Detect weak glass transition of polyurethane acrylate on DSC8000

Authors: Michelle Lee, Peng Ye

Introduction

Polyurethane acrylate resin can be synthesized by either thermal curing or UV curing. The final product has two separate phases---the soft-segment and the hard-segment. The glass transition temperature (Tg) of these two phases depends on the chemical composition and molecular weight of these two phases. The interesting mechanical property of polyurethane acrylate material is largely due to the two phase morphology. Polyurethane acrylate is widely used as a coating for metals, paper, optical fibers, and other materials.

Since the two phase structure is important to Polyurethane acrylate material's function, the glass transition temperatures of these two phases are important parameters to know. Differential scanning calorimetry (DSC) is generally used to detect glass transition temperature of polymer. However for Polyurethane acrylate, the two glass transitions are weak and one of them is sub-ambient. The conventional slow heating rate of 10 ˚C/min makes it difficult to detect these two Tg. The sensitivity of DSC can be increased by increasing heating rate because the heat flow signal of DSC is proportional to scanning rate according to the basic heat flow equation:

Heat flow=sample mass*Cp*scanning rate

The fast scanning rate DSC technique is proven to be very effective in detecting weak glass transition in highly crystalline polymer like HDPE, or the low amorphous content (<10%) of lactose in pharmaceutical formulation.

In this study, the polyurethane acrylate sample is from a coating on mold release paper which is used during artificial leather molding. The new DSC8000 double furnace power compensation DSC with liquid nitrogen cooling accessory CLN2 was used to detect Tg.

DSC8000/8500 with Autosampler

Method

DSC8000 is the new PerkinElmer high end double furnace power controlled DSC. It utilizes the unique PerkinElmer power compensation scheme. Compared with the conventional heat flux DSC, it features:

- Two independently controlled low mass furnaces
- Fast response time
- Direct and accurate energy measurement
- Use platinum resistance thermometers (PRT) instead of thermocouples for the most accurate temperature measurement.

The maximum heating rate on DSC8000 is 300 ˚C/min which can cover most fast scanning applications. If faster heating or cooling rates are required, then the DSC8500 (heating and cooling up to 750 ˚C/min) is the choice.

Four cooling accessories are available for DSC8000 to cover the full experimental temperature range of which two are relevant for this application:

- Intracooler 3 (-100 ˚C to +750 ˚C)
  - New feature to control On/Off by Pyris Software
  - New Vacuum Tube Transfer Line = frost free
- CLN2 (-190 ˚C to +750 ˚C)
  - New feature to control On/Off by Pyris Software
  - Dial-a-temp feature -190 ˚C to +35 ˚C
  - New Vacuum Tube Transfer Line = frost free

The Intracooler 3 and CLN2 are new cooling accessories available only on DSC8000/8500. The Intracooler 3 is a three stage mechanical cooling accessory. It further extends the lowest operation temperature to -100 ˚C while at the same time operates as easy as Intracooler 2. The CLN2 is a brand new liquid nitrogen cooling accessory. It is a truly versatile cooling accessory. The CLN2 cooling block temperature can be set anywhere between -190 ˚C to +35 ˚C. Nitrogen purge gas can be used instead of helium depending on the block temperature setting. The liquid nitrogen consumption is low which means significant operational cost reduction for user.

A brand new, reliable autosampler is also available for increased productivity.

DSC8000 with CLN2 cooling accessory was used for this study. The block temperature was set at -190 ˚C and helium purge gas at 20 ml/min was used. The sample was in the form of white powder and sample mass was 7.134 mg.

The method started with a one minute isothermal holding at -70 ˚C, and then heating from -70 ˚C to 250 ˚C at 200 ˚C/min and followed by a one minute isothermal holding at 250 ˚C. For comparison purpose, a conventional slow heating at 10 ˚C/min was also performed.

CLN2 liquid nitrogen cooling accessory

Intracooler 3 cooling accessory

Result

Figure 1 is the data from the 200 ˚C/min heating scan. The start-up transition indicated that the instrument was in control and started to collect meaningful data only 0.1 min or 6 seconds after the heating step started. Such a quick response is critical for low temperature transition detection, especially at fast scanning rates because the lowest starting temperature of experiment is often limited by the cooling accessory. The quick DSC response is only available on a double furnace power controlled DSC , due to the two low mass furnaces.

Figures 2 and 3 are zoomed into the two Tg of the polyurethane acrylate sample. The red curve is from the fast heating scan of 200 ˚C/min while the black curve is from the conventional 10 ˚C/min heating. As can be seen clearly, the weak Tg of polyurethane acrylate can only be detected at fast scanning rates. A slow scanning rate does not have enough sensitivity to detect this transition.

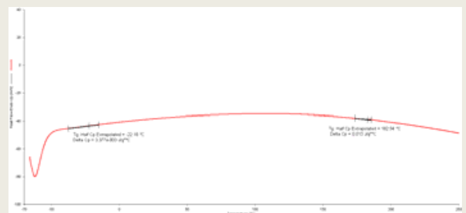

Figure 1. DSC heating curve of PU acrylate at 200 ˚C/min

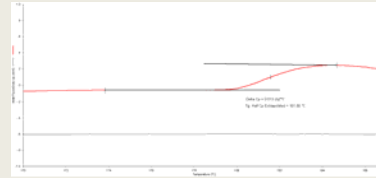

Figure 2. High temperature Tg detection at different heating rates.
Red curve: 200 ˚C/min; Black curve: 10 ˚C/min

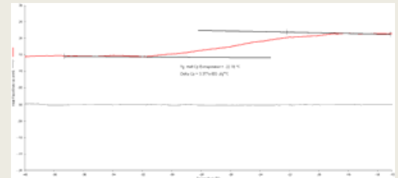

Figure 3. Low temperature Tg detection at different heating rates.
Red curve: 200 ˚C/min; Black curve: 10 ˚C/min

Summary

The polyurethane acrylate resin has two separated phases due to its soft segment and hard segment. The glass transition temperatures of these two phases are important technical parameter to characterize. The weak Tg transitions demands fast scan DSC technology. The new DSC8000 with CLN2 liquid nitrogen cooling accessory is the ideal analytical tool. Its power compensation design, quick response time and high sensitivity enable it to detect these two weak Tg, which is not possible using conventional DSC.

PerkinElmer, Inc., 940 Winter Street, Waltham, MA USA (800) 762-4000 or (+1) 203 925-4602 www.perkinelmer.com