

Thermal Analysis

Better Characterization of Hot Melt Adhesives Using the Double Furnace DSC



DSC 8500

Introduction

Hot melt adhesives are a copolymer consisting of ethylene and vinyl acetate (VA). The end use properties of EVA copolymers, such as packaging films and hot melt adhesives, are very much dependent upon the level of the amorphous vinyl acetate component contained in the copolymer. Low levels of vinyl acetate result in a material which is more rigid, since the crystalline ethylene component becomes dominant. Higher levels of vinyl acetate result in a more flexible product with a higher degree of toughness.

Hot melt adhesives are solvent-free adhesives, that are characteristically solid at temperatures below 80 °C, are low viscosity fluids above 80 °C, and rapidly set upon cooling. The development of hot melt adhesive technology stemmed from the previous use of molten wax for bonding. When this method no longer satisfied performance needs, 100 percent thermoplastic systems were introduced. Hot melt adhesives are used in a variety of manufacturing processes, including bookbinding, product assembly, and box and carton heat sealing.

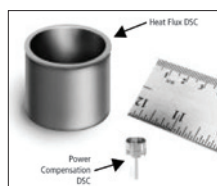
The characterization of the thermal properties of EVA copolymers and hot melt adhesives is important for process optimization, product improvement and for quality assurance purposes. Differential scanning calorimetry (DSC) provides an ideal means of assessing the thermal characteristics of EVA copolymers and hot melt adhesives. Given that hot melt adhesives are subjected to very fast heating and cooling conditions in real-life, it is essential to have a DSC instrument which can simulate these processing conditions.

Double Furnace DSC

The Double Furnace DSC uses two independently controlled, low mass (1 g) sample and reference furnaces. The low mass of the Double Furnace furnaces yields a DSC with low thermal inertia and the fastest response time of any DSC instrument available.

The Double Furnace DSC allows samples to be linearly heated and/or cooled at rates as fast as 500 °C/min. This is important when dealing with hot melt adhesives which are subjected to very fast heating and cooling conditions during use.

In contrast, heat flux DSC instruments employ a large mass furnace. Some DSC devices use a silver block with a mass of 100 g or more. This provides a much higher thermal inertia and a slower inherent DSC response time. The heat flux DSC instruments cannot achieve the very fast cooling and heating provided by the Double Furnace DSC. The large difference in masses between the heat flux DSC and the Double Furnace DSC may be seen in the following figure.



Experimental

In order to demonstrate the use of the Double Furnace DSC for the better and more complete characterization of hot melt adhesives, a two stage adhesive (from Bostik™) was analyzed. The following conditions were used to measure the thermal properties of the hot melt adhesive.

Experimental Conditions

Instrument	PYRIS Double Furnace DSC
Sample mass	Approx. 20 mg
Heating rate	20 °C/min
Cooling rate	400 °C/min (linear)
Temperature range	-60 to 180 °C
Purge gas	Helium
Sample pan	Open aluminum pan

The DSC instrument was calibrated for temperature and enthalpic response using high purity indium metal.

Results

The use of the fast cooling ramp (400 °C/min) simulates the conditions to which a hot melt adhesive is subjected when it is ejected from the hot melt gun. The adhesive is quickly melted in the gun and then experiences very rapid cooling back to room temperature. The Double Furnace permits the simulation of these real-life cooling conditions for hot melts.

The ability of the Double Furnace DSC to provide fast cooling (at 400 °C/min) may be seen in Figure 1. In this example, the hot melt adhesive was cooled from 180 °C down to -60 °C at a rate of 400 °C/min. The plot shows the actual sample temperature and the program temperature, as well as the hot melt hot flow signal, as a function of time. The sample tracks the program temperature linearly down to -20 °C as these results show, even at the ballistic cooling rate of 400 °C/min.

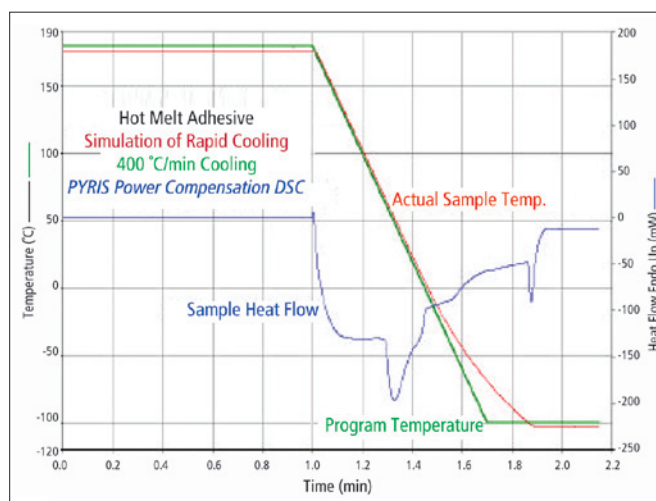


Figure 1. DSC results obtained during cooling of the hot melt adhesive at a rate of 400 °C/min showing heat flow, sample temperature and program temperature.

The ability to perform rapid cooling experiments on the hot melt adhesives is important as different sample crystalline morphologies can develop in the ethylene component at different cooling rates. The Double Furnace DSC provides the very fast response times necessary to be able to perform these high velocity measurements.

With the heat flux DSC instruments, the fastest controlled cooling rates achievable, over this hot melt temperature range, would only be a maximum of 100 °C/min (at best). The Double Furnace DSC provides the flexibility to be able to perform both normal and ballistic heating and cooling experiments.

The effect of the cooling rate on the resulting crystallization of the ethylene component may be seen in Figure 2. This figure shows an overlay of the DSC cooling data at linear rates of 400, 200, 100 and 50 °C/min. The crystallization onset temperature is moved to lower temperatures with respect to increasing cooling rate and the nature of the crystallization is different (as exemplified by the different shapes of the crystallization peaks). The Double Furnace DSC is the only DSC capable of providing this type of information at such a range of cooling rates.

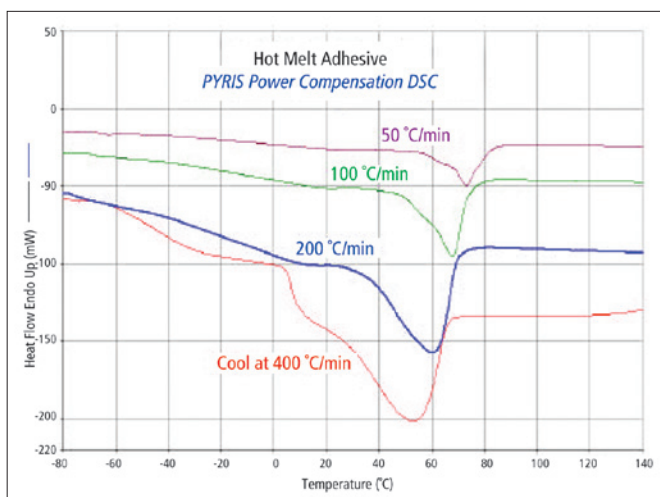


Figure 2. DSC results showing crystallization of hot melt adhesive at cooling rates of 400, 200, 100 and 50 °C/min.

The Double Furnace DSC provides outstanding reproducibility even at the ballistic cooling rate of 400 °C/min, as may be seen in Figure 3. This plot shows an overlay of 5 cooling experiments performed at the rate of 400 °C/min on the hot melt adhesive sample.

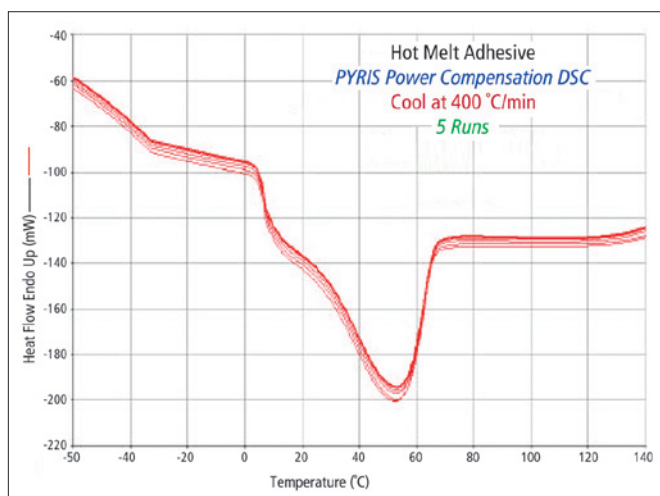


Figure 3. Five cooling experiments performed on hot melt adhesive using a cooling rate of 400 °C/min.

Shown in Figure 4 are the DSC results obtained on the as-received hot melt adhesive. The glass transition event of the vinyl acetate component is observed as a stepwise change in the DSC heat flow at -12 °C. Above T_g, the ethylene component undergoes melting beginning at 38 °C with peaks occurring at 53, 93 and 115 °C. The total heat of melting is 94.4 J/g and this value reflects the percent crystallinity possessed by the as-received hot melt adhesive.

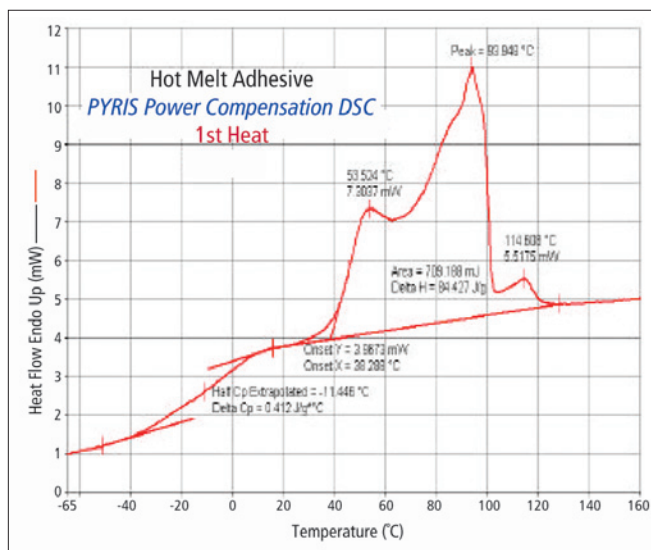


Figure 4. DSC results for as-received hot melt adhesive sample.

The hot melt sample was cooled back to room temperature at a ballistic rate of 400 °C/min (to simulate real life conditions) and then held at room temperature for 10 minutes. The sample was then cooled back to -60 °C, and reheated to 180 °C at a rate of 20 °C/min. Displayed in Figure 5 are the DSC results generated during the reheat experiment reflecting the new thermal history of the adhesive. The sample yields its T_g at -21 °C and immediately begins melting upon passing through T_g. The ethylene component yields melting peaks at 31 and 91 °C with a heat of melting of 74.5 J/g.

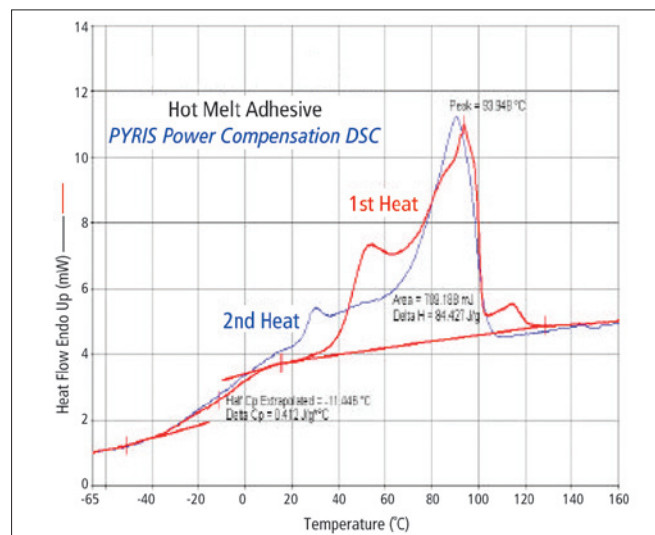


Figure 6. Overlay of first and second heating experiments for hot melt adhesive sample.

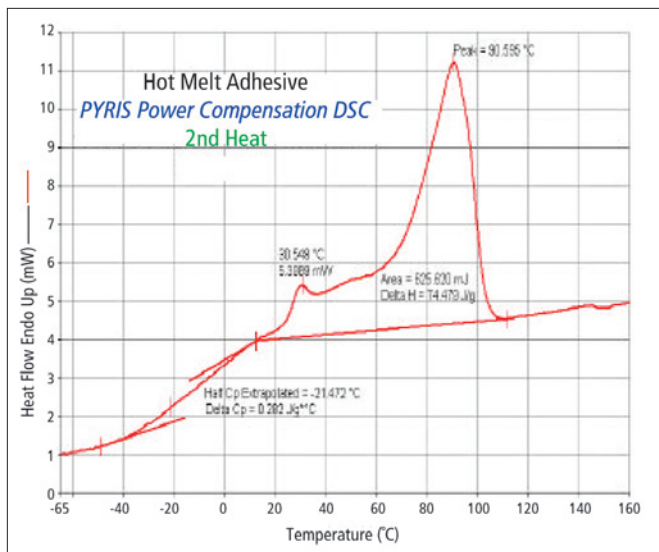


Figure 5. DSC results during second heating of hot melt adhesive sample (after cooling back to RT at 400 °C/min).

A direct comparison of the DSC results obtained for the hot melt adhesive during the first and second heating segments may be seen in Figure 6. The effects of the thermal history on the properties of the hot melt sample are very evident from these results.

Summary

The Double Furnace DSC provides outstanding characterization information on hot melt adhesives. The adhesives are generally a copolymer of ethylene (crystalline) and vinyl acetate (amorphous). The thermophysical properties of the ethylene component are particularly susceptible to the cooling conditions from the melt. Since hot melt adhesives are heated to the melt in a gun and then rapidly ejected, it becomes important to have a DSC instrument which can heat and cool quickly to provide better processing simulation data. The Double Furnace DSC can ballistically heat and cool at rates up to 500 °C/min. This provides better, real-life data on hot melt adhesives. The Double Furnace DSC is the only DSC available which can provide this very rapid heating and cooling.