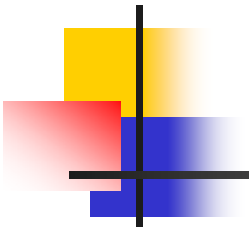
Composite materials characterization by means DSC



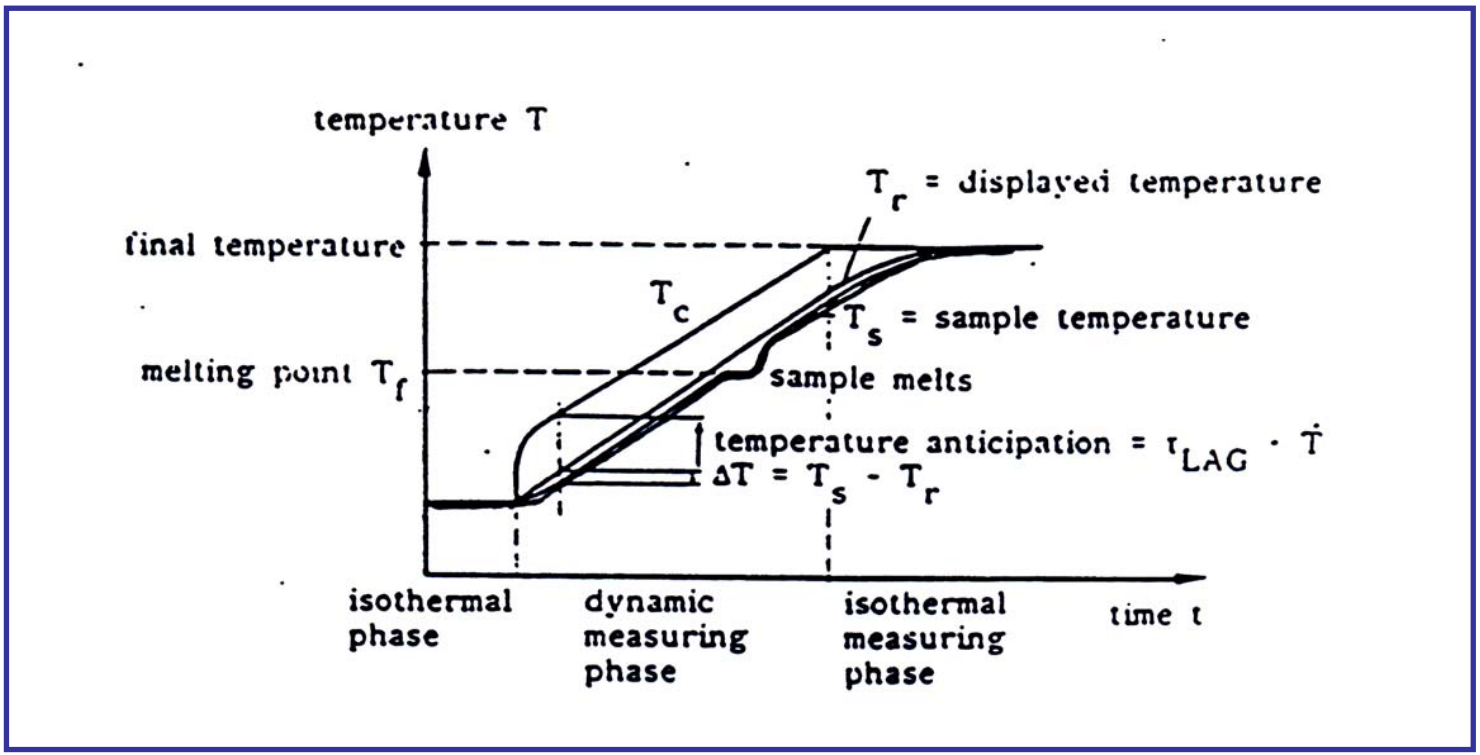
THERMAL ANALYSIS IN COMPOSITES

Introduction to Thermal Analysis

- ✓ Thermal analysis covers a group of techniques where properties of a sample are investigated as a function of temperature or time.
- ✓ The applied temperature program consist of a sequence of segments where the sample is heated or cooled at a constant rate or held at constant temperature.
- ✓ In many experiments the atmosphere also plays and important role, the most common are inert and oxidazing gases.

Differential Scanning Calorimetry

✓ When the sample absorbs energy the enthalpy change is called ENDOTHERMAL.



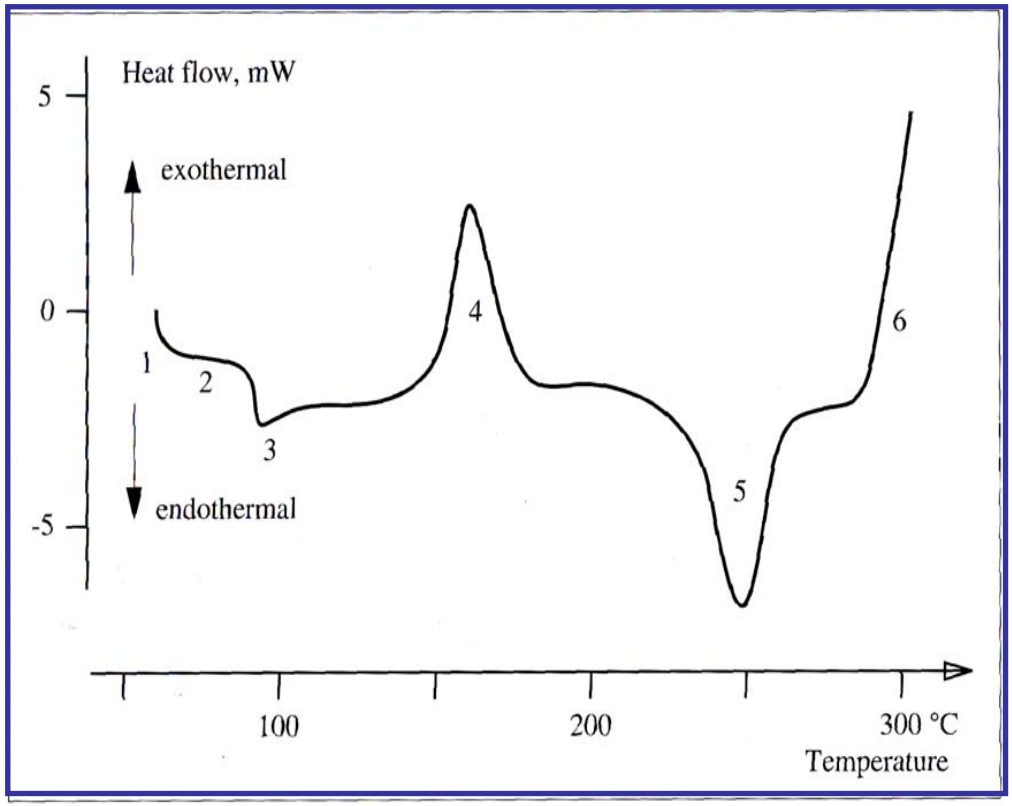
Differential Scanning Calorimetry

✓ A heat flow corresponds to a transmitted power and thus is measured in mW. Integrating power with respect to time results in an amount of energy expressed in mWs=mJ. The transmitted energy corresponds to an equal change in enthalpy of the sample.

Differential Scanning Calorimetry

- ✓ When the sample realease energy the process change is called EXOTHERMAL.
- ✓ A DSC measures provide information about: Thermal effects shaped as peak, characterized by their enthalpy change and temperature range (e.g. melting, crystallization, chemical reaction)
- ✓ In addition the especific heat capacity is obtained, DSC also observes thermal effects caused by a change in heat capacity (e.g. glass transition)

Differential Scanning Calorimetry



1. Initial deflection that is proportional to the sample's heat capacity
2. DSC curve with no thermal effects "baseline"
3. Glass transition of amorphous fraction
4. Peak of cold crystallization
5. Melting peak of the crystalline fraction
6. Beginning oxidative degradation in air

Thermogravimetric Analysis

- ✓ In the TGA the mass of the sample is measured while it is subjected to a temperature program.
- ✓ The measurement is performed in a defined atmosphere, usually in N2, inert conditions, or in oxigen.
- ✓ The mass is recorded with a highly sensitive electronic balance. Interfering buoyancy and drag force effects are compensated by blank curve substraction.

Thermogravimetric Analysis

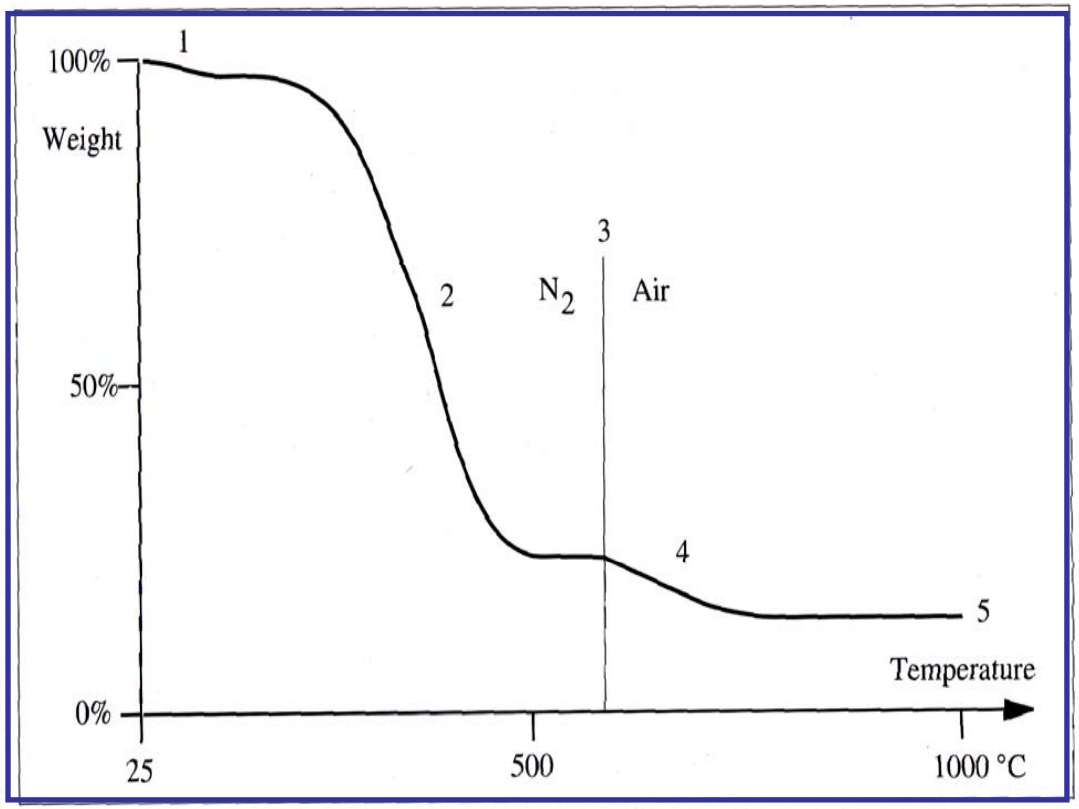
TG provide the following results

✓ Content of highly volatile matter (e.g. moisture, solvents); polymer content, carbon black, ash or filler content.

✓ From the temperature range of the polymer pyrolisis qualitative information is obtained since the kinetics of decomposition is different from polymer to polymer

✓ About the temperature and course of decomposition reactions in inert atmosphere, as well as burning profiles in air or oxygen

Thermogravimetric Analysis



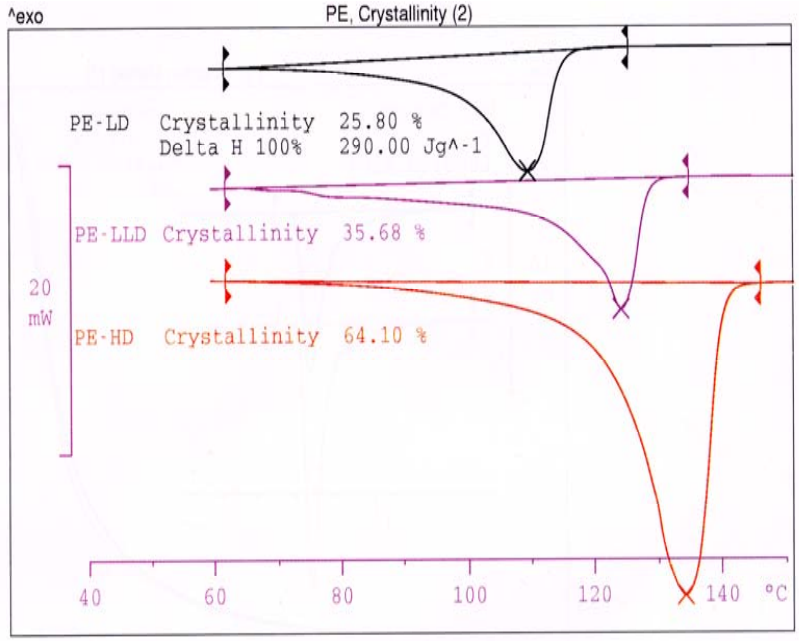
1. Volatiles (moisture, solvents, monomers)
2. Polymer decomposition
3. Change of atmosphere
4. Burning step of carbon (carbon black or fillers)
5. Residue (ash, fillers, glass fiber)

HDPE characterizing by crystallinity

- The area under the peak represents the heat of fusion of the sample. It is proportional to amount of crystals present in the sample. The crystallinity is determined by comparing the measured heat of fusion with the theorical heat of fusion of 100% crystalline HDPE (290 J/g)

Polymer	LDPE	LLDPE	HDPE
crystallinity	25.8	35.78	64.1
Heat of fusion	74.7	103.5	186.0

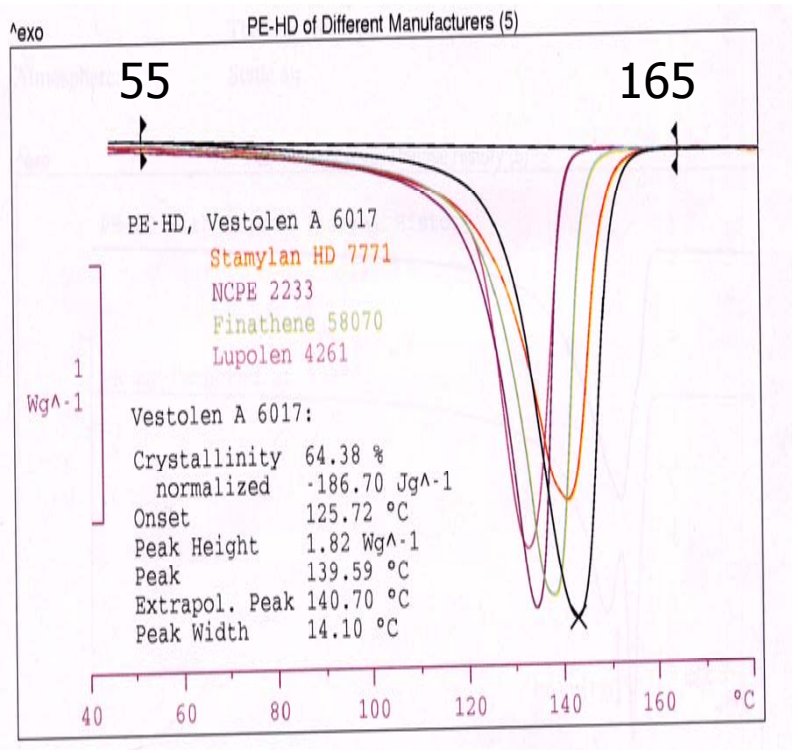
- The DSC crystallinity shows what percentage of the material is crystalline versus being amorphous. The crystallinity depends on the regularity of the molecule structure and on the thermal history. The DSC corroborates to the mechanical properties.



HDPE of different manufacturers

The DSC curve of all samples begins to deviate from baseline between 60 and 70ºC. Between 145 and 160ºC the signal returns to the BL.

Name	crystall	Peak Temp	Peak width	Sample mass
Vestolen	64.6	142.6	14.1	13.3
Stamylan	56.3	139.6	15.2	22.5
NCPE	52.9	133.1	10.6	4.9
Finathene	59.0	135.2	12.4	11.3
Lupolen	48.7	131.4	11.5	4.5



The reference heat of fusion of 100% crystalline PE is taken to be 290 J/g. 55 and 165ºC are the applied integration limits.

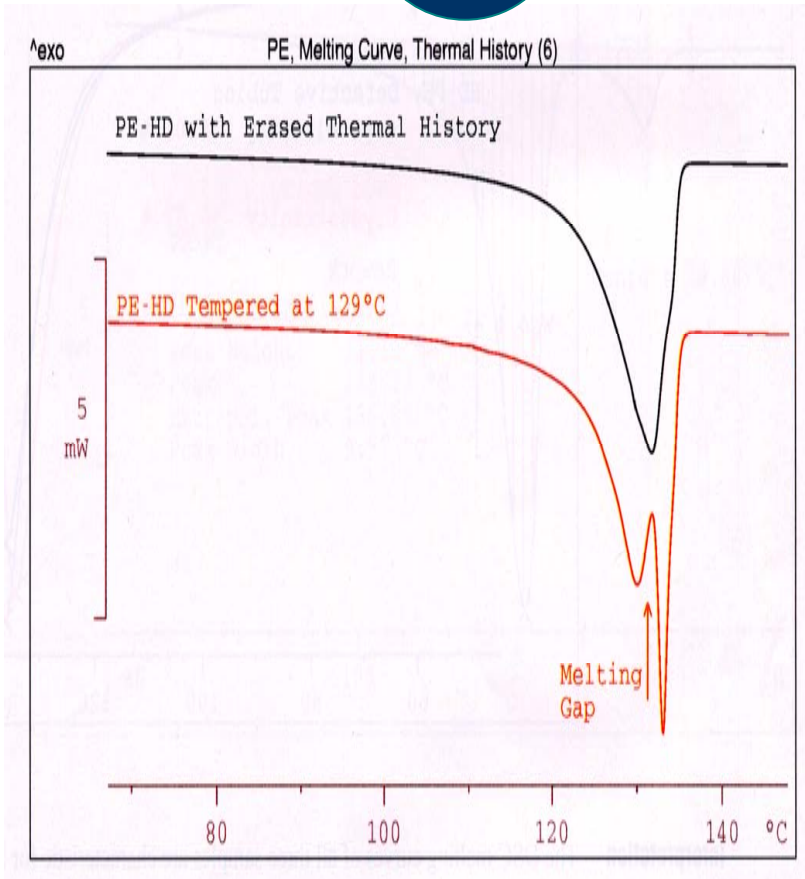
HDPE melting curve and the

Tempering 60’ 129 °C
Cooling to 40°C at 5K/min
Heating 30 to 180
Cooling 160 to 40 at 5K/mi
Heating 30 to 180 at 5

- During tempering at 129ºC crystal segregation ocurrs: amorphous domains of highest order in molecular structural can form crystallites with melting points higher than 129ºC. Naturally crystallites with melting points at 129ºC or lower cant form during this tempering. As the sample is cooled, additional crystallites with lower melting points can form but a gap at 129ºC appears on the reheating curve of sample

- The melting gap can be evaluated as an onset, however the most important information it reveals at what T the tempering was done.

- The shape of DSC melting curve depends on the thermal history of the sample. The melting gap is often used to check for correct process T (annealing of HDPE high voltage cables)



Heating 30 to 200

DSC of sheets made of rework, said to be HDPE

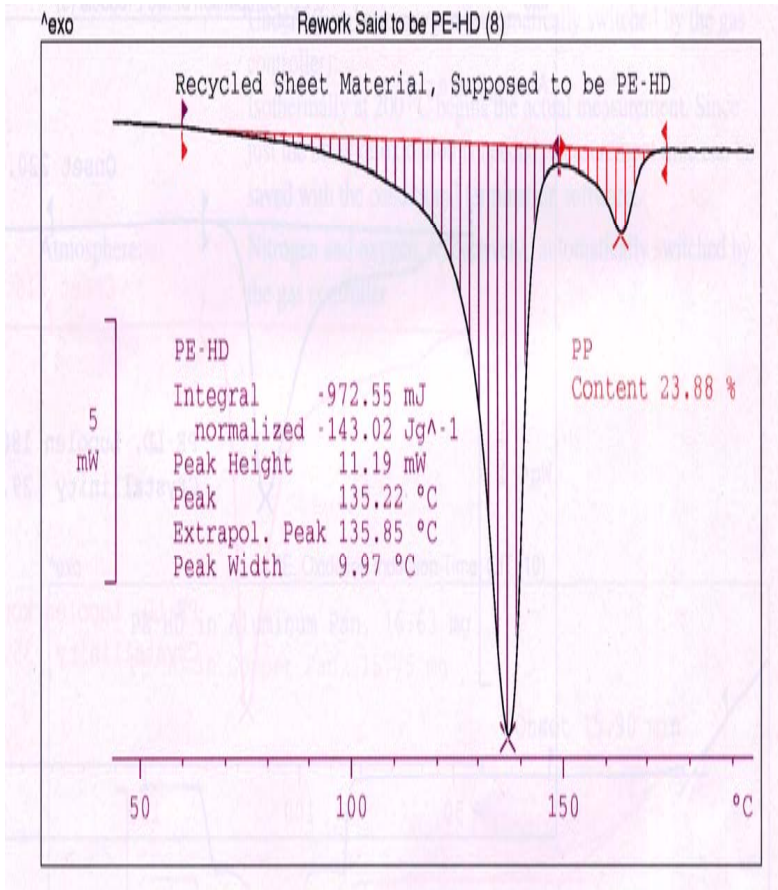
- The melting curve cleary shows the material is a blend of HDPE (PT 135ºC) and PP (PT= 163ºC) instead of pure HDPE

- The determined heat of fusion of the PP peak at 14.3 J/g enables the calculation of the aprox. content of PP. If the heat of fusion of pure PP is determined to be 60 J/g then the following calculation is true:

- Cryst PP Content = ΔH/ ΔHpp thus 14.3/60=23.9%

- Cryst HDPE Content = ΔH/ ΔHhdpe thus 143/290=49%

- DSC proves the material doesn't match the agree quality.



1st 30 °C t 180°C

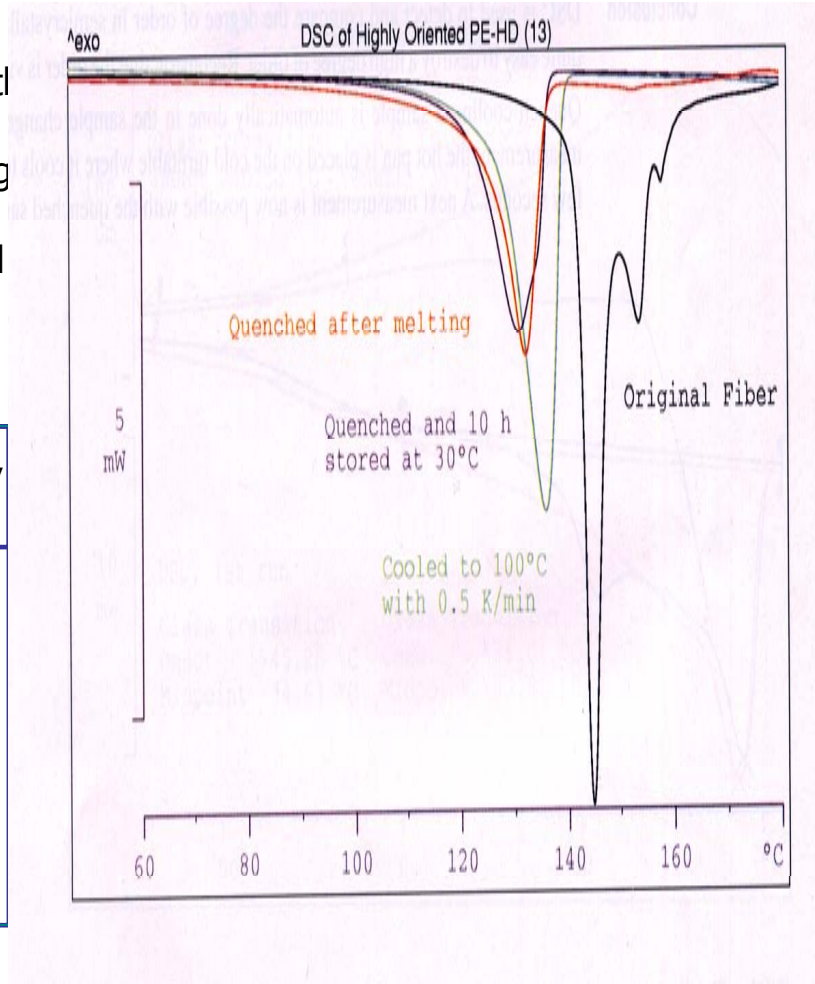
2on quenched

3st quenched (10h stored 30°C)

DSC of highly oriented HDPE fiber

- All heating curves shown endothermal effects caused by tl fusion of the crystalline areas of the polymer. The 1st fusion peak is completly different from the following curves. The hig degree of order in the fiber shift the melting range to much higher T. On melting this higher degree of order is destroyed irreversibly.

Thermomechanical hist	Peak Temp	heat fusion	crystallinity
Original gel spinning	144	253	87
Quenched	132	147	51
Quenched (10h) Stored 30ºC	131	139	48
With 0.5K/min cooled	136	183	63



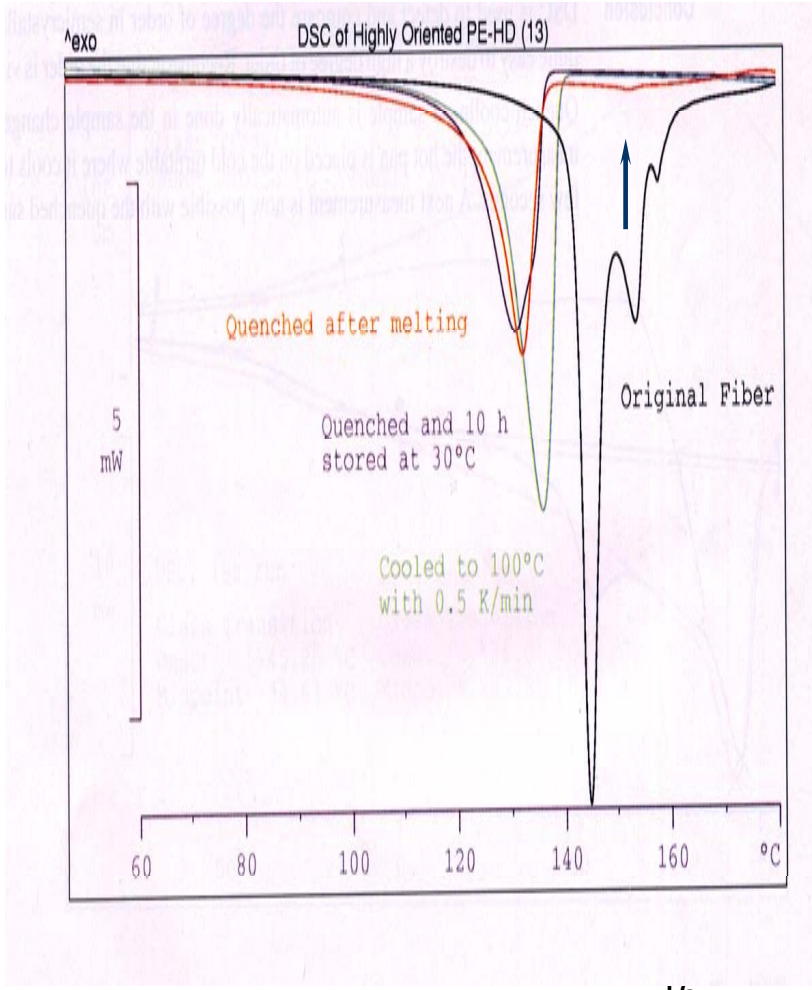
1st 30 °C t 180°C

2on quenched

3st quenched (10h stored 30°C)

DSC of highly oriented HDPE fiber

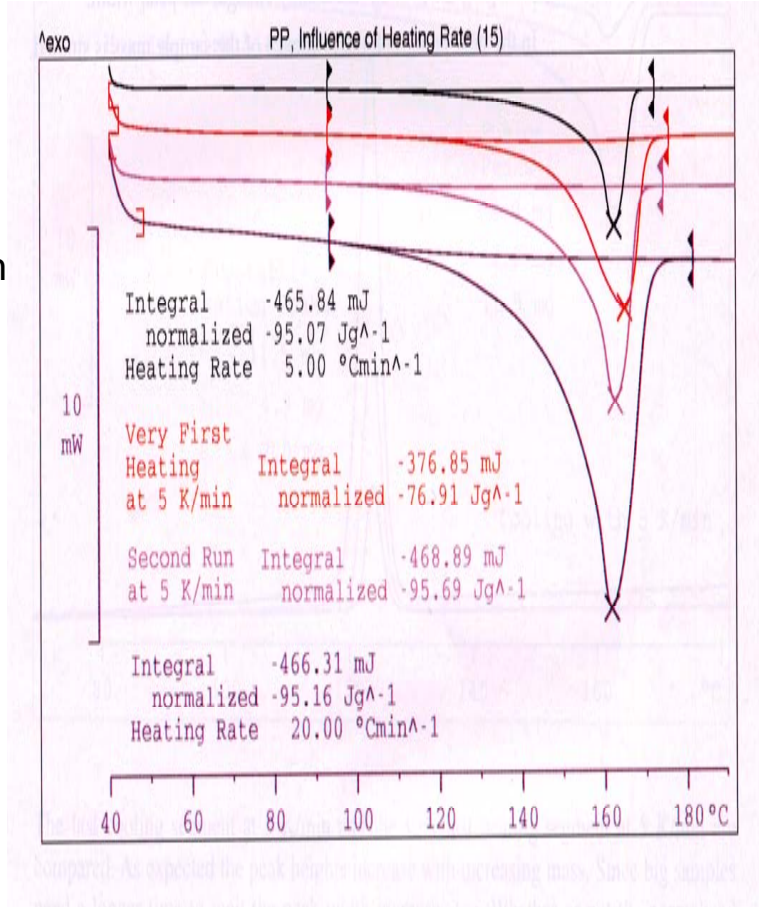
- All the experiment have been done with a single sample. This explains the relatively high crystallinity after the first quenching. The sample "remembered" the hight degree of order and produced a few second peak at 150ºC. With out of peak the crystallinity would amount to only 42%.
- DSC is used to detect and compare the degree of order in semicrystalline polymers. It's a quite easy to destroy a high degree of order. Reconstructing the order is virtually impossible. Quench cooling a sample is automatically done in the sample changer: at the end of the measurement the hot pan is placed on the cold turntable where it cools to ambient within a few seconds.



PP influence of heating rate

- As expected the very first and second melting curves at 10K/min are different due to their diffent thermal history. Changing the heating rate, influences both the peak height and width.
- The reference heat of fusion of 100% crystalline PP is taken to be 190 J/g (between 95 to 180ºC with straight baseline)

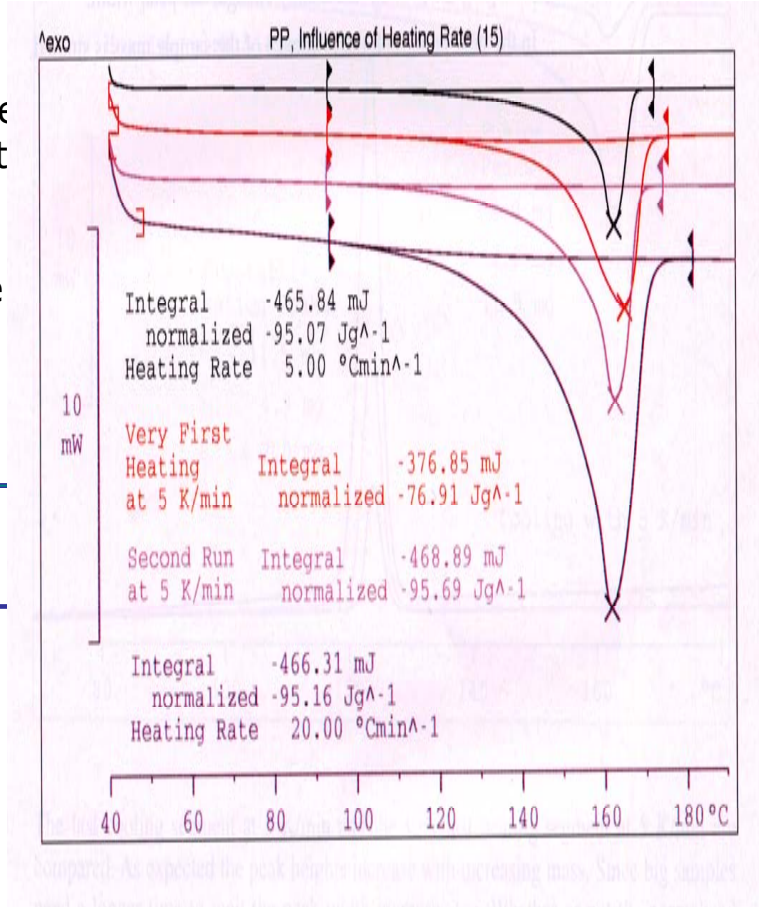
	1st heating 5 K/min	2on heating 10 K/min	3rd heating 20 K/min	4rt heating 5 k/min
Heat of fusion	76	95.7	95.2	95.1
Peak height	4.1	5.2	8.4	3.3 mW
Peak Temp	164.6	162.2	161.1	162 ºC
Peak widht	13.2	10.4	14.2	6.8



PP influence of heating rate

- The melting behaviour of semicrystalline polymers depends on thermal history. The low heat of fusion on first heating is due to incomplete crystallization of the pellets. To compare different lots of raw materials the 2on DSC melting curves should be used after both samples have been subjected to the same thermal history by carrying out a controlled coolingrun after the samples are melted.
- Changing the heating rate mainly changes the peak width

	1st heating 5 K/min	2on heating 10 K/min	3rd heating 20 K/min	4rt heating 5 k/min
Heat of fusion	76	95.7	95.2	95.1
Peak height	4.1	5.2	8.4	3.3 mW
Peak Temp	164.6	162.2	161.1	162 ºC
Peak widht	13.2	10.4	14.2	6.8

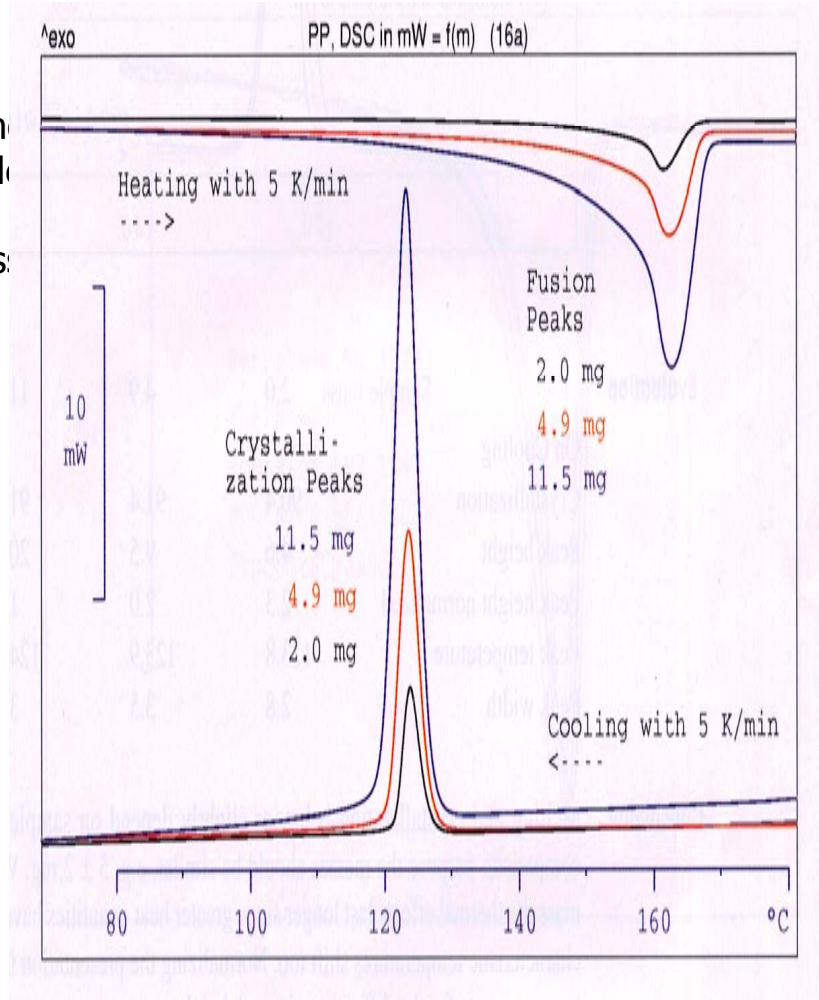


PP influence of sample mass

- The last cooling segments at 5 K/min and the very last heating segments at 5 K/min are compared. As expected th peak heights increase with increasing mass. Since big sampl need a longer time to melt the peak width increases too. Whether or not the normalized representation in W/g is mas independent

On heating

sample mass	2.0	4.9	11.5 mg
Heat of fusion	88.8	95.1	94.1 J/g
Peak height	1.6	3.3	7.2 mW
Peak height norm	0.8	0.7	0.7 W/g
Peak Temp	161.3	162.2	163.3 °C
Peak widht	5.2	6.8	7.7 °C

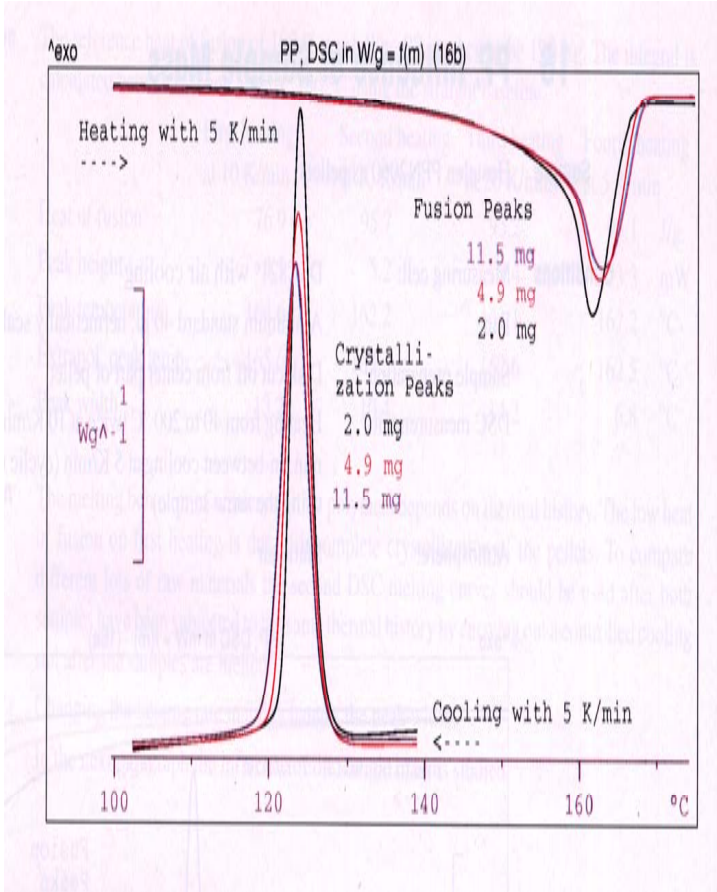


PP influence of sample mass

- Melting and crystallization behaviour slightly depend on sample mas. Therefore, for comparasion purpose the masses should be similar (5 -/+2 mg) With increasing sample mass the thermal effects last longer since greater heat quantities have to be transferred. The characteristic temperature shift too.

On cooling

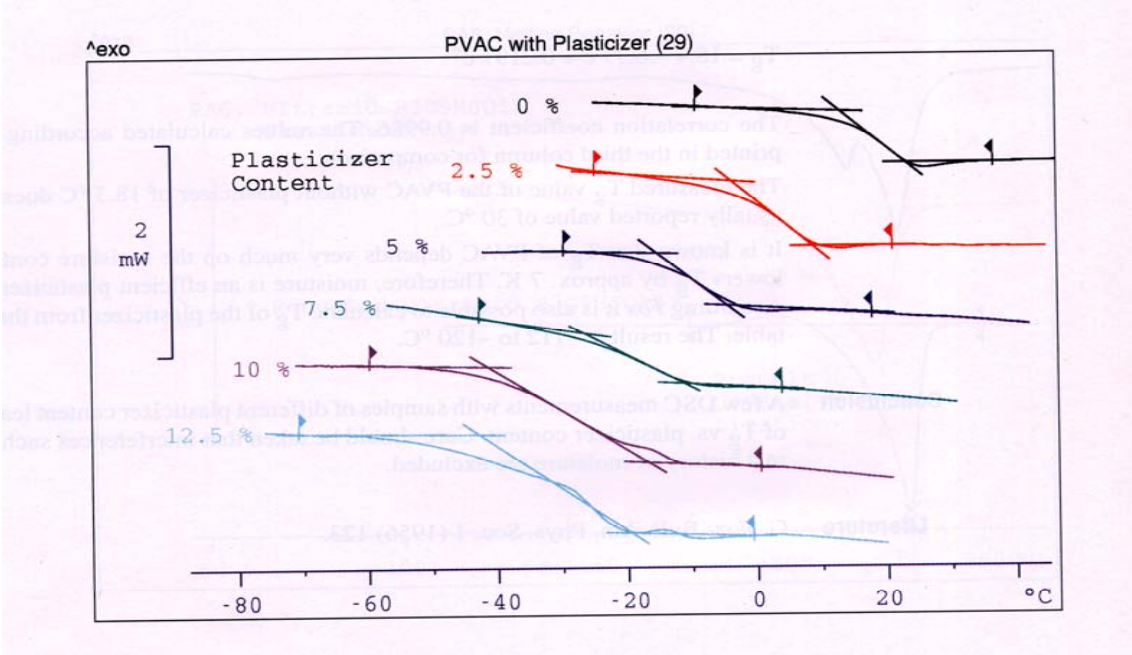
sample mass	2.0	4.9	11.5 mg
crystallization	90.4	91.4	91.0 J/g
Peak height	4.6	9.5	20.0 mW
Peak height norm	2.3	2.0	1.8 W/g
Peak Temp	123.3	123.9	124.0 ºC
Peak widht	2.8	3.5	3.8 ºC



PVAC Glass Transition Temperature and Plasticizer

To obtain a clear diagram the region has been cut out of the DSC curves. As expected Tg is lowered by the plasticizer. With increasing plasticizer content the transition become less pronounced (wider)

Sample mass	plasticizer	Tg (°C)
9,285	0	18.3
9,877	2.5	2.8
8,716	5.0	-10.2
9,410	7.5	-18.7
14,293	10.0	-29.1
13.795	12.5	-31.3



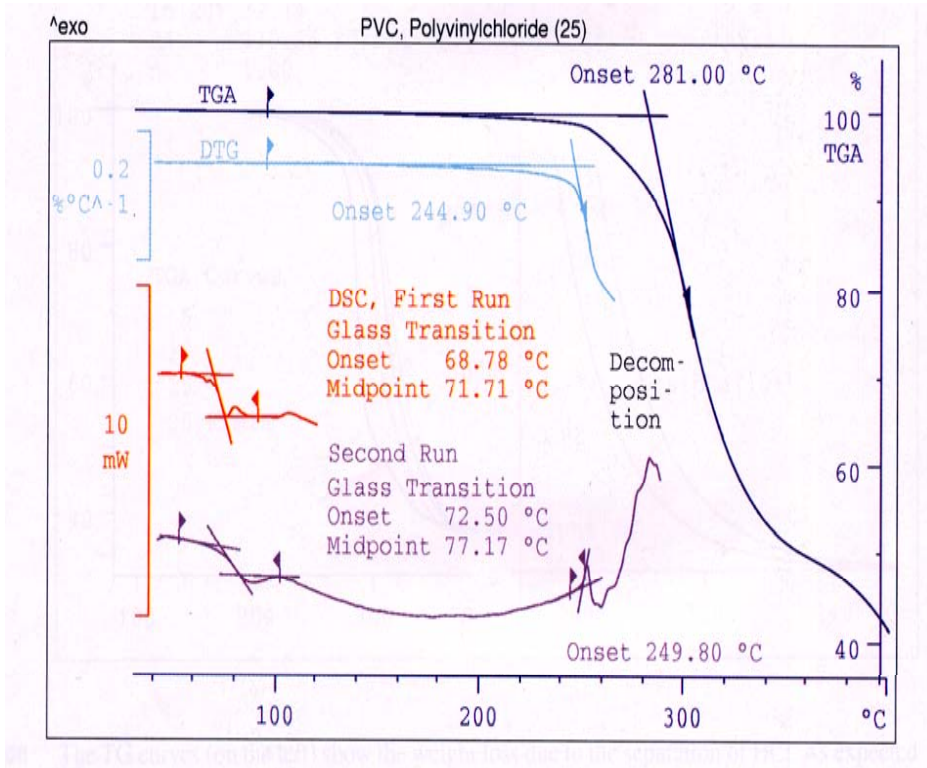
The measured Tg value of the PVAC without plasticizer of 18.3 doesn't agree with the usually reported value of 30ºC. This is due to the moisture (1% decrease 7K the Tg)

PVC investigated by DSC and TGA

There are typical distortions on the first DSC curve. They are caused by stress relief, enthalpy relaxation and drying. Usually the second run gives undisturbed glass transitions

Above aprox. 200ºC the thermal decomposition begins often with and exothermal peak (DSC) and always with a weigth loss due to the separation of HCl (TGA). The HCl could attack the cell. Purging it with N2 is a countermeasure to reduce any damage.

Part of the exothermal decomposition is caused by the chemical reaction of the formed HCl with the Al pan

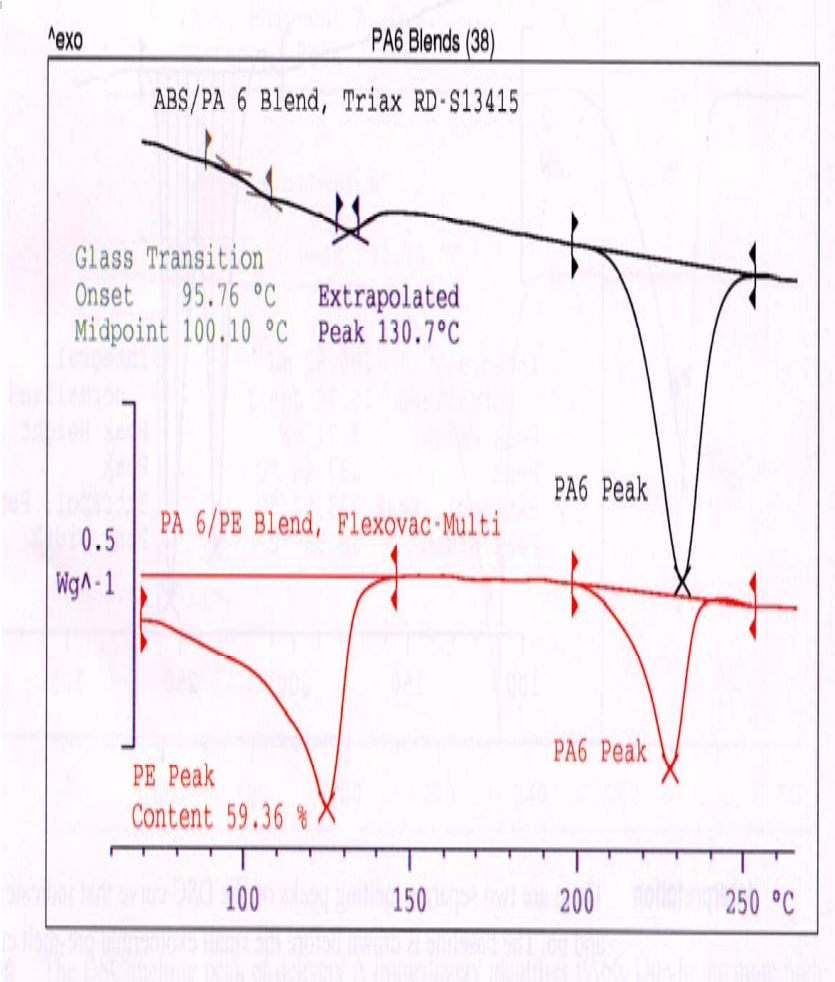


PA 6 / ABS Blends
PA 6 / PE Blends

Heating from 30 to 280ºC at 20K/min

As expected on both DSC curves there is the PA6 fusion peak of 230ºC. The ABS component show the Tg of PS at 100ºC and of PAN at 130ºC. The PE component of 2º blend gives a fusion peak of 124ºC (100J/g).

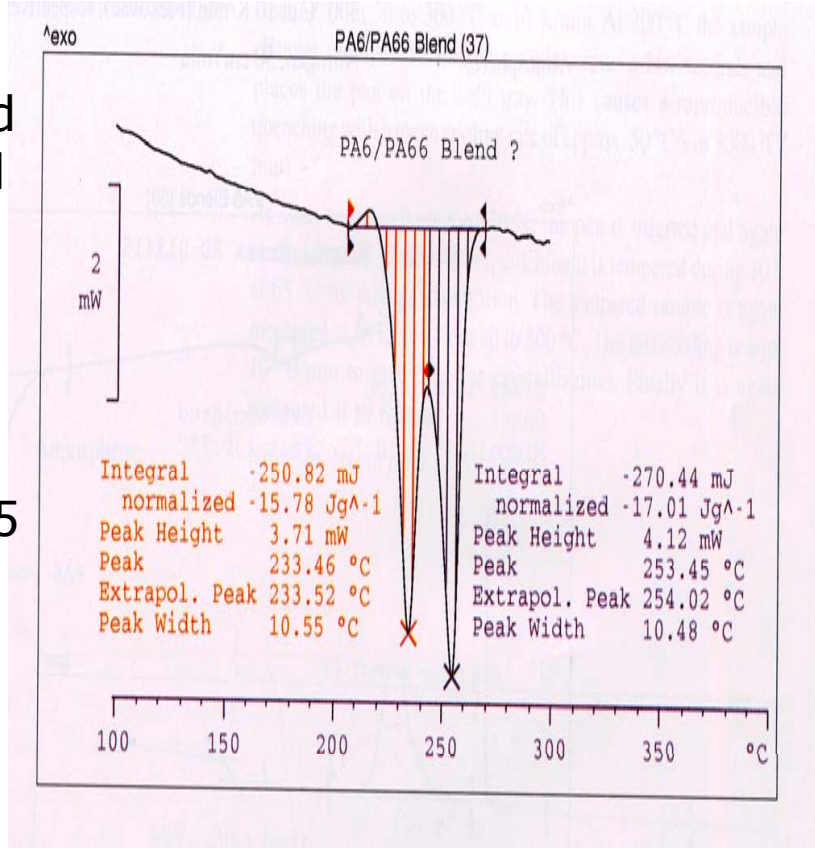
The heat of fusion of PA6 is aprox. 50J/g. Both samples show 20 J/g, therefore their PA6 is aprox 40%. The calculation of the content is automatic when the reference heat of fusion has been entered. In the same way the content of PE in PE/PA6 blend is 59%.



PA6/PA66 Blend

There are two separate melting peaks on the DSC curve that indicate the presence of PA6 and 66. The BL is drawn before the small exothernal pre-melt crystallization peak to get the original heat of fusion.

From the peak areas contents can be estimated if the respective heats of fusion are known. If 45 J/g is assumed to be the heat of fusion for both materials, contents of 35 and 38% would result for the two blends. Some blends with known formulation for serve for calibration to get even more accurate results.

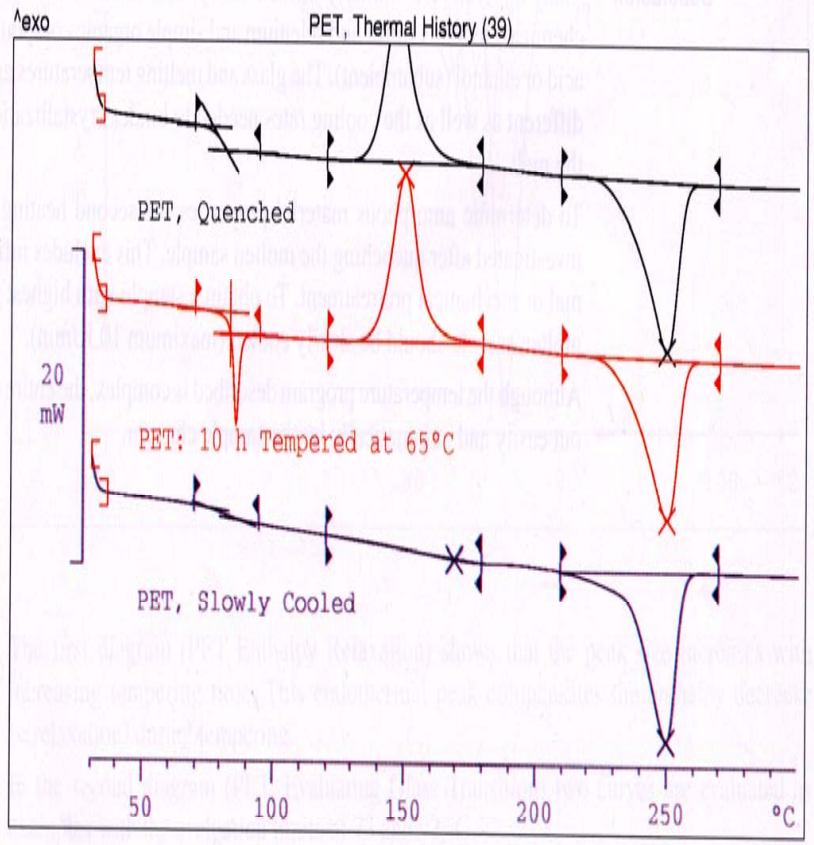


Polyethylene Terephtalate Thermal History

Heating from 30 to 300 at 10K/min quenching with a mean cooling rate of 50ºC/s. When the cell reached 30ºC the pan is heating at 10 K/min. After quenching it's tempered at 65ºC (10h), The tempered sample is again measured at 10k/min from 30 to 300. Finally the sample suffer a slowly cooling

All DSC curves are shown with their initial deflections that are proportional to the sample's capacity. The quenched sample as usual exhibits the ideal shape of the Tg. Tempering at 65ºC causes the relaxation peak. The transition of the slowly cooled sample is less pronounced since a portion of the polymer is now in the crystalline state.

	Quenched	Tempered	Slowly
Tg	76.2	82.7	75.6
H Crys	35.4	34.3	0.1
H fusion	42.3	39.9	39.9
P temp	248.6	248.6	248.6



Polyethylene Terephtalate, Thermal History

Many materials are similarly influenced by their thermal history.

The glass and melting temperature are, individually different as well as the cooling rates needed to hinder crystallization when quenching from the melt.

To determine amorphous material properties the second heating curve should always be investigated after quenching the molten samples. To obtain a samples with highest possible crystallinity, the molten samples should be slowly cooled (10K/min).

Although the temperature program described is complex, the entire experiment can be carried out easily and automatically by the sample changer

any question ?