

# Morphology and Thermal Properties of Expanded Graphite (EG)/Poly(ethylene terephthalate) (PET) Nanocomposites

Sandra PASZKIEWICZ, Zbigniew ROSŁANIEC – Institute of Materials Science and Engineering, West Pomeranian University of Technology, Szczecin, Poland; Anna SZYMCZYK – Institute of Physics, West Pomeranian University of Technology, Szczecin, Poland; Zdenko SPITALSKY – Department of Composite Materials, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia; Jaroslav MOSNACEK – Center of Excellence FUN-MAT, Department of Synthesis and Characterization of Polymers, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

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## Introduction

In recent years, a significant increase in interest of polymer nanocomposites, a relatively new group of materials is observed [1]. Polymer nanocomposites are obtained by modification of traditional materials by dispersing the filler in the polymer matrix with dimensions of several nanometers. So there are materials that consist of two or more phases (continuous and dispersed), with clear separation of the surfaces of which at least one component is characterized by diffuse at least one dimension on a nanometric scale ( $10^{-9}$  m) [2]. It is assumed that this dimension can not exceed 200 nm, and is usually much less than 100 nm. As nanofillers different materials are used as terms of the chemical nature (inorganic, organic), physical structure (crystalline, amorphous, gaseous inclusions nanofoams) and particle shape (3D - „powder”, 2D - platelets, 1D - linear).

Nanocomposites with nanoparticles can be prepared by direct melt mixing in molten state, mixing with the polymer in the solution or *in situ* polymerization. *In situ* polymerization technique enables loading and dispersion of nanoparticles during manufacturing of nanocomposite (synthesis of polymer). Nanoparticles are dispersed in the monomer, which is then input to the reaction mixture [3]. The advantage of this method is the ability of formation of physical or chemical bonding between functional groups of the monomer, and groups on the surface of nanofillers, which provides improved dispersibility [4]. The increasing viscosity of preparing polymer provides *in situ* preparation of appropriate interphase interactions and stabilizes the dispersion. Properties of polymer nanocomposites depend significantly not only on the type of polymer matrix and the nature of the nanofiller, but also on the degree of granularity and uniform dispersion of nanoparticles [5]. In the case of the thermoplastic matrix, nanofiller may affect the crystallization rate, degree of crystallinity and the nature of the crystalline phase [6].

Introduction of the nanofiller to the polymer matrix, aims to give composites relevant / new mechanical, thermal, electrical, optical, gas barrier and/or biological properties, depending on the type of the nanofiller [7÷9]. Significant improvement in properties of the composites depends mainly on the size and shape of nanofiller particles [10], surface area, degree of surface development, surface energy and spatial distribution of the nanoparticles in a polymer matrix.

Since the discovery of graphene in 2004 by A. Geim and K. Novoselov there is a growing interest in using it as a filler of polymer materials. Graphene is an atomically thick, two-dimensional (2-D) sheet composed of  $sp^2$  carbon atoms arranged in a plane structure [1]. Graphene system has very high electron mobility (high electrical conductivity) at room temperature ( $2 \cdot 10^5$  cm<sup>2</sup>/Vs), very high thermal conductivity of about 5000 W/m·K, and extraordinary mechanical strength (with Young modulus of 1 TPa and ultimate strength of 130 GPa) approximately 100 times greater than steel and is the strongest material ever measured. [11]. Single-layer graphene also

features a very high electrical conductivity (up to 6000 S/cm) [12], and unlike CNT, chirality is not a factor in its electrical conductivity. It is a light, almost transparent material (absorbs only 2% of the light), with extremely high surface area (theoretical limit: 2630 m<sup>2</sup>/g) and is gas impermeable [13]. Graphene is not naturally abundant due to its instability and tendency to form three-dimensional structures (agglomeration). It can be synthesized by a variety of methods divided by Kim at: Top-Down and Bottom-Up [1] i.e.: CVD, epitaxial growth, thermal exfoliation (expanding) and then reduction of GO (the oxidized form of graphene) as well as micromechanical methods [14]. For example, starting from pyrolytic graphite, structures with a thickness of from one to several graphene layers can be isolated [14]. The unique properties of graphene, mentioned above, explain great interest in innovative nanocomposite materials with their participation. Their very small size and large aspect ratio may lead to improved applicative characteristics of many polymeric materials.

The aim of our work was to determine the conditions for obtaining nanocomposites PET/EG during polycondensation (*in situ*), polymer matrix, initially described for poly(ester-ethers) copolymers [15] and PBT/CNT nanocomposites [16], and examines the impact of expanded graphite content on their structure and thermal properties.

## Experimental section

### Materials

For the poly (ethylene terephthalate) (PET) synthesis were used following substrates: dimethyl terephthalate (DMT) (Sigma - Aldrich); ethanediol (ED) (Sigma - Aldrich), catalysts: zinc acetate (ester exchange catalyst)  $Zn(CH_3COO)_2$  (Sigma - Aldrich); antimony trioxide – polycondensation catalyst -  $Sb_2O_3$  (Sigma - Aldrich); thermal stabilizer Irganox 1010 (Ciba – Geigy, Switzerland). Expanded graphite was prepared by thermal expansion (SGL Carbon SE, Germany); average thickness of the agglomerates after expanding was  $450 \div 560$  nm. Graphene platelets size ranged from  $16 \mu m$  to  $46 \mu m$  (99%). Before adding the nanofiller (expanded graphite) to the reaction mixture it was combined with ethanediol, dispersed to split agglomerates and exfoliated.

### Preparation of nanocomposites

Nanocomposites PET/EG were prepared by *in situ* polymerization in the synthesis of PET in the polycondensation reactor (Autoclave Engineers, Pennsylvania, USA) capacity of 1000 cm<sup>3</sup>. The process was conducted in two stages. In the first stage, at atmospheric pressure and temperature range of  $160 \div 180^\circ C$ , took place transesterification reaction between both dimethyl terephthalate (DMT) and ethylene glycol with the addition of nanofiller (EG), which was initially dispersed using high-speed stirrer (Ultra-Turax T25) and sonicator (Homogenizer HD 2200, Sonoplus). To carry out the dispersion ultra-power lower sonic bath

(BANDELIN, Sonorex digitec) was used, resulting in the precipitation of methanol. When a precipitated amount of alcohol was close to the theoretical amount, the pressure was gradually lowered to about 0.1hPa and the second stage was begun—polycondensation carried in temperature to 275°C by the stirrer speed 40 rot/min. The progress of the PET polymerization was monitored based on observations of the changing viscosity of the reaction mixture (polymer), which was in turn monitored on the basis of observations of changes in torque stirrer during the synthesis. The reaction was considered complete when the viscosity in the system rose to 14Pa·s. The obtained polymer/nanocomposite was extruded from the reactor at a pressure of nitrogen in the form of polymer wire.

**Methods of characterization**

Thermal and thermo-oxidative stability of investigated polymer nanocomposites were evaluated by thermogravimetry (TGA 92-16.18 Setaram) using the system to measure the simultaneous TG-DSC. Measurements were carried out in an oxidizing atmosphere i.e. dry, synthetic air (N<sub>2</sub> : O<sub>2</sub> = 80 : 20vol.%) and in argon. The study was conducted at a heating rate of 1°C/min in the temperature range from 20 to 700°C. Measurements were conducted in accordance with the principles contained in the PN-EN ISO 11358:2004 Activation energy was determined by Freeman-Carroll method [17]:

$$\frac{dm}{dt} = k_0 c^n e^{-\frac{E_a}{RT}} \quad (1)$$

where: *m* - order of reaction, *E<sub>a</sub>*- activation energy, *c*- mole fraction of reactant, *k<sub>0</sub>*-specific rate, *R*- gas constant, *T*- temperature.

Measurements by differential scanning calorimetry (DSC) were performed using a differential calorimeter Q-100 (TA Instruments, USA, 2004) in cycle: heating – cooling – heating, the heating and cooling rate 10°C/min in the temperature range from 25 to 300°C, the glass transition temperature *T<sub>g</sub>*, crystallization *T<sub>c</sub>* and melting *T<sub>t</sub>* temperatures were determined and the degree of crystallinity systems was investigated *X<sub>c</sub>*. The degree of crystallinity was determined using the formula:

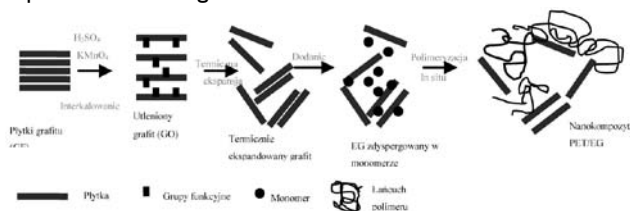
$$X_c = \frac{\Delta H_m}{\Delta H_m^0} 100\% \quad (2)$$

where:  $\Delta H_m$  – enthalpy of melting material sample, J/g;  $\Delta H_m^0 = 140,01 \text{ J/g}$  – the theoretical value of enthalpy for 100% crystalline PET [18].

The structure of nanoparticles and nanocomposites were observed by scanning electron microscopy (SEM) of Company JEOL JSM 6100 SEM and transmission electron microscope (TEM) (JEOL JEM-1200 EX Electron Microscope). The samples were cryofractured in liquid nitrogen, and then vacuum coated with a thin gold film before being analyzed using SEM.

**Result and discussion**

Carbon nanoplates (graphene) obtained by expansion and exfoliation of graphite in ethanediol (ED) were introduced to poly(ethylene terephthalate) (PET) during its synthesis (*in situ*) in molten state. The steps are shown in Fig. 1.

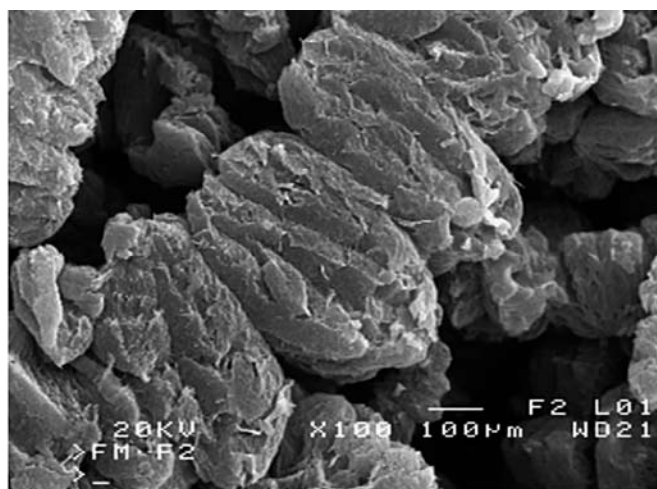


**Fig. 1. Schematically illustration of formation of EG and the synthesis of PET/EG nanocomposites**

The prepared nanocomposites of PET / EG contained 0.025, 0.05, 0.1, 0.2 and 0.4 wt%. of expanded graphite. Additionally,

in order to compare synthesized and characterized unmodified PET obtained in the same way as nanocomposites.

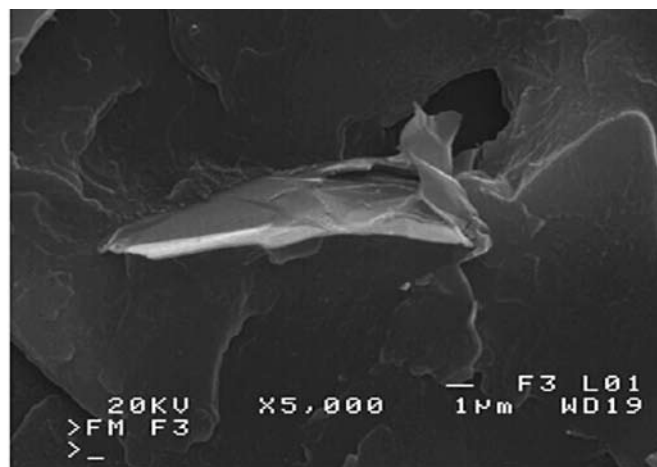
The effectiveness of expanding graphite depends on the degree of oxidation. Expanded graphite (EG) used in this work was obtained from rapid oxidized graphite, therefore as a result of expansion single plane graphene sheets and loosely (mostly) bonded graphene packages. Such aggregates (initial agglomerates) have a size of about 200µm, which can be seen clearly on the SEM images (Fig. 2).



**Fig. 2. SEM image of expanded graphite**

However, they are loosely bonded together as shown in the SEM images (Fig. 3 and 4). During the dispersion of EG in ethanediol took place their further exfoliation, however, its effectiveness depends on method and process time. The usage of sonicator was due to split the existing agglomerates of expanded graphite nanosheets, and distributed in the entire volume of ethanediol. As a result of intensive mixing took place the increase of temperature, which lowers its viscosity and thus facilitated its distribution. The mixing time was determined experimentally. Conducting dispersion alternately with high-speed stirrer and high power for 30 min, as in earlier work in relation to carbon nanotubes [3, 16 ], was not effective. In nanocomposite occur then aggregates with a diameter of 100÷400nm (Fig. 5). Further dispersion carried in low-power sonic bath for 10–12 hours leads to much better exfoliation (Fig. 6). In nanocomposite 2-3 graphene platelets occur very rarely. (Fig.7).

The process of polymer synthesis was conducted in two steps. The presence in the reaction mixture of expanded graphite essentially did not effect on progress of the ester exchange, but it was seen the effect on the polycondensation process. Polycondensation reaction involving EG was getting slower, as evidenced by a slower increase in viscosity of the system (torque stirrer) in the last stage of synthesis.



**Fig. 3. SEM image of PET/EG 0.05wt.% nanocomposites, x5000**

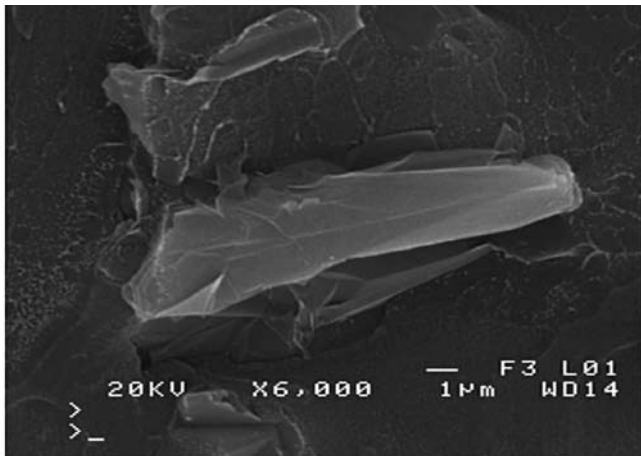


Fig. 4. SEM image of PET/EG 0.2wt.% nanocomposites

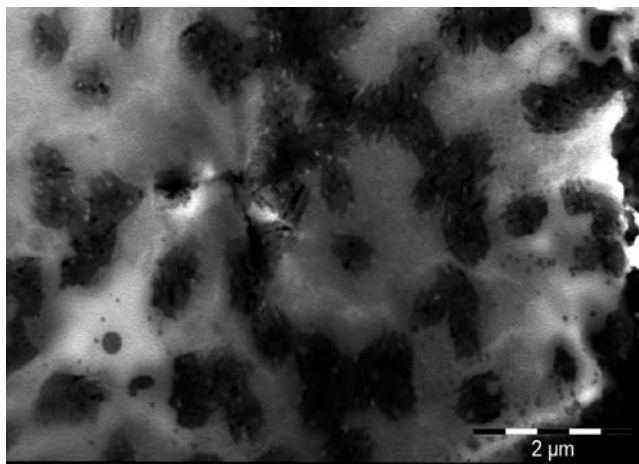


Fig. 5. TEM image of PET/EG 0.2wt.% nanocomposites

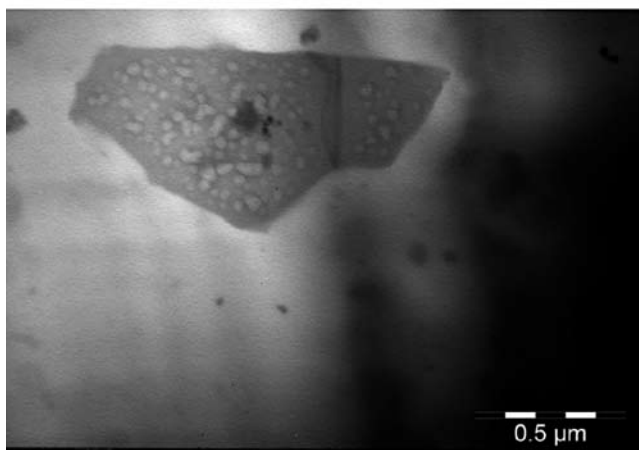


Fig. 6. TEM image of PET/EG 0.05wt.% nanocomposites, x120000

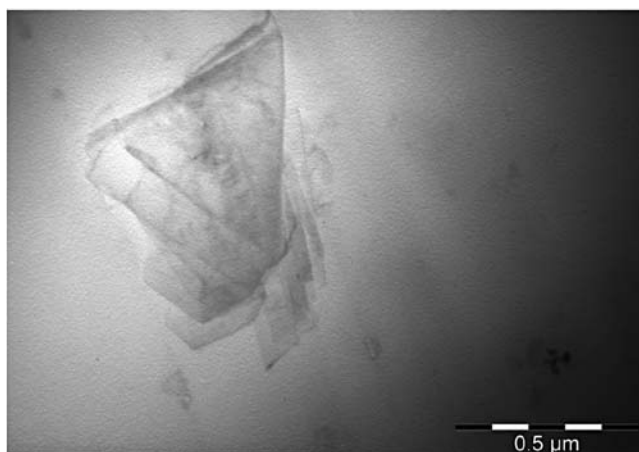


Fig. 7. TEM image of PET/EG 0.1wt.% nanocomposite

Nanofillers usually affect the ability to crystallize semi-crystalline polymers [19÷23]. Distributed in the polymer matrix nanoparticles assisted by nucleation and growth of crystallites. In the case of characterized in this work nanocomposites, there was no significant effect of nanoparticles on the physical transitions in PET or they were very small. Only for the highest content of EG in investigated nanocomposites based on PET it can be stated repeatedly the increase of crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) (fig. 8 and 9). EG content does not significantly affect the degree of crystallinity of PET, which is between 34,4÷36,1 (Tab. I). This is probably due to the fact that the sizes of individual expanded graphite nanoplatelets were below the critical nucleation agents, as a result, may not constitute active centers of growth of crystallites. It also describes the lack of changes in the glass transition temperature ( $T_g$ ) of semi-crystalline PET regardless of the EG content

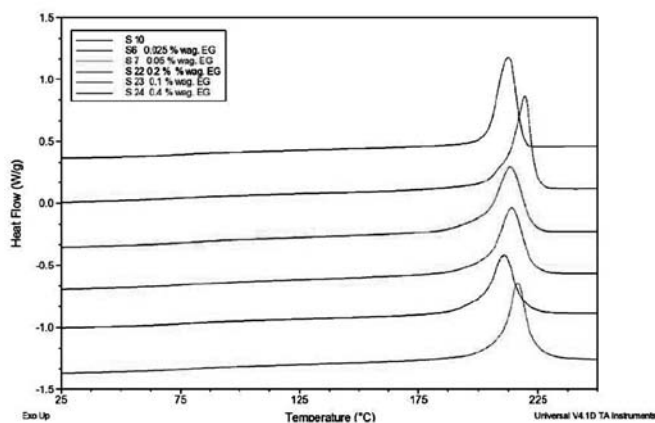


Fig. 8. DSC thermograms for PET and PET/EG nanocomposites during the cooling

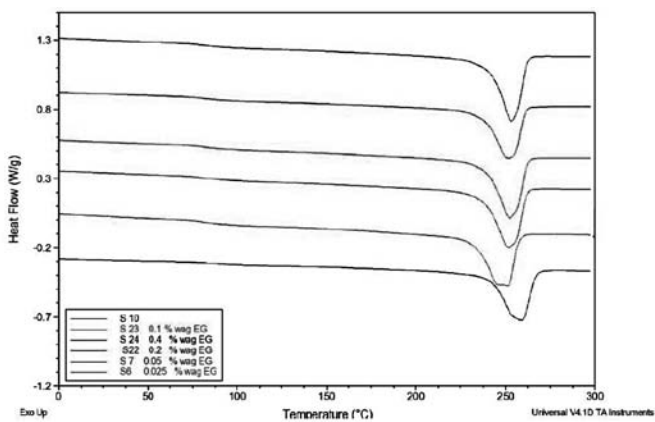


Fig. 9. DSC thermograms for PET and PET/EG nanocomposites during the heating

Table I  
Physical transition temperature and the degree of crystallinity of PET and PET/EG nanocomposites

Symbol	$T_g$ , °C	$T_m$ , °C	$T_c$ , °C	$X_c$ , %
PET	85	257	214	36.1
PET/EG-0.025wt%	83	251	207	35.3
PET/EG-0.05wt%	83	253	210	36.1
PET/EG 0.1wt%	83	252	214	36.0
PET/EG 0.2wt%	83	252	217	34.4
PET/EG 0.4wt%	83	253	217	35.8

In the literature [24÷26], it was found that the addition of expanded graphite into the polymer matrix (PVC, PLA) improves the thermal stability both in oxidizing atmosphere and in an inert atmosphere. The studies of graphene influence on thermal properties of PET showed that 0.025% increase in graphene affects the thermo-oxidative resistance of nanocomposites (Fig. 10). Of course, in an inert atmosphere in the process of degradation occurred at approximately 20°C higher than in an oxidizing atmosphere. The nanocomposite containing 0.1 wt% of graphene exhibit the highest temperature of 2% mass loss in an inert atmosphere. However, the differences between the temperatures corresponding to 2, 10 and 50% weight loss and the temperature of maximum rate of weight loss for obtained PET / EG nanocomposites and unmodified PET at 3 to 5°C are within the measurement error. The value of activation energy ( $E_a$ ) for the PET / EG nanocomposites increased with increasing content of expanded graphite, both when the measurement was carried out in an oxidizing atmosphere and in argon. The values of  $E_a$  for the measurement carried out in air ranged between 247-268 kJ / mol, while for the measurement carried out in argon these values were in the range 304-318 kJ / mol. The results of research carried out in an oxidizing atmosphere and in argon are presented in Table 2.

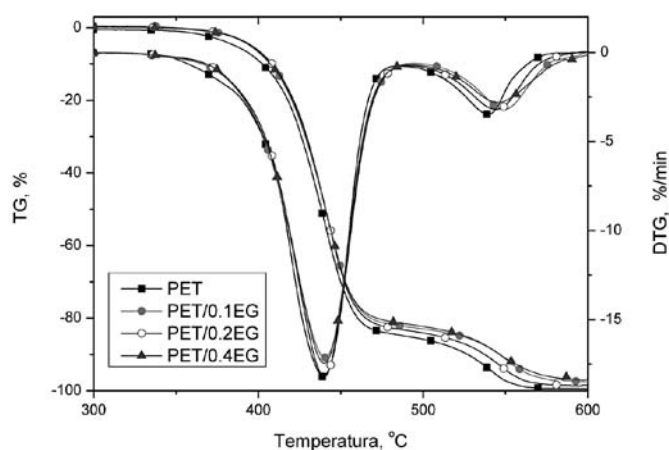


Fig. 10. Weight loss and derivative weight loss versus temperature for the PET/EG nanocomposites in air at a heating rate of 10°C/min

In an oxidizing and inert atmosphere in the thermal degradation process, PET/EG nanocomposites showed improved thermal stability. In an inert atmosphere the degradation process does not depend on the participation of EG. It can therefore be assumed that the mechanism of thermo-oxidative stability of PET by graphene sheets is related to the annihilation of free radicals by carbon planes. Probable mechanism of thermal degradation of PET is the free radical reaction. This has been shown previously [27-29] by analyzing the process of model compounds (Fig. 11). This phenomenon of improving the stability has also been observed for composites with carbon nanotubes. So it can be assumed that the mechanism of increasing the stability of PET is due to the transfer of free radicals on the carbon planes and its deactivation. Expanded graphite therefore fulfills the role of antioxidant operating at higher temperatures.

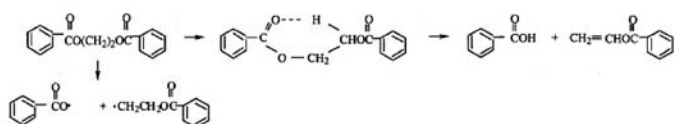


Fig. 11. The mechanism of thermal degradation of PET [28]

This is why the 2% weight loss temperature of nanocomposites with expanded graphite content of 0.1, 0.2 and 0.4wt.% was significantly higher than for PET without carbon nanoparticles.

Table 2

Temperatures corresponding to 2, 10 and 50% weight loss activation energy and the maximum temperature of the mass loss rate for the nanocomposites obtained in an oxidizing atmosphere and in argon

Symbol	$T_{2\%}$ , °C	$T_{10\%}$ , °C	$T_{50\%}$ , °C	$E_a$ , kJ/mol	$T_{DTG1}$ , °C	$T_{DTG2}$ , °C
Measurement carried out in an oxidizing atmosphere						
PET	366	402	438	257.07	440	539
PET/EG 0.1	382	408	441	247.02	440	545
PET/EG 0.2	381	407	441	255.25	441	549
PET/EG 0.4	381	407	441	268.34	441	545
Measurement carried out in argon						
PET	387	413	442	313.53	441	-
PET/EG 0.1	400	418	444	304.30	442	-
PET/EG 0.2	395	415	443	316.36	441	-
PET/EG 0.4	389	389	414	318.32	441	-

## Conclusions

The aim of his work was preparation of polymer nanocomposites based on PET (matrix) and expanded graphite as a nanofiller. The method of dispersion of EG in ethanediol and then maintaining the dispersion during the synthesis of PET is a good way of obtaining PET / EG nanocomposites. Investigated materials were prepared by *in situ* by the introduction of nanofiller into the polymer during the synthesis. Structure surveys support the effectiveness of the method from the viewpoint of uniformity of distribution of the dispersed phase; however, to eliminate the observed agglomerates of nanofillers should result in further research into the way of expanded graphite dispersion in glycol.

DSC studies show that the addition of expanded graphite does not affect the melting point and glass transition temperature of PET. These temperatures for all samples were very similar. Furthermore it was found that the addition of nanofillers does not affect the crystallization temperature or the degree of crystallinity of PET. In an oxidizing and inert atmosphere in the thermal degradation process PET/EG nanocomposites showed improved thermal stability. The mechanism of PET stabilization by graphene is associated with the transfer of free radicals on the carbon planes. For a 2% weight loss nanocomposites containing expanded graphite already more than 0.1% by weight possessed higher thermo-oxidative stability.

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Sandra PASZKIEWICZ – M.Sc., graduated from the Faculty of Chemical Technology and Engineering (2009), and in 2010 the second specialization at the Faculty of Mechanical Engineering and Mechatronics, West Pomeranian University of Technology in Szczecin. Since 2009 she is the Ph.D. student in Institute of Materials Science and Engineering, Faculty of Mechanical Engineering and Mechatronics, WUT. Research interests: polymer nanocomposites containing carbon nanotubes and graphene, polymer hybrid nanocomposites.

e-mail contact: sandra.paszkievicz@zut.edu.pl

Zbigniew ROSŁANIEC - Professor, graduated from Szczecin University of Technology, now West Pomeranian University of Technology in Szczecin (1969). He is the head of Department of Polymer Materials in the Institute of Materials Science and Engineering and director of the Institute at the Faculty of Mechanical Engineering and Mechatronics. Specialty-research reactive polymer systems, thermoplastic elastomers and polymer nanocomposites containing carbon nanotubes and graphene.

Anna SZYMCZYK – Ph.D., graduated from the Faculty of Chemical Technology and Engineering Szczecin University of Technology (1994), now West Pomeranian University of Technology in Szczecin. Since 2002 he is employed as a lecturer at the Institute of Physics, at the Faculty of Mechanical Engineering and Mechatronics, WUT. She received the PhD title in 1999 at Faculty of Chemical Technology and Engineering Szczecin University of Technology. Specialty: chemistry and technology of polymer.

Zdenko SPITALSKY – Ph.D., graduated in organic chemistry at Comenius University, Faculty of Natural Sciences, Department of Organic Chemistry (1998). He received Ph.D. degree in Macromolecular chemistry in 2002 Slovak Academy of Sciences, Polymer Institute, Bratislava. His current research focuses, among others, to surface modification of carbon nanomaterials, preparation of nanocomposites and organic synthesis.

Jaroslav MOSNACEK – Ph.D., graduated in organic chemistry at Comenius University, Faculty of Natural Sciences, Department of Organic Chemistry (1998). He received Ph.D. degree in Macromolecular chemistry in 2002 Slovak Academy of Sciences, Polymer Institute, Bratislava. He was awarded in 2004 as Slovak Young Scientist of the Year for "Preparation of photo-reactive compounds, monomers and polymers, and modification and stabilization of polymers". His current research interests are focused on synthesis of organic compounds for polymer chemistry and physics; synthesis, modification, degradation and stabilization of polymers; and covalent modifications of inorganic, carbon and polymer surfaces.