

## HOW DID WE FIND THE RIGID AMORPHOUS PHASE?

J. D. Menczel<sup>1\*</sup> and M. Jaffe<sup>2</sup>

<sup>1</sup>Alcon Laboratories, 6201 South Freeway, R8-9, Fort Worth, TX 76123, USA

<sup>2</sup>New Jersey Institute of Technology, 111 Lock Street, Newark, NJ 07103, USA

The first experimental evidence of the existence of the rigid amorphous phase was reported by Menczel and Wunderlich [1]: when trying to clarify the glass transition characteristics of the first main chain liquid crystalline polymers [poly(ethylene terephthalate-co-*p*-oxybenzoate) with 60 and 80 mol% ethylene terephthalate units] [2], the absence of the hysteresis peak at the lower temperature glass transition became evident when the sample of this copolymer was heated much faster than it had previously been cooled. Since this glass transition involved the ethylene terephthalate-rich segments of the copolymer, we searched for the source of the absence of the hysteresis peak in PET. There, the gradual disappearance of the hysteresis peak with increasing crystallinity was confirmed [1]. At the same time it was noted that the higher crystallinity samples showed a much smaller  $\Delta C_p$  than could be expected on the basis of the crystallinity calculated from the heat of fusion (provided that the crystallinity concept works). Later it was confirmed that the hysteresis peak is also missing at the glass transition of nematic glasses of polymers.

When checking other semicrystalline polymers, the sum of the amorphous content calculated from the  $\Delta C_p$  at the glass transition, and the crystallinity calculated from the heat of fusion was far from 100% for a number of semicrystalline polymers. For most of these polymers, the sum of the amorphous content and the crystalline fraction was 0.7, meaning that ca. 30% rigid amorphous fraction was present in these samples after a cooling at 0.5 K min<sup>-1</sup> rate. Thus, the presence of the rigid amorphous phase was confirmed in five semicrystalline polymers: PET, Nylon 6, PVF, Nylon 66 and polycaprolactone [1]. Somewhat later poly(butylene terephthalate) and bisphenol-A polycarbonate [3] were added to this list.

In this paper we also report details on a special effect of the rigid amorphous phase (RAP) on the mobile amorphous phase (MAP): the hysteresis peak at the glass transition of the MAF disappears under the influence of the RAP, and this raises the question whether the glass transition of the MAF becomes time independent in semicrystalline polymers.

**Keywords:** crystallinity, DSC, glass transition, mobile amorphous phase, rigid amorphous phase, semicrystalline polymers

### Introduction

More than twenty years passed since we found the rigid amorphous phase (RAP) in the ATHAS Laboratory of Rensselaer Polytechnic Institute (RPI). Before introducing the RAF, the crystallinity concept had assumed that the fractional crystallinity by itself was able to describe the structure insensitive thermal properties of semicrystalline polymers. Since the heat capacity jump at the glass transition for semicrystalline polymers is smaller than the value calculated from the crystallinity, the rigid amorphous phase was introduced so that all the phases in a semicrystalline polymer make up 100%.

### Experimental

The DSC measurements during the time period since 1980, were performed using a DuPont (today TA Instruments) DSC 910 connected to a DuPont 990 and 1090 Thermal Analyzers, a Perkin-Elmer DSC4, several Perkin-Elmer DSC7s, a TA Instruments

2100-910 DSC, a TA Instruments 3200-DSC 2920, and a TA Instruments Q100 DSC. Most of these instruments (except the DSC 910-Thermal Analyzer 990) were cooled with some FTS mechanical cooling accessory having a head temperature of -100°C. The instruments were calibrated with In, Sn and Pb on heating. When cooling calibration was necessary, this was done using (4-*n*-octyloxy-2-hydroxybenzal)-4'-*n*-butylaniline [4], (+)-(4-(2'-methylbutyl) phenyl-4'-*n*-octylbiphenyl-4-carboxylate (with a commercial name of CE-8) and (+)-4-*n*-hexyloxyphenyl-4'--(2''-methylbutyl)-biphenyl-4-carboxylate having a commercial name of CE-3. CE-3 and CE-8 were purchased from BDH Chemicals Ltd., Poole, Gt. Britain [5, 6] purified to 99.9% as described in [7].

The listed polymers were: PET, Nylon 6, PVF, Nylon 66, polypropylene and polycaprolactone (Scientific Polymer Products); fiber grade PET of Hoechst Celanese with IV of 0.65; Gafite 1600 PBT from GAF Corporation; Lexan polycarbonate from GE (crystalline polycarbonate was prepared as described in Ref. [8]), poly(ethylene naphthalate) (PEN) prepared at Hoechst Celanese.

\* Author for correspondence: joseph.menczel@alconlabs.com

## Results and discussion

The two-phase model of semicrystalline polymers assumes that any semicrystalline sample is composed of a crystalline fraction and an amorphous fraction. This means that according to the two-phase model

$$C_p(T) = x C_x(T) + y C_m(T) = x C_x(T) + (1-x) C_m(T) \quad (1)$$

where  $C_p(T)$  is the temperature dependence of the specific heat capacity of the semicrystalline polymer;  $C_x(T)$  is the temperature dependence of the specific heat capacity of the crystalline phase,  $C_m(T)$  is the temperature dependence of the specific heat capacity of the amorphous phase;  $x$  is the crystallinity (crystalline fraction) calculated from the heat of fusion, and  $y$  is the amorphous fraction calculated from the heat capacity jump at the glass transition. Therefore, according to the two-phase model,

$$y = 1 - x \quad (2)$$

As it was suggested in our first two papers on the rigid amorphous phase [1, 3], the rigid amorphous phase can be determined if the fraction of the 'mobile' (or traditional) amorphous phase is determined from the heat capacity jump at the glass transition, and the crystallinity is calculated from the heat of fusion. In this case,

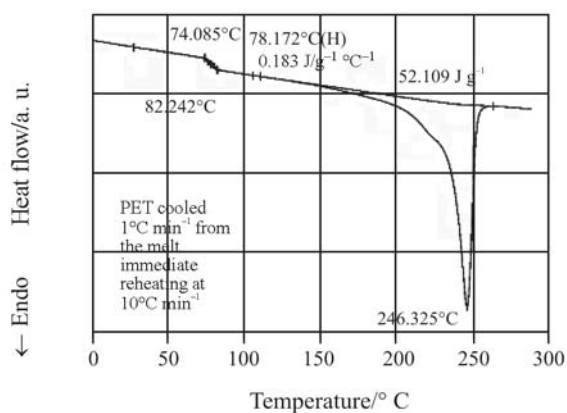
$$y \neq 1 - x \quad (3)$$

and

$$\text{RAF} = 1 - x - y \quad (4)$$

where RAF is the rigid amorphous fraction.

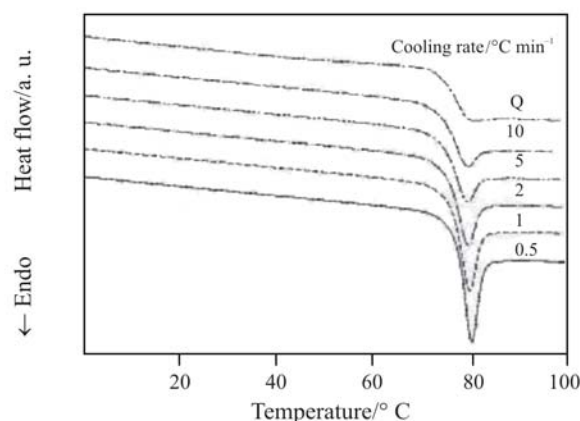
A DSC curve representing the first case of the rigid amorphous case [1] is shown in Fig. 1 which corresponds to ca. 18% rigid amorphous fraction. For amorphous PET we found normal hysteresis behavior



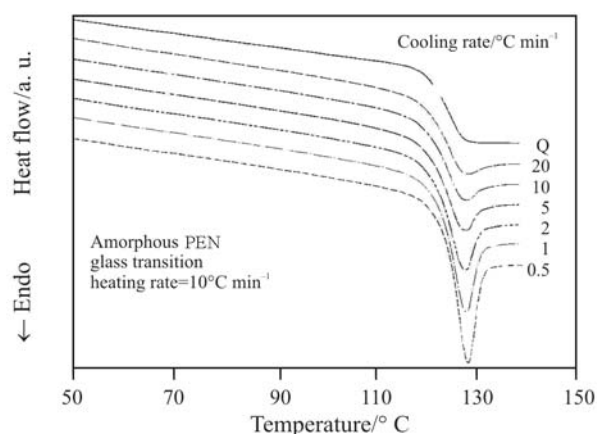
**Fig. 1** Heating curve of PET crystallized from the melt at a rate of cooling of  $1^\circ\text{C min}^{-1}$  (heating rate =  $10^\circ\text{C min}^{-1}$ ). It is obvious that  $x + y < 1$ , i.e., a considerable rigid amorphous fraction is present in the sample

at the glass transition, i.e. when the sample is heated faster than it had previously been cooled, an endothermic hysteresis peak appears at the high temperature side of the glass transition. As expected for amorphous polymers, the magnitude of the endothermic hysteresis peak increases with decreasing cooling rate (see Figs 2 and 3 for amorphous PET and amorphous PEN).

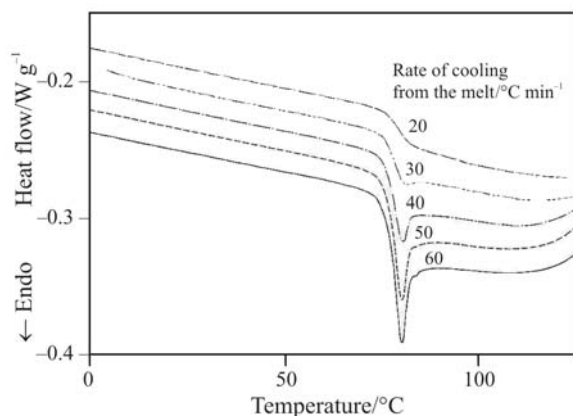
However, when crystallinity is introduced into the sample, the intensity of the hysteresis peak gradually decreases, and disappears at a crystallinity value of 29% as shown in Figs 4 and 5 (in the original paper of [1], 30% was obtained).



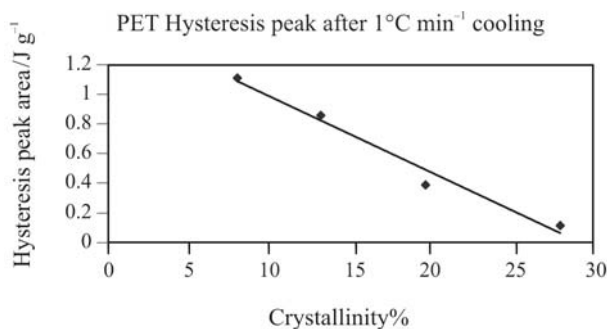
**Fig. 2** Amorphous PET: heating curves at  $\text{HR} = 10^\circ\text{C min}^{-1}$ . Amorphous PET was prepared by quenching from  $290^\circ\text{C}$ , i.e. from beyond the equilibrium melting point of PET by liquid nitrogen. Then, the samples were heated to  $100^\circ\text{C}$ , and cooled at the rates indicated at the curves ( $Q$  – a sample quenched from the melt)



**Fig. 3** Amorphous PEN: heating curves at  $\text{HR} = 10^\circ\text{C min}^{-1}$ . Amorphous PEN was prepared by quenching from  $340^\circ\text{C}$ , i.e. from beyond the equilibrium melting point of PEN by liquid nitrogen. Then, the samples were heated to  $140^\circ\text{C}$ , and cooled at the rates indicated at the curves ( $Q$  – a sample quenched from the melt)



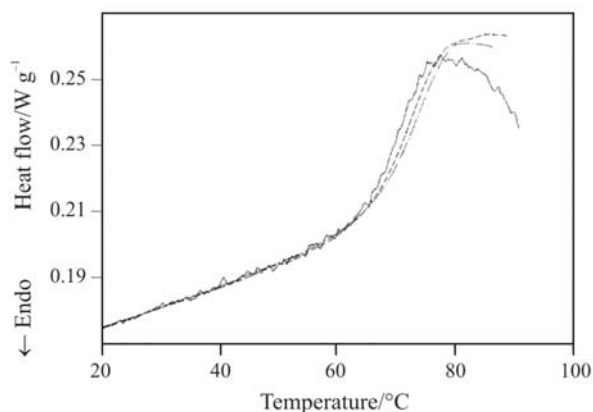
**Fig. 4** The glass transition of PET samples of various crystallinities recorded on heating. The samples were prepared by cooling from 290 to  $-20^{\circ}\text{C}$  at various rates, then heating them to  $105^{\circ}\text{C}$ , and cooling at  $1^{\circ}\text{C min}^{-1}$ . The final heating for analysis was done at  $10^{\circ}\text{C min}^{-1}$



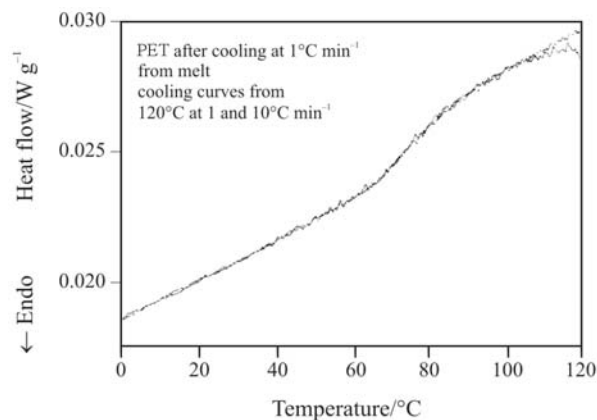
**Fig. 5** The area under the hysteresis peak of samples from Fig. 4 as a function of crystallinity

It was suggested [1] that the time dependency of the glass transition disappears at high crystallinity values, since the hysteresis peak that is indicative of the time dependency, disappears at high crystallinities. It is well known that the glass transition is a time dependent transition. This can be illustrated by recording the glass transition of amorphous PET on cooling at various rates (Fig. 6): when the cooling rate of amorphous PET decreases from  $20^{\circ}\text{C min}^{-1}$ , and then to  $5^{\circ}\text{C min}^{-1}$ , and then to  $1^{\circ}\text{C min}^{-1}$ , the glass transition temperature measured on cooling, visibly decreases.

In 1980 the thermal analysis instrumentation was not good enough to record the glass transition accurately on cooling. That time the quench cooler (stainless steel cooling can) or cold purge gas were the only available cooling accessories. Of course, the baseline on cooling was not reproducible, therefore superposition of the cooling curves, similar to those shown in Figs 6–8 was impossible. In addition, the temperature calibration on cooling was not available, that was only developed in the early 90's [4, 7, 9]. However, later with introduction of the FTS mechanical



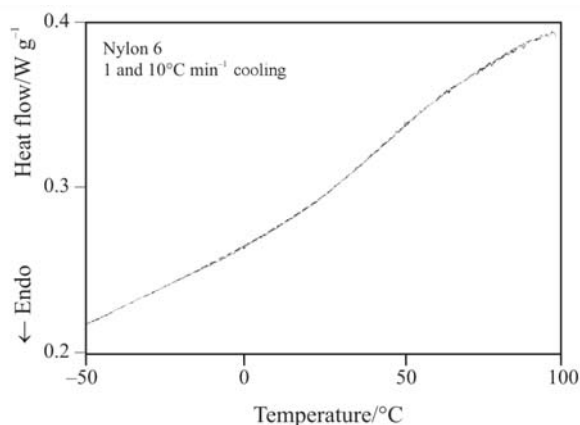
**Fig. 6** Cooling curves of amorphous PET in the glass transition region. Cooling rates:  $1^{\circ}\text{C min}^{-1}$  (noisy curve),  $5^{\circ}\text{C min}^{-1}$  (dashed curve) and  $20^{\circ}\text{C min}^{-1}$  (dotted curve)



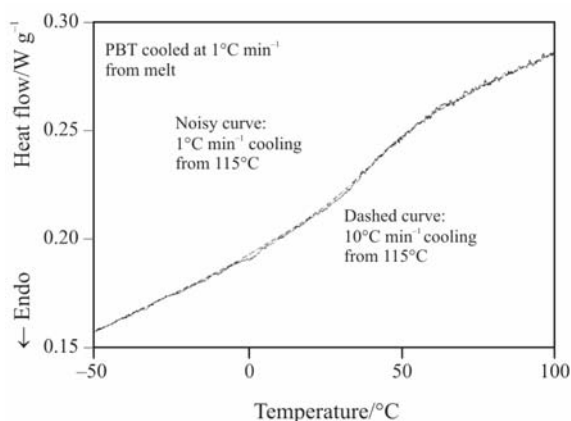
**Fig. 7** The cooling curves of semicrystalline PET in the glass transition region. Cooling rates were 1 and  $10^{\circ}\text{C min}^{-1}$ . The sample has been prepared by cooling at  $1^{\circ}\text{C min}^{-1}$  from  $290^{\circ}\text{C}$ , and then heating to  $120^{\circ}\text{C}$

cooling accessories, and especially with the DSC of Tzero technology this task became much easier. When using mechanical cooling accessories, the temperature control is not lost during cooling, and the baselines are well reproducible during cooling at various rates. Therefore, it is relatively easy to check whether the glass transition of semicrystalline samples is really a time independent phenomenon.

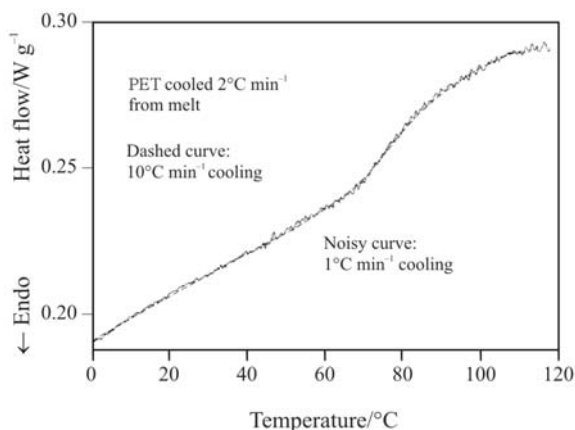
Therefore, samples of three polymers (PET, Nylon 6 and PBT) were prepared by crystallizing them at a cooling rate of  $1^{\circ}\text{C min}^{-1}$  from the melt, then these samples were heated to a temperature beyond the glass transition temperature of the mobile amorphous phase, and cooled again at 1 and  $10^{\circ}\text{C min}^{-1}$ . The DSC curves recorded during this second cooling at 1 and  $10^{\circ}\text{C min}^{-1}$  are overlaid and shown in Figs 7–9. The temperature correction due to the different cooling rates is only  $0.4\text{--}0.5^{\circ}\text{C}$  [9], therefore there was no need to shift the curves. These figures indicate that the cooling curves can be fully overlaid, thus,



**Fig. 8** The cooling curves of Nylon 6 in the glass transition region. Cooling rates were  $1^{\circ}\text{C min}^{-1}$  (noisy curve) and  $10^{\circ}\text{C min}^{-1}$  (dashed curve). The sample has been prepared by cooling at  $1^{\circ}\text{C min}^{-1}$  from  $280^{\circ}\text{C}$ , and then by heating them to  $100^{\circ}\text{C}$



**Fig. 9** The cooling curves of PBT in the glass transition region. Cooling rates were  $1^{\circ}\text{C min}^{-1}$  and  $10^{\circ}\text{C min}^{-1}$ . The sample has been prepared by cooling at  $1^{\circ}\text{C min}^{-1}$  from  $245^{\circ}\text{C}$ , and then by heating them to  $100^{\circ}\text{C}$

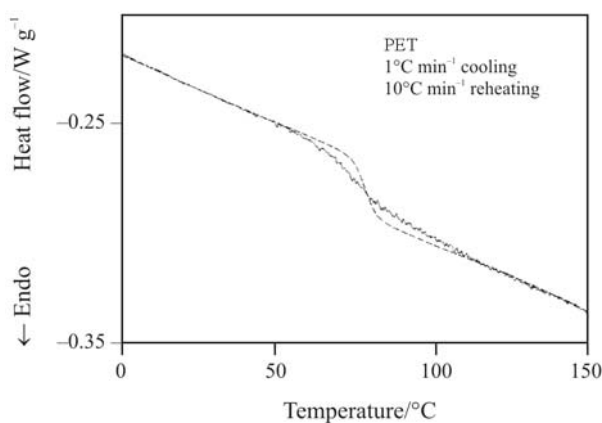


**Fig. 10** The cooling curves of PET in the glass transition region. Cooling rates were  $1^{\circ}\text{C min}^{-1}$  and  $10^{\circ}\text{C min}^{-1}$ . The sample has been prepared by cooling at  $2^{\circ}\text{C min}^{-1}$  from  $290^{\circ}\text{C}$  and heating it up to  $120^{\circ}\text{C}$ . The two curves are still superimposable

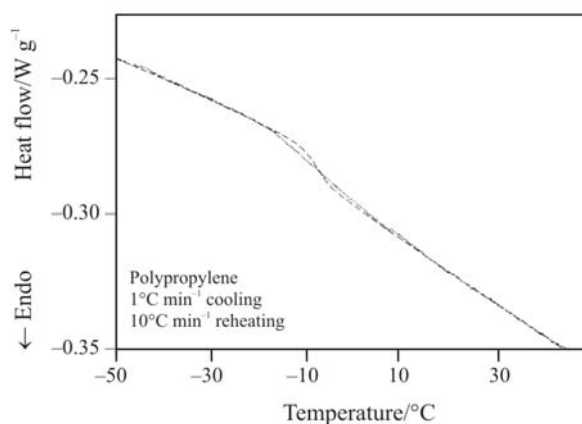
according to these measurements, the glass transition really becomes time independent, at least in the mentioned cooling rate range.

Further experiments showed that this time independence for PET is valid at crystallinity values at which no cold crystallization is observed during a subsequent heat-up. Thus, at  $2^{\circ}\text{C min}^{-1}$  cooling from the melt (and up to ca.  $10^{\circ}\text{C min}^{-1}$ ), the curves recorded at various cooling rates from above the glass transition temperature, can still be overlaid (Fig. 10).

Therefore, it seems that the absence of time dependence can explain the absence of the hysteresis peak during the subsequent heat-up at higher rates. However, the curves recorded during the cooling and heating experiments cannot be overlaid as shown in Figs 11–13 for PET, PP and Nylon 6. It is clear that the glass transition during a  $10^{\circ}\text{C min}^{-1}$  heat-up is narrower than during a  $1^{\circ}\text{C min}^{-1}$  cooling, but there is no hysteresis peak on the curve recorded on heating.

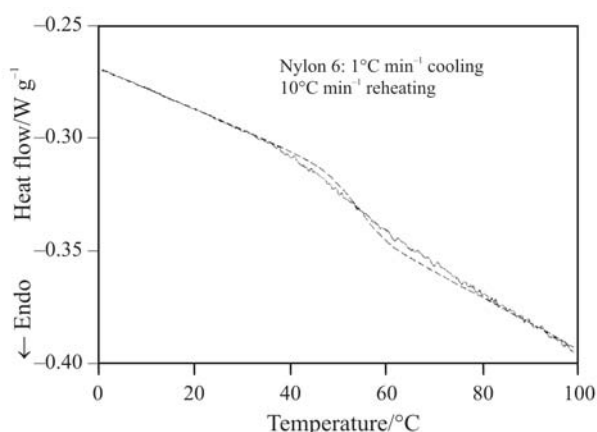


**Fig. 11** The glass transition curves of PET on cooling at  $1^{\circ}\text{C min}^{-1}$  from the melt (noisy curve), and on reheating the sample at  $10^{\circ}\text{C min}^{-1}$  (dashed curve)



**Fig. 12** The glass transition curves of polypropylene on cooling at  $1^{\circ}\text{C min}^{-1}$  from the melt (noisy curve), and on reheating the sample at  $10^{\circ}\text{C min}^{-1}$  (dashed curve)

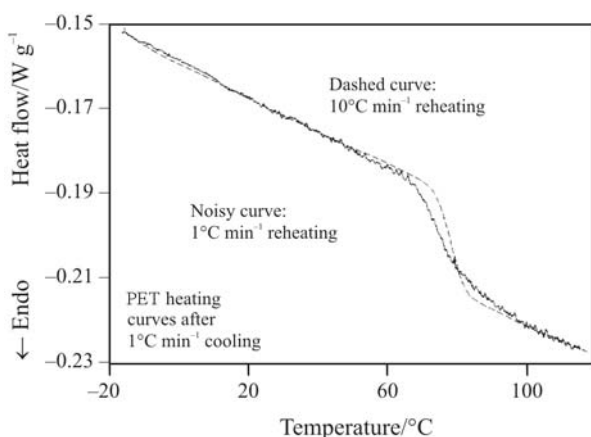
## HOW DID WE FIND THE RIGID AMORPHOUS PHASE?



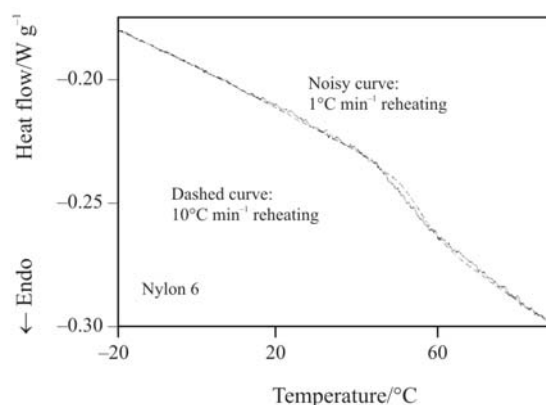
**Fig. 13** The glass transition curves of Nylon 6 on cooling at  $1^{\circ}\text{C min}^{-1}$  from the melt (noisy curve), and on reheating the sample at  $10^{\circ}\text{C min}^{-1}$  (dashed curve)

These curves indicate that the glass transition is not fully time independent, but only the midpoint stays constant. The width of the glass transition depends on whether the transition was recorded on cooling or heating. This phenomenon seems to be similar for all semicrystalline polymers. The absence of the hysteresis peak can be explained by the equal areas between the two curves below and beyond the midpoint of the glass transition as shown in Figs 11–13.

Figures 14 and 15 (PET and Nylon 6) indicate that the DSC curves recorded on heating at various rates ( $1$  and  $10^{\circ}\text{C min}^{-1}$ ) of semicrystalline samples crystallized at very slow cooling ( $1^{\circ}\text{C min}^{-1}$ ) are different: even the midpoint is somewhat different for these curves, and the width of the glass transition increases with decreasing heating rate, but there is no hysteresis peak. However, as mentioned at the comparison of the cooling at heating curves, the areas between the curves at the lower and higher



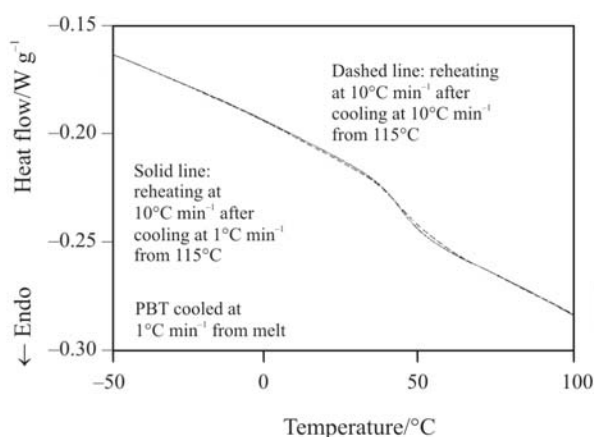
**Fig. 14** PET sample prepared by  $1^{\circ}\text{C min}^{-1}$  cooling from the melt, then heated at  $1$  and  $10^{\circ}\text{C min}^{-1}$



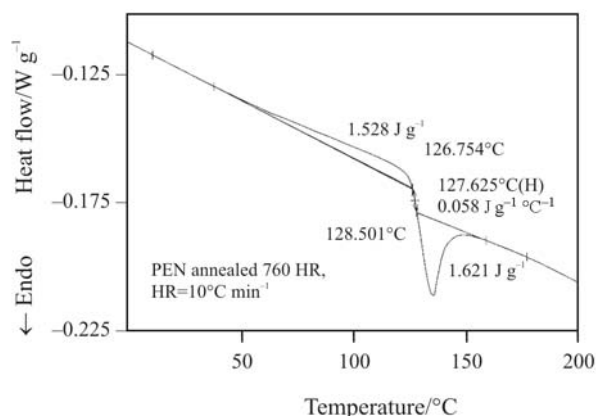
**Fig. 15** Nylon 6 sample prepared by  $1^{\circ}\text{C min}^{-1}$  cooling from the melt, then heated at  $1$  and  $10^{\circ}\text{C min}^{-1}$  after  $1^{\circ}\text{C min}^{-1}$  cooling from  $90^{\circ}\text{C}$

temperature regions of the glass transition are somewhat equal, which again, can explain the missing hysteresis behavior. Similar phenomenon can be observed in case of highly crystallizable polymers (PBT): the width of the glass transition on heating curves of samples prepared at various cooling rates is different, and the areas between the curves below and above the glass transition temperature (midpoint) are similar (Fig. 16).

All these experiments indicate that the glass transition as a whole in general does not fully lose its time dependence at various cooling and heating rates. Let us see what is happening on the example of Fig. 11. It is obvious that the two areas between the cooling and heating curves must be equal in order to satisfy the first law of thermodynamics. If that can be achieved with a simple change of the width of the glass transition, like in Fig. 11, there is no need for a hysteresis peak. If, however, there is a considerable difference between the two areas, a hysteresis peak must appear in order



**Fig. 16** PBT sample prepared by  $1^{\circ}\text{C min}^{-1}$  cooling from the melt, then reheated to  $100^{\circ}\text{C}$ , and cooled at  $1$  and  $10^{\circ}\text{C min}^{-1}$ , and finally, re-heated again at  $10^{\circ}\text{C min}^{-1}$  for analysis



**Fig. 17** PEN sample prepared by  $1^{\circ}\text{C min}^{-1}$  cooling from the melt, then annealed at  $102^{\circ}\text{C}$ , cooled at  $10^{\circ}\text{C min}^{-1}$ , and heated again at  $10^{\circ}\text{C min}^{-1}$ .  $\Delta C_p$  calculation at midpoint (since TAI software gives an option for calculation of  $\Delta C_p$  from start or onset to end or stop as well)

to satisfy the first law, and thus, making an adjustment for the two areas to become equal.

Finally, we need to mention another interesting phenomenon on annealed samples. Figure 17 shows the DSC curve of semicrystalline poly(ethylene naphthalate) prepared by crystallization from the melt at slow cooling ( $1^{\circ}\text{C min}^{-1}$ ) after a 12.7 day annealing at  $102^{\circ}\text{C}$ . It is easily visible that the effect of the annealing is not similar to the effect of the slow cooling rate. First, an endothermic hysteresis peak appears on the high temperature side of the glass transition, but this is not the only change in the shape of the DSC curve: another, broad, exothermic hysteresis peak precedes the glass transition, whose area is similar to the area of the endothermic hysteresis peak. Also, the glass transition temperature shifts when compared to the un-annealed sample. All this indicates, that, as suggested in [1] for PET, the kinetics of the glass transition must be changed.

## Conclusions

- Semicrystalline polymers must be described by co-existence of two amorphous phases (mobile or traditional amorphous phase and rigid amorphous phase) and the crystalline phase.
- Slow cooling followed by fast re-heating of semicrystalline polymeric samples does not introduce an endothermic hysteresis peak. The absence of the hysteresis peak can be explained by a drastic decrease of the time dependence of the glass transition. Nevertheless, some time dependence can be seen even for these samples.
- Annealing of semicrystalline samples does induce a hysteresis peak, but with a simultaneous appearance of a broad pre-glass transition exothermic hysteresis peak indicating changes in the kinetics of the glass transition.

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