Infrared thermometers only measure surface temperature. Although the sheet absorbs the same amount of energy, increased mineral loading will indicate increased surface temperature.

11.7 Infrared Energy Absorption for Specific Polymers

Electromagnetic radiation band width

Essentially all light-gauge sheet and a substantial portion of heavy-gauge sheet are radiantly heated. The electromagnetic radiation bandwidth or wavelength is usually given in microns or μm. The entire electromagnetic radiation band, from the very short radio and microwave wavelengths to the extremely long wavelengths of nuclear and cosmic rays, was depicted in Fig. 8.1. The visible wavelength spectrum is very narrow, from 0.4 μm to about 0.7 μm. The near-infrared wavelength spectrum is from about 0.7 μm to about 2.5 μm. The far-infrared wavelength spectrum is from about 2.5 μm to about 100 μm. Most commercial thermoforming heaters emit energy in the far-infrared wavelengths. The usual far-infrared wavelength range for heating polymer sheet is from about 2.5 μm to around 15 μm.

FTIR

The chemical make-up of a polymer determines how much radiant energy a polymer absorbs and how much is transmitted through the polymer. Figure 11.11 is a transmission spectrum for polystyrene (PS). It is instructive to examine this figure in some detail. First, the data are obtained using a Fourier transform infrared (FTIR) scanning device [39]. A thin film of polymer is scanned with infrared energy from a black body source. The beam passes through an interferometer where it is encoded. It then passes through the polymer film. As the frequency of the beam energy is altered, the amount of energy absorbed by the polymer and the amount transmitted through the polymer at that frequency are recorded electronically. The frequency spectrum data are then analyzed using Fourier transformation mathematics. The results are presented in graphical form, as seen in Fig. 11.11, where the amount of energy transmission through the polymer is given as a function of beam wavelength.

FTIR analysis is a fundamental analysis tool in organic chemistry. By electronically comparing specific wavelength peaks with databases containing literally thousands of pure organic substances, polymers, additives, and organic contaminants can be identified and their concentrations determined in minutes.

Example

FTIR analysis is also an important teaching tool for the thermoformer. Re-examination of Fig. 11.11 shows that two curves are shown. The thinner top curve is for 0.001 in (25 μm) thick film. Except for the regions around 3.5 μm and 6.5–7 μm, the film is approx. 90% transparent. The heavier lower curve is for 0.010 in (250 μm) thick film. Again, except for regions around 3.5 μm and 6.5–7 μm, the film is 30–50% transparent. In the 3.5 μm and 6.5–7 μm regions, the film has zero or near-zero transparency. Chemically, these regions represent carbon-hydrogen bond activity[28]. In other words, all carbon-hydrogen polymers should show complete or nearly complete energy absorption in these wavelengths.

Now consider regions away from these regions. It is apparent that as the PS film gets thicker, it absorbs more far-infrared energy and therefore transmits less far-infrared energy. In fact, it has been mathematically verified that the amount of energy absorbed increases exponentially with film thickness. This also implies that during heating, the sheet is absorbing radiant energy volumetrically and not just on the surface.

Now compare the FTIR curves in Fig. 11.11 for PS with Fig. 11.12 for polyethylene (PE), Fig. 11.13 for polyvinyl chloride (PVC), and Fig. 11.14 for polyethylene terephthalate (PET).

All three sets of curves show zero or near-zero film transparency in the 3.5 μm and in the 6.5–7 μm regions. Note, however, that 0.010 in (250 μm) thick PE film is still nearly 70% transparent in the far-infrared energy range. This is why it is more difficult to radiantly heat light-gauge PE sheet than to radiantly heat light-gauge PVC sheet of the same thickness.

Influence of fillers, pigments, and reinforcing agents

As noted earlier, opaque substances such as pigments, fillers, and reinforcing elements, block a portion of inbound radiant energy. The amount of blocking is proportional to the opaque substance loading level. As expected, blocking alters the energy distribution to the sheet, meaning that more energy is absorbed on the surface and less transmitted to the sheet interior. The result is an altered temperature profile in the polymer residing near the sheet surface.

Keep in mind that the FTIR scan presents energy transmission as a function of wavelength in microns (μm). Any solid or semi-solid particles having dimensions in the range of 2.5 μm to, say, 15 μm will interfere with far-infrared radiant energy transmission. Such particles

[28] –CH stretch occurs in the 3.0–3.7 μm region and –CH bend occurs in the 6.5–7 μm region.

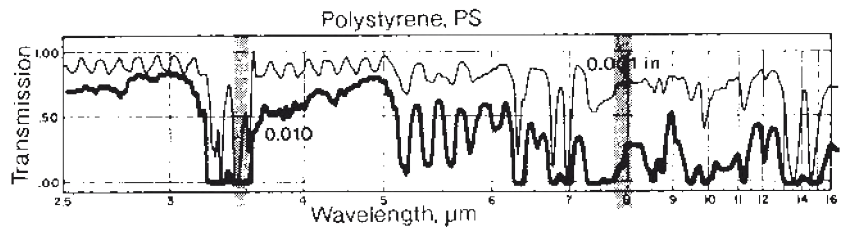

Figure 11.11: Infrared transmission spectrum for polystyrene (PS)

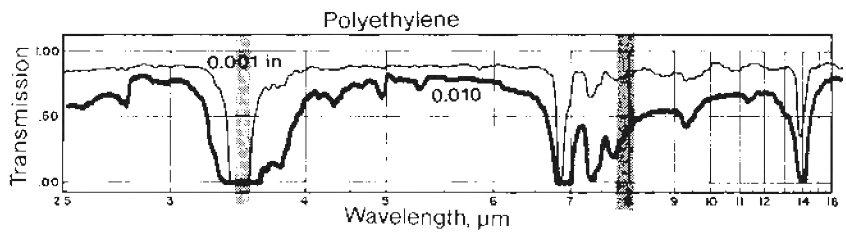

Figure 11.12: Infrared transmission spectrum for polyethylene (PE)

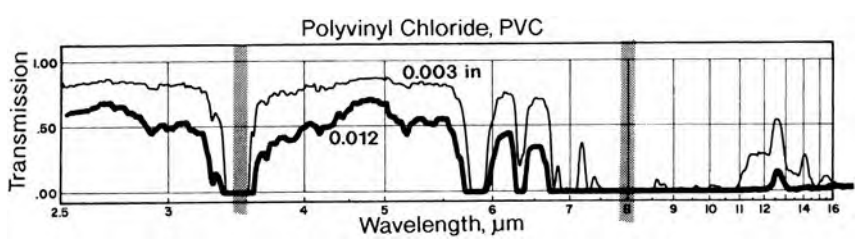

Figure 11.13: Infrared transmission spectrum for polyvinyl chloride (PVC)

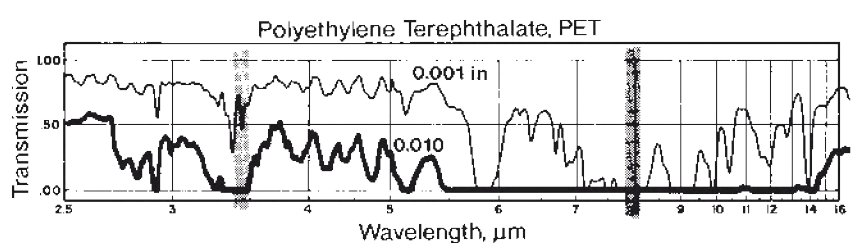

Figure 11.14: Infrared transmission spectrum for polyethylene terephthalate (PET)

might include pigments, nucleating agents, gelled and/or crosslinked polymers, and other detritus. Dyes and tints are normally organics and should appear in FTIR scans as specific peaks. Unless they agglomerate, particles with dimensions less than, say, 2.5 μm, will usually not interfere with far-infrared radiant energy transmission. In particular, particles that are added to alter the polymer appearance in the visible wavelength range usually will not alter the heating performance of the plastic sheet. Opacifiers such as titanium dioxide are additives in this class.

Relation between peak radiation wavelength and temperature

There is a strict mathematical equation relating peak radiation wavelength with temperature. The equation is:

$$T + 273\ ^\circ\mathrm{C} = \frac{2897.6}{\lambda_{\max}} \tag{11.10}$$

Where T is the temperature of the energy source and $\lambda_{\max}$ is the peak radiation wavelength. At 2.5 μm peak wavelength, for example, the temperature of the energy source is 1625 °F (885 °C). At 3 μm, it is 1280 °F (695 °C) and at 4 μm, it is 845 °F (450 °C). These represent the peak wavelengths generated by thermoforming heaters at their respective temperatures.

The relative heating characteristics of polymers can be surmised from examining their FTIR scans, side by side. Compare, for example, the FTIR scan for 0.010 in (0.25 mm) thick PE (Fig. 11.12) with that for 0.010 in (0.25 mm) thick PET (Fig. 11.14). It is apparent that the transmission rate through each film at a peak wavelength of 3.5 microns (3.5 μm) is nearly zero. As a result, the two sheets should heat at relatively the same rates if their heater temperatures are both set at 1030 °F (555 °C). On the other hand, at 490 °F (255 °C), the peak radiant energy wavelength is about 5.5 microns (5.5 μm). As a result, at this heater temperature, transmission through PE will be about 65% while that for PET will be nearly zero. In other words, PET will absorb nearly 3 times more energy than PE will at this lower temperature. In short, the energy absorption character of the polymer must be taken into account whenever initial heater temperature is determined and any time heater temperatures are to be adjusted.