

Thermal Analysis

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Characterization of Polyketone Copolymer by High Speed DSC

Introduction

The aliphatic polyketone copolymer (PK copolymer) is a perfectly alternating copolymer of ethylene and carbon monoxide.¹ It exhibits many desirable engineering thermoplastic properties, such as a high tensile yield stress and

an excellent impact performance. Its high degree of chemical resistance and superior barrier properties make this polymer an interesting, new thermoplastic for engineering applications.

After a washing and drying procedure, the reactor product consists of a white, semi-crystalline powder, soluble only in a few exotic solvents, like hexafluoroisopropanol (HFIPA) and meta-cresol. The crystalline phase of this polymer is built of orthorhombic unit cells with a polymer chain at each corner and one in the center. These polymer chains crystallize into two different modifications the alpha and the beta modification. The alpha modification changes into the beta form material at temperatures higher than about 120 °C. The beta form material, which is the dominant unit cell for the (unoriented) PK copolymer, fuses at about 250 °C. Lommerts *et al*,² calculated the dimensions of both cell types. Alpha form $a = 6.91 \text{ \AA}$, $b = 5.12 \text{ \AA}$, $c = 7.60 \text{ \AA}$; cryst. density = 1.382 g/cm^3 . For the beta form, $a = 7.97 \text{ \AA}$, $b = 4.76 \text{ \AA}$, $c = 7.57 \text{ \AA}$; cryst. density = 1.297 g/cm^3 .

The density increase obtained when the standard beta phase material is converted into the alpha phase material might improve the barrier properties even more (the structure and extent of the crystalline phase are important barrier-properties determining parameters). To see if and how the beta phase material could be changed into the alpha phase material PK copolymer was studied.

Polymerization-solvent induced and pressure/shear forces induced alpha crystallinity effects prove to be (partly) irreversible after heating through the alpha/beta crystal transition, indicated by T_m^* . A third method found, thermally induced alpha crystallinity, annealing at a temperature just below the melting of the beta crystalline phase, proved to be completely reversible.³ So, this method was used to make PK copolymer systems with high alpha/beta crystal ratios. A series of three such samples were put aside to measure possible effects of storage time on the alpha/beta ratio.

The conventional DSC analysis of these samples using a PerkinElmer® DSC 7 had many problems. The three main problems were:

- Uncertainty about T_{m1} (max) value, (cross-linking reactions, possibly already started during the fusion, might influence the measured T_{m1} values).
- Uncertainty about proper T_{m1} values in connection with clearly present re-crystallization effects during the main fusion process.
- Investigation of the amorphous phase, i.e. determination of the T_g -value by conventional DSC was not possible for PK copolymer.

Recent developments in high speed DSC provide many advantages over conventional DSC. HyperDSC® is the premier fast scan DSC technique from PerkinElmer. It requires a DSC instrument with an extremely fast response time and very high resolution. It allows very fast linear heating and cooling scanning (up to 500 °C/min) over a broad temperature range. Not only does HyperDSC provide higher sensitivity, but it can also suppress kinetic events during scanning, thus analyzing the sample as received. During the discussions about the advantages of the HyperDSC, we realized that this improved technique might give the answers we were still looking for.

Experiment

The samples used for this study and the sample treatment as a function of temperature and time are schematically shown in Appendix I. The following experiment conditions were used to measure these samples in 2005:

Instrument: PerkinElmer Pyris™ 1 DSC

Sample mass: 1 mg (approximately)

Heating/cooling rate: 300 °C/min

Number of scans: First and second heating scans taken for each sample

Temperature range: -100 °C to +300 °C

The HyperDSC was calibrated for temperature and enthalpy responses using high purity indium and lead. The systems' base-line was checked before and after the measurements (Figure 1).

In 1993, the data was obtained by using a PerkinElmer DSC 7 with a scanning rate of 20 °C/min.

Results

Experiment and calculated values

This study was started with a number of scouting experiments to check our reported T_{m1} (max) value of 258 °C ± 1 °C (20 °C/min).³ A reactor powder sample measured at a heating rate of 300 °C/min resulted in T_{m1} (powder) = 258.6 °C and 256.6 °C. Hence, the T_{m1} value determination proved that it was not hampered, or hardly hampered by possible cross-linking effects.

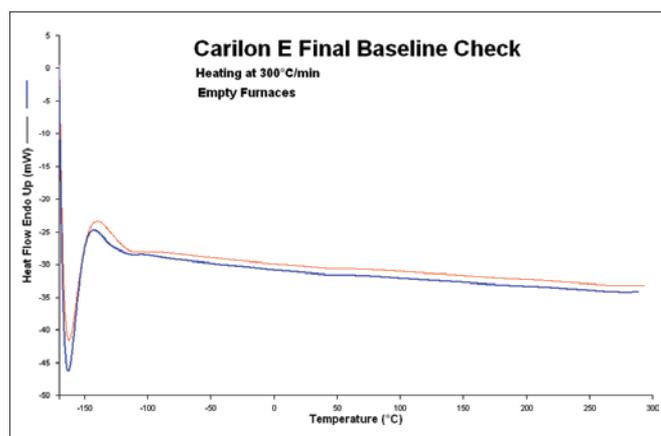


Figure 1. System baseline before and after the experiments (red: before, blue: after).

Figure 2 shows the first and second heating scan results measured on sample 1 in 2005. Both curves clearly illustrate that the alpha phase crystallinity present in this sample (see alpha/beta crystal transition between about 100 °C and 150 °C) completely disappeared at the start of the second heating scan. But then, the second scan clearly showed a shifted fusion process of the beta crystalline phase to lower temperatures. This raised the question; might both effects be coupled? We started to summarize both fusion effects in T_m and H_f values (results shown in Table 1) and used Figures 3 and 4 to get a better look at the fusion processes. Figure 3A shows the fusion endotherms of the three samples at the standard heating rate in 1993. Figure 3B gives the same results, but measure at 300 °C/min. in 2005. Both figures show that the fusion endotherms of the samples 2 and 3 in 1993 were clearly influenced by recrystallization effects during the fusion process. These effects were (barely) present in the three endotherms measured at a high rate in 2005.

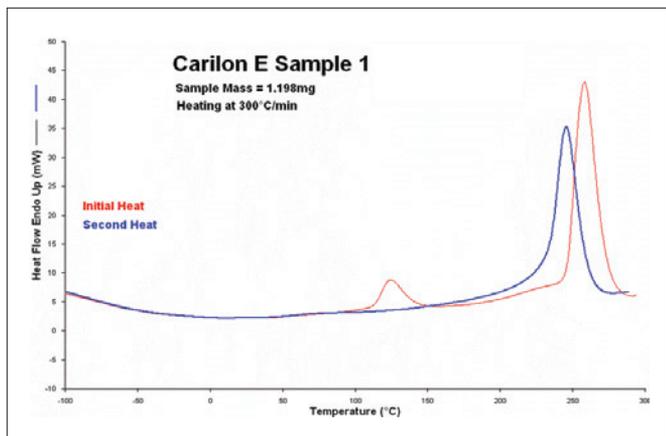


Figure 2. First and second heating scans measured on sample 1. (in 2005). Red curve is initial heating and blue curve is second heating.

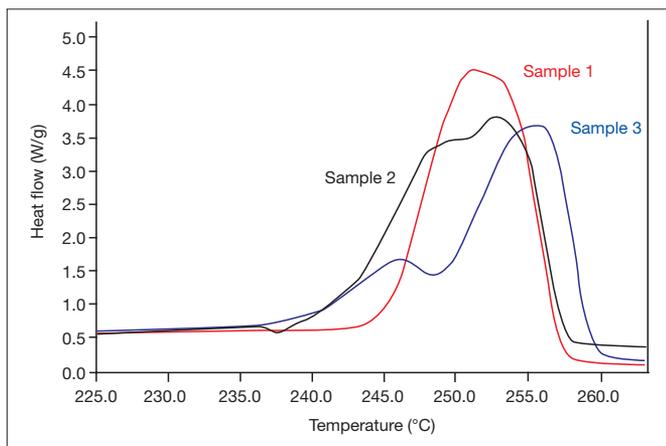


Figure 3A. The beta phase fusion effects of the systems 1, 2, and 3 (in 1993), i.e. heating rate 20 °C/min.

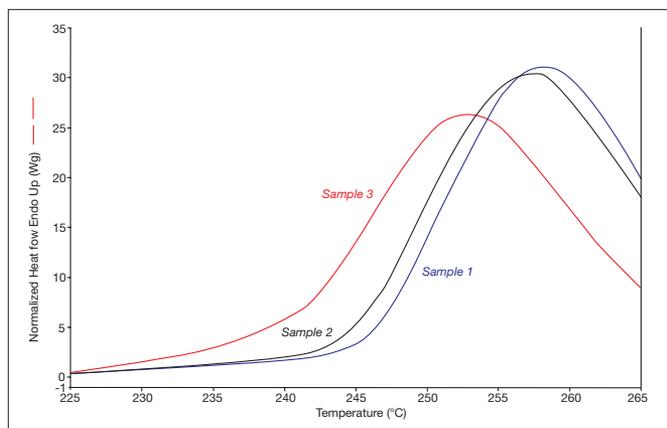


Figure 3B. The beta phase fusion effects of the systems 1, 2 and 3 (in 2005), i.e. heating rate 300 °C/min.

Figures 4A and B show the alpha/beta crystal transitions of these samples. Figure 4A shows the expected result, i.e. no annealing – no alpha crystallinity – no alpha/beta crystal transition in sample 3 (1993), besides, an increasing strength of the alpha/beta crystal transition with increasing annealing times. The alpha/beta crystal transitions measured in 2005 at a high heating rate are shown in Figure 4B. The strength of the crystal transition of the two annealed samples (1 and 2) are not only increased, but that the non-annealed reference sample 3 is also now showing a clear crystal transition. Thus, during the longtime storage at 20 °C of this sample, beta crystallinity has been partly changed into alpha crystallinity due to the release of built-in stress during the compression molding procedure. This important aspect will be discussed later on separately.

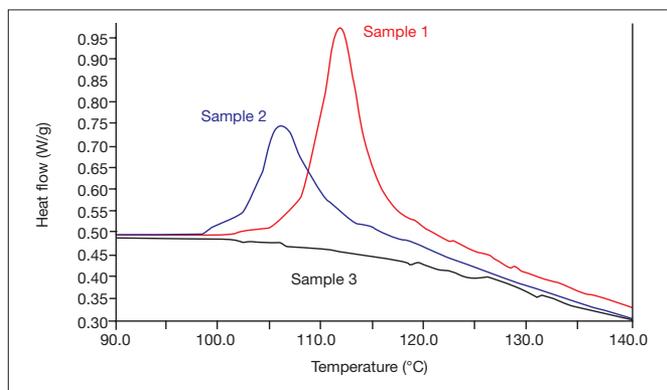


Figure 4A. The alpha phase fusion effects of the systems 1, 2 and 3 (in 1993), i.e. heating rate 20 °C/min.

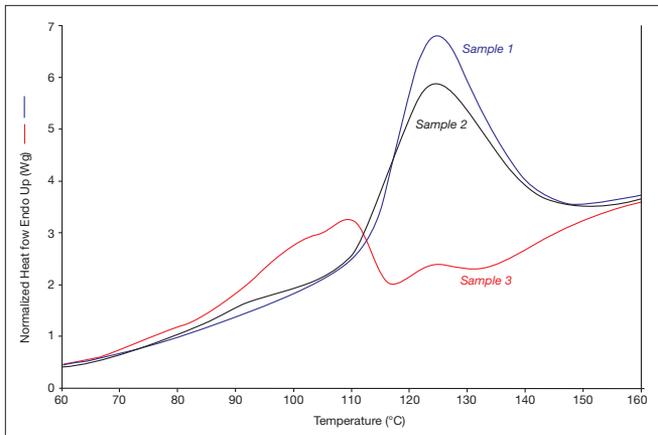


Figure 4B. The alpha phase fusion effects of the systems 1, 2 and 3 (in 2005), i.e. heating rate 300 °C/min.

Table 1. High and low heating rate results measured on PK copolymers.

Sample Code	Alpha Cryst. Phase		Beta Cryst. Phase	
	T_m^* °C	H_f^* J/g	T_{m1} °C	H_{f1} J/g
1. 1993**	111.8	8.3	252	116.1
1. 2005***	124.4	18.2	258	126.9
2. 1993	106.3	5.1	251.8 *	116.0*
2. 2005	124.2	15.8	257	126.1
3. 1993	-	-	249.4 *	112.0*
3. 2005	109	4.3	252.7	118.2

* corrected by calculation, see text.

** (1993) low, i.e. 20 °C/minute heating rate experiments.

*** (2005) high, i.e. 300 °C/minute heating rate experiments.

In order to check the consistency of all fusion effects measured, we first tried to find a manner to correct for the recrystallization effects during the fusion of samples 2 and 3 (1993). It soon became clear that especially strong coupling between the alpha/beta fusion effects offered correction possibilities.

The H_{f1} values of the four other samples were plotted as a function of H_f^* . The linear relation fitting these values was extrapolated to $H_f^* = 0.0$ with a H_{f1} value of 112.8 J/g. This value of 112.8 was subsequently changed in small steps between 114.0 and 110.0 to find the H_{f1} value for $H_f^* = 0.0$, giving the highest correlation factor value. Using this value as a 'calculated' data point, an 'optimized' H_{f1}/H_f^* relation was calculated i.e.:

$$H_{f1} = 0.8497 \times (H_f^*) + 111.89 \quad (n = 5, R_{val} = 0.9537) \quad (1)$$

Substitution of $H_f^* = 0.0$ for sample 3 (1993) resulted in a corrected H_{f1} value of ≤ 111.7 , i.e. 112 J/g instead of the experimental value 110.6 J/g. Substitution of $H_f^* = 5.1$ J/g for sample 2 (1993) resulted in a corrected H_{f1} value of 116 J/g instead of the experimental value of 119.1 J/g.

The linear relation T_{m1}/H_f^* was used in the same way to calculate the corrected T_{m1} values for both samples 2 and 3 (1993). The corrected T_{m1} value of sample 2 (1993) was calculated at 251.8 °C. The corrected T_{m1} value of sample 3 (1993) was calculated at ≤ 249.4 °C.

These four calculated values are also listed in Table 1, with the warning: calculated values.

Calculation of beta phase T_{m1} and H_{f1} values based on the alpha phase T_m^* value.

The differences in the T_{m1} and H_{f1} values listed in Table 1 are not straightforward. Hence, we tried to calculate these values to see if they fit in one model. The used model is simple: assuming that the T_m^* values are known, it calculates the other three parameters i.e., the H_f^* , T_{m1} and H_{f1} values with three derived equations:

$$H_f^* = 0.7200 \times (T_m^*) - 72.5678 \quad (2)$$

$$T_{m1} = 0.4668 \times (H_f^*) + 249.4099 \quad (3)$$

$$H_{f1} = 0.8497 \times (H_f^*) + 111.7243 \quad (4)$$

with T_{m1} and T_m^* : °C

H_{f1} and H_f^* : J/g and

$100 \text{ °C} < T_m^* < 125 \text{ °C}$

It is important to realize that these equations only hold for compression molded PK copolymer systems.

Subsequently, the four T_m^* values listed in Table 1 with corresponding experimental T_{m1} and H_{f1} values were used to calculate the fusion values of their beta crystalline phase, see Table 2. The comparison of the calculated values with the reported measured values is satisfactory. It indicates that the measured differences in T_{m1} and H_{f1} of both important properties are correct. Continuation of this research is necessary to obtain further/better understanding of this fascinating behavior. But, in fact these results obtained with experimental data:

- differ in time more than twelve years
- are measured at different locations and by different persons
- are performed on different DSC systems

and are, in our eyes the best proof of the excellent quality, high stability and reliability of PerkinElmer's Thermal Analysis Systems.

Table 2. Testing the consistency of the results of high and low heating rate DSC experiments performed in 1993 and 2005.

Beta Phase T_{m1} Values			
Sample Code	T_{m1} (calc.)°C	T_{m1} (meas.)°C	$ \Delta T $ °C
1.(1993)	253.1	252	1.1
1.(2005)	257.3	258	0.7
2.(2005)	257.3	257	0.3
3.(2005)	252.2	252.7	0.5
		$ \Delta T $ °C average	0.7

Beta Phase H_{f1} Values			
Sample Code	H_{f1} (calc.) J/g	H_{f1} (meas.) J/g	$ \Delta H_f $ J/g
1.(1993)	118.5	116.1	2.4
1.(2005)	126.2	126.9	0.7
2.(2005)	126	126.1	0.1
3.(2005)	116.8	118.2	1.5
		$ \Delta T $ °C average	1.2

The glass-rubber transition

The Tg value determination of high crystalline polymers by DSC is, for most systems, not possible, or at least difficult. Earlier, we reported our attempts to determine the Tg values of PK co- and terpolymer by conventional DSC. The conclusion then was the DSC Tg value determination of PK co- and terpolymers is only possible on PK terpolymers after a proper thermal pre-treatment. The DSC Tg (onset) value reported for these systems was $4\text{ °C} \pm 3\text{ °C}$.³

The heat flow/temperature curves of the present three samples were blown-up to see if any Tg effect was present. A clear Tg effect was measured for the systems 1 and 3 (2005), see Figure 5. For system 2 (2005) only the Tg onset was detected. So we found:

1. (2005) DSC Tg (onset) = 7 °C
2. (2005) DSC Tg (onset) = 2 °C
3. (2005) DSC Tg (onset) = 9 °C

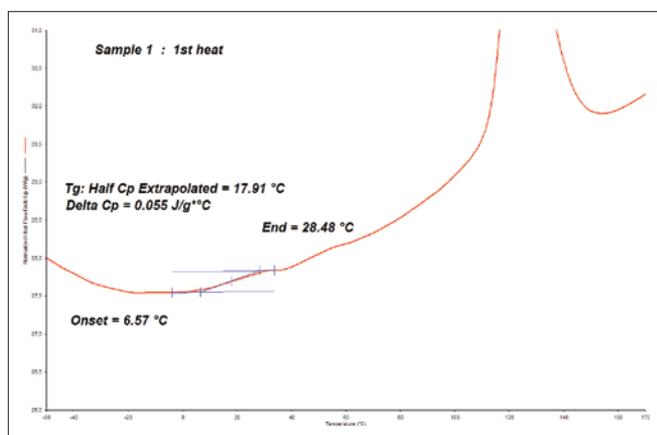


Figure 5. The DSC Tg value determination of sample 1 at 300 °C/min (in 2005).

This result is much better than we ever measured for such semi-crystalline polymers. We do think that a proper optimization in terms of sample mass, sample shape and sample pre-treatment³ will improve these results even more.

Summary and conclusions

Two simple HyperDSC heating scans on three PK copolymer samples provided more information about the amorphous and crystalline phases of this high crystalline polymer than a lot of standard DSC heating rate measurements did in the past. The high heating rate measurements (300 °C/min) dismissed the doubts that the reported maximum T_{m1} value, i.e. 258 °C, and the alpha- and beta-phase fusion effects were measured without any hampering due to recrystallization effects during both processes. The results of both the recent high rate and the old low rate measurements fit perfectly in the proposed alpha/beta fusion model. Besides, Tg effects were clearly detected in these scans without any pre-treatment (this is rare for such high crystalline polymers). The results of these measurements show that the HyperDSC technique is really the most effective and most sensitive DSC technique available at the moment for the characterization of both the crystalline and the amorphous phase of a polymeric system.

References

1. E. Drent, European Patent 121,96 (Shell), 1984.
2. B.J. Lommerts et al., J. of Pol. Sc. : Part B: Polymer Physics, Vol. 31, p. 1319 – 1330 (1993).
3. W.M. Groenewoud: Characterization of Polymers by Thermal Analysis, Elsevier Science Amsterdam/New York, ISBN:0-444-50604-7 (2001).

Appendix I: Thermal history of investigated PK copolymer samples

I. Reactor powder PK copolymer (Carilon E) – MDU batch 91.091

$$T_{m1} = 258 \pm 1 \text{ } ^\circ\text{C}^*$$

$$H_{f1} = 152 \pm 6 \text{ J/g}^*$$

II. Sample sheet molding i.e. Compression molded for 2.5 min. at 280 °C

III. Annealing procedure

10 min. at 240 °C
DSC sample 1. (1993)

6 min. at 240 °C
DSC sample 2. (1993)

no annealing
reference DSC sampe 3. (1993)

IV. Storage time 1993-2005 storage in darkness at 20 °C and 50% R.H.

DSC sample 1. (2005)

DSC sample 2. (2005)

DSC sample 3. (2005)

* reported average values; specific batch values 257.0 °C / 151.8 J/g