

## XRD INVESTIGATION OF THERMAL DEGRADATION EFFECT ON SOME COMMERCIAL PET SAMPLES

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**ABSTRACT.** The structural changes of some commercial PET samples, submitted to different thermal treatments, were investigated by XRD method. Rapid cooling of melted samples, leads to partial destruction of the initial local ordered structure. A tendency of polymeric chain to conglomerate into new small crystalline structures is observed. At slow cooling this tendency is accentuated, but the initial ordered structure is almost entirely destroyed.

**Keywords:** PET, thermal degradation, XRD method

### INTRODUCTION

Solid polyethylene terephthalate, (PET), in its solid form, is one of the most popular polymers used for various packaging, often for food products and alimentary liquids as water or soft drinks. It is cheap, easy to produce, and as a container, acceptably maintains the quality of the aliments or liquid within over long periods of time.

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Due to the continuous accumulation of PET wastes, with small rate of recycling, this polymer is one of the most pollutant material produced by the humanity, for what reason the investigation of its potential reuse or recycling is being conducted constantly. At the most basic level, PET bottles are often recycled by grinding and milling into lower grade packing material, or fibers. Dissolving these materials with specific solvents and then repolymerization is possible, but the procedure is not frequently used because it is expensive and takes more effort than simply creating more new material. One of the simples method of destroying or recycling these materials is the thermal degradation, but this process could produces other secondary pollutant products, or can induces irreversible modification of the structure the polymer, avoiding its use for new applications, [1,2]. It is a reason for which the study of the thermal effects on the molecular structure of these materials is important. XRD is a suitable technique for investigation such local ordering modification and can offer information concerning the reuse of these materials, [3].

## **EXPERIMENTAL**

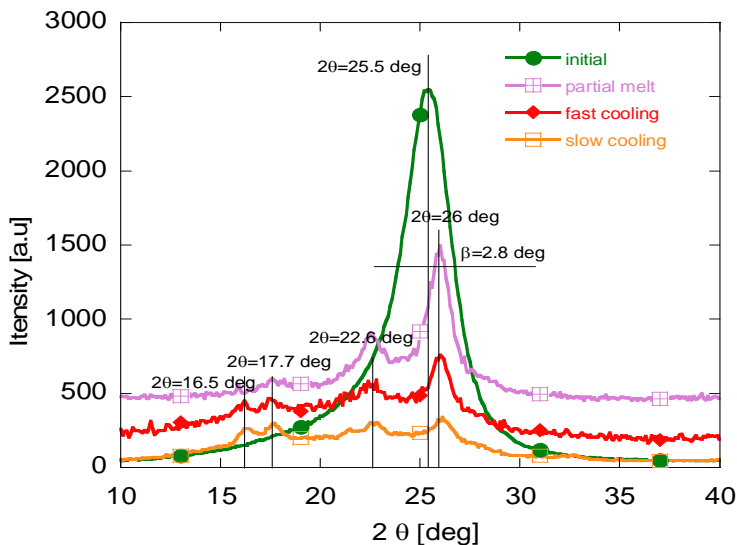
We used for ours investigation small square pieces, with the dimensions 20x20 mm and the thickness about 0.3 mm, taken off from commercial PET water bottles. The samples were heated progressively on aluminum plate, up to 300°C, until an even melt was obtained. Once the samples were completely melted, there were maintained at this temperature 1-2 minutes for homogenization. We did not leave samples on for much longer, to prevent decomposition of PET chains. After that the samples were cooled. The crystallization of PET is greatly affected by cooling rate, and we wished to investigate this effect as well. To facilitate this, we employed two simple cooling methods. The first was to take off the plate with the melt from the heating system and leave it in open air, at room temperature, to cool progressively by passively convection. This process takes approximately 3 minutes. For further discussions we refer this as the slow cooling process.

The second cooling procedure, referred as fast cooling, was achieved by immersing rapidly the melted sample in cold water. This cooling process is estimated to take about 2-5 seconds. Using this procedure, all samples remain transparent and flexible, mostly in amorphous phase, without crystallization.

The X-ray diffraction was performed with Bruker X-ray diffractometer, with  $\text{Cu K}\alpha$   $\lambda=1.54 \text{ \AA}$ , at 45 KV and 40 mA. The  $2\theta$  range of  $10\text{--}40^\circ$  was recorded, within  $0.1^\circ$  resolution.

## RESULTS AND DISCUSSION

Generally the polymers are known as amorphous materials due to the disordered arrangement of the chains, [4, 5]. However, some times, parts of different neighboring chains, or different parts of the same chain, can adopt a parallel local arrangement, giving a local ordered character to the sample. This situation is called crystalline phase.



**Fig. 1.** The XRD data recorded for PET in initial state, partially melted, melted and fast cooled, melted and slow cooled.

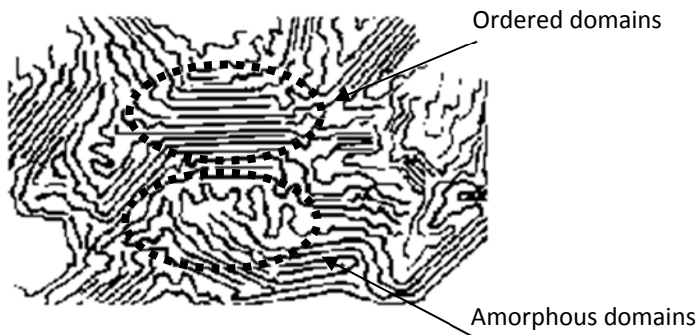
The crystallization is determined by the particularities of polymerization process or by the action of different external factors, as the heating-cooling process. In function of the amount of crystalline phase, we speak about crystalline, semi-crystalline or amorphous polymers. The distance between the parallel portions of the polymeric chains, in the crystalline phase, is of the same order of magnitude as the inter-planar distance of solid crystals, and behaves in the same manner as a solid crystal, when they are investigated by XRD method. It is the reason for which XRD can be successfully used for structural polymeric investigation. From the diffraction theory we can calculate the inter-planar distance with the Bragg equation:

$$d = \frac{k \cdot \lambda}{2 \sin \theta} \quad (1)$$

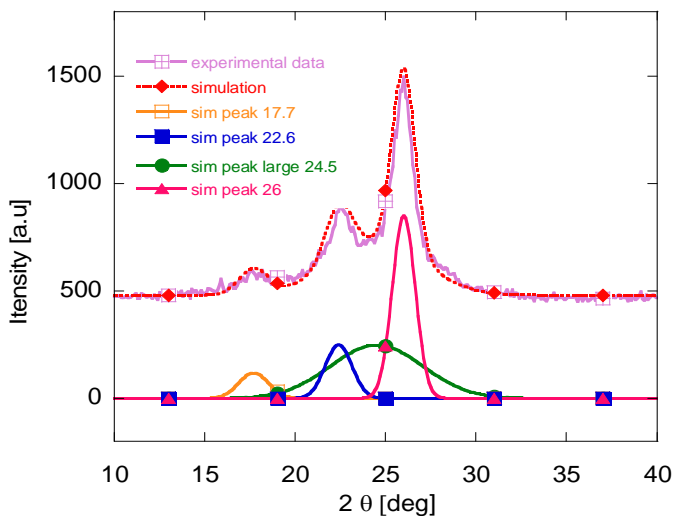
where  $k$  is the diffraction order and  $2\theta$  is the diffraction angle. The area  $S$  under the diffraction peak is proportional with the concentration of the ordered domains in the sample, [6-9].

In native state, the PET is a semi-crystalline polymer, containing both the amorphous and crystalline phase, [10]. This affirmation is confirmed by the XRD pattern of the PET sample before any heating process. The spectrum contains a high peak centered at the diffraction angle  $2\theta = 25.5^\circ$ , with a great area. That corresponds to a large fraction of the polymeric chains, in parallel arrangement, with the inter-planar distance  $d=3.48\text{\AA}$ . However the peak is not narrow, (like in the case of the solid crystals), it is large, with the half line width  $\beta = 2.8^\circ$ , between  $2\theta = 23.9^\circ$  and  $26.7^\circ$ , (Fig. 1). That shows a dispersion of the inter-planar distances between  $d_1=3.33\text{\AA}$  and  $d_2=3.74\text{\AA}$ . That shows that the sample contains many ordered domains with parallel arrangement of the chains, with inter-planar distances ranging between  $d_1$  and  $d_2$ . Outside these crystalline domains, the polymeric chains are in the amorphous phase. A simplified sketch of such structure is presented in figure 2. The amorphous phase leads to the broadening of the spectrum.

The crystallinity of a PET is greatly dependent on the thermal treatment, especially the heating-cooling rate, [2, 11]. The heating process increases the dynamics of the polymeric chains, which have the tendency to disengage from the ordered arrangement and become freely.



**Fig. 2.** Schematic representation of the semicrystalline polymer.



**Fig. 3.** Simulation of the experimental XRD data for PET partially melted.

As result, the fraction occupied by the crystalline phase into the whole sample decreases. Moreover it is possible that new nucleation centers appear in the sample, giving rise to new ordered domains, generally with different inter-planar distances and different sizes. Consequently the XRD spectrum changes. We can see this effect for partially melted samples, (Fig. 1). The XRD spectrum of these samples contains three peaks, at  $2\theta = 26^\circ$ ,  $22.6^\circ$  and  $17.7^\circ$ . The first peak at  $26^\circ$  is the correspondent one of the high peak at  $2\theta = 25.5^\circ$  of the unheated PET, but its amplitude is reduced and it shifts towards higher angles. That means that the initial ordered phase of the polymer, responsible for the peak  $2\theta = 25.5^\circ$ , occupies smaller fraction into the partially melted samples, and becomes more compact, with smaller inter-planar distance,  $d=3.42 \text{ \AA}$ . The new peaks at  $2\theta = 22.6^\circ$  and  $17.7^\circ$  indicate the apparition of new crystalline domains, with greater inter-planar distance. Theirs small amplitude shows only small fraction occupied into the sample. The fractions occupied by each ordered structure are proportional with area of the peak. To calculate these parameters we simulated the spectrum using Gaussian function for each peak.

$$f(\theta) = A \exp \left[ -\frac{(\theta - \theta_0)^2}{\beta} \right] \quad (2)$$

There  $\theta_0$  is the diffraction angle of the maximum of the peak and  $\beta$  is the half line width. The result of simulation, for the partially melted sample, is shown in figure 3. The parameters of the simulation are listed in Table 1. In this table S denotes the area under each peak,  $S_{\text{tot}}=3635 \text{ a.u.}$  is the area of the entire spectrum,  $d$  is the inter-planar distance corresponding to the maximum of the peaks and  $S/S_{\text{tot}}$  represents the fraction of the crystalline phase corresponding to each peak into the entire sample. The simulation shows also the existence of a broad peak, centered at  $2\theta = 24.5^\circ$ , superimposed over the main three peaks. This peak corresponds to the completely disordered phase which appears into the polymer after the melting.

In the un-melted sample this peak is difficult to be seen because it is hidden by the high peak at  $2\theta = 25.5^\circ$ . However it exists and enlarges the whole spectrum.

**Table 1.**

$2\theta_0$ [deg]	$\beta$ [deg]	S [a.u.]	S/S <sub>tot</sub> [%]	d [Å]
17.7	1.3	240	6.61	5.01
22.6	1.1	464	12.76	3.96
26	0.8	1347	37.06	3.42
24.5	1.3	1584	43.57	3.62

As the sample become to melt, the initial crystalline phase diminishes in the detriment of the amorphous phase, but additionally new small crystalline domains, designed by the peak at  $2\theta = 22.6^\circ$  and  $17.7^\circ$ , appear. When the samples are completely melted and then cooled, the situation is different. The degree of crystallinity is noticeable in the sample depending on whether it's opaque or transparent [2]. At fast cooling rate we can see a drastic decrease of the intensities of the peaks at  $2\theta = 22.6^\circ$  and  $26^\circ$ , small increase of the peak at  $2\theta = 17.7^\circ$ , and the apparition of a new peak at  $2\theta = 16.5^\circ$  (Fig. 1). That means massive destruction of the initial crystalline phase and the apparition of new centers of crystallization with higher inter-planar distance. At slow cooling rate, the decrease of the intensities of the peaks at  $2\theta = 22.6^\circ$  and  $26^\circ$  is more pronounced than in the case of fast cooling, but the peaks at  $2\theta = 17.7^\circ$  and  $16.5^\circ$  appears more clearly into the spectrum. That means intensification of the degradation of the initial crystalline phase and accentuation of the tendency of the polymeric chains to form new small ordered domains. To explain this behavior we must take into account the fact that the crystallization process takes time to spread from nucleation centers towards the amorphous places. At fast cooling rate the polymeric

chains have not enough time to disengage completely from the ordered domains that result in the persistence of an important proportion of ordered phase. However a great fraction of the chains have enough time to escapes from the ordered phase and become free. The result is the growing of the amorphous phase. A small fraction of them have enough time to conglomerate into new small ordered domains, responsible for the new peaks at  $2\theta = 17.7^\circ$  and  $16.5^\circ$ . At slow cooling rate, the polymeric chains have enough time to disengage from the ordered domains, determining almost complete destruction of the initial ordered phase. The intensity of the peak  $2\theta = 22.6^\circ$  and  $26^\circ$  decreases considerable. On the other hand, the chains have more time to self assembling in the new ordered domains, that explains the refinement of the shape of the peaks at  $2\theta = 17.7^\circ$  and  $16.5^\circ$ .

## CONCLUSION

The thermal degradation of commercial PET was investigated by XRD method. The initial samples, before any heating process, have a semi-crystalline structure dominated by the crystalline phase. The XRD spectrum shows an intense peak at  $2\theta = 25.5^\circ$ . The structure of the samples changes in function of the thermal treatment. In the partially melted samples the fraction of the amorphous phase increases in the detriment of the ordered phase. Moreover the inter-planar distance of the crystalline phase decreases and new crystallization centers becomes to appear. At fast cooling rate the fraction of the initial crystalline phase decreases again and the tendency of crystallization in new domains is accentuated. At slow cooling rate, the initial ordered phase is almost completely destroyed, the amorphous phase is dominant, and the tendency of crystallization in new centers appear more clearly. As final conclusion we can affirm that changes of local structure of the PET depend strongly on the particularities of heating-cooling process.



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