Abstract

I consider the respective roles of inbound radiant energy absorption and internal scattering for plastics containing particulates.

Introduction

For some time now, I have been considering plastic sheet response to inbound far-infrared energy. My epiphany has been reconciling the classic one-dimensional transient heat conduction model for energy uptake by plastic sheet with wavelength-dependent transmissivities of thin plastic films as determined by Fourier Transform Infrared spectroscopy.

To review, the classic mathematical model is shown in Figure 1 where energy interchange, be it convection (energy interchange between environmental air and sheet) or heating from radiant sources (electromagnetic energy interchange between an emitter and the sheet) takes place only at the sheet surface.

The general equation is:

\[
\rho c_p \frac{\partial T}{\partial \theta} = k \frac{\partial^2 T}{\partial x^2},
\]

Where \( T \) is the sheet temperature, \( k \) is its thermal conductivity, \( \rho \) is its density, \( c_p \) is its heat capacity, \( x \) is the distance into the sheet from the surface, and \( \theta \) is time. The classic boundary conditions are:

\[
k \frac{\partial T}{\partial x} (x = L, \theta > 0) = h(T_{air} - T) + \alpha \frac{\partial T}{\partial x} (x = L, \theta > 0) = h(T_{air} - T) + G(T^*_{heater} - T^*_{air})
\]

\[
-k \frac{\partial T}{\partial x} (x = 0, \theta > 0) = h(T_{air} - T) + G(T^*_{heater} - T^*_{air})
\]

Where \( T_{air} \) is the ambient air temperature, \( h \) is the convective heat transfer coefficient, \( T^*R \) is the absolute radiant heater temperature, \( T \) is the surface temperature, \( T^* \) is the absolute surface temperature, \( T^*_{heater} \) is the absolute heater temperature, and \( G \) is a complex geometric parameter that includes emissivities of both the heater and the sheet surface.

The classic initial condition is

\[ T(0 \leq x \leq L; \theta = 0) = T_0 \]

Where \( T_0 \) is the initial sheet temperature, usually considered to be constant.

As I’ve stated in the past, these equations have been solved many times in many texts. The standard method is to write the equations in differential form. Beginning at time \( \theta = 0 \), the equation is stepped forward an incremental \( \Delta \theta \), and new values for sheet temperature are determined at every differential value of \( x \), viz, \( x + \Delta x \). These values are then used to determine the new temperature values at time \( \theta + \Delta \theta \). And so on. The classic equation is linear parabolic second order PDE.

In an earlier paper, I referred to this model as “radiopaque,” meaning that the plastic is assumed to receive and emit inbound energy only at its surface (1).

While this sounds rational for thick sheet, I believe that there is sufficient evidence to refute this rationality. I will imbed this argument in some discourse below.

Now to the Epiphany

For a long time, I preached that thermoformers should realize that different plastics absorb energy at differing far infrared wavelengths. To illustrate this, I referred them to far-infrared wavelength charts known as FTIR spectra. An example, that of polyethylene is Figure 2.
Figure 2. Fourier Transform Infrared Spectrophotometer Scan of Two Thicknesses of Polyethylene

The vertical axis is transmissivity with values ranging from 1 (totally transparent) to 0 (totally opaque). The horizontal axis is wavelength with the range of 2.5 μm to 16 μm. The typical range for thermoforming is about 4 μm to 7 μm. These FTIR charts are designed to help polymer chemists determine chemical compositions of polymers as well as general make-up and concentrations of various organic additives. As a footnote, FTIR scans are used by forensic crime scene investigators to determine the makeup of evidence left at crime scenes.

My epiphany was that essentially all plastics have 100% transmissivity at zero thickness. This meant to me that plastics heat by volumetrically absorbing inbound radiant energy. Even more, this meant that I have been using the wrong mathematical model for plastics.

How so, you ask? If no energy is absorbed on the plastic surface, the boundary conditions, equations 2 and 3, are wrong. And if that is wrong, then the conduction equation 1 is also wrong. Why? Because it does not include the effect of volumetric absorption. I discussed this issue at great length in a recent paper (1) and so will not regurgitate it here. However, I will leave a carrot out there for a future examination of infrared spectra used to argue various aspects of transmission and absorption of neat plastics.

So, What is the Purpose of this Paper?

I spent several months drafting a paper that focused on energy uptake in multilayer sheet. Examples include PMMA film on ABS for exterior UV protection and multilayer packaging – PS-tie-EVOH-tie-PP for instance. While doing so, I focused on the energy issues at the interfaces between two plies. The problem I faced was how to consider the mismatch in indices of refraction at the interface. And this led me to the Kubelka-Munk theory (2) and all of its subsequent analyses.

To “set the table,” so to speak, consider this. Energy uptake or conversely energy transmission, in monolithic “pure” films is best described by the Beer-Lambert extinction model. I have used this to try ot understand energy transmission through thin plastic films using published FTIR spectra. The equation is developed in this way.

Consider I to be the inbound radiant flux. The flux I(x) at any point x within the plastic is diminished or extinguished according to equation 5:

\[ \frac{dI(x)}{dx} = - I \beta dx \quad \text{or} \quad \frac{dI}{I} = \beta dx \]  

(5)

Where \( \beta \) is the extinction coefficient, a property of the plastic that can be (and probably is) wavelength- and thickness-dependent.

Equation 6 results after integrating equation 5:

\[ I(x) = e^{-\varepsilon x} \]  

(6)

Where I have assumed that \( \varepsilon \) is a constant and independent of wavelength and thickness. This equation is either called Beer-Lambert Law or Bouguer Law (3). This equation, by definition, describes transmission of electromagnetic energy into a solid. When \( x = 0 \), \( I(0)=1 \) and when \( x = \infty \), \( I(\infty)=0 \). Of course, this was the crux for my epiphany that the radiopaque model is incorrect.

In this epistle, I take an overview of the role particulates play in transmission, absorption, and (unlike my other discussions) reflectance of inbound electromagnetic energy, particularly in the far infrared region so very important to thermoformers.

The True Meaning of Hiding Power

Recall that my original objective was to understand the radiant flux issue at the interface between two plies of plastic. Early on in my research for background information I discovered a many decades old theory that considered the hiding power of white paint over a black substrate. At first I wondered if this theory – known henceforth as the Kubelka-Munk theory or simply the K-M theory – was applicable to my multiple-layer plastic sheets or films. Then it occurred to me that perhaps the ply problem was a simplified aspect of the broader problem of energy uptake of plastics that contain dispersed particulates.

What kinds of particulates? Fillers, fibers, foams, plastics such as rubber-modified polystyrene? What about pigment and opacifiers – TiO\(_2\), calcium carbonate, tale – among those used in paint? And so on.

The questions I then posed are:

- What is the K-M theory?
- Can it be applied to homogeneously dispersed particulate-filled plastics?
The K-M Theory

In 1931, Paul Kubelka and Franz Munk proposed a mathematical model for albedo or reflection of diffuse visible light from a matte, planar parallel paint surface of thickness X covering a substrate (2). The inbound light or electromagnetic radiation has an energy intensity of I. A portion of that energy RI = J is reflected back to the source. K-M call R the albedo of the paint. I’ll call it the reflectivity and the paint layer the coating. The geometry that follows is given in Figure 3.

At a point x into the coating from the substrate, the energy intensity moving away from the source is i and that moving toward the source is j. The differential layer of coating, dx, absorbs energy as a dx and it scatters energy as s dx, where a is the absorption coefficient and s is the scattering coefficient. The source energy passing through the differential layer is:

\[ i \Delta X \] (7)

The reflected energy passing through the differential layer is:

\[ j \Delta X \] (8)

The total energy intensity in the differential layer is written as:

\[ -d i = -(a+s)i \Delta x + sj \Delta x \] (9)

\[ dj = -(a+s)j \Delta x + si \Delta x \] (10)

In short, this is a net balance of energy intensities from the source and from the reflected coating. If these equations are added, the following equation results:

\[ \frac{d j}{i} = \frac{d i}{j} \equiv d \ln \frac{i}{j} = -2(a+s)dx + \left( \frac{s}{j} + \frac{i}{j} \right) s dx \] (11)

Recall that \( R = I/I \). If \( r = j/i \) in the equation above, I get

\[ d \ln r = -2(a+s)dx + (r + r^{-1})dx \] (12)

Or:

\[ \int \frac{dr}{r^2-2\left(\frac{a+s}{s}\right)r+1} = -s \int dx \] (13)

Now \( r = R \) when \( x = X \). I will assume that \( R = R_0 \) when \( x = 0 \) (at the surface of the substrate). Further, I let \( b = (a+s)/s = a/s + 1 \). I integrate this by partial fractions to yield the functional K-M theory:

\[ \ln \left( \frac{R_0}{R} \right) = -b \left( \frac{a+s}{s} \right) x + \left( \frac{s}{s} + \frac{1}{1} \right) s x \] (14)

I now have the working K-M equation.

What about Pigmented Plastics?

However, I found that carrying through K-M’s examples require some redefinitions that do not necessarily yield to easy interpretation. Further research yielded the Saunderson interpretation for analysis of the color in pigmented plastics (4). Saunderson recasts the K-M equation in the following form:

\[ T(x) = \frac{2be^{-bx}}{a+s-(a+s-b)e^{-2bx}} \] (15)

\[ R(x) = \frac{s(1-e^{-2bx})}{a+s-(a+s-b)e^{-2bx}} \] (16)

Where \( T \) is transmittance and \( R \) is the reflectance through the coating of \( x \) thickness.

If the plastic coating only absorbs, such as would be the case with dyes, \( s=0 \). The equation for transmittance, equation x, becomes:

\[ T(x) = e^{-ax} \] (17)

And I get the Beer-Lambert-Bouguer law as I expected.

On the other hand, if my plastic layer is opaque, viz, \( x = \infty \), I get \( T=0 \), as expected and reflectance is:

\[ R(x) = \frac{s}{a+s+b} = \frac{1}{a/s+1+\sqrt{(a/s)^2+4}} \] (18)

Suppose scattering and absorbing coefficients are equal, viz, \( a=s \). The reflectance from an opaque plastic, \( R=0.27 \). Because transmittance is zero, absorptance, \( A \), is \( 1-0.27 = 0.73 \). Table 1 gives some values for opaque plastics.
Table 1
Absorptance and Reflectance as Functions of Absorbing to Scattering Coefficient Ratio, a/s
For a Radiopaque Plastic

<table>
<thead>
<tr>
<th>a/s</th>
<th>Reflectance</th>
<th>Absorptance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.01</td>
<td>0.87</td>
<td>0.13</td>
</tr>
<tr>
<td>0.1</td>
<td>0.64</td>
<td>0.46</td>
</tr>
<tr>
<td>0.316</td>
<td>0.46</td>
<td>0.54</td>
</tr>
<tr>
<td>1.0</td>
<td>0.27</td>
<td>0.73</td>
</tr>
<tr>
<td>3.16</td>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td>31.6</td>
<td>0.02</td>
<td>0.98</td>
</tr>
<tr>
<td>∞</td>
<td>0</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Recall that I began this paper with my argument against the adoption of the general equation for radiopaque plastics. I agree that the Kubelka-Munk and Saunderson methodologies are for visible light impinging on paint and colored plastics. But I see no impediment to extending these arguments to any and all electromagnetic radiation, whether visible wavelength radiation, or far infrared radiation.

**What about Particulates in Plastic?**

In my opinion, plastics that have zero transmissivities (viz, radiopaque plastics) may absorb and reflect inbound energy, the ratio being strongly dependent on the scattering characteristics of the plastic. Of course, in the extreme, if the plastic totally reflects inbound energy, such as with a mirrored surface, absorption is zero, and the sheet does not hear, regardless of its thickness.

On the flip side, when reflectivity is zero, all inbound energy is absorbed. Suppose the “occlusions” are organic but with a different index of refraction to that of the polymer. The proper form for the specular reflectance at the interface is Snell’s Law. For normal incidence such that developed by K-M and Saunderson, reflectance, R, is given by Fresnel’s law:

\[ R = \frac{(n_1-n_2)^2}{(n_1+n_2)^2} \]  

(19)

Where \( n_1 \) and \( n_2 \) are refractive indices of the interfacing materials.

Refractive index for air = 1. Refractive index for PTFE is 1.35 and for HDPE is 1.54. Consider an interface between PMMA as a UV absorber and chemical barrier \( n=1.49 \) and the fire-retardant PVC \( n=1.54 \). The reflectance, R, is 0.003. I view this as insignificant. However, the reflectance between PMMA and air is 0.04. This could be significant. What about minerals? Table 2 gives refractive indices for several additives to plastics.

Table 2
Refractive Indices for Plastic Additives

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass fiber</td>
<td>1.54</td>
</tr>
<tr>
<td>Talc</td>
<td>1.62</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1.84</td>
</tr>
<tr>
<td>Iron</td>
<td>1.94</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.90</td>
</tr>
</tbody>
</table>

So why is TiO₂ an excellent opacifier? Its reflectance with air is \( R = 0.24 \). The reflectance between talc and air, \( R = 0.06 \), meaning that it is not a suitable opacifier. On the other hand, consider the reflectance between E-glass fibers and PP \( n=1.47 \). \( R=0.04 \). Ergo, there is very little reflectance issue in e-glass fiber-reinforced PP, regardless of the glass concentration. Or with carbon black in HDPE where \( R=0.008 \).

**What is the Role of Particulate Concentration?**

Remember I am considering only the far infrared energy spectrum of importance to thermoformers, viz, 4 \( \mu \)m to 7 \( \mu \)m. Optical opacity focuses on the wavelength range of 0.38 \( \mu \)m to 0.7 \( \mu \)m. Organic dyes rarely affect the far infrared spectrum. The extent of pigment concentration is usually conservative. Again the objective is visual.

Here’s an example. Consider carbon black A typical dosage in polystyrene is usually 1-2 weight percent and certainly not more than 1 weight percent. High concentrations of carbon black tend to embrittle even the toughest impact PS. The density of carbon is 2260 kg/m³. The density of PS is 1050 kg/m³. 2.2 wt percent of carbon black occupies only 1 percent by volume in PS. Ergo, 99 volume percent of PS has no pigment.

Now I contrast this to 40 weight percent talc-filled PP. Talc has a specific gravity of 2750 kg/m³ and PP density 1s 910 kg/m³. Talc is nearly 20 percent by volume in the filled PP.

Recall my earlier musings on the relative roles of reflectivity and absorptivity for this material. The functional equation is the ratio of absorptivity to scattering, a/s, as shown in Table 1. According to Saunderson, the aggregate value for a/s should be the sum of the absorption coefficients for all species divided by the scattering coefficients for all species:

\[ \frac{a}{s} = \frac{\sum c_i a_i}{\sum c_i s_i} = \frac{c_1 a_1 + c_2 a_2 + \ldots}{c_1 s_1 + c_2 s_2 + \ldots} \]  

(20)

I think I can extract measurable values for the absorption coefficient for PP and am pretty sure that the scattering effect is zero (or technically very small). With some digging, I can probably find the absorption...
coefficient for the mineral. But my cursory investigation has yet to yield a suitable value for its scattering coefficient. In short, at this point I doubt that I can ascertain appropriate guidelines for determining the effect of particulate loading in plastics.

However, following Saunderson’s lead, I propose a simple example to illustrate how these models might be used. Consider a plastic that absorbs but does not scatter inbound radiation. The correct model for absorption/transmission is the Beer-Lambert-Bouguer equation 17. Ergo, finite $a_1$ and $s_1$.

Suppose I add a particulate to the plastic - one that does not absorb but scatters inbound radiation. For this, $a_2=0$ and $s_2$ is finite. Equation 20 becomes:

$$
\frac{a}{s} = \frac{C_1 a_1}{C_2 s_2} = \frac{(1-C_2)a_1}{C_2 s_2}
$$

Where $C_1$ and $C_2$ are the wt fractions of the plastic and particulate, respectively. Consider now transmittance, equation 15 for this combination.

$$
T(x) = \frac{2b e^{-bx}}{a+b-(a+b)e^{-2bx}}
$$

Where $b=(1-C_2)a_1/C_2 s_2 + 1$. I now want to assume that the plastic absorptance coefficient is low (meaning that transmission of inbound radiant energy is high. And I assume that the particulate scattering coefficient is high. The numerator in equation 15 is small and the denominator is large, yielding $b \approx 1$. I get the following for the transmissivity equation.

$$
T(x) \approx \frac{2e^{-x}}{s_2 (1-e^{-2x})}
$$

(22)

Because the first term in the general equation for $b$ has disappeared, the particulate concentration does not enter into this equation. Now if $s_2 \gg 1$, I can write equation 22 as:

$$
T(x) \approx \frac{2e^{-x}}{s_2 (1-e^{-2x})}
$$

(23)

For relatively thick plastic sheets, $e^{-2x} \ll e^{-x}$. As a result the transmissivity reduces simply to a modified version of the Beer-Lambert-Bouguer equation.

$$
T(x) \approx \frac{1}{s_2} e^{-x}
$$

(24)

I conclude that the higher the particulate scattering coefficient becomes, the lower the transmissivity becomes, even though the absorption coefficient of the plastic is very low. To me, this emphasizes the importance of particulate scattering on volumetric absorption of inbound far infrared radiation.

### Conclusion

So how does this translate to the heating characteristics of pigments or dyes that are specifically added to affect the visual appearance of the plastic?

I think I can best summarize this portion of the paper as follows. If the concentration of particulates is low, as is the case with opacifiers and pigmented colorants, traditional transmissivity and absorptivity coefficient values for the unmodified plastics are probably sufficient when using the volumetric absorption heat transfer models.

On the other hand, how does this translate to the heating characteristics of highly particulate-filled plastics?

Here’s my take on this. As the concentration of particulates increases, as is the case with filled and reinforced plastics, absorptivity coefficients for those particulates must be included. More importantly, it is my belief that the effect of particulate scattering becomes more critical to the prediction of energy uptake in filled plastics. Certainly transmissivity and absorptivity in the non-particulate portion of the plastic can be determined. But I believe that it is the energy scattering effects of particulates that dictate temperature profiles in plastics regardless of the absorption characteristics of the neat plastic.

### References


File: SPE-Parametric Radiant Energy Absorption in Plastics