Characterization of Foams by Thermal Analysis

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Structural and nonrigid foams have continued to expand their position in the plastics marketplace. The unique properties of these materials have resulted in their increased use in many areas of plastics manufacturing:

- Blown film extrusion
- Pipe and sheet extrusion
- Extrusion coating
- Blow molding
- Wire coatings
- PVC pipes
- Home finishing and insulation materials
- Packaging materials
- Automotive components

The thin-walled cellular structure affords foamed polymers their unique properties. In addition to the obvious advantages of low density these cellular plastics provide enhanced thermal, acoustical and electrical insulation properties as compared to their higher density or solid counterparts. Because of the presence of the cellular air pockets, the foams also provide better mechanical/damping properties and superior flexibility.

The process of making a foamed thermoplastic involves three basic processing steps:

1. Getting the polymer into a viscous, liquid state
2. Introducing a gas to produce significant expansion
3. Solidification of the foamed thermoplastic to stabilize or freeze the structure

Thermoplastics are generally heated to bring the polymer to the desired viscosity range before introducing the foaming gas. The gas is introduced into the molten polymer by a liquid dispersed in the melt or by the reaction of a chemical foaming agent. Usually the chemical foaming agents are compounds that release nitrogen during thermal decomposition. The choice of the particular foaming agent depends on the viscosity of the thermoplastic at the temperature at which the agent decomposes.

The properties of the foam can be tailored by adjusting the blowing agent and/or the polymer to get the desired foam density and structure. The foam density can be altered by adjusting the concentration of the foaming agent or by incorporating additives which will alter the decomposition of the agent. The viscosity of the thermoplastic is critical. Less foaming will take place at higher resin viscosities. Conversely, if the melt viscosity is too low, the gas will overflow, rupturing the cells and blemishing the surface of the end product. In general, optimal foaming is achieved by modifying the viscosity of the resin through additives, blending or crosslinking.

One of the best means of characterizing the properties of foams is thermal analysis, which comprises a series of techniques including:

- Differential scanning calorimetry (DSC) for measuring the heat flow properties of materials when heated, cooled or held isothermally.
- Thermogravimetric analysis (TGA) for the determination of the weight loss properties of samples when heated or held under isothermal conditions.
- Thermomechanical analysis (TMA) for measuring the dimensional properties of materials when heated, cooled or held isothermally.
- Dynamic mechanical analysis (DMA) for the characterization of the mechanical or viscoelastic properties of samples when heated, cooled or held isothermally.
- Thermoconductivity (TC) for the assessment of the ability of a material to conduct heat.

PerkinElmer offers a complete line of all of these thermal analytical instruments and has played a major role in the development and enhancement of this field of analytical instrumentation. The extensive thermal analysis line of products offered by PerkinElmer encompasses R&D as well as QA applications.

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Figure 1. DSC results obtained on LDPE sample with blowing agent.

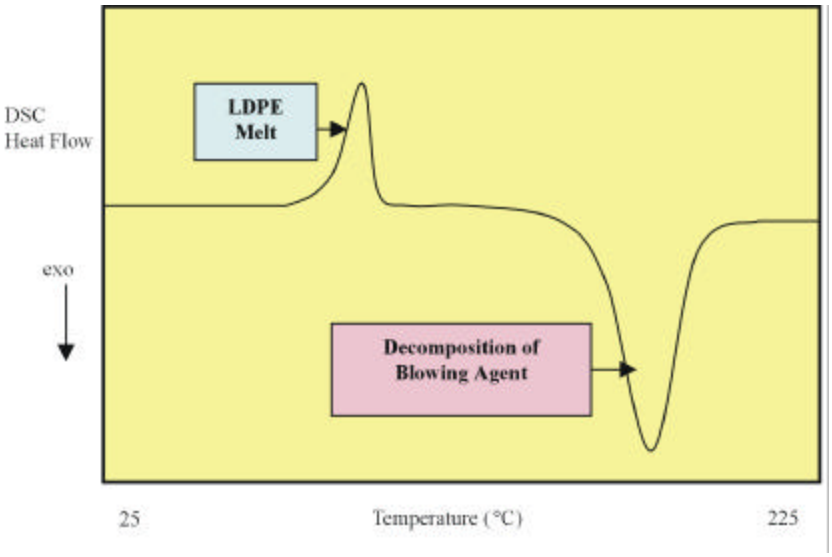
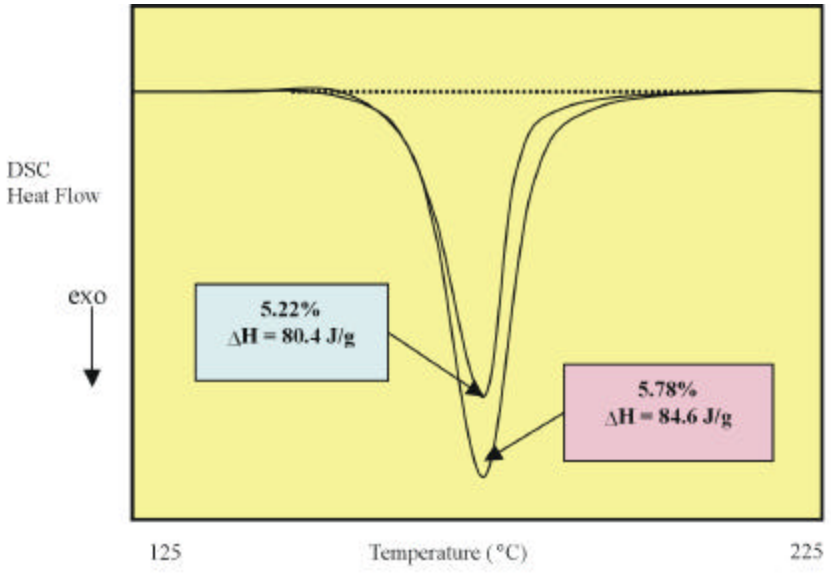


Figure 2. Quantitative determination of blowing agent in LDPE resin by DSC.



DSC

The most widely utilized thermal analysis technique is DSC and is used to measure important thermal properties such as glass transition temperatures (Tg), melting points (Tm), heats of transitions, percent crystallinities and crystallization temperatures. For the characterization of foams, DSC provides valuable data on the melting properties of the polymer as well as the assessment of the decomposition of the foaming agent.

A sample of low density polyethylene (LDPE) containing a blowing agent was analyzed using the PerkinElmer DSC. Figure 1 shows the DSC results generated on the LDPE sample with the blowing agent.

The first endothermic peak at 105 C is that melting of the crystalline component of the low density polyethylene resin. Above the melt, the resin becomes a viscous liquid. Upon further heating, a large exothermic peak is obtained at approximately 180 C, which is due to the thermal decomposition of the blowing agent and the subsequent release of nitrogen gas. The DSC results provide valuable information on the melting of the thermoplastic resin and the temperature interval over which the blowing agent undergoes decomposition. The peak maximum at 180 C represents the maximum rate of decomposition under the given experimental conditions. Different blowing agents may degrade over a different temperature range and DSC can easily assess the range. Higher decomposition temperatures may result in a greater degree of foaming as the thermoplastic resin viscosity

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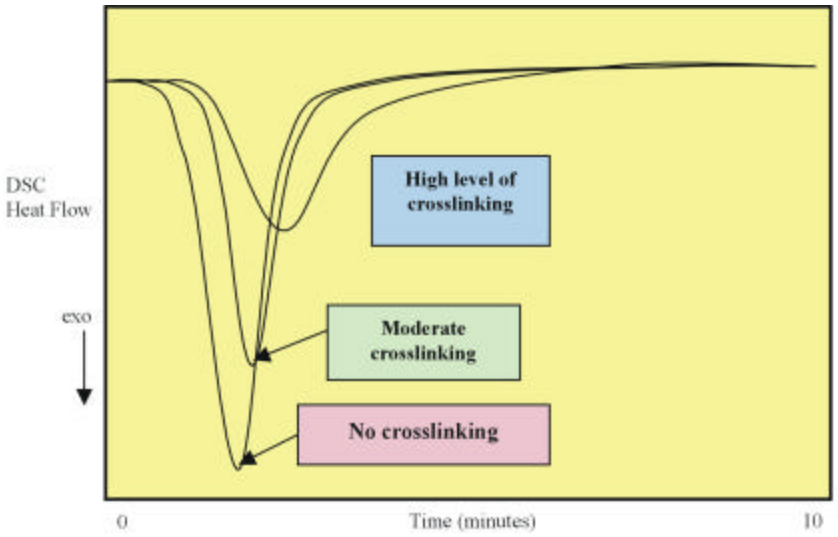
Figure 3. Isothermal crystallization of different crosslinked LDPE resins by DSC.



will be lower as the temperature increases.

The second example of the use of DSC shows how the technique can be used to assess the amount and rate of release of blowing agents. The overall heat of decomposition is directly proportional to the amount of blowing agent present in the resin. Figure 2 shows the DSC results generated a LDPE resin containing different concentrations of the blowing agent. One sample contains 5.22% of blowing agent while the other contains 5.78%.

The DSC results show the measurement of the heat of decomposition can be used to assess the level or concentration of blowing agent in the resin. A difference of only 0.03% in concentration would be detectable using the PerkinElmer DSC.

DSC can also be used to examine the relative viscosities of resins. The viscosity achieved by the thermoplastic during the foaming operation will have a major impact on the degree of foaming that occurs. Higher resin viscosities will generally result in a greater degree of foaming, while less foaming will take place at higher resin viscosities. The viscosity of LDPE can be adjusted by subjecting the polymer to irradiation. This produces additional crosslinking, which then increasing the viscosity of the resin in the molten state.

The effects of this crosslinking on the resin's relative viscosity can be studied by DSC isothermal crystallization measurements. With this test, a sample of the resin is heated through its melt and held for 5 minutes to destroy the existing crystalline phase. The sample is then quickly cooled to a temperature below the melting point and held under isothermal conditions to monitor the resulting crystallization of the resin. A given polymer, which has a higher viscosity due to crosslinking, will take longer to crystallize and have a smaller overall heat of crystallization. Resins will little or no additional crosslinking will crystallize more rapidly.

The PerkinElmer power compensated DSC is ideal for performing the highly sensitive isothermal crystallization test. The low mass furnaces (1 g) on the sample and reference sides permit both rapid cooling and thermal equilibration, necessary for accurately and reproducibly measuring the isothermal crystallization behaviors of the resins. In contrast, heat flux DSC instruments have a single large mass furnace (up to 200 g), which precludes rapid cooling and making the instrument sluggish when attempting to thermally equilibrate at isothermal conditions.

In the next DSC example, three LDPE resins of different crosslink densities, were tested using the isothermal crystallization approach. The samples were heated to 130 C, to permit the sample to melt, held for 5 minutes, and then cooled at a rate of 320 C/min to an isothermal temperature of 97 C. The resulting crystallization responses of the resins were monitored using the power compensated DSC as a function of time.

These DSC results show that, as the resin becomes more crosslinked and its viscosity becomes higher, it takes increasingly longer for the polymer to crystallize. The DSC

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isothermal crystallization measurement provides an easy-to-

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Figure 4. Determination of level of blowing agent in LDPE by TGA.

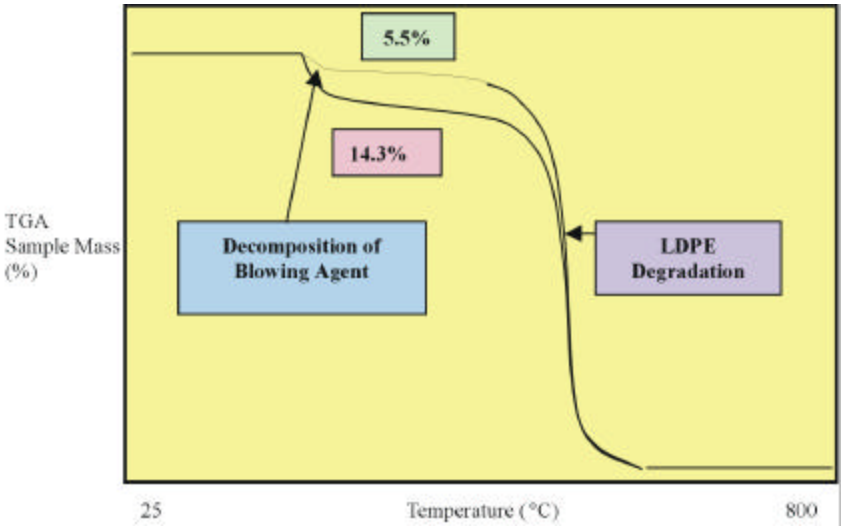
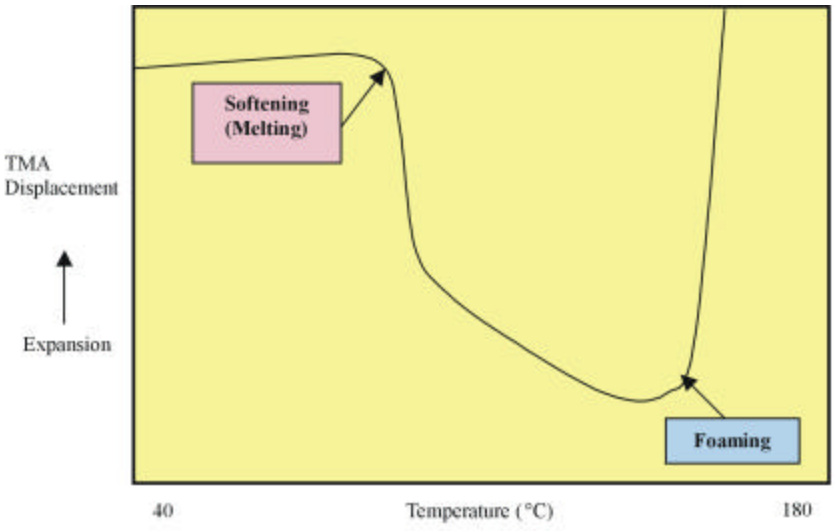


Figure 5. Characterization of LDPE foam by TMA (compression mode).



perform, yet highly sensitive screening or QA test for examining resins for foaming propensity. It should be noted that the standard DSC heating test showed little or no significant differences on this series of crosslinked LDPE resins.

TGA

Thermogravimetric analysis is a very useful technique for measuring weight losses, due to loss of volatiles or to chemical degradation, degradation onset temperatures, and rates of degradation. Samples can be subjected to different purge gas environments to allow for different degradation processes to be observed. The most commonly used inert purge gases (to study pyrolysis or thermal degradation) are nitrogen and argon, while air and oxygen can be used to measure oxidative degradation. Using the PerkinElmer Thermal Analysis Gas Station (TAGS), the flow rate of the purge gases can be precisely and digitally controlled. The TAGS also permits automatic switching of one purge gas to another during an experiment and gases can even be mixed with the device.

TGA is a valuable technique for the characterization of foaming polymers including the assessment of thermo-oxidative stabilities, compositional analysis including the amount of blowing agent, flammability studies, and the measurement of inert ash or residue. Since blowing agents release nitrogen gas during degradation, the temperatures and concentrations of the agents can be easily assessed by TGA.

Shown in Figure 4 are the TGA results generated on two different LDPE samples containing different levels of blowing agents.

The decomposition of the blowing agent at approximately 200 C is easily measured by TGA, and the level of the mass loss is directly proportional to the amount of blowing agent contained in the polymer.

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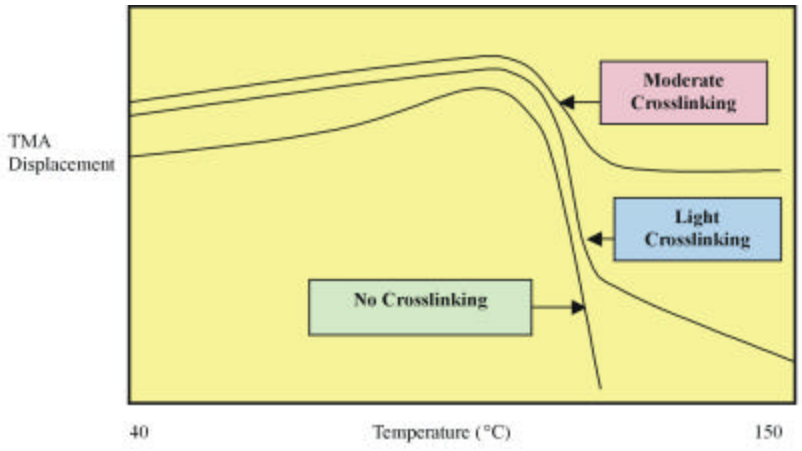
Figure 6. Assessing crosslink density of LDPE polymers using compression mode of TMA.



TMA

Thermomechanical analysis is a valuable technique for measuring the dimensional properties of materials, including softening temperatures, heat deflection temperatures, expansion, penetration, coefficients of thermal expansion (CTE), swelling and shrinkages. The actual foaming or the swelling of a polymer can be measured using TMA. As the material foams, it undergoes significant expansion and this is monitored using the TMA approach. Shown in Figure 5 are the TMA results generated on a sample of LDPE with blowing agent. The sample was analyzed using the TMA compression mode which provides outstanding data on foams.

The TMA results show that the LDPE sample undergoes a small amount of expansion between 40 and the melting temperature. At approximately 100 C, the sample melts and the lightly loaded probe penetrates the sample and a rapid decrease in the thickness of the sample is observed. A quasi-linear response is obtained in the viscous region above the melting point and the slope of this reflects the degree of crosslinking achieved by the resin. Upon further heating a large increase in the expansion of the polymer is observed and this reflects the swelling causes by the release of the nitrogen gas from the blowing agent. These results demonstrate that the TMA results can provide valuable information on the melting temperature, relative crosslink density and foaming temperature.

As was discussed in the DSC section, the relative crosslink density or viscosity of the polymer above the melting point can have a major effect upon the degree of foaming that occurs. The compression mode of the TMA provides a sensitive means of assessing the relative degree of crosslinking (and viscosity) of the polymer.

Shown in Figure 6 are the TMA results generated on 3 different LDPE samples with different levels of crosslinking.

These results show that the moderately crosslinked LDPE sample exhibits the least amount of displacement change at the melting temperature and that the slope of the quasi-linear response above Tm is close to 0. The more lightly crosslinked LDPE material yields a large change in its displacement at the melting point and has a significant slope in the viscous region above 100 C. The non-crosslinked LDPE has the largest change in penetration at the melting point and this is because of the lack of crosslinks to hold the material together in the liquid phase. As the small force is applied, via the TMA probe, the non-crosslinked sample continuously flows and a large and constant amount of penetration is obtained.

Summary

Thermal analysis offers the plastics engineer and development scientist a very wide range of information on the formulation and thermal-physical properties of polymers. The family of techniques (DSC, TGA, TMA, DMA and Thermoconductivity) provides the following valuable processing parameters:

- Softening or glass transition temperatures
- Melting temperatures
- Percent crystallinities
- Amount of blowing agents
- Effectiveness of blowing agents
- Relative resin crosslink densities
- Decomposition properties of blowing agents

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- Polymer degradation temperatures
- Flammability information and effectiveness of flame retardants
- Stiffness (modulus) and damping (energy absorbing) properties
- Relative foam densities from thermoconductivity measurements

PerkinElmer offers a complete line of state-of-the art thermal analysis instruments to provide the valuable characterization information on polymers and foams.

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