

Alphabet Soup?

It seems that plastics people never tire of their alphabet soup – ABS, PTFE, PVC, PUR, and on and on. The soup continues when we consider evaluating the characteristics of plastics. In this short series, we consider a few of the letters in this soup.

Tg, Tm and DSC

We've already discussed the first two. Tg is glass transition temperature, or the temperature above which polymers become rubbery rather than glassy. Tg's for polystyrene and acrylic are around 210°F (100°C). Tg for rigid PVC is around 185°F (85°C) but can be as low as -25°F (-30°C) when highly plasticized. The glass transition temperature for nylon 6 is only 122°F (50°C). The Tg for polyethylene is around -125°F (-90°C) and that for homopolymer PP is 15°F (-10°C).

You'll recall that Tm is the melting temperature for crystalline polymers such as polyethylene, polypropylene and nylon. The melting temperature for HDPE is around 275°F (135°C). The melting temperature for homopolymers PP is 330°F (165°C), and that for nylon 6 is 430°F (220°C).

One popular method for measuring Tg and Tm is with DSC. So, what is DSC? Differential scanning calorimetry. Consider heating a substance from room temperature, say, to a specific processing temperature. Let's use water as an example. It takes exactly one calorie of energy to heat one gram of water one degree Centigrade. In British units, it takes one British Thermal Unit of energy to heat one pound of water one degree Fahrenheit. This rule works until water reaches its boiling point of 212°F (100°C). At the boiling point, the temperature remains constant even though substantial energy is inputted to the water. If we were to compare the energy uptake of a substance that did not boil with that of water, we would see that the temperature of the non-boiling substance would continue to climb while that of water would remain constant until all the water had evaporated.

Conversely, if we cool water from room temperature to 32°F (0°C), it freezes. At the freezing point, the temperature remains constant even though substantial energy is removed from the water.

Physical changes that take up energy with little or no temperature change, such as boiling or melting, are called endothermic changes. Physical changes that give off energy with little or no temperature change, such as freezing or crystallizing, are called exothermic changes.

We can build a device that compensates for these temperature differentials. The device uses a well-characterized substance as its reference. The substance to be tested is then heated at the same rate as the reference substance. This is done by carefully controlling the energy ratio between the reference substance and the test substance. Since the device is measuring calories or units of energy, it is called a calorimeter. Since the device measures the temperature difference between two substances as they heat, it is a scanning device. And since the device is looking at the difference between the two substances, it is a differential device. If we put this all together we see that the device is a differential scanning calorimeter, or DSC!

What Can We Learn From DSC?

First, we must realize that the DSC can be used either in a heating mode or in a cooling mode. Samples are usually heated beginning at room temperature and they are usually heated at a fixed temperature rate such as 10°C/minute. The temperature range and energy requirements of transitions are the primary information gathered from heating DSCs. The most common transitions are the glass transition temperature and the melting temperature, if any.

Between transitions, the DSC provides relative energy uptake by the test substance. This is directly related to that for water, as specific heat or



heat capacity. As we saw above, the amount of energy absorbed by water is 1 cal/gm°C or 1 Btu/lb°F. So its heat capacity is 1.0. It takes 100 cal/gm°C or 180 Btu/lb°F to heat water from 32°F to 212°F. We find that polystyrene has about 55% of the heat capacity of water and that for PVC has about 37% of that of water. PP has about 85% of the heat capacity of water and that for LDPE is about the same as that of water. Remember, now that these values are between transitions.

DSC is important when trying to determine the extent of crystallization of a polymer. Consider the case for a 100% crystalline polymer that requires 100 cal/g to melt. If that polymer is cooled from the melt and DSC determines that only 50 cal/g was liberated during recrystallization, it is safe to say that the polymer at room temperature is only 50% crystalline.

In the last lesson, we learned that coPP melts around 155°C but recrystallizes at around 100°C. How did we know that? From DSC, of course.

The DSC can teach us another aspect to polymer characterization. As we increase the cooling rate for some crystalline polymers, we retard the temperature at which recrystallization begins. And we reduce the final level of crystallinity. How do we know this? Consider PET. It has a melting temperature of 510°F (265°C). If we cool PET very slowly, we find that it recrystallizes at around 250°C to about 40-45%. If we cool PET very rapidly, we find that there is no recrystallization region. PET remains amorphous at room temperature and beyond. DSC is therefore a tool for determining how rapidly a plastic crystallizes. ■

Keywords: glass transition, melting, recrystallization, calorimeter, endothermic, exothermic

ABCs of Alphabet Soup?

In our last lesson, we learned about T_g, T_m, and DSC. These are important letters in our alphabet soup. In this lesson, we look at some new letters.

IR and FTIR

IR means infrared and FTIR means Fourier-transform infrared. We usually heat our plastic sheet with radiant heaters. These heaters emit infrared energy or IR. Infrared energy is part of the electromagnetic spectrum of energy. The spectrum is usually defined in terms of the length of the emitting rays. And the length is usually given in microns. The length is identified by the symbol μm . Radio waves are long-length waves, in the range of 10^7 to 10^{10} μm . They reside near one end of the electromagnetic spectrum. Gamma rays are short-length waves, in the range of 10^{-4} to 10^{-7} μm . They reside near the other end of the electromagnetic spectrum.

In contrast, visible light has the wavelength range of 0.4 to 0.7 μm . It is about in the middle of the electromagnetic spectrum. Energy of shorter wavelengths, between 0.4 μm and about 10^{-2} μm , is ultraviolet energy. Energy of longer wavelengths, between 0.7 μm and about 10^3 μm , is called infrared energy. The infrared energy wavelength range is usually separated into near infrared energy, having wavelengths between 0.7 μm and about 2.5 μm , and far infrared energy, having wavelengths between about 2.5 μm and 10^3 μm .

Our thermoforming radiant heaters typically operate in the wavelength range of about 3.5 μm to about 20 μm or so. Or in the far infrared energy wavelength range. As you might expect, as the temperature of the radiating body increases, the peak wavelength shifts to short and shorter wavelengths. And as the radiating body temperature increases, the amount of energy emitted increases as well.

For example, if your heater temperature is 400°F (~200°C), the peak wavelength is 6.06 μm , and the maximum amount of energy emitted at this wavelength is 2.94 units¹. If you raise the



heater temperature to 600°F (~315°C), the peak wavelength is 4.92 μm , and the maximum amount of energy emitted is 6.78 units. If you raise the heater temperature to, say, 900°F (~480°C), the peak wavelength is 3.83 μm , and the maximum amount of energy emitted is 17.3 units.

A couple of reference points, please! Certainly! The sun radiates at 12,000°F (~6500°C), its peak wavelength is 0.43 μm , and the maximum amount of energy it emits is nearly 120,000 units²! What about us! Because radiation is electromagnetic energy interchange, we radiate back to the sun at 98.6°F (37°C). Our peak wavelength is 9.35 μm , and we emit about 0.52 units. We're pretty feeble radiators!

Okay, what about the sheet we're trying to heat? Well, as the sheet heats, the amount of energy it radiates increases. Suppose the heater temperature is 600°F. If the sheet reaches 400°F, it radiates a maximum of 2.94/6.78 = 43% of the energy it gets from the heater *back to the heater!* Really! Isn't infrared energy fun?

Okay, what is FTIR? Keep in mind that heaters emit and sheet absorbs far infrared energy. However, plastics do not absorb energy uniformly. The amount of energy absorbed at any given wavelength depends on the type of plastic being heated. Very few plastics uniformly absorb radiant energy only on their surfaces. When the radiant energy is not entirely absorbed in the surface layer, some of it is transmitted into the plastic. If the sheet is thick enough, all the radiant energy that impinges the sheet surface is absorbed in the polymer. Plastics such as polyethylene are notoriously poor at absorbing energy on the sheet surfaces. Others, such as PVC, absorb a substantial portion of the incoming energy on the sheet surface.

But how can we tell whether a sheet of plastic is absorbing most of its energy on its surface or inside the sheet? That's where FTIR comes in. For the moment, ignore the "FT" part of the alphabet soup. I take a thin film of my plastic, place it in an infrared or IR

scanner, and pass a monochromatic³ infrared beam through it. I measure the decrease in energy transmitted through the plastic film at that wavelength. I change the wavelength of the infrared beam and again measure the transmitted energy. If I scan the film with an infrared beam of wavelength range of 2 μm , say, to 20 μm , I will have covered the majority of the wavelength range of our heaters.

Now, I double the film thickness and repeat the scan. This tells me how deep the infrared energy penetrates into my film. I continue doubling the film thickness until none of the infrared energy is transmitted through the film.

The IR scanner is mostly used in an analytical polymer laboratory, where polymer chemists determine the general composition of the polymer and its additive packages. The various peaks that are generated at specific wavelengths are directly related to the molecular confirmation of the polymer. For example, the carbon-hydrogen bond is stretched at a frequency of about 3.5 μm . As a result, all polymers containing C-H bonds absorb 100% of the 3.5 μm infrared energy. PP does. PE does. PTFE doesn't because it has no C-H bonds.

What about the "FT" portion of FTIR? The polymer chemist obtains infrared scans of various recipes in order to compare the ingredients. These scans are then mathematically encoded so that the polymer chemist (or his computer software) can arithmetically subtract the infrared spectrum of the polymer, say, from the spectrum of the recipe. What's left must be the additive package. By subtracting the infrared spectrum from a known additive package, for example, the polymer chemist can determine the composition of any unknown in the recipe. The mathematical encoding is called Fourier Transformation or "FT." And we've just put the "FT" back into FTIR.

Do we care what the recipe of our plastic is? Not really. We just need to know how much infrared energy our plastic absorbs. So we just "piggyback" on the polymer chemist's FTIR device. ■

Keywords: Infrared, far infrared, electromagnetic energy, wavelength, Fourier Transform

¹ The units are kW/m² - μm .

² Think Clearwater Beach, Florida at 1400 hours on July Fourth!

³ Monochromatic: Of or composed of radiation of only one wavelength.

XYZs of Alphabet Soup?

This is the third in a series on plastics alphabet soup. So far, we've tackled Tg and Tm. And we spent time with DSC and IR and FTIR. Are there more acronyms¹ that we should know about? Sure. Lots. In this discourse, we look at four more – HDT, DTA, DMA, and DTMA.

What is HDT?

HDT stands for heat deflection temperature². It is an ASTM test (D648) and an ISO test (75-1, 75-2)³. The test focuses on the three-point deflection of a plastic bar of very specific dimensions⁴. The bar is placed in an oil bath. A dead weight is placed in the center⁵. The oil bath is heated at a very specific rate⁶. As the plastic increases in temperature, it softens. HDT is the temperature at which it sags a fixed amount⁷. This test, without ASTM or ISO numbers, is more than 60 years old.

HDT is often used to sort or rank plastics. And it is often used for quality control. In thermoforming, it provides a crude, early estimate of the lower temperature for forming. Unfortunately, it is not a very good test. For example, it has no value for plastics that are relatively soft at room temperature, such as some plasticized PVCs and TPOs. The test yields a single data point that should not be used to predict long-term behavior. The test is often tricked by residual stress in the test specimen. And it is tricked if the polymer has very low

¹ Acronym: a word formed from the initial letters of a multi-word name.

² HDT was originally called heat distortion temperature.

³ Another acronym used for the ASTM test is DTUL, meaning deflection temperature under load.

⁴ 5 inches long by 1/2-inch thick by a width not to exceed 1/2-inch. ISO specifications are similar but in metric units.

⁵ The weight is equivalent to either 66 or 264 lb/in² fiber stress. ISO specifications are similar but in metric units.

⁶ 2 +/- 0.2°C/min.

⁷ 0.010 inches. ISO specifications are similar but in metric units.

thermal conductivity or if the oil bath is not vigorously stirred.

Here is another way the data can mislead. Consider HDT values for polycarbonate and nylon 6 for two loads:

Plastic	HDT @ 66 psi	HDT @ 264 psi
Polycarbonate	290°F	275°F
Nylon 6	370°F	150°F

What is the real HDT value for nylon 6?

And one more reason to avoid HDT values. Consider glass-reinforced polycarbonate and nylon 6 HDT values:

Plastic	Unreinforced @ 264 psi	Reinforced HDT @ 264 psi
Polycarbonate	275°F	295°F
Nylon	150°F	420°F

Again, what is the HDT of nylon 6? Nuff, said!

DTA, DMA, and DTMA. Are These the Same?

First, DTA. DTA stands for differential thermal analysis. Remember our discussion on DSC, differential scanning calorimetry? Well, DTA uses the same equipment and the same analysis as that for DSC. The difference is that the data are interpreted differently for DTA. For example, DTA yields specific heat, or the amount of heat absorbed by the plastic as a function of temperature. Time-dependent changes such as rate of crystallization are obtained by running the DSC/DTA at different heating (or cooling) rates.

DMA is the acronym for differential mechanical analysis and DTMA is the acronym for differential thermal mechanical analysis. The earliest device is described in ASTM D 2236. A review of various mechanical testing techniques is described in ASTM D 4065. In gen-



eral, a solid plastic test bar is subjected to torsional or flexural oscillation.

Usually, if the device is operated at a fixed temperature and the frequency of oscillation is varied, the test is called DMA. If the device is operated at a fixed oscillation frequency and the temperature is varied, the test is called DTMA. There is an imperfect correlation between these two testing procedures.

What is DMA/DTMA used for? If the plastic is elastic, its resistance matches that of the oscillating device. If the plastic is fluid or viscous, its resistance is out-of-phase with that of the oscillating device. As the temperature or frequency is changed, device detects shifts from elastic to viscous or viscous to elastic character in the polymer. As a result, the data will yield the glass transition temperature of the polymer. More importantly, however, the test will show plastic resistance to applied load over a temperature range up to its melting temperature. This is important for thermoformers, since we are stretching the plastic while it is primarily in its rubbery solid state. For example, we can quickly assess the forming temperature range of the plastic. And within a given polymer family, we can determine which polymer recipe yields the broadest forming window. DMA/DTMA will probably be the subject for a TF 101 lesson.

DMA/DTMA data obviate single-point values such as those obtained with HDT/DTUL devices. ■

Keywords: *mechanical analysis, heat deflection, heat distortion, oscillation frequency*