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Characterization of poly(ethylene terephthalate) used in commercial bottled water

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Abstract. The aim of this study is to determine which compounds are present into drinking water packaged in poly(ethylene terephthalate) bottles and to know the origin of these substances in relationship with the material.

A screening procedure was established for the detection of unknown compounds into bottled water. A panel of water bottles has been tested after exposure to extreme conditions of temperature and UV radiation to accelerate the possible migration of substances.

At the same time, physico-chemical characterization of polymeric material has been performed namely calorimetric analysis, IRTF and low-frequency mechanical spectroscopy. The results thus obtained allow understanding in a better way the migration kinetics of molecules inside the polymer, it means the pollution of the bottled water.

1. Introduction

Poly(ethylene terephthalate) (PET E) is a polyester used in a wide number of applications. Its chemical inertness and physical properties made it particularly suitable in food packaging applications especially in beverages and drinking water [1]. Indeed, PET E packaging combines adequate gas barrier properties for the retention of carbonation with a glass like transparency, light weight and good recyclability.

The most common process to produce PET E involves the polycondensation of dimethyl terephthalate and ethylene glycol with antimony (Sb), germanium or titanium based catalyst [2]. Sb catalysts are used in 90% of the worldwide production of PET E [3]. Several studies have shown the presence of compounds not expected *a priori* in bottled water, sometimes in non negligible concentrations. Acetaldehyde, a thermal degradation compound formed during the polymerization reaction and the hot step process in the bottle water manufacture, has widely been reported in PET E packaged water [4]. Formaldehyde and acetone have also been detected in some cases [4, 5]. Sb in commercial PET E bottled water was found after the exposure to different conditions of temperature, storage and sunlight [3, 6]. Substances relative to additives used in the plastic material processing have been reported [7, 8] in water packaged in PET E.

The origin of several substances is not clearly established and remains controversy. One of the possible sources is the diffusion of constituents from PET E to water, namely (i) monomer, (ii)

catalyst, (iii) additives or degradation products formed in the manufactures or a long storage of the bottle, (iv) the impurities contained in the starting substances or additives [9] and (v) the polyethylene (or polypropylene) caps of water bottles.

2. Aim of the work

The aim of our study is twofold: on one hand to study the effect of physical properties of the packaging material (caps and bottles) on the presence of substances from it to water. Such a physical characterization was performed to determine crystallinity ratio, the glass transition temperature (T_g), the vibrational spectrum of PET E assessed by IR spectroscopy and the nature of bottles caps, generally polyethylene (PEHD) or polypropylene (i-PP).

On the other hand, a screening analytical method was designed to identify unknown compounds in water. In order to accelerate the diffusion of compounds, a panel of commercial water bottles was subjected for 15 days at 65°C (equivalent to an exposure between $300 < t < 700$ days [10]) and UV radiation dose of 9 hours (1.7 W/cm^2).

3. Materials and techniques.

The techniques employed for chemical and morphological characterization are presented.

3.1. Sampling

Some brands of French market PET E plastic drinking water was purchased in a local shop. The bottle water panel was selected according to visual parameters like bottle color, volume, thickness of plastic material and type of water like non-carbonated or carbonated water. Some PET E bottles containing carbonated water are of the multilayer type: a functional barrier (usually PA-6) is placed between two PET E layers. In this case, only the PET E in contact with water was tested.

3.2. Water analysis

3.2.1. Screening method for water samples

The accelerated conditions test was carried out in a steamroom APT.line™ KBF-ICH (BINDER, Germany). Several water extraction methods were performed to extract a large number of substances from water. Dichloromethane was used for the liquid-liquid extraction (LLE) and the elution of solid-phase extraction (SPE) cartridges (Oasis HLB, Waters) was carried out in ethyl acetate. Analyses were run on a Varian 450-GC Gas Chromatograph connected to Varian 240-MS Ion-Trap Mass Spectrometer. The GC-MS was equipped with an autosampler COMBIPAL (CTC Analytics AG, Switzerland). The separation column was a Restek Rxi5MS capillary column, $30 \text{ m} \times 0.25 \text{ mm}$ i.d., $0.25 \mu\text{m}$ film thickness. A IP deactivated guard column Restek $5 \text{ m} \times 0.53 \text{ mm}$ was placed before the separation column. Extracts of water samples were analyzed in the full scan mode and the mass spectral were identified by comparison with a conventional NIST MS Library Search (The National Institute of Standards and Technology Mass Spectral Library, version 2.0).

3.3. PET E bottles

3.3.1. IRTF spectroscopy

IRTF spectroscopy was carried out in order to determine the nature of polymer material and its structural state. Spectra were performed on a Nicolet 460 Spectrometer E.S.P. Each spectrum was obtained with a resolution of 4 cm^{-1} . Sample preparation (few μm thick) was achieved by mechanical polishing of PET E cuts of stretched parts of the water bottle.

3.3.2. Differential scanning calorimetry (DSC)

The crystallinity ratio and the glass transition temperature of PET E samples were assessed *via* calorimetric measurements using a Setaram DSC-131 instrument. Specimens (few mg) were heated from 20°C to 350°C at 10°K/min. The crystallinity ratio was determined according to, $(\Delta H_f - \Delta H_c)/(\Delta H_f^0)$, where: $\Delta H_c, \Delta H_f$ are the heats of crystallization and of melting of the specimen, respectively. ΔH_f^0 is the melting heat of the PET E ideal crystal: 140 J/g [11]

4. Results and discussion

The IR spectra exhibited PET E commercial bottle is displayed in Fig. 1.

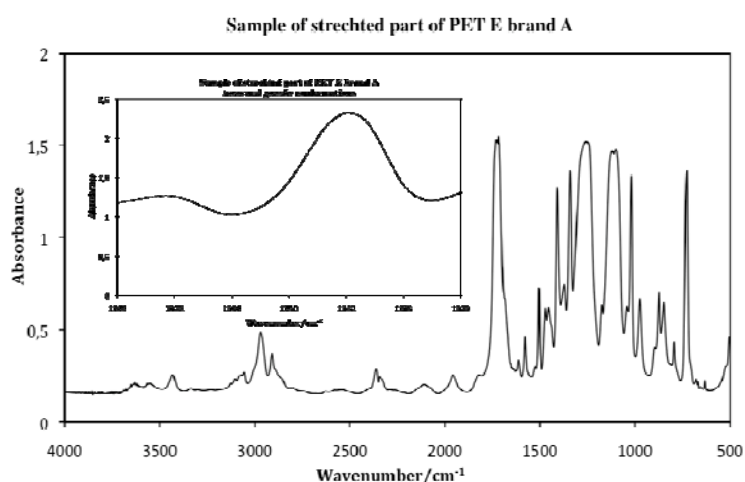


Figure 1. Infrared spectrum of the stretched part of a PET E bottle. The characteristic bands at 1340 cm⁻¹ and 1370 cm⁻¹ are shown in the insert.

Chemical additives present as traces and related to polymer or bottle manufacture are not observed. But these traces and degradation products could migrate from bottle to water. Thus, analytical methods allowing the detection of these substances into water with low detection limits (down to µg/l) were developed. To yield this goal, a screening analytical method was designed and the separation and identification of these compounds is in progress.

Nevertheless, the characteristic bands at 1340 cm⁻¹ and at 1370 cm⁻¹ are clearly observed. These bands correspond to the wagging mode of ethylene units in *trans* conformations and *gauche* conformations respectively [12]. The *trans* form is made more favorable by crystallization and stretching, while the *gauche* conformations are characteristic of the amorphous state [13].

Results of DSC measurements are displayed in Fig. 2. It is shown that the bottle neck was practically amorphous with a crystallinity ratio not exceeding 14% and a glass transition temperature T_g of 72°C *e.g.* typical value of PET E [14]. In addition, the absence of the exothermic peak on heating confirms the crystallization of PET E in the stretched part of the bottle due to the blowing process. As an example, Table 1 shows the crystallinity ratios found in two brands of commercial bottles in PET E. Also, it is obvious that this technique is not sensitive enough to determine the T_g of the semicrystalline part of the bottle. Low frequency mechanical spectroscopy (LFMS) experiments are in progress to determine this value which is 10°C higher in semicrystalline PET E comparing to the amorphous state. First results (not shown here), indicate that a structural relaxation appears near 40°C with a module shear decrease about 20%. This effect is not present on the second heating run. The T_g at 88°C is clearly revealed with a drastic module shear decrease. LFMS is a very sensitive method to characterize the dynamics of molecular motions in the polymer. This point is particularly attractive because these motions are suspected to make the molecule diffusion faster in the polymer.

The nature of the caps for two brands of bottles is also shown in Table 1. The identification was possible due to a large difference of the melting points of PEHD and i-PP: 120-130°C and 150-175°C,

respectively [15]. Results revealed that the nature of caps depends on the type of water stored in the bottle.

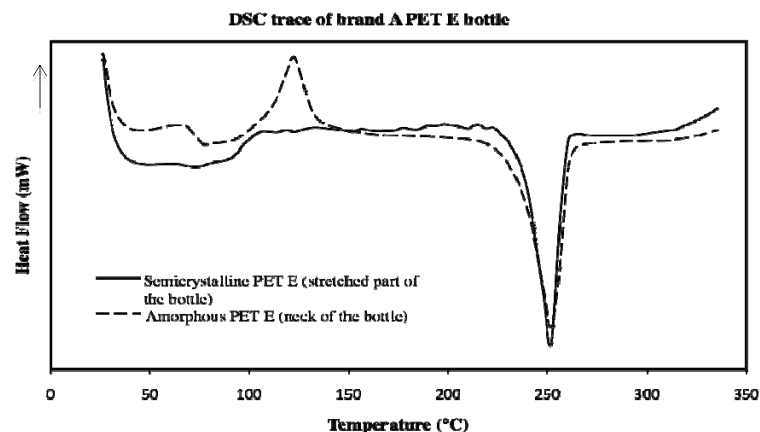


Figure 2. DSC analyses of the stretched part and the neck of a PET E bottle.

Table 1. Crystallinity ratio and nature of caps in two commercial PET E water bottles.

Water Bottles	Type of water	Bottle Layers	Crystallinity ratio (stretched zone)	Nature of caps (melting temperature)
Brand A	Carbonated mineral water	PET E-PA-PET E	31%	i-PP (174°C)
Brand B	Non-carbonated water	PET E	21%	PEHD (125°C)

5. Conclusions and Perspectives

The physical characterization of PET E in commercial bottles of drinking water is important to explain the interaction of packaging with water. The blowing process during the bottle manufacture induces the polymer crystallization by stretching. DSC measurements shown the crystallization ratios between 20 to 30% in the stretched part of the bottle tested, but are not able to reveal the orientation of these crystals. The X-ray scattering (SAXS and WAXS) will be carried out to characterize more in detail the structure and arrangement of PET E polymeric chains in the bottle.

Using the screening method in bottled subjected to extreme conditions, several substances relative to additives have been found in water. The confirmation of their presence and quantification of these substances is in progress. Also, it is necessary to determine the relative roles of the bottle (PET E) or caps (PEHD or i-PP).

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