Selected thermal methods for study of the waste PET material

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Abstract

The aim of the paper is to study selected PET thermoplastics, using dynamic mechanical analysis (DMA). DMA is one of the most progressive and suitable methods for study of the viscoelastic properties relating to the thermoplastic polymers. In dynamic mechanical analysis, the tested material is not exposed only to a certain temperature range but also to mechanical stress in the form of selected frequencies. Based on these facts, the melting point and glass transition temperature, material crystallization, softening points, elastic and loss moduli, tan δ, and many others parameters can be detected for thermoplastic materials. PET-based waste materials with different coloring were used as predetermined tested samples.

Keywords: Dynamic mechanical analysis, dispersive X-ray spectroscopy, thermoplastics, polyethylene terephthalate, differential scanning calorimetry

Introduction

Methods of thermal analysis for input control, quality control or research and development of material have been used more frequently. The increasing degree in automation of analytical instruments decreases the difficulty in their operating. The consequence is the development of standardization of thermoanalytical methods [1-4]. Dynamic mechanical analysis (DMA) along with differential scanning calorimetry (DSC) can be included among the experimental methods of thermal analysis for determination of changes in composition and properties of the studied material where the stimulus of the given changes is the heat load. In addition, the sample may be exposed to other influences, such as, reactive atmosphere, static or dynamic mechanical load. During the heat load, the reversible and irreversible changes in dimensions occur in the sample and they depend on the material properties, initial dimensions and the used temperature range [5, 6].

In relation to the dynamic mechanical analysis (DMA), the tested material is not exposed only to a certain temperature range but also to mechanical stress in the form of selected frequencies. Based on this fact, it is possible to detect the melting temperature and glass transition temperature, material crystallization, softening points, elastic and loss moduli, tan δ as well as other parameters in thermoplastic materials [7, 8, 11]. From the aspect of differential scanning calorimetry (DSC), the tested material is subjected to linear heating, whereby there is the rate of heat flow, which is measured continuously in the material and it is proportional to the instantaneous heat of measurement. This method allows the determination of significant thermodynamic parameters of the tested thermoplastic polymers. In other words, this method is mainly based on determination of the melting and crystallization temperature, the glass transition temperature as well as determination of the material crystallinity [9, 10].

Furthermore, the energy dispersive X-ray spectroscopy (EDX) provides elemental and chemical analysis of the sample. This method is important for the identification of potential harmful substances occurring in plastic bottles [11].

Materials and methods

For the experiment, four types of polyethylene terephthalate (PET) were selected as the materials for testing. The samples, which were used for examination, were represented by the waste of the plastic bottles from different manufacturers of sweet drinks and each one tested sample had a different color, namely: pink (PET P1) , blue (PET B1), green (PET G1) and transparent (PET T1) without any coloring additive (Fig. 1).

During DMA analysis, the temperature of sample is scanned and the storage modulus, loss modulus and loss factor (tan δ) are constantly measured. At the glass transition temperature (T_g), the storage modulus decreases and the peak can be observed for the loss modulus and loss factor [5]. Dynamic mechanical analysis was performed, using the DMA Q800 from TA Instruments (Fig. 3a). The samples were mounted between film tension fixtures by the chosen tension-film geometry and it can be seen in the Fig. 2. The dimensions of each sample were 45 x 10 x 3 mm. The temperature range for the measurement was chosen from -25 ºC to 170 ºC, with a heating rate of 3 ºC per minute and frequency was set to 10 Hz.

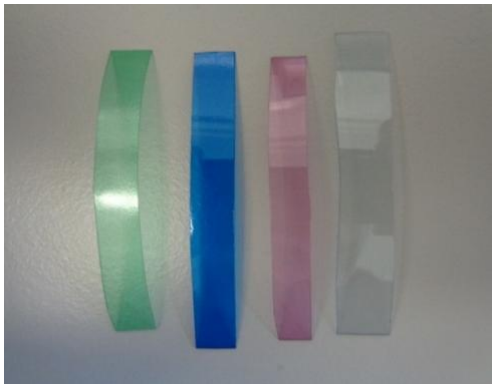

Fig.1 Tested PET samples

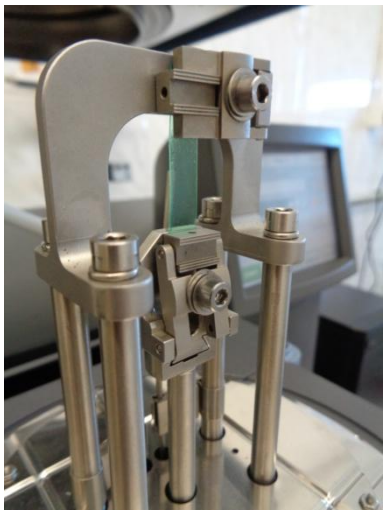

Fig.2 Geometry tension - film for DMA analysis

DSC analysis was performed by help of Mettler Toledo, TGA/DSC 2 (Fig.3b). The weight of the tested samples was about 20 mg and they were heated from 0 °C to 300 °C, with a selected heating rate of 10 °C per minute.

Using energy-dispersive EDX-7000 X-ray fluorescence spectrometer, the elemental and chemical analysis of the samples was carried out. All measurements were carried out at the CEDITEK (Center for quality testing and diagnostics of materials) workplace at Faculty of Industrial Technologies in Púchov.

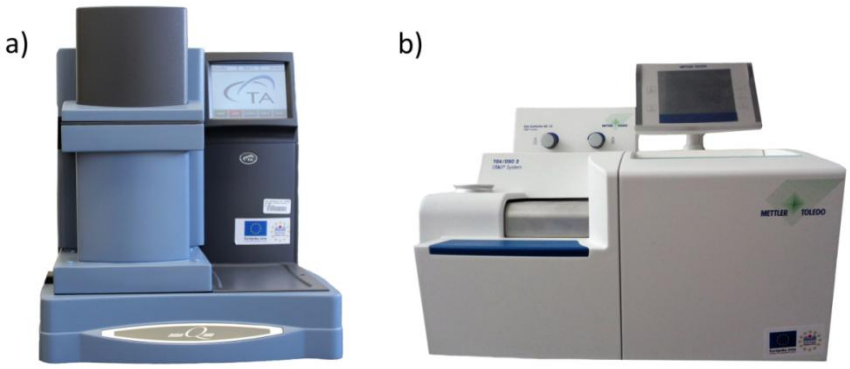

Fig.3 Instruments a) TA Instruments DMA Q 800, b) Mettler Toledo, TGA/DSC 2

Discussion and results

Dynamic mechanical analysis was performed for PET samples. Fig. 4 shows the measured tan δ curves for individual samples, depending on the temperature at frequency of 10 Hz.The loss factor (tan δ) represents the internal friction of the macromolecule segments and can be characterized as a ratio of the loss modulus and elastic modulus.The relaxation maximum for individual PET samples ranges from 105 °C to 118 °C, which corresponds to the glass transition of the tested materials.

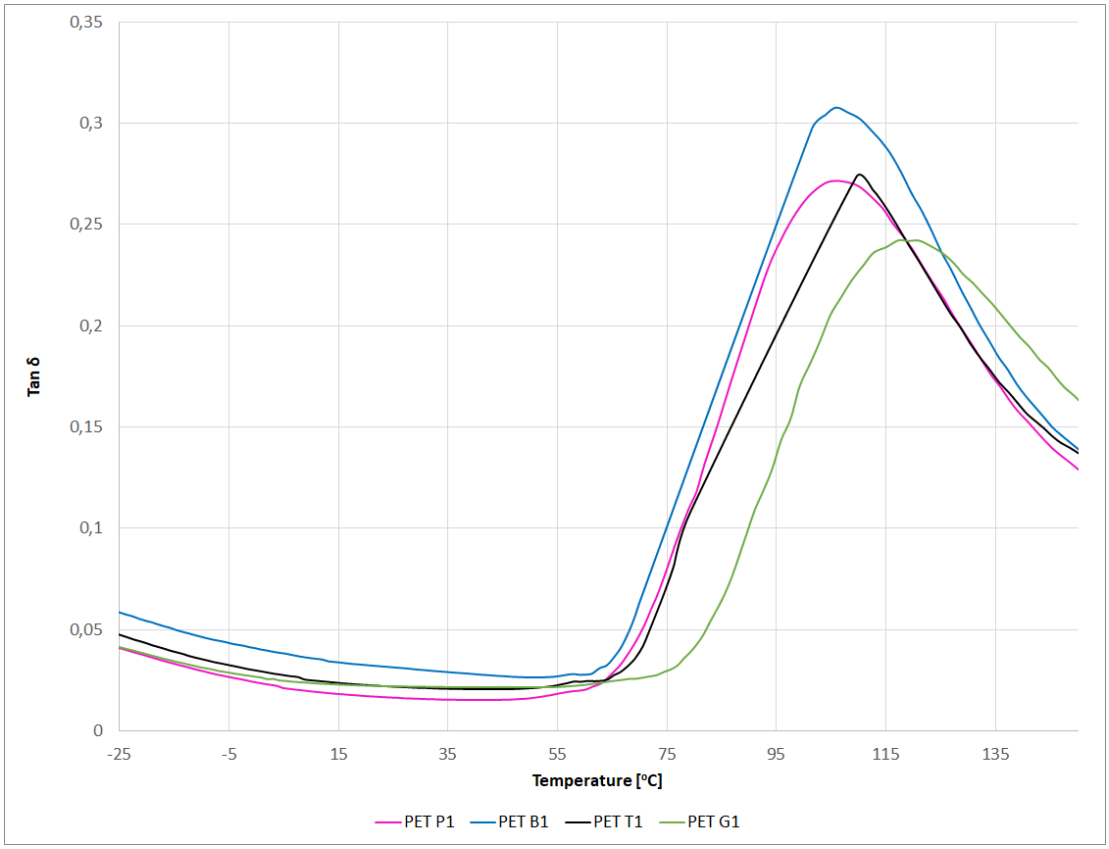

Fig.4 tan δ for PET samples

As it can be seen in the Fig. 4, the glass transition temperature (T_g) for the PET B1 and the PET P1 sample was at approximately 105 ° C. Glass transition temperature was also measured for PET T1 and PET G1 sample, where the measured temperature was higher by~ 5 ° C for PET T1, and for PET G1 sample, it was higher by ~ 12 °C. All the measured glass transition temperatures from tan δ curves for individual samples are shown in Tab.1.

Table1 Measured glass transition temperatures from DMA analysis

Tested sample	Glass transition temperature - T_g (ºC)
PET B1	105.9
PET P1	105.5
PET G1	117.2
PET T1	112.6

The graph shown in Fig. 5, represents the storage modulus, which is a measure of the apparent stiffness of the base units. It represents part of the ideal elastic resistance of the material against the elastic dynamic stress at the given frequency and temperature conditions. There is a decrease in storage modulus. The first transition, from the rigid glassy state to the softer state, is observed at around 50 – 60 °C for samples PET T1, PET B1, PET P1, and around 60 - 80 °C for PET G1. This is so called glass transition and it leads to a drop in the Young's modulus. The second transition, at around 60 – 70 °C (80 °C for PET G1), is crystallization of initially amorphous PET. This transition leads to a significant increase in the Young's modulus It is worth mentioning that this transition is unusual.

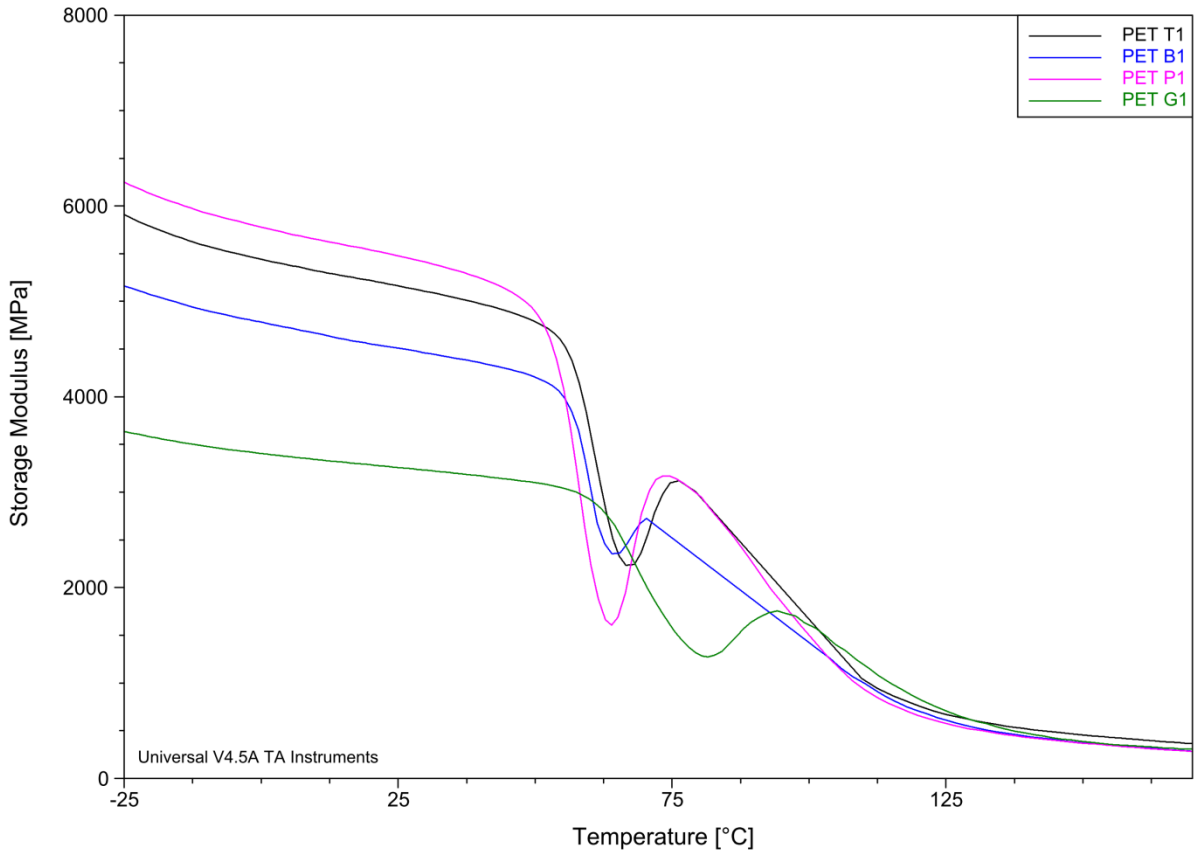

Fig. 5 Storage modulus of PET samples

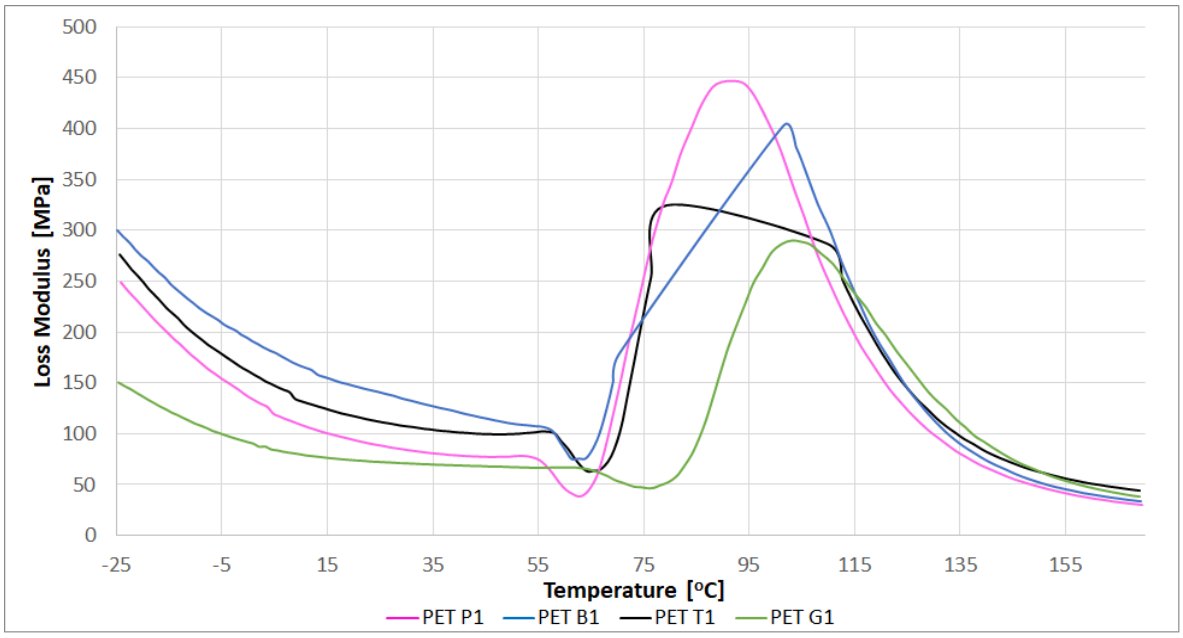

Fig. 6 Loss modulus of PET samples

The graph shown in Fig. 5, represents the loss modulus, which expresses the rate of energy transfer between molecules and is proportional to the amount of energy between molecules. It characterizes mechanical losses and determines the amount of energy that convert in heat during one deformation period. There is a increase in loss modulus around 65 °C (80 °C for PET G1 sample). This increase is associated with α-transition so called glass transition of polyethylene terephthalate.

The samples were subsequently subjected to DSC analysis, where the melting point (T_m) was observed. The melting point of each PET sample is shown in Table 2. There were no significant differences in the mutual comparison of melting temperatures of the tested materials (temperatures were ~ 250 °C, with minor variations).

The different conditions of the technological production of individual materials, the influence of the used dye and the proportion of the semicrystalline and amorphous phase in the material can be included among the factors influencing the glass transition temperature and melting temperature.

Table 2 Measured melting points from DSC analysis

Tested sample	Melting point – T_m (ºC)
PET B1	250.3
PET P1	250.7
PET G1	250.9
PET T1	250.6

Thermoplastics, which were used for plastic bottles can contain concentrations of heavy metals. Used antioxidants can contain Ni, while thermal stabilizers can contain Ni, Pb and Sb. The polymerization process is often carried out with an antimony (Sb), germanium (Ge), titanium (Ti), cobalt (Co), magnesium (Mg) or zinc (Zn) based catalyst [11].

EDX analysis revealed weight percentage presence of individual elements in samples and it is shown in Table 3. It can be seen that samples contain amount of sulphur, while PET P1 sample also contains increased amount of antimony which was obviously used in the form of catalyst during polycondensation of PET. PET P1 sample also contains little amount of phosphorus. All samples contain little amount of calcium. The presence of these elements can be due to used coloring additives or UV stabilizers.

Table 3 EDX analysis

PET B1		PET P1	
Element	***Contents (weight %)***	***Element***	***Contents (weight %)***
S	0.020	Sb	0.017
Ca	0.003	S	0.016
K	0.002	P	0.011
Fe	0.001	Ca	0.005
Sb	0.001	K	0.001
Cu	0.001	Cu	0.001
PET G1		**PET T1**	
Element	***Contents (weight %)***	***Element***	***Contents (weight %)***
S	0.019	S	0.026
Ca	0.004	Ca	0.005
K	0.002	K	0.002
Co	0.001	Co	0.001
Cu	0.001	Cu	0.001
Fe	0.001	Fe	0.001

Conclusion

The aim of this paper was to focus on dynamic mechanical analysis and its practical application in relation to the study of polyethylene terephthalate. The measurements were carried out for four PET samples, using DMA and DSC analysis and from the resulting graphs, the glass transition temperature and the melting point of the each sample were determined. Storage modulus, loss modulus and loss factor (tan δ) obtained from DMA analysis, were described for each sample. It is important to mention the frequency along with the glass transition temperature, because the frequency can have effect on the temperature at which the glass transition is detected. Based on the measurements, it can be concluded that DMA and DSC analysis are the most progressive and suitable methods for evaluating and testing thermoplastic materials. Furthermore, the EDX analysis revealed the presence of some elements and heavy metals in tested polymers, such as antimony, sulphur and phosphorus.

Acknowledgments

KEGA 007TnUAD-4/2017, VEGA grant No. 1/0649/17, project "Center for quality testing and diagnostics of materials", ITMS code 26210120046 relating to the Operational Program Research and Development, EF of Reg. Development.

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