Determination of Rigid and Mobile Amorphous Content of Semicrystalline Polymers Using DSC

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Introduction

Crystallinity of semicrystalline polymers is the most important thermodynamic parameter affecting mechanical, chemical, and thermal properties of its final product. Several techniques, such as Infrared Spectroscopy, X-ray diffraction, and optical analysis, can be used for determining the amorphous content or the crystallinity.

For a semicrystalline polymer, the relationship of crystallinity and amorphous content can be described as following:

$$a_{crystal} + a_{amorphous} = 100\%$$

where $\alpha_{crystal}$ is the percentage of the crystallinity of a semicrystalline polymer and $\alpha_{amorphous}$ is the percentage of the amorphous content of a semicrystalline polymer. The determination of the crystallinity of semicrystalline polymers by DSC has recently discussed (1-4).

For polymers which melt over a narrow temperature range with no cold crystallization on heating the initial crystallinity can be determined by simply dividing the heat of fusion taken from DSC analysis by the theoretical heat of fusion of 100% crystalline material taken from the literature, such as the ATHAS data bank (5). For more complicated systems, like PET, Gray (6) and Mathot (7) have demonstrated a more quantitative method of treating DSC data. This method has been incorporated in the temperature dependent crystallinity software that was used in this work.

Although the total amorphous content of most semicrystalline polymers can be calculated through the relationship as above, the contribution to the relaxation strength at the glass transition can be different. At glass transition temperature, some of the amorphous chains or segments are free to move, defined as mobile amorphous, while some are rigid and have less freedom, defined as rigid amorphous. Due to this difference in molecular mobility, scientists have tried to use analytical techniques such as infrared spectroscopy (IR) and NMR to understand and measure the mobile amorphous content and the rigid amorphous content. It seems there is no a quick and easy method for this determination.

Recently, a practical method has been reported using DSC specific heat measurement by Schick (8). Since heat capacity is a quantitative method for measuring the change of the degree of freedom in the glass transition region, it is sensitive enough to differentiate the mobility of the rigid amorphous and the mobile amorphous. Therefore, the following relation can be obtained:

$$a_{crystal} + a_{rigid-amorphous} + a_{mobile-amorphous} = 100\%$$

where

$$a_{mobile-amorphous} = \Delta C_{p,semicrystdline} \Big/ \Delta C_{p,amorphous}$$

where $\alpha_{mobile-amorphous}$ is the percentage of the mobile amorphous and $\alpha_{rigid-amorphous}$ is the percentage of the rigid amorphous of a semicrystalline polymer. $\Delta C_{p,semicrystdline}$ is the specific heat increment of the semicrystalline polymer during the glass transition and $\Delta C_{p,amorphous}$ is the specific heat increment of the total amorphous polymer during the glass transition.

This study will demonstrate the methodology for the determination of the rigid amorphous content and the mobile amorphous content using DSC. Two commercial PET semicrystalline polymer products have been evaluated.

Experimental

A new generation of Power Compensated Calorimeter (PerkinElmer Instruments PYRIS Diamond DSC) was used to measure the heat of fusion during melting. The latest release of the Pyris Software for Windows (V4.01) with StepScan software was used to determine the specific heat change in the glass transition region.

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A typical PYRIS StepScan method has been shown as Fig. 1.

Figure 2 illustrates a typical DSC sample temperature profile used to determine the pure amorphous state. Very rapid cooling rates (400 °C/min) are required to obtain the "pure" amorphous state. The PYRIS Power Compensation DSC provides the fastest controlled (linear) heating and cooling of any DSC instrument available.

Two PET samples were taken from commercially available products. One was from the soda bottle and the second was from a computer floppy disk. They were first punched into disks and then loaded into DSC aluminum standard sample pans for the measurements. The sample size was in the range of 12-15mg.

Results and Discussion

A thermal curve resulting from the heating segments of the PET from the beverage bottle is shown in Fig. 3. The dashed line is the data from the initial heat. This shows the original or as received semicrystalline state before fast cooling down. The solid line represents the results of the second heat after super fast cooling "quench cooling". It is this cooling cycle when the total amorphous state was formed. The Tg is calculated on this heating cycle.
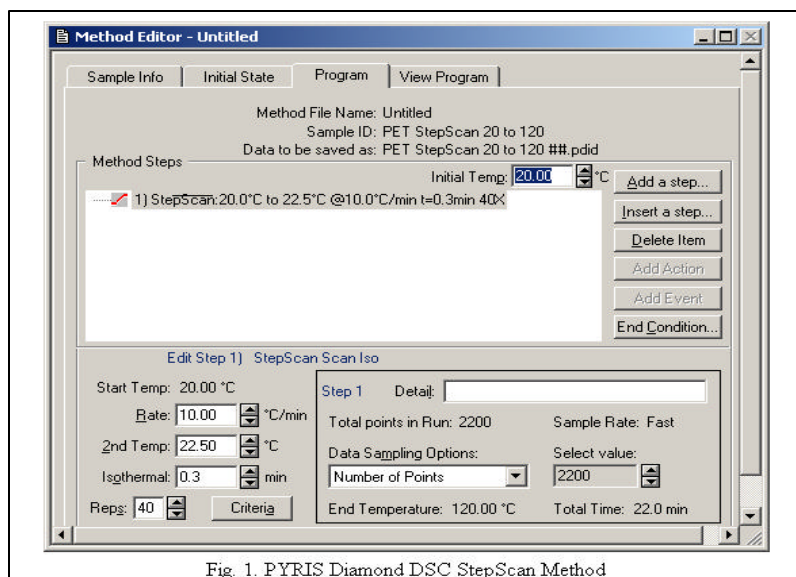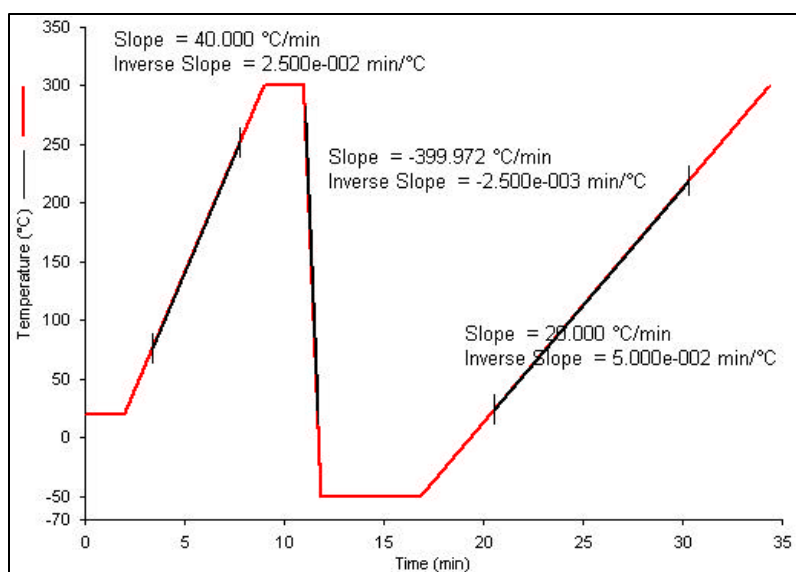

Fig. 1. PYRIS Diamond DSC StepScan Method

Figure 2. PYRIS Diamond temperature program demonstrating the ability of the Diamond DSC to cool at very fast rates

The StepScan result is also displayed in Fig. 4. (It is noteworthy the excellent correlation between the ΔCp measurement of the conventional DSC experiment and that obtained in the StepScan Cp experiment. 0.290 J/g*°C versus 0.291 J/g*°C respectively)

Table 1 lists the calculation results of ΔCp at the glass transition temperature in both amorphous state and semicrystalline state. The percentage of crystallinity was calculated using the temperature dependent crystallinity feature of the PYRIS Software for Windows. Three samples of each PET polymer were measured and the mean results were calculated.

Table 2 lists the calculated results of the percentage of the crystallinity, the mobile and the rigid amorphous contents based upon the relationship as discussed in the introduction.

From Table 1, it can be found that PET from the soda bottle has much smaller ΔCp increment change during Tg comparing with PET from the floppy disk film. However, the measured glass transition temperatures were in the same temperature range. This can be clearly explained by the calculated rigid amorphous content listed at Table 2. When the rigid amorphous content is higher, it will have less contribution to the relaxation strength of amorphous during the glass transition. Glass transition is a complicated process of amorphous and semicrystalline polymers, and a complete theoretical understanding is not yet available. Several theoretical models from free volume to thermodynamics and kinetics have been developed to describe the glass transition phenomenon (9-11).
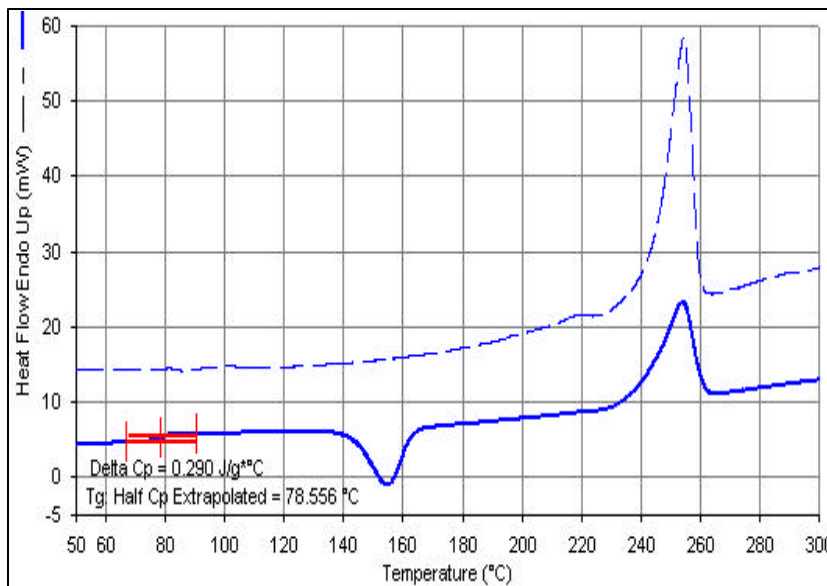

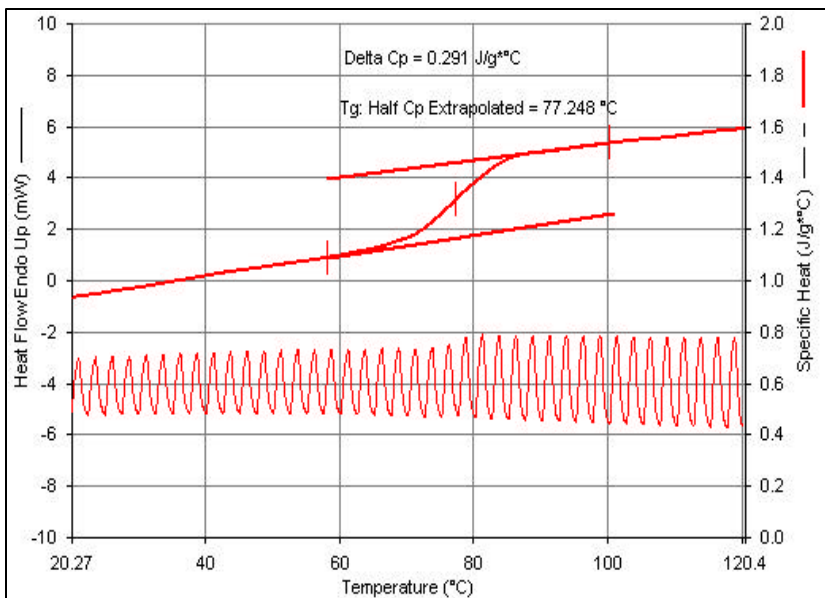Figure 3. DSC results from PET soda bottle before and after cooling

Figure 4. StepScan DSC results for PET soda bottle in Tg region

In general, the free movement behavior of amorphous segments during the glass transition contributes the increment change of the specific heat. When some amorphous segments are locked between the crystalline chains or do not contribute to the glass transition change, the increment change of the specific heat capacity will be reduced dramatically when compared with the pure amorphous polymers.

From this analysis it is was found that the PET from the soda bottle contains about 20% rigid amorphous content whereas the PET from the floppy disk has much lower or almost no rigid amorphous segment. Both PET materials have a similar percentage of crystallinity. One explanation for the higher content of rigid amorphous content in the beverage container is the possibility of the addition of recycled PET polymers and/or some other additives, which participates less in the relaxation strength during the glass transition.

Although these two kinds of PET have quite different rigid amorphous percentage, their glass transition temperatures and crystallinities are very similar. Therefore, mobile amorphous and rigid amorphous contents can affect the properties of the semicrystalline polymers though they may not interrupt the glass transition temperature and crystallinity of the semicrystalline polymers.

PET Material	ΔCp @ Tg semicrystalline	ΔCp @ Tg amorphous	Glass Transition (Tg)
Soda Bottle	0.12±0.02 J/g.$^{\circ}$C	0.28±0.01 J/g.$^{\circ}$C	78.7 $^{\circ}$C
Floppy Disk Film	0.21±0.02 J/g.$^{\circ}$C	0.32±0.01 J/g.$^{\circ}$C	78.3 $^{\circ}$C

Table 1. Properties of PET soda bottle and floppy diskette

PET Materials	Crystallinity (%) @ Tg	Mobile Amorphous @ Tg (%)	Rigid Amorphous @ Tg (%)
Soda Bottle	37	43	20
Floppy Disk Film	36	64	<1

Table 2. Results of crystallinity, mobile and rigid amorphous contents

Summary

In conclusion, the following summary can be drawn:

1. DSC specific heat and heat of fusion measurement is an efficient method for determining rigid and mobile amorphous contents of the semicrystalline polymers.
2. The rigid amorphous segment of the semicrystalline polymers will affect the relaxation strength but may not affect the glass transition temperature and the crystallinity.
3. StepScan method of the PYRIS Diamond DSC is an accurate technique for measuring specific heat of the polymers. Temperature dependent crystallinity is a quantitative method for calculating the crystallinity of the semicrystalline polymers. The results generated can be used accurately for calculating the mobile and rigid amorphous contents.

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