Thermal Analysis for the Characterization of Polymer Impact Resistance

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One of the more important mechanical properties exhibited by a polymeric material is its impact resistance. This refers to the ability of a material to undergo a deformation without cracking or shattering.

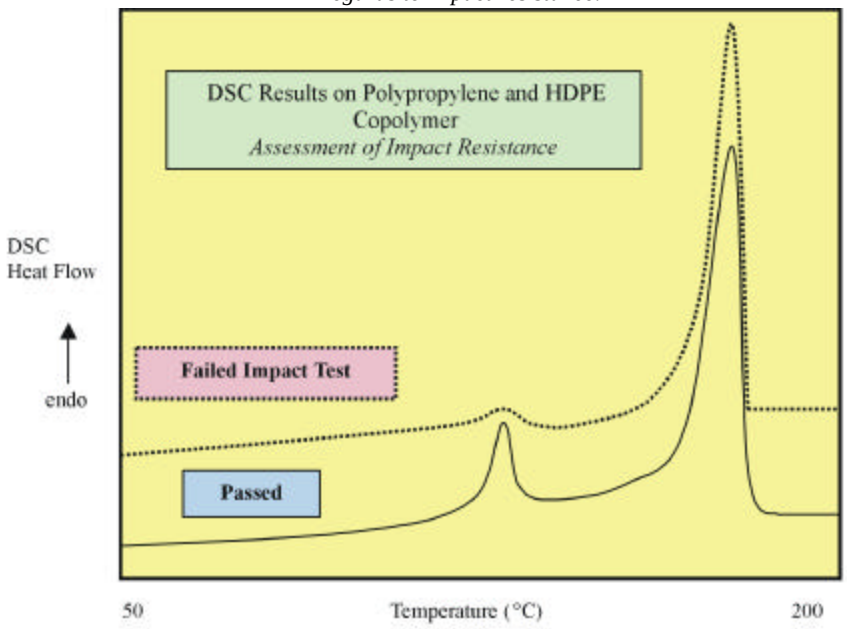
The impact resistance of a polymer is critical for certain applications including:

- Plastic bumpers or components for automobiles
- Polymeric windshields for commercial aircraft
- Plastic bottles
- Housings or casings for personal computers
- Plastic storage containers
- Toys made from plastics
- Garbage bags
- Casings for automotive batteries
- Composites used for golf clubs and bicycle frames
- Electronic components

The impact resistance exhibited by polymers is a primarily a function of the following:

- The particular polymer chemistry (main chain molecular motions)
- Incorporation of a rubber phase or component
- Addition of a second component (with good impact properties) to form a blend or copolymer system
- Addition of plasticizing agents
- Crystallinity of polymer

Figure 1. DSC results on the melting responses of polypropylene blends with regards to impact resistance.



Thermal analysis provides a series of techniques for characterizing polymers with regards to their impact resistance properties. The two most valuable techniques for this application are differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC measures heat flow into or from a sample under heating, cooling or isothermal conditions. DMA measures the viscoelastic properties of materials including stiffness (modulus) and energy absorption (damping) as a function of temperature and time (frequency).

DSC is the most commonly utilized thermal analysis technique and is used to measure:

- Softening or glass transition temperatures (Tg)
- Melting temperatures (Tm)
- Heats of melting
- Percent crystallinities of semi-crystalline polymers

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Figure 2. DSC measurement of Tg's of ABS copolymer.

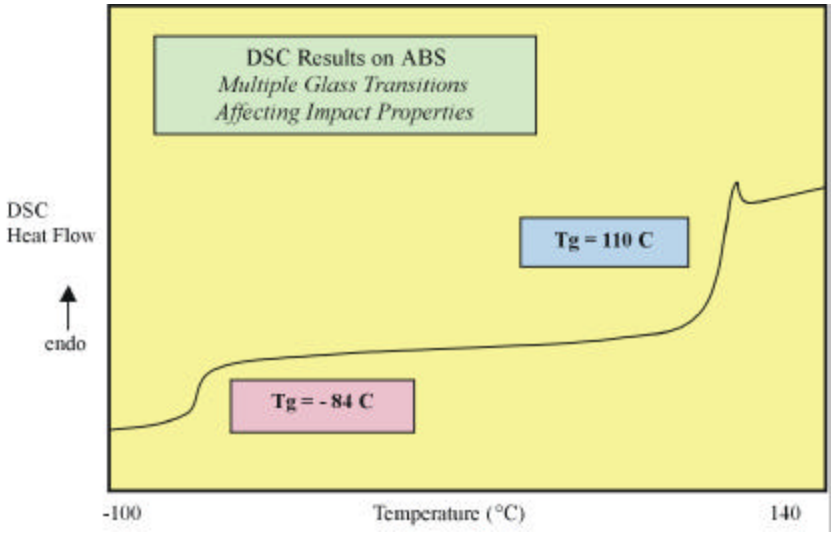
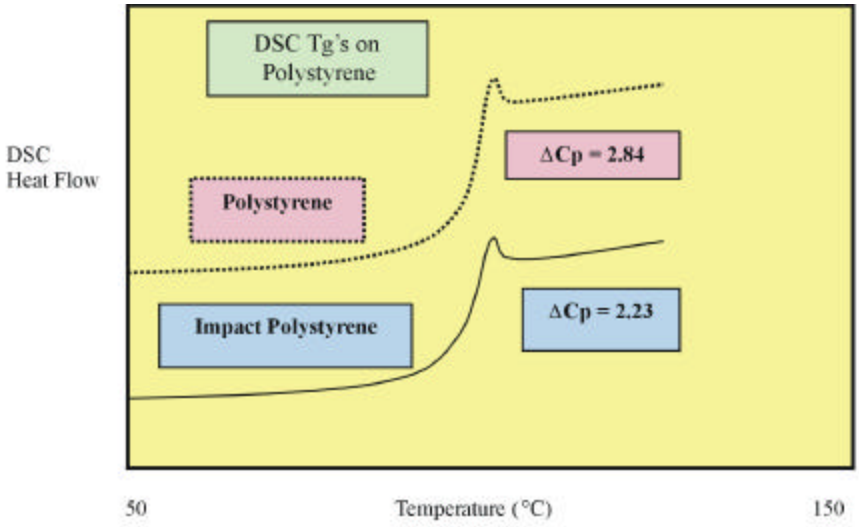


Figure 3. DSC Tg results on regular and impact-modified polystyrenes.



- Heats and temperatures of crystallization

The DSC results can be used to assess impact resistance of many thermoplastic materials, based on data obtained at the glass transition event and/or the melting transition. As an example, polypropylene (PP) exhibits poor impact resistance. However, high density polyethylene (HDPE) has excellent impact strength; and, adding HDPE to PP will significantly improve the impact resistance exhibited by the blend. The melting of the HDPE and PP components in the blend can be quantified using DSC and the data can be used to make predictions regarding the impact resistance of the PP-HDPE blend. The larger the HDPE melting component, the better the impact properties of the blend. An example of this is shown in the Figure 1.

The melting of the HDPE component is observed as a small endothermic peak at about 120 C. The greater the concentration of the HDPE (and, therefore, better impact properties), the larger the magnitude of the peak at 120 C. The melting of the polypropylene component is observed as the larger endotherm at about 180 C.

Another means of improving the impact resistance of thermoplastics is to add or graft a rubbery component to the main polymer. The presence of the rubber phase gives enhanced toughness characteristics. An excellent example of this is ABS (acrylonitrile – butadiene – styrene) which contains a rubbery component. The presence of this rubber phase results in the occurrence of a subambient glass transition event. This is shown in the DSC results obtained for ABS in Figure 2.

The Tg of the rubbery phase is observed at –84 C and this transition is related to the good impact properties exhibited by the ABS copolymer. The glass transition of the main polymeric component (SAN) occurs at 110 C. The excellent subambient performance of the PerkinElmer DSC allows for the

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Figure 4. DSC Tg's on plasticized and unplasticized PVC resins.

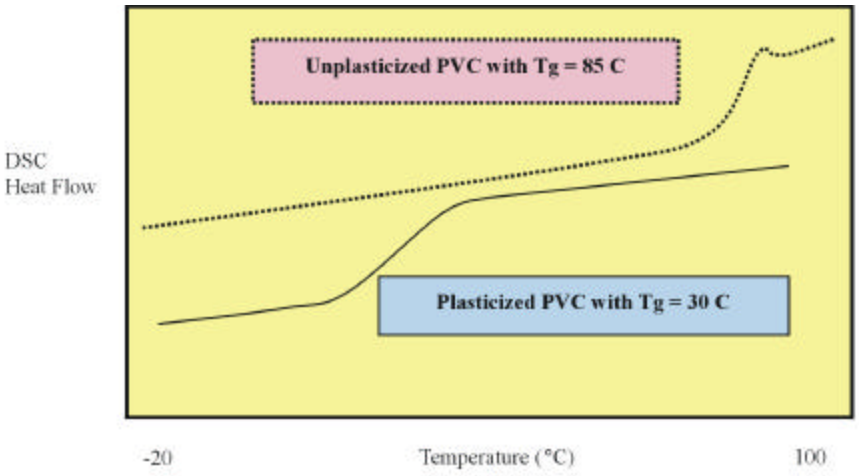
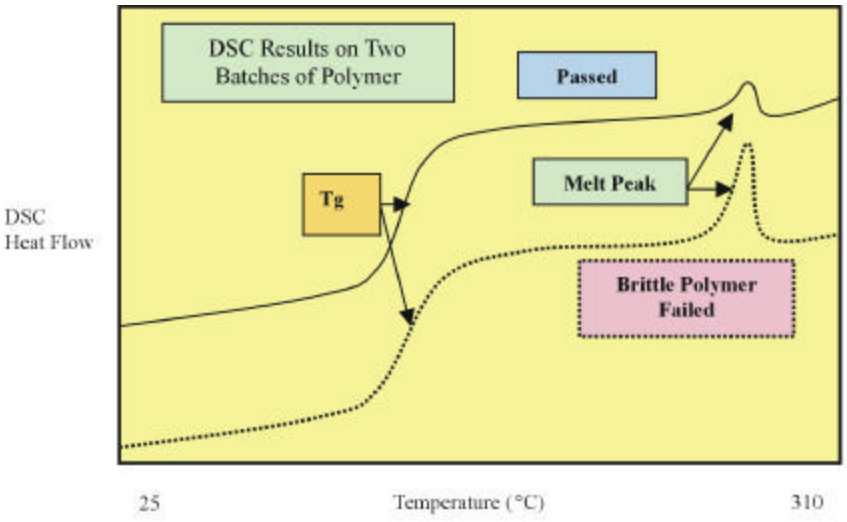


Figure 5. DSC results on the melting of two different lots of polymers for tolerance testing.



rubbery phase transition at –84 C to be clearly measured.

DSC can examine the Tg's of standard polystyrene and impact-modified polystyrene and the differences in the change in the heat capacity at Tg (ΔCP) can be used to of the polymers. In the following applications example, two samples of polystyrene (regular and impact-modified) were tested by DSC. The standard polystyrene contained 100% while the modified resin had 78% polystyrene and 22% of the modifier. The effect of diluting the PS component reduces the intensity or magnitude of the glass transition event of the impact-modified polystyrene.

Figure 3 shows the DSC results obtained on regular polystyrene and impact polystyrene.

Other polymers are strongly affected by the presence of plasticizing agents, which reduce the glass transition temperature and make the polymer more flexible. An example of this is PVC (polyvinyl chloride), which is plasticized by the addition of DOP (di-octyl phthalate). Higher concentrations of DOP in PVC will reduce the Tg of the polymer as is shown in the Figure 4.

In this example, the unplasticized PVC yielded a Tg of 85 C while the plasticized resin (with 20% DOP) had a significantly lower Tg of 30 C. The flexibility of the PVC polymer will be altered with the addition of the DOP. For applications where rigidity are required (such as pipes), then the unplasticized PVC would be desired. For other applications, where flexibility is necessary, PVC with the DOP plasticizer would be preferred. The greater the level of DOP, the lower the Tg will be. The DSC can thus provide information on the plasticization of the PVC polymer.

In some polymers, the level of crystallinity can have a major affect on key properties such as stiffness, optical clarity, barrier resistance and brittleness. As an example, the lot-to-lot variability of a semi-crystalline polymer was tested for the level of crystallinity using DSC. Displayed in the Figure 5 are the results generated on two different lots of the polymer.

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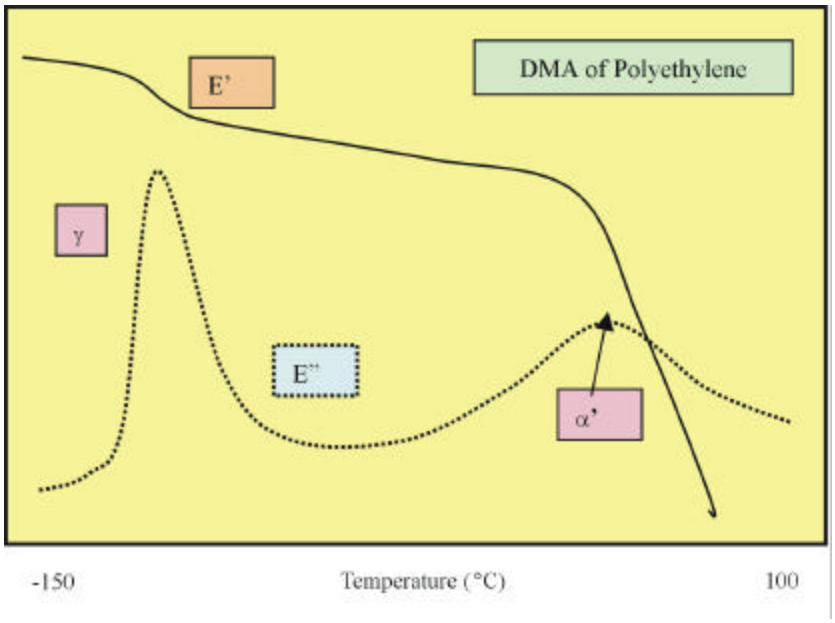
Figure 6. DMA results on high-density polyethylene showing storage modulus and loss modulus responses.



In Figure 5, the lower curve represents the data obtained on the polymer lot, which failed the tolerance testing as the material exhibited excessive and unacceptable brittleness. The upper curve is that obtained on the acceptable polymer, which passed the brittleness test. The unacceptable polymer had a significantly larger value of the heat of melting (4.0 J/g) as compared to the acceptable material (1.8 J/g). In this case the larger heat of melting, reflecting a higher level of crystallinity, resulted in the failed polymer being more brittle. The company using this particular polymer implemented DSC as a quality assurance tolerance test for assessing the brittleness of the material. When the DSC heat of melting exceeded 3.0 J/g, the polymer was deemed unsatisfactory.

One of the best means of assessing a polymer's given impact resistance propensity is DMA, which measures the mechanical or viscoelastic properties of a sample. DMA determines the stiffness and energy absorbing characteristics of a material as a function of temperature as well as frequency or time. The DMA loss properties (energy absorption) are related to the impact resistance of the sample. In general, polymers, which exhibit a large loss transition at temperature below –50 C, will exhibit good impact properties at room temperature. The molecular motions associated with the subambient loss transition are related to the material's impact resistance or toughness.

As an example, high-density polyethylene has excellent impact properties. Figure 6 shows the DMA results obtained on a sample of HDPE. The E' response represents the change in stiffness of the sample with regards to temperature, while the E" curve reflects the damping or energy absorbing characteristics. The α' loss transition at about 50 C is a pre-melting transition and is believed to be due to the movement of small crystallites. The intense γ subambient loss peak at –125 C is due to rotational molecular motions of 4 to 6 methylene groups in the polymer main chain. It is known that the intensity of this particular subambient loss transition is related to the polymer's impact resistance. The more intense the γ transition, the better the material's impact properties are.

Summary

Thermal analysis provides a valuable means of assessing a polymer's impact properties. In particular, DSC and DMA are useful for this particular application. DSC can be used to measure the changes in melting and/or glass transition properties, which are related to impact resistance. DMA measures stiffness and damping properties and, in general, a polymer, which yields a significant damping or loss transition below –50 C, will have good impact properties. PerkinElmer offers a number of DSC and DMA systems for the assessment of impact resistance.

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