Image analysis as a useful tool for fast detection of dimensional and structural changes of poly(ethylene terephthalate) containers

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Abstract

The aim of this paper is to present image analysis as a useful technique for fast, reliable and non-destructive detection of dimensional and structural changes in polymers. The possibility of applying image analysis was demonstrated in the case of solvent-induced crystallization of poly(ethylene terephthalate) (PET) containers filled with commonly used organic solvents: chlorobenzene, isophorone, xylene, Espesol, Shellsol A 100, Solvesso 150, propylene glycol, glycerin and water and subjected to the storage stability test at 54 °C for 14 days (CIPAC 1-MT 46.1.3). In addition, the obtained results were analyzed using one-step analysis of variance (ANOVA) combined with the Duncan's statistical test ($p<0.05$). According to the achieved results, three main impacts of the presented paper could be distinguished: 1) dimensional and transparency changes could be precisely followed by image analysis in both following cases: for small changes in water, as well as for significant ones in chlorobenzene; 2) a correlation between the changes in the degree of crystallinity and transparency could be obtained without the continuous material testing by DSC; 3) image analysis is potentially applicable for assessment of other crystalline polymers.

Keywords: *image analysis; fast detection; ageing; solvent diffusion; poly(ethylene terephthalate)*

1. INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most widely used polymeric materials [1,2]. It is cheap, easy to process, has an extraordinary clarity, and is presumed to have barrier properties that are sufficient for most packaging applications. Due to its common use as a beverage packaging material, the main focus has been on its food packaging properties. Still, PET packaging is not only limited to food packaging and nowadays many other products are packed in PET containers, such as pesticides, cosmetics, household products, etc. However, many products contain diverse, mainly organic solvents. Therefore, numerous investigations have focused on the possible migration of various chemical species stored in PET packaging into PET containers [3]. For example, Plotan *et al.* showed that endocrine disruptors, alkylphenyls and phthalates were partly leeching from PET containers [4]. Further, Dombre *et al.* found out that permeability of volatile organic compounds affects properties of the virgin and recycled PET (e.g. thermal, crystallinity, oxygen and carbon dioxide barrier properties) [5]. Welle and Franz investigated diffusion of low molecular weight molecules in PET bottles in order to define basic parameter set for migration modeling of PET and found that the key parameters for more realistic migration modeling are activation energies of diffusion in the polymer [6]. Additionally, organic solvents could influence barrier properties of the PET packaging. In cases when a significant amount of organic solvent penetrates into PET, swelling occurs followed by the increase in the polymer chains mobility that further increases diffusion coefficients of the penetrant [7,8]. Bearing in mind that PET can be crystalline up to 60 %, its permeability toward gases and liquids and corresponding diffusivities can be significantly influenced by the degree of

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crystallinity [9]. In the case of contact of crystallizable polymers and small molecules that can diffuse into that material, so called solvent-induced crystallization can take place [10-12]. As a result of solvent transport through the polymer, crystallization occurs in different phases of the process. In the beginning the amorphous regions undergo reorganization, forming small crystallites, and further transforming to lamellar zones that eventually lead to well defined crystalline regions [13].

The described structural changes in polymeric packaging can have many negative effects on its use, recycling and processability. The most important of these negative effects refer to the lowering of the barrier properties of PET packaging and narrowing the possibilities for its recycling and reuse. Worsened barrier properties can threaten the storage stability of the packed products. Beside the significantly shortened shelf lifetime of the product, this can also cause numerous harmful effects on humans as well as the environment in general. In addition, the EU plastics industry and the leading plastics federations have defined Plastics 2020 Challenges, recognizing the recycling and reuse of plastics as one of the main challenges [14]. Determination of the quality of the used plastic packaging became important for further processing possibilities in order to help doubling the recycling rate of plastic packaging.

Therefore, it is necessary to find a fast method to check whether there are changes occurring in the packaging itself. At the same time, this method has to be precise and capable to evaluate if any individual container is prone to failure during the storage time of its content or its appropriateness for recycling/reuse at the end of its service life. As the modern industry of polymer packaging deals with mass production and a huge number of items, a cost-effective approach to the described analysis is another important demand [15].

Structural changes in polymers, especially changes in crystallinity may be detected by several techniques, such as scanning electron microscopy (SEM), wide-angle x-ray diffraction (WAXD), differential scanning calorimetry (DSC), optical microscopy, Fourier-transformed infrared spectroscopy (FTIR), *etc.* [16,17]. Some of these methods are costly and time-consuming, especially when the number of samples to be investigated is high. On the other hand, image analysis is a fast and convenient method which could be used to follow structural changes in polymers.

The purpose of image analysis using Image Pro Plus (Media Cybernetics) is to obtain a quantitative description of an image if morphological characteristics can be attributed to the properties of the object studied. It can be applied in various areas of science – materials science, coatings, metallurgy, polymers, semiconductors, textile/fibers, cables and connectors, *etc* [18,19].

Signals that are collected by the visual unit (e.g. a camera) can be processed to compare and analyze various object characteristics, such as a maximum and minimum radius, characteristic angles, different areas, roundness levels of hue and saturation, and many others. This method can be of great value when performing repetitive tasks, in particular in areas where a certain visual parameter can be a measure of quality of the entire product. In these cases, fast and accurate image analysis can be performed automatically to eliminate bad products or divide products into various quality categories. It can also be applied online at the production line, so the quality of the product is assured during production. Such systems have been already reported in the food industry, e.g. in the production of cereal flakes [20] and industrial snack food processes [21]. Although less prominent, image analysis has proven to be successful in polymer beads analysis [22], offering a simple and inexpensive way to obtain useful results. Also, on the industrial level, dimensional deviations of poly(ethylene terephthalate) bottle cups have been assessed using the analysis of a cup image. Each cup with a dimension deviation that is above the determined standard would be removed instantly by the air waft. The rate of such analysis is very high so that around 500 items can be checked per minute.

The main goal of the present paper is to demonstrate image analysis as a useful tool for fast detection of dimensional and structural changes in polymers, such as in the case of solvent-induced crystallization in PET containers. Transparent PET containers were filled with commonly used organic solvents: chlorobenzene, isophorone, xylene, Espesol, Shellsol A 100, Solvesso 150, propylene glycol, glycerin and water, in order to evaluate changes that occurred during the storage stability test. Structural changes, detected by image analysis, were confirmed and analyzed by DSC to examine the degree of crystallinity in the affected zones. The essence of the research was to speed up characterization of huge number of samples by eliminating DSC measurements from the sample analysis on the industrial level. In addition, one-step ANOVA combined with the Duncan’s statistical test ($p<0.05$) was used to identify the most significant parameters.

2. EXPERIMENTAL

2. 1. Materials

Poly(ethylene terephthalate) (PET poly JADE, China, Brand „CZ 302“ Container grade polyester chips) was used to produce 50 mL containers (90 x 28 mm) by injection molding on an ASB 50 injection molding unit (at Hemotehna PET Plant, Subotica, Serbia). The organic solvents, applied in this investigation, were: chlorobenzene (Sigma-Aldrich, USA, *p.a.*), 3,5,5-trimethylcyclohex-2-en-1-one (Isophorone, Brentag, Belgium, *p.a.*), xylene (J.T. Baker, USA, *p.a.*), Espesol (Charter Oil Co., USA) - a mixture of aromatic compounds, Solvesso 150 (Tonengeneral Sekiyu K.K, Japan) – a mixture of aromatic compounds, Shellsol A 100 (Shell Chemicals, Netherlands) - a mixture of aromatic components, propylene glycol (Merck, Germany) , glycerin (Merck, Germany) and distilled water. The sample labels and significant physical and chemical parameters of the applied solvents are presented in Table 1.

2. 2. Storage stability test

Empty containers or ones filled with organic solvents and water were closed and sealed with high-density polyethylene (HDPE) caps, after which they were subjected to the storage stability test (CIPAC 1-MT 46.1.3). According to the method, all the investigated containers were kept at 54 °C for 14 days, which simulates 2 years of shelf life. After 14 days, the containers were cooled to the room temperature, opened and the content was removed. The empty containers were left at ambient temperature without any washing to dry to the constant weight.

2. 3. Image analysis

Images of the samples were acquired by using a NIKON D80 digital camera with the maximum resolution of 10.3 MPixels. The distance between the camera and samples was set to 30 cm, with a 50 cm focus, using a flash against a non-reflecting black background. Each container was photographed in two different positions. Frontal pictures of the entire container bottle were taken before and after the storage stability test in order to establish dimensional changes. In addition, the container bottom was photographed before and after the experiment to establish the amount of non-transparent areas that were not present in the sample before the storage stability test.

Table 1: Sample numbers and significant physical and chemical parameters of the applied solvents [23,24]

Sample number	Solvent	Density, g/cm^3	Boiling point, ^{0}C	Vapor pressure at 20 ^{0}C, Pa	δ / SI (J/m^3)$^{1/2}$·10^{-3} (type of interactions)	δ / (cal/cm^3)$^{1/2}$
1-6	Empty container	-	-	-	-	-
7-12	Water	1.00	100	2300	47.9 (strong H bonding)	23.4
13-18	Chlorobenzene	1.11	132	1173	19.4 (poor H bonding)	9.50
19-24	Espesol	0.900	169	200	16.8 (poor H bonding)	-
25-30	Isophorone	0.923	213	26.6	18.6 (medium H bonding)	9.10
31-36	Shellsol A 100	0.868-0.885	155-185	210-1300	18.1 (poor H bonding)	-
37-42	Xylene	0.864	138.5	900	18.0 (poor H bonding)	8.80
43-48	Solvesso 150	0.900	178	100	17.4 (poor H bonding)	-
49-54	Propylene Glycol	1.04	188	0	25.8 (strong H bonding)	12.6
55-60	Glycerin	1.25	182	130	33.8 (strong H bonding)	16.5
	PET				21.9	10.7

The obtained images were then processed using Adobe Photoshop CS3, and saved as .tiff and .jpg format images. In order to determine the transparency level of the containers before and after the storage stability test, these images were analyzed by Image Pro plus 4.0 software (Media Cybernetics, Serbia).

In order to measure dimensional changes of containers during the storage stability test, an image of the container contour of a virgin sample (that was not subjected to the storage stability test) was acquired by using Image Pro Plus, and 30 points on the contour were selected. The reference points were chosen at equidistant lengths on the contour, except at some places where it was considered important to measure any potential difference (*e.g.* points on contour curvatures). By superposing images of containers that were subjected to the storage stability test, contour differences with respect to the virgin container could be assessed and measured at the reference points. This protocol was repeated for all the samples, and their contours were compared to the virgin sample contour by establishing a reference point in the middle of the container contour height and measuring the difference of all the other points from the virgin contour (Figure 1).

As mentioned before, after the storage stability test some parts of the bottom developed non-transparent areas, which may be connected to a change in the degree of crystallinity of the sample. To define the observed changes on the container bottom, characteristic parameters (the perimeter and the area of the object of interest, roundness, area of the bottom and the area of the changed transparency at the bottom) were determined by the tools in the program Image Pro Plus. An object of interest is defined as a part of the container bottom with changed transparency.

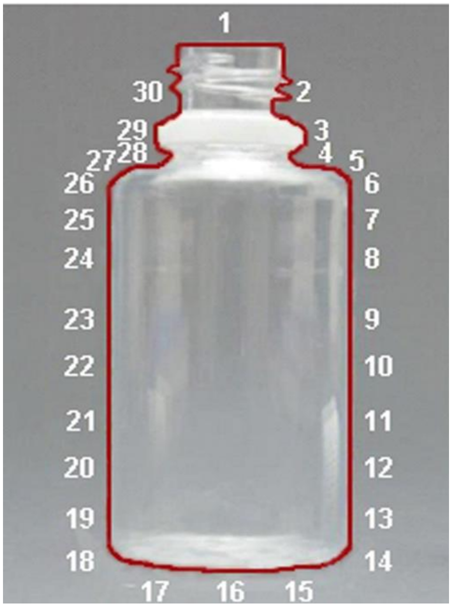

Fig. 1. Reference points on the sample bottle

Measurement starts with projected two-dimensional area. The area of the container bottom with changed transparency, A, is usually expressed in µm^2 and calculated as the sum of the areas of each individual pixel a_p, within the borders [25]:

$$A = \Sigma a_{\mathrm{p}} \quad (1)$$

The perimeter of the changed transparency, *P*, is defined as the total length of the object boundary, most often expressed in µm. It is calculated from the Cauchy-Crofton equation [25]:

$$P = \frac{\pi}{N}\sum_{\alpha}^{\pi} I_{\alpha} d_{\mathrm{L}} \quad (2)$$

where *I* is the number of intercepts formed by a series of parallel lines with the spacing d_{L}; *N* is the number of directions, from α to π.

Roundness (R_{d}) is defined as:

$$R_{\mathrm{d}} = \frac{P^2}{4\pi A} \quad (3)$$

where *P* is the perimeter (the total length of the defined object boundary); *A* is the area of the object of interest. A perfect circle has R_{d} value of 1, while larger values indicate deviation from the perfect circular shape.

A distance filter was used to select an area containing white zones at the bottom of the container. This filter enables the distinction between white and dark parts of the image and to clearly see the area affected by the changes that occurred in the material. This transformation was applied to every image with a typical result presented in the sample image in Figure 2 (middle). Transparency levels were measured by choosing six points at each base of the container and measuring the whiteness level at each point before and after the storage stability test. As the images were taken against a black background, the fully transparent part of the container is 100 % black in the image, while an increase in the whiteness level is a direct measure of the transparency decrease.

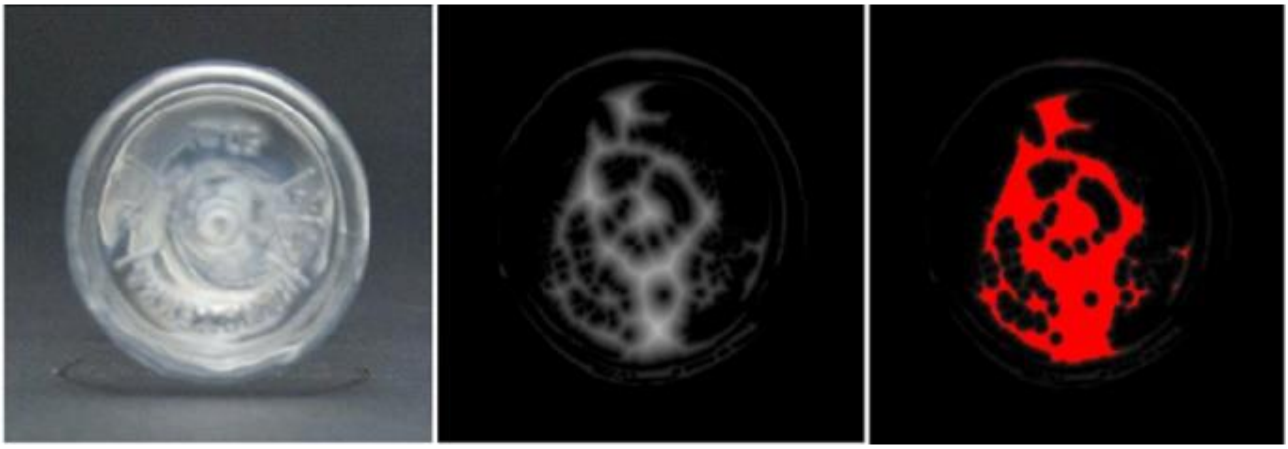

Fig. 2. The image of the container bottom (left), the container bottom after the application of the distance filter (middle) and the area of interest marked in red (right) (solvent: xylene)

The resulting image was then transformed to a 256 gray level image wherein the threshold function was used to extract the affected area (the area of interest). In most systems, grayscale is defined by the intensity of white light [23]. An intensity value of zero indicates absence of white light; hence, it is black. Likewise, a value of 255 indicates a white light of the highest intensity. The edge of an object of interest was defined by a threshold. Here, the intensity value of the background of an image was measured as 0 ("black") and the threshold was chosen to be 90 % (26) ("dark gray"). So, anywhere in the field of view where the pixel intensity value exceeded 26 was considered as the edge or interior of an object. The area of interest, which included all gray zones wherein the pixel intensity was above the threshold, was marked red (Fig. 2, right).

2. 4. Differential scanning calorimetry

DSC curves were recorded using a Perkin-Elmer PE II in the temperature range 50-180 °C under a nitrogen flow of 26 mL min^{-1} at the heating rate of 10 °C min^{-1}. Samples for DSC measurements were taken from the container bottom by cutting the areas of interest (15-20 mg) and put in an aluminum pan.

2. 5. Data analysis

All experimental data of non-transparent zones at the base of containers (roundness, object area, area with changed transparency), transparency, grayness and degree of crystallinity were analyzed using the statistical package for social sciences, version 20 (SPSS Inc., Chicago, IL, USA). The obtained results are presented as mean values of sixty samples for each solvent ± SD (standard deviation) and further subjected to one-way analysis of variance (ANOVA) in order to determine differences between multiple means in continuous variables. Statistical significance was set at $p < 0.05$. For those parameters for which the significance of mean values differences by samples is found, the Duncan test was used for *post hoc* analysis.

3. RESULTS AND DISCUSSION

Changes in the PET containers that were subjected to the storage stability test were monitored by using image analysis. The basis for this monitoring was a change in the container's mass, their shape and transparency.

The initial masses of all the containers were 12.05 ± 0.05 g. After the end of the experiment they were measured to evaluate any possible change of mass, after which they were analysed by one-step ANOVA. The obtained results are presented in Figure 3.

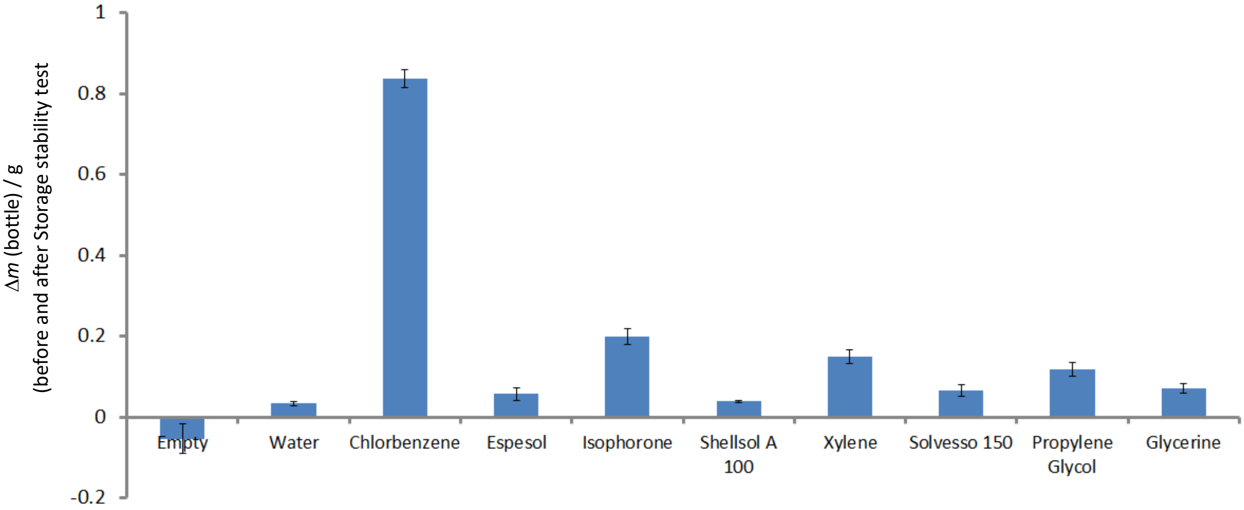

*Figure 3**.** The mass change of PET containers after the storage stability test compared to the reference bottle (no solvent). Mean deviations that were under the 0.01 % are also presented but are too small to be seen*

It was found that the mass change for the containers filled with water was very small showing that the amount of water penetrating into the material was negligible (Δm = 0.033±0.005 g). When organic solvents were present, the results were somewhat different. All organic solvents used in the experiments penetrated into the PET containers. Masses of the corresponding containers were higher than the initial ones in all cases, wherein the most significant mass increase was noticed in the cases of chlorobenzene (Δm = 0.837±0.022 g), isophorone (Δm = 0.199±0.019 g) and xylene (Δm = 0.15±0.017 g).

Diffusion of chlorobenzene and isophorone into the bottle material can be explained based on the solubility parameters shown in Table 1. It is well known that two substances are miscible if their values of the solubility parameter δ are close to each other. Values of the solubility parameter δ of chlorobenzene, isophorone and xylene are similar (9.5, 9.1 and 8.8, (cal/cm^3)$^{1/2}$, respectively) and also are not far from the solubility parameter corresponding to PET (δ_{PET}=10.7 (cal/cm^3)$^{1/2}$). Maximal PET-solvent interactions have been detected for solvents with certain values of the solubility parameter [23,24]. The first group consists of solvents with a solubility parameter around 9.8, capable of interacting with the aromatic groups in PET. The second group comprises solvents with the solubility parameter around 12.1 that interact with the aliphatic groups in PET [23,24]. These findings are in accordance with the results of the storage stability tests performed within this study. The greater relative diffusion of chlorobenzene to isophorone is a consequence of the smaller size of the molecule of chlorobenzene (112.56 g mol^{-1}) to that of isophorone (132.21 g mol^{-1}) and its diffusion is facilitated. On the other hand, propylene glycol and glycerin exhibit a greater tendency toward formation of hydrogen bonds between the individual molecules of the solvent with respect to the polymer/solvent interactions, which explains the lower diffusion into PET and, consequently, smaller changes in mass for these two solvents.

The difference between interactions of chlorobenzene and xylene with PET can be related to the difference in values of the refractive index (n) and the dipole moment (μ(D)) corresponding to these two solvents (chlorobenzene: n = 1.52481, μ = 1.54 D, xylene: n = 1.49722, μ = 0.45 D). Values of these two parameters directly affect dispersion and polar solubility in PET that are evidently greater in the case of chlorobenzene (δ_d = 9.28 (cal/cm^3)$^{1/2}$, δ_p = 2.1 (cal/cm^3)$^{1/2}$) as compared to xylene (δ_d = 8.65 (cal/cm^3)$^{1/2}$, δ_p = 0.5 (cal/cm^3)$^{1/2}$) [26-28].

Based on the mass change, bottles that have undergone the biggest changes during the storage stability test (bottles filled with chlorobenzene, isophorone, xylene), as well the ones filled with water and propylene glycole, were used for further testing.

Image analysis was employed to investigate how solvent penetration and its subsequent diffusion through PET influenced changes in sample dimensions and crystallinity. Two parameters were followed – the change of sample dimensions and the decrease in transparency observed at the sample container bottoms.

By comparing the contours of all sample containers to the reference container that was not subjected to the storage stability test, values of dimensional changes and locations of greatest deviations from the reference container contour were established (Fig. 4).

Figure 4 shows that the most pronounced deviation from the reference contour for all investigated samples is at the container neck where the screw thread is located and where the container contour changes its angle (measuring points 2-6 and 26-30 as marked in Figure 1). These changes proved that the dimensional change of the container as a result of the storage stability test can compromise the quality of the sealing properties of the containers. The largest dimensional changes that are seen in the screw thread zone imply that the contact between the screw cap and the container can be reduced, letting some of the solvent evaporate. This also happens to samples that were exposed to chlorobenzene and isophorone at the lower part of the container, at the point where the base of the container begins, but to a lesser extent.

As can be seen, the most intense deviation from the reference contour occurred in the case of the container exposed to chlorobenzene. This behavior was expected because, according to the general chemical resistance of PET products [14], the resistance of PET toward chlorobenzene is evaluated as 3, meaning that PET exhibits poor resistance to attack and should not be considered for this application. According to the same source, PET resistance toward water, isophorone and xylene is defined as 1, meaning that PET exhibits good resistance to attack and chances for successful testing are very high. Notable deviations for samples exposed to these solvents were found mainly at the container neck, implying that with corrections in the neck design, these solvents could be stored in PET containers if only this aspect is considered. However, testing is necessary especially due to possible structural changes induced by latter solvents.

It was also noted that initially completely transparent containers developed non-transparent zones at the neck and the bottom after the storage stability test (Fig. 5). So, the next step was to investigate how the solvents used influenced changes in transparency of the PET containers. It was assumed that the reason might be development of zones with higher crystallinity that decreased transparency.

It is known that recycling of PET produces material with higher crystallinity, so it may be assumed that solvent penetration should facilitate relaxation of polymer chains and enable formation of zones with increased crystallinity. Analysis of this process can give clues about the solvent penetration mechanism in the given material.

By using the image analysis it is possible to recognize grey levels and calculate the average level of grayness of affected zones that were detected as the zones with changed transparency (the higher the grayness, the lower the transparency). Container bottoms were used for further analysis. The total surface area of non-transparent zones, roundness and other basic image analysis parameters of container bottoms, depending on the solvent, were determined by Image analysis, analyzed by ANOVA and presented in Table 2.

It is noticeable that non-transparency in the case of water is very small, only two-three zones, covering less than 3% of the total area. Three times larger area was detected in the case of isophorone, and more than a third of the entire bottom area became non-transparent in the case of chlorobenzene.

Roundness, as defined in Eq. 1, was used in this study since this parameter may indicate uniformity of the structure around the solvent entry point. When a solvent enters the material, it diffuses in all directions, forming a circular area.

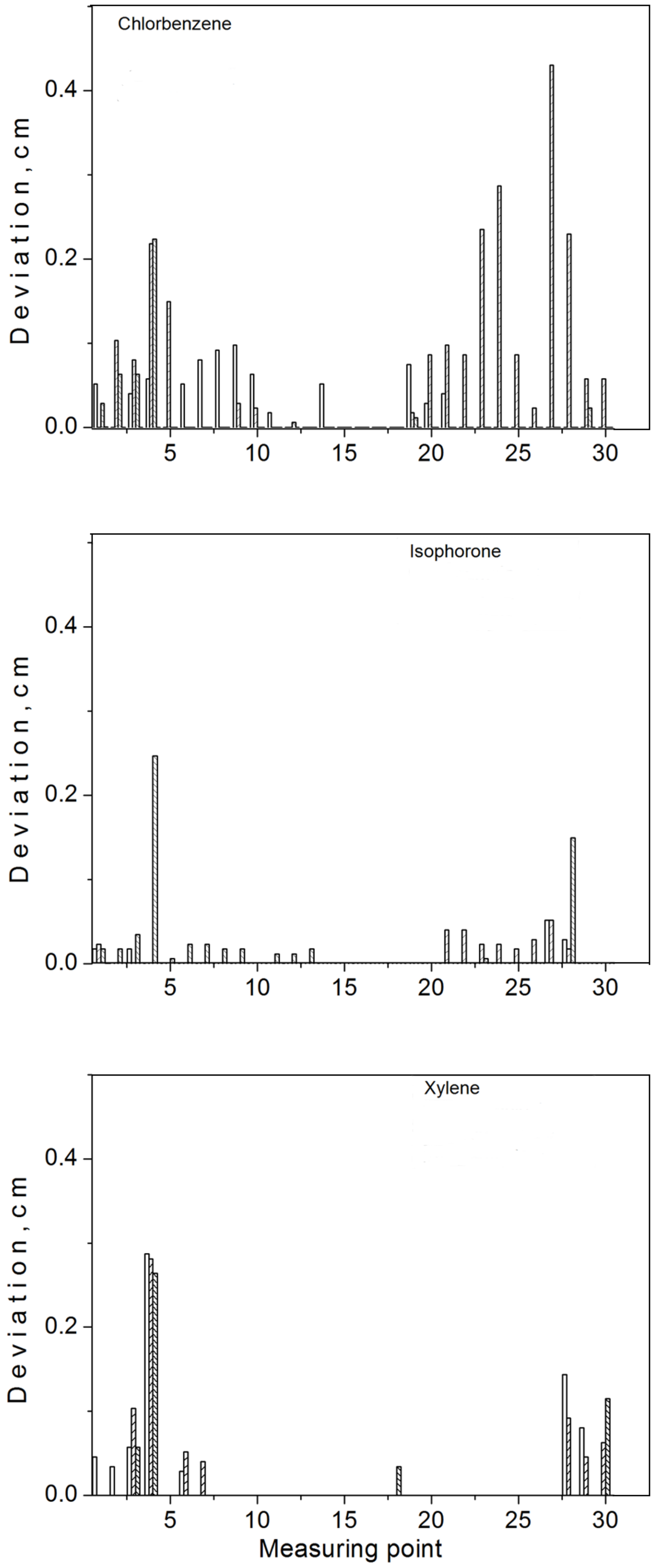

Figure 4. The Deviations of experimental points from the reference contour of the container. The end zones refer to the screw thread zone; while the zone around point 15 is the container base (see Figure 1). The reference sample in all cases was an empty container that was not subjected to the storage stability test.

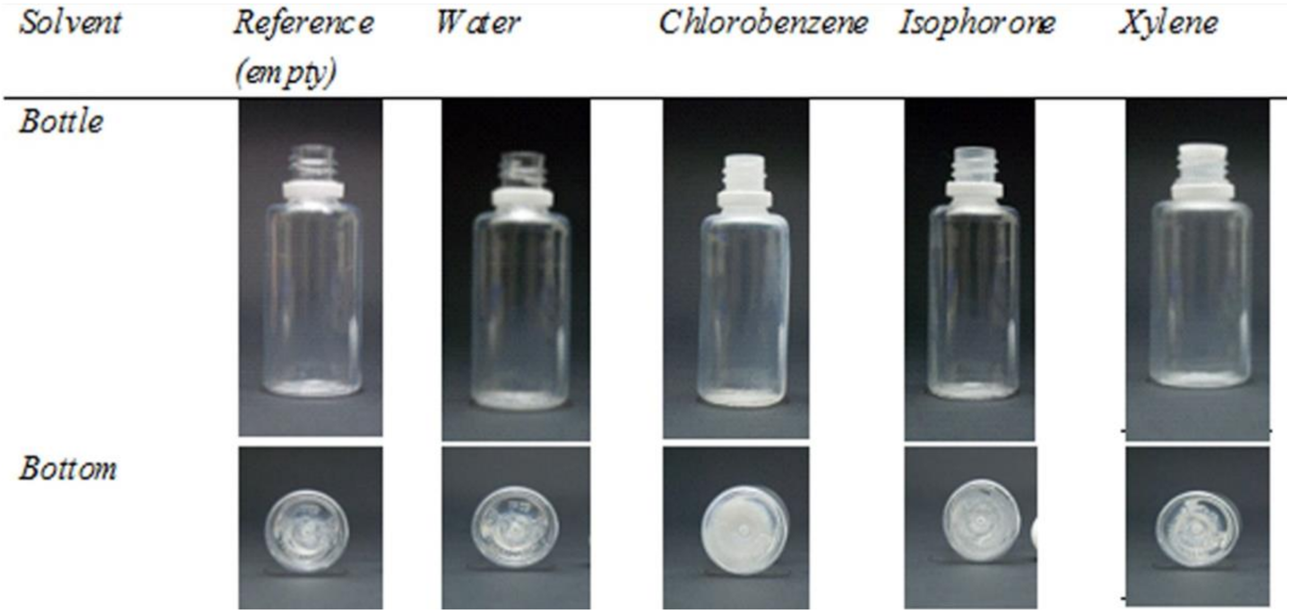

Fig. 5. Photographs of representative containers and their bottoms used in image analysis

Table 2. Characterization of non-transparent zones at container bottoms after the storage stability test

Solvent	Roundness	Object area, cm^2	Area of the container bottom with changed transparency, %
Empty	4.02±0.148^{c}	0.340±0.030^{ab}	0.013±0.019^{a}
Water	9.08±0.629^{g}	0.430±0.055^{ab}	2.69±0.076^{b}
Chlorobenzene	3.55±1.33^{bc}	2.53±0.530^{c}	34.3±1.56^{f}
Espesol	4.71±0.168^{d}	0.730±0.057^{b}	4.71±0.345^{c}
Isophorone	4.09±0.196^{c}	0.160±0.014^{a}	5.63±1.42^{d}
Shellsol A 100	2.75±0.149^{a}	3.55±1.09^{d}	4.55±0.069^{c}
Xylene	3.24±0.108^{ab}	0.50±0.052^{ab}	21.9±0.912^{e}
Solvesso 150	7.03±0.277^{e}	0.240±0.021^{ab}	3.83±0.237^{c}
Propylene Glycol	8.15±0.378^{f}	0.360±0.137^{ab}	4.13±0.237^{c}
Glycerin	5.13±0.327^{d}	0.300±0.114^{ab}	4.25±0.149^{c}

*Values in the same column bearing different superscripts are significantly different ($p<0.05$).

As long as the structure is uniform, without any imperfections, roundness will be close to 1, and diffusion through non-uniform parts of the material will be different, increasing the roundness level. Based on measurements of container masses and areas of non-transparent zones, water is considered as the least penetrating solvent among those that were investigated. The highest roundness values confirm that water diffuses mostly through micro-cracks in the material, thus forming a very uneven circle around the entry point. Roundness of zones was similar when larger areas were covered.

It is also interesting to note that the non-transparent zones concentrate around the middle of the base of the container (Fig. 5). This behavior indicates that the observed changes are linked to irregularities in the structure. Commonly, at the center of the container base there is a trace of the mould riser inducing formation of a different structure. Present investigations show that this area is the location where a solvent penetrates.

Image analysis of the investigated solvent-induced changes on the bottoms of PET containers further involved correlation between the changed transparency in the affected zones, *i.e.* grayness = 100 %-transparency, and structural changes in the PET. Transparency of the affected zones was determined by image analysis as described in the experimental section (0 % is black, 100 % is white) and listed together with grayness in Table 3. For the sake of clarity, the grayness in Table 3 relates to the level of gray of non-transparent parts at the bottom (detected objects), while the area of changed transparency (Table 2) relates to their ratio with respect to the total bottom surface.

Based on the obtained data, we can conclude that significant changes in transparency, along with bottles filled with chlorobenzene (for which this change was expected), also occurred in bottles filled with isophorone and xylene. These changes were the result of changes in the structure of PET subjected to the influence of these solvents.

Table 3. Transparency, grayness and degree of crystallinity of PET container bottoms

Solvent	Transparency, %	Grayness, %	Degree of crystallinity, %
Empty	98.2±0.3^{i}	1.76±0.3^{a}	27.7±0.5^{a}
Water	81.7±0.8^{h}	18.2±0.8 ^{b}	28.4±0.2^{b}
Chlorobenzene	30.7±0.9^{a}	69.3±0.9^{i}	32.5±0.3^{g}
Espesol	75.1±0.8^{f}	24.9±0.8^{d}	28.6±0.1^{bcd}
Isophorone	66.3±1.0^{c}	33.7±1.0^{g}	29.3±0.1^{e}
Shellsol A 100	79.0±1.2^{g}	20.9±1.2^{c}	28.5±0.1^{bc}
Xylene	52.4±0.7^{b}	47.5±0.7^{h}	31.5±0.2^{f}
Solvesso 150	76.0±0.7^{f}	23.9±0.6^{d}	28.5±0.1^{bc}
Propylene Glycol	72.9±0.7^{e}	27.1±0.7^{e}	28.8±0.1^{cd}
Glycerin	70.3±1.2^{d}	29.7±1.2^{f}	28.9±0.1^{d}

*Values in the same column bearing different superscripts are significantly different ($p<0.05$).

DSC analysis was used to determine if the non-transparency stemmed from a higher level of crystallinity. In this case, it would be the result of solvent penetration giving the polymer chains room to reorganize and increase the level of crystallinity.

DSC analysis of both transparent and non-transparent zones from the same container bottom was performed for each sample. Sample DSC curves obtained for PET containers exposed to chlorobenzene are shown in Figure 6.

Peaks that correspond to melting of PET were compared to the theoretical value of 140.1 J g^{-1} for 100 % crystalline PET [28], and the results show that the transparent part was 27.7 % crystalline, while the crystallinity of the non-transparent part was 32.5 %. This finding confirmed that non-transparency originated from a higher degree of crystallinity, as was presumed at the beginning. The obtained results for crystallinity degrees in non-transparent zones for all investigated containers are presented in Table 3 as a mean value of all samples in each group.

Finding a connection between the new approach to studying structural changes in PET by Image analysis and DSC as a conventional, but expensive and time consuming experimental method, would provide a cheap, easy and fast tool for monitoring the quality of consumed PET containers.

Thereby, we correlated the change of grayness of PET container bottoms, as compared to that of the empty bottle, to the experimentally obtained change in crystallinity degree detected by DSC. The obtained dependence is presented in Figure 7.

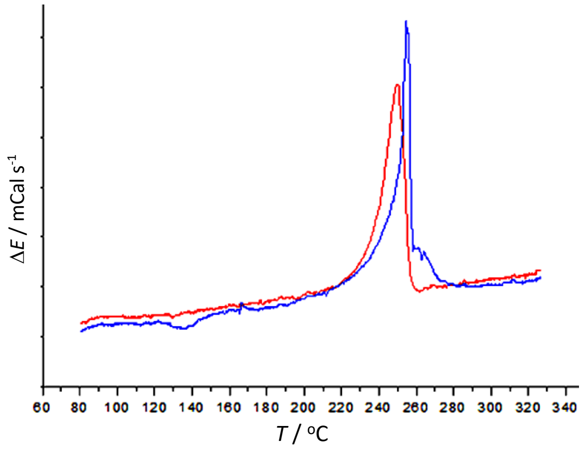

Fig. 6. DSC curves of the transparent (red line) and non-transparent part (blue line) of the container bottom after the storage stability test using chlorobenzene

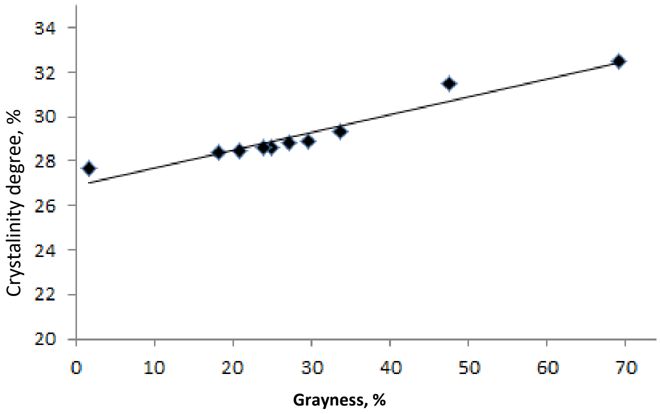

Figure 7. Crystallinity degree vs. grayness (with respect to the reference sample - transparent PET)

As may be seen from the Figure 7, the dependence of the change in crystallinity on the change in grayness was linear with the slope value of 0.07, and independent of the solvent used. The linear correlation coefficient between the degree of grayness and the degree of crystallinity is 0.953 and is statistically significant (p <0.001). Hence, there is a strong positive linear correlation between these two parameters.

Therefore, the presented method provided the possibility for calculation of the change in the crystallinity degree of PET by simple analysis of its image, *i.e*. acquiring the change in material grayness. The presented linear dependence of the change in crystallinity on the change in grayness for PET samples (Fig. 7) thus becomes a master curve for given conditions and PET and may be used to calculate the degree of crystallinity of a PET sample (without DSC measurements) using transparency change of that sample at given conditions. It could be assumed that this analysis could be applied to other crystalline polymers. This can significantly speed up characterization of PET and facilitate selection when processing an enormous number of samples.

4. CONCLUSIONS

Image analysis and the related software Image Pro Plus were successfully applied to determine structural changes in the polymer and evaluate effects of various solvents on PET containers during the storage stability test. It was shown that dimensional changes of containers could be recorded in great detail by using the image analysis software. The observed changes in sample crystallinity were confirmed by DSC. The most important finding is that the same software could enable calculation of the degree of crystallinity of PET, based on simple analysis of the material image, *i.e*. by determining the transparency change of the material. Then the time consuming and costly DSC measurements could be used only to obtain the master curve and not to test the entire production line (that would be done by the image analysis).

This investigation thus showed that image analysis is an easy and fast method to detect dimensional and structural changes in transparent PET products during their shelf-life. The achieved results could be of great benefit in applications where quick analysis of a large number of samples must be performed. Finally, this analysis potentially could be applied to other crystalline polymers, the structure of which might change during their service lifetime.

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REFERENCES

[1] Tavares AA, Silva DFA, Lima PS, Andrade DLACS, Silva SML, Canedo EL. Chain extension of virgin and recycled polyethylene terephthalate. Polym. Test. 2016; 50:26-32.

[2] Xu Y, Song Y, Zheng Q. Effects of nanosilica on crystallization and thermal ageing behaviors of polyethylene terephthalate. Chinese J. Polym. Sci. 2015; 33(5):697-708.

[3] Dombre C, Rigou P, Chalier P. The use of active PET to package rosé wine: Changes of aromatic profile by chemical evolution and by transfers. Food Res. Inter. 2015; 74:63-71.

[4] Plotan M, Frizzell C, Robinson V, Elliot CT. Connolly L. Endocrine disruptor activity in bottled mineral and flavoured water. Food Chem. 2013; 136(3-4):1590-1596.

[5] Dombre C, Marais S, Chappey C, Lixon-Buquet C, Chalier P. The behaviour of wine aroma compounds related to structure and barrier properties of virgin, recycled and active PET membranes. J. Membr. Sci. 2014; 463:215–225.

[6] Welle F, Franz R. Diffusion coefficients and activation energies of diffusion of low molecular weight migrants in Poly(ethylene terephthalate) bottles. Polym. Test. 2012; 93(31):93-101.

[7] Welle F, Bayer F, Franz R. Quantification of the Sorption Behavior of Polyethylene Terephthalate Polymer versus PET/PA Polymer Blends towards Organic Compounds. Packag. Technol. Sci. 2012; 25:341–349.

[8] Chandra P, Koros WJ. Sorption and transport of methanol in poly(ethylene terephthalate). Polymer 2009; 50:236–244.

[9] Khanum R, Takarada W, Aneja A, Kikutani T. Crystallization of poly(ethylene terephthalate) filaments by infusion of ethanol upon cold drawing. Polymer 2015; 59:26-34.

[10] Ali W, Sultana P, Joshi M, Rajendran S. A solvent induced crystallization method to imbue bioactive ingredients of neem oil into the compact structure of poly (ethylene terephthalate) polyester. Materials Sci. Eng.: C. 2016; 64:399-406.

[11] Andjelić S, Scogna RC. Polymer crystallization rate challenges: The art of chemistry and Processing. J. Appl. Polym. Sci. 2015; 132:42066.

[12] Aharoni SM, Murthy NS. Effects of Solvent-induced Crystallization on the Amorphous Phase of Polycarbonate of bisphenol A). Inter. J. Polym. Mater. 1998; 42(3-4):275-283.

[13] Radhakrishnan J, Kaito A. Structure formation during the isothermal crystallization of oriented amorphous poly(ethylene terephthalate) films. Polymer 2001; 42:3859-3866.

[14] Plastics 2020 Challenges.www.plasticseurope.org/en/focus-areas/strategy-plastics. Accessed May, 2018.

[15] Monitor & control PET bottle crystallinity & barrier properties, in: Plastics Technology. Gardner Publications, Inc. 2015. www.ptonline.com/Products/zone/blowmolding/6.Accessed May, 2018.

[16] Ouyang H, Lee WH, Ouyang W, Shuie ST, Wu TM. Solvent-Induced crystallization in poly(ethylene terephthalate) during mass transport: Mechanism and boundary condition. Macromolecules 2004; 37:7719-7723.

[17] Ouyang H, Lee WH, Shih MC. Three stages of crystallization in poly(ethylene terephthalate) during mass transport. Macromolecules 2002; 35:8428-8432.

[18] Image Pro Plus. www.mediacy.com/imageproplus. Accessed May, 2018.

[19] Fernandes-Santos C, Souza-Mello V, da Silva Faria T, Mandarim-de-Lacerda CA. Quantitative Morphology Update: Image Analysis. Int. J. Morphol. 2013; 31(1):23-30.

[20] Pereira AC, Reis MS, Saraiva PM. Quality Control of Food Products using Image Analysis and Multivariate Statistical Tools. Ind. Eng. Chem. Res. 2009; 48:988-998.

[21] Honglu Y, MacGregor JF, Haarsma G, Bourg W. Digital imaging for online monitoring and control of industrial snack food processes. Ind. Eng. Chem. Res. 2003; 42:3036-3044.

[22] Jose AJ, Wong LS, Merrington J, Bradley M. Automated image analysis of polymer beads and size distribution. Ind. Eng. Chem. Res. 2005; 44:8659-8662.

[23] Chidambaram D, Venkatraj R, Manisankar P. Solvent-induced modifications in poly(ethylene terephthalate) structure, properties and dye ability. Indian J. Fibre Text. Res. 2002; 27:199-210.

[24] Weast RC. Handbook of chemistry and physics**.** 55th ed., Cleveland, Ohio; 1974.

[25] Olson E. Particle Shape Factors and Their Use in Image Analysis–Part 1: Theory. Summer 2011; 15(3):85-96.

[26] McClellan AL. Tables of experimental dipole moments. Freeman, San Francisco; 1963.

[27] Hansen CM, Skaarup K. The three dimensional solubility parameter - key to paint component Affinities III. - Independent calculation of the parameter components. J. Paint Techn. 1967; 39(511):511-514.

[28] PerkinElmer.www.perkinelmer.com/Content/applicationnotes/app_thermalcrystallinitythermoplastics.pdf. Accessed May, 2018.

SAŽETAK

Analiza slike – korisna tehnika za brzu detekciju dimenzionih i strukturnih promena boca od poli(etilen tereftalata)

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(Naučni rad)

Cilj ovog rada je da pokaže da je analiza slike brza, pouzdana i nedestruktivna metoda koja može da se koristi za detekciju dimenzionih i strukturnih promena u polimerima. Mogućnost primene analize slike pokazana je na primeru rastvaračima indukovane kristalizacije boca od poli(etilen tereftalata) (PET), koje su izložene testu starenja na 54 °C tokom 14 dana (CIPAC 1-MT 46.1.3). Za ispitivanje su korišćeni sledeći organski rastvarači: hlorbenzen, izoforon, ksilen, "Espesol", "Shellsol A100", "Solvesso 150", propilen glikol, glicerin i voda. Za analizu rezultata korišćena je jednofaktorska analiza varijanse (ANOVA) u kombinaciji sa Dankanovim statističkim testom ($p<0,05$). Na osnovu postignutih rezultata utvrđeno je: 1) analizom slike se precizno mogu detektovati promene dimenzija i transparentnosti PET bez obzira da li prisutan rastvarač izaziva male (voda) ili velike (hlorbenzen) promene; 2) moguće je uspostaviti vezu između promena u stepenu kristaliničnosti i transparentnosti PET bez primene DSC metode. Analiza slika se može potencijalno primeniti in a druge kristalinične polimere.

Ključne reči: analiza slike; brza detekcija; starenje; difuzija rastvarača; poli(etilen tereftalat)