

THERMAL AND MECHANICAL PROPERTIES OF POLYESTER COMPOSITES WITH GRAPHENE OXIDE AND GRAPHITE

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Thermal behavior of polyester composite with graphene oxide/graphite was investigated using DMA, TGA and SEM. The influence of graphene oxide/graphite on mechanical and thermal properties of polyester composites were studied in case of small contents. The study allowed to conclude that graphene oxide and graphite have a different effect on polyester composites due to their different chemical bonds with polyester matrix. Analytical inference of the storage modulus was done using Einstein relationship, while the Nielsen equation was used for the damping factor. Glass transition temperature of polyester composites was inferred by DMA method. Thermal stability and mass loss were investigated through TGA tests. Images obtained by scanning electron microscopy allowed morphological analysis of the composite specimens.

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1. Introduction

The unique mechanical and thermal characteristics of graphene drew the scientific world attention. Thus the graphene have been used as additive in different polymers so as to obtain polymer/graphene nanocomposites. Polymer mixing with graphene has as a result better mechanical and thermal characteristics in comparison with carbon nanotubes [1-7]. However, there is a problem when using graphene in composites, namely their tendency to agglomerate into the polyester matrix due to the large specific surface as well as to the van der Waals bonds among the graphene layers [8,9]. In order to obtain a better strengthening effect of graphene in polymer composites, a better dispersion into the matrix and strong chemical bond between graphene and polymer matrix must be obtained [10,11]. There are two types of graphene structures, namely graphene oxide and reduced graphene which are often used as additives in composites. Graphene oxide contains oxygen based groups such as carbonyl, hydroxyl or oxygen, as these are linked to the graphene [12]. There have been discovered more methods in order to make the graphene oxide functional and for their better dispersion into the polymers [13-16]. Polyester is one of the most used thermosetting polymers. Due to the fact that it is easily processed, as well as to its excellent mechanical characteristics and its relatively small price, polyester like the epoxy, is widely used in industry, for example in car industry, aeronautics, or building materials industry [17-19].

This study is focused on studying the polyester composites mixed with graphene oxide and graphite. These composites were tested using DMA in order to find out its mechanical behavior not only in glassy state as well as rubber state. In order to find out additives influence on composite mass loss in the heating process, TGA method was applied. By using Einstein's equation, the experimental and the theoretical values of the storage modulus and the damping factor were compared.

Graphite and graphene are two allotropic states of carbon which can interact differently with polyester resin which is the matrix of the composite materials. Potential chemical bonds can

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be considered firstly as van der Waals bonds when referring to number and secondly as hydrogen bonds. The latter, hydrogen bonds, are stronger than van der Waals bonds but less numerous and they can be found among the macromolecules of the polyester resin, namely among the atoms of the ester groups and the carboxyl and carbonyl groups which are formed during the chemical process for obtaining graphene oxide from graphite. When having the same concentration of graphite and graphene in a composite material with polyester matrix it is obvious that the number of the chemical bonds which appear between polyester macromolecules atoms to be higher when referring to graphene than when referring to graphite. This is due to separating the graphite layers and to increasing the number of graphene flakes. The graphene flakes discharge a bigger number of carbon atoms through their much larger surface compared with the surface of the graphite they come from. Thus the number of van der Waals bonds will be higher between the polyester matrix and the graphene compared with composite materials formed from polyester matrix and graphite. In case of composite materials formed from polyester matrix and graphene oxide there also appear hydrogen bonds between the oxygen atoms of ester groups and hydrogen atoms of carboxyl groups which are formed during the oxidation process. The number of these bonds is smaller than that of van der Waals bonds because of the small number of carboxyl groups which are linked to the graphene but in this case the strength of the hydrogen bonds is much bigger.

2. Experimental

2.1. Materials

The research was carried out on two types of composite materials, made of polyester with graphene oxide and polyester with graphite. Graphite used was purchased from Koh-I-Noor, and the polyester resin, trade name Norsodyne H 13 271 TA, was purchased from Rompolimer. Graphene were obtained through chemical reactions as a version of Staudenmaier method from graphite. In a 500 mL beaker was placed 5 g of graphite. Then it was added a volume of 200 mL perchloric acid 70%, purchased from Merck and the obtained mixture was homogenized using a magnetic stirring for 20 minutes (1500 rpm). Then the mixture was cooled in an ice bath before the addition of potassium permanganate (achieved from Fluka).

The addition reaction is highly exothermic, so that the permanganate was added in four steps of 5g each. The temperature during the reaction process increased from 25°C to 35°C. In order to keep the temperature below 35°C, it was applied a cooling procedure of the entire reaction mass using an ice bath. The global reaction time was 24 hours. Then, at this mixture was added the hydrogen peroxide 30% in ten steps of 1 ml. The total reaction time was 3h. After the reaction is finished (CO₂ emission ceased), the resulting suspension was centrifuged at 18,000 rpm. The clear phase was separated, washed with distilled water in 5 stages; the total distilled water was 1500 ml. Finally the solution achieved the pH value of 6.5 (identical with distilled water one). At the end the solution was washed for two times using absolute ethanol in a total volume of 500 ml and then it was centrifuged. The resulting residue was placed into a crystallizer vessel as a thin film and dried in an oven at 105°C for 8h. In order to obtain polyester-graphite (G) and polyester-graphene oxide (GO) nanocomposites respectively, it was introduced the determined quantities of G and GO into resin mass, achieving finally a total amount of 100 g of nanocomposite.

According to the concentrations established for the experiment, it was weighed at the analytical balance appropriate quantity of G and GO respectively and it was placed in a mortar. A dry grinding stage was performed for 30 minutes. Then it was added 1-2 g of polyester resin and followed a wet grinding stage for another 30 minutes. The mixture was sampled by a washing procedure, using new quantities of resin till the final amount of 100 g. The entire mixture was sloped in a 200 ml stirred tank and it was stirred for 1h using a magnetic stirrer (1500 rpm). After this step, it was continued the dispersion of the particles into the matrix by sonication in two stages of 5 minutes. In order to keep the temperature under control during the reaction process at 50°C, the mixture was cooled in an ice bath. The reaction mass was then degassed under vacuum (1-2 torr) for 1 minute. After that, the catalyst (2% PMEK) was added under continuously stirring. This

stage was followed by a mechanical homogenization for another 1 minute. Then, the reaction mixture was poured into rubber molds. The gelling time was 17 minutes. After an hour the nanocomposite was draw out from the mold and placed into the oven to complete the reaction at 60°C for 4h.

2.2. Methods

2.2.1. Dynamical mechanical analysis

Dynamical mechanical analysis (DMA) is a technique through which a small deformation is applied on the sample in a cyclic way. This experiment allows determination of the material's response to effort according to the temperature and/or deformation frequency.

Dynamic mechanical properties of the samples have been determined using "Dynamic Mechanical Analyzer" DMA Q800 by TA Instruments. The results of the measurements have been processed using the software Universal Analysis 2000. DMA analysis was made using unsaturated polyester resin samples additivated at three concentrations: 0.05 wt%, 0.10 wt%, 0.15 wt% by using two additives: graphene oxide and graphite. Test conditions were as follows: measurements were made in the open air, measurement method was dual cantilever, loading frequency 1Hz, temperature interval 25 – 250°C, heating speed 3°C/min, samples sizes, imposed by clamp for dual cantilever lenght 60 mm, width 11 mm, thickness 5 mm. The samples have been scanned according to their visco- elastic response including storage modulus (E'), loss modulus (E'') and damping factor ($\tan \delta$) in order to assess -the effect of graphene oxide and graphite as well as the variation of their concentration on these characteristics.

2.2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique which consists in measuring mass changes of a sample at the same time with increasing temperature in a controlled atmosphere. Results are recorded as weight loss – time (for isothermal analysis) or mass loss-temperature (for analysis made with a constant heating speed). The instrument used for Termogravimetric analysis was TGA Q5000 IR, TA Universal Analysis, the melting crucible was made of platinum, the gas was 5.0 purity air, the temperature range 25-600°C and the heating speed was of 10 °C/min.

2.2.3. Scanning electron microscopy

SEM observations of polyester/graphene oxide, polyester/graphite and the fracture surface of polyester and polyester nanocomposites were examined using a QUANTA 20 scanning electron microscope. The fracture surfaces were gold coated prior to SEM investigation to make them conductive.

3. Results and discussion

3.1. Dynamical mechanical analysis

The complex modulus (E^*) of composites subjected to DMA test consists of storage modulus (E') and loss modulus(E''):

$$E^* = E' + E'' \quad (1)$$

Storage modulus(E') represents the elastic energy received during deformation and stored into the material during a loading cycle, energy which is released at the end of the loading. Loss modulus (E'') represents the energy dissipated into the composite as heat during a loading cycle, and it is a means of measuring the vibration energy which changes itself into heat due to internal friction and it cannot be recovered.

3.1.1. Storage modulus

In different graphene oxide composites, increasing the value of storage modulus is due to graphene flakes which only limit the movement of polymeric chain [20-27], and also due to lack of molecular polyester chain ramification [28]. Also, another factor of increasing the polyester storage modulus is aging the material which results in limiting the movement of polyester chain, which becomes more rigid with the time [29]. Another factor which influences the stiffness of the polymer and implicitly of storage modulus is decreasing the length of the polymeric chain as well as of the number of rigid particles from the polymeric matrix [30]. The decrease of storage modulus during glass transition temperature (T_g) is because of the rise of molecular mobility [31-38].

In Figures 1 and 2 there are shown three areas: the elastic area which is shown between the temperatures interval 30-50°C, where the storage modulus slowly decreases; the second area is between the temperature interval 50-90°C, where the storage modulus abruptly decreases; the third area corresponds to the rubbery plateau domain where the storage modulus is almost null. In Figure 1 it can be noticed that the storage modulus doesn't have a strong dependence on the graphene oxide content. The only concentration when the storage modulus of the composite is bigger than that of the pure polyester is with 0.05 wt% graphene oxide. Similar results for concentrations bigger than 0.1 wt% have been obtained with carbon nanotube polyester composite [39]. An explanation for decreasing of E' can be that of chemical bond deterioration between graphene oxide and the polyester matrix [40]. Another explanation may be that during the composite making, the tendency for graphene oxide agglomeration is stronger for concentrations of 0.1 wt% and 0.15 wt% graphene oxide, and the chemical bonds which are formed with the polyester chain are weaker. The same tendency is manifested during the temperatures interval 50-90°C.

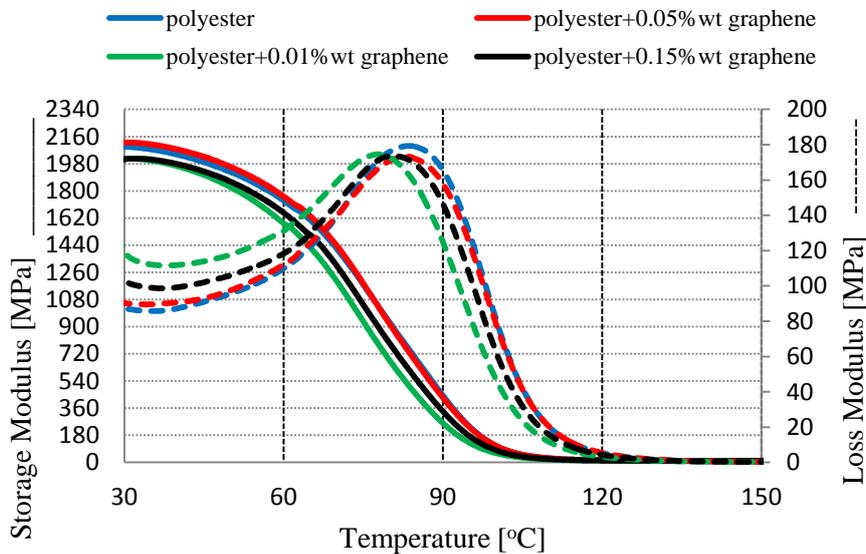


Fig.1. Storage modulus and loss modulus vs temperature for polyester/graphene composites

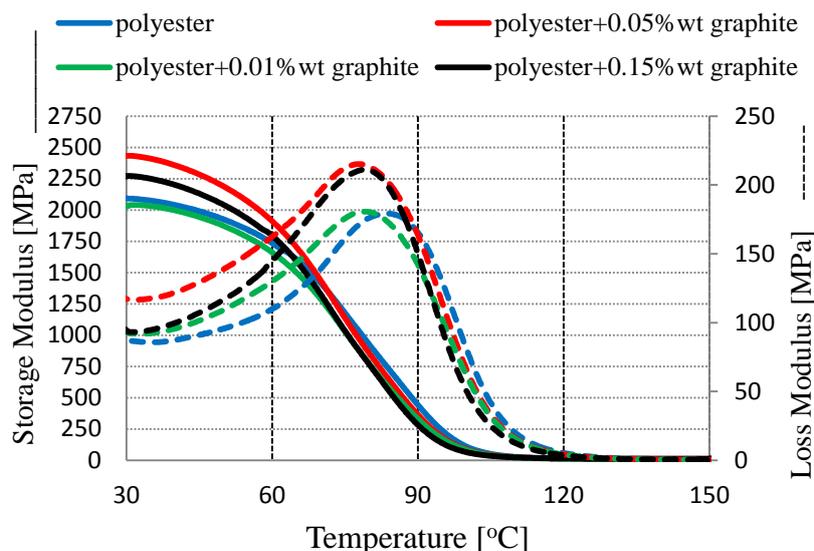


Fig.2. Storage modulus and loss modulus vs temperature for polyester/graphite composites

Figure 2 shows the increase of the storage modulus during the temperatures interval lower than T_g , except for the composite containing 0.1 wt% graphite. Lower values of the storage modulus are measured for the concentration of 0.1 wt%. The biggest values of storage modulus are noticed for the polyester composite with 0.05 wt% graphite. This is due to the strong chemical bonds between graphite and the polyester chain. In Figures 1 and 2 can be noticed that the values of the storage modulus increase for small concentrations of the graphene and the graphite from composites. This aspect demonstrates that the strong graphene oxide-polyester and graphite-polyester chemical bonds take place even in case of small concentrations of the additives.

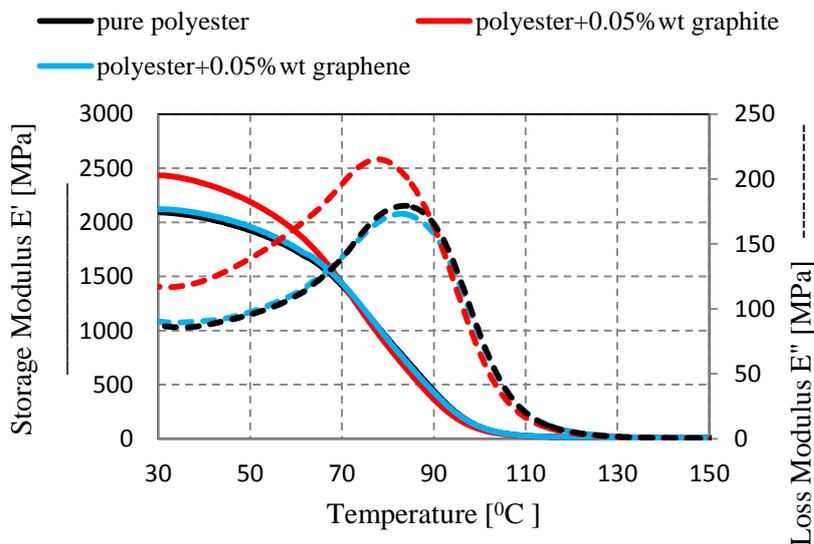


Fig. 3. Storage modulus and loss modulus, vs temperature for polyester+0.05 wt % grapheme and polyester+0.05 wt % graphite

In Figure 3 it can be seen the values of the storage modulus for polyester-graphene oxide and polyester-graphite composites where the additive's influence was the strongest. This strong influence manifested itself in the polyester+0.05 wt% graphene and polyester+0.05 wt% graphite composites. Bigger values have been obtained for polyester+0.05 wt% graphite composite, which

emphasizes one more time the fact that the chemical bonds between the graphite and the polyester chain are stronger than those between the graphene oxide and the polyester chain.

3.1.3. Loss modulus

Loss modulus (E'') represents the result of the viscous behaviour of the composite and it also represents the dissipated energy changed into heat. The fast increase of it indicates the increase of the polyester chains mobility. In the glassy transition area, all jellified cross-linked are capable of increasing their degrees of freedom. Loss modulus values are also smaller for polyester – graphene oxide composites compared with the pure polyester. Graphene has a bigger thermal conductivity (5000 W/mK) [43], which allows the heat release faster than pure polyester. Loss modulus increases in the glass transition area due to the increasing molecular movement which occurs in the polyester chain. In Figure 1 it can be noticed that the maximum loss modulus decreases because of the influence of the graphene oxide, but there are no significant differences due to different concentrations of graphene oxide. The maximum values of the loss modulus for composites are towards higher temperatures than the maximum of loss modulus obtained for the pure polyester. The biggest difference of the maximum of the loss modulus can be noticed in case of the polyester+0.05 wt% graphene oxide composite.

Figure 2 shows that the maximum values of the loss modulus are higher for the polyester-graphite composites comparing with the values obtained for the pure polyester. These maximum values are moved to smaller values of the temperature compared with the maximum obtained for the loss modulus of the pure polyester. The maximum values of the E'' , for the pure polyester, are obtained for higher temperatures of the glass transition interval. The increase in temperature brings a decrease in the elastic response of the polymer in favour of the plastic feature, which becomes dominant during the glass transition. The maximum values of the loss modulus are obtained for the polyester+0.05 wt% graphite composite.

In Figure 3 it can be noticed that the values of the loss modulus are bigger for the graphite composites compared with the values obtained in polyester-graphene oxide composites. It can also be stated that the mobility of the polymer chains is higher for graphite composites, resulting in a bigger plastic effect than for graphene composites. Chemical bonds between the oxidized graphene and the polyester matrix are weaker in comparison with the chemical bonds formed by graphite and the polyester matrix and the bigger tendency for graphene to agglomerate determines a smaller loss of energy inside the composite.

3.1.2. Theoretical modelling of the storage modulus

Using Einstein's equation [31, 32, 41, 42] we can compare the experimental values of the storage modulus with the theoretical ones:

$$E'_c = E'_m (1 + V_f) \quad (2)$$

where: E'_c is the storage modulus of the composite, E'_m – the storage modulus of the matrix, V_f – volum fraction of additives from the composite.

In Figure 4 there are shown the experimental values and theoretical values of the storage modulus for the temperatures of 50°C, 90°C and 130°C. The symbol (t) represents the theoretical values of the storage modulus for the respective temperatures. The experimental values are smaller than those which calculated, which shows the insignificant influence of the graphene oxide on the storage modulus. The small differences between the experimental and the theoretical values are only seen in case of the composite with the concentration of 0.05 wt% graphene oxide and for temperatures over 90°C. For temperatures between the interval 50-90°C there are differences between the experimental and the theoretical values of the storage modulus only for the composites which have the concentration of 0.15 wt% graphene oxide.

From Figure 5, it results that there are the same insignificant differences between the theoretical and the experimental values for the storage modulus of the polyester-graphite composites both below T_g temperatures and over them. Significant differences only appear for temperatures in the glassy transition area and for the concentration of 0.15 wt% graphite. Figures 4

and 5 show a good relation between the experimental values and those given by the theoretical model of Einstein's equation.

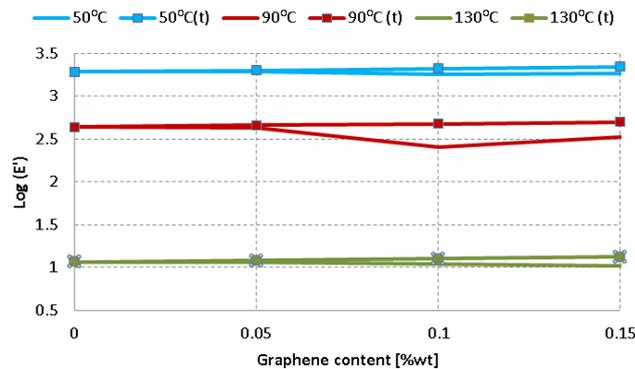


Fig.4. Theoretical and experimental storage modulus for polyester with graphene oxide composites

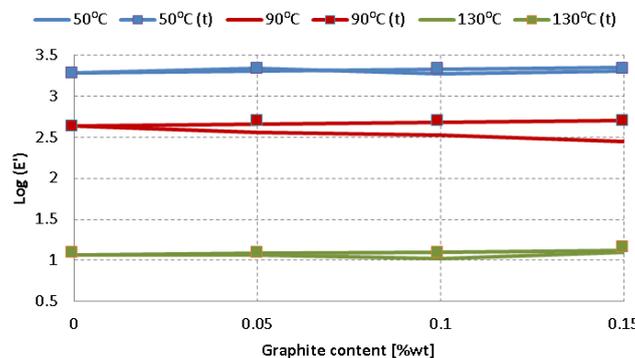


Fig.5. Theoretical and experimental storage modulus for polyester with graphite composites

3.1.4 Damping factor

Damping represents the capacity of the material to absorb the deformation energy during a cyclic loading and gives information about the lost energy into the material as dissipated heat. *Damping factor* ($\tan\delta$) represents the ratio between the loss modulus and the storage modulus of the energy. The temperature when the damping factor has its maximum value represents the temperature where the composite does not come back to its initial state. The decrease of the maximum value of the damping factor under the influence of the graphene oxide has also been noticed for other composites [25]. Damping factor is done by following relationship:

$$\tan \delta = \frac{E''}{E'} \quad (3)$$

Nielsen's equation can be used for theoretical calculus of damping factor in order to be compared with the experimental values [31]:

$$\tan \delta_c = \tan \delta_m (1 - V_f) \quad (4)$$

where $\tan\delta_c$ is damping factor for composite, $\tan \delta_m$ is damping factor for matrix, V_f – volum fraction of additives into the composite. Figure 6 shows that the values of the damping factor are higher in polyester-graphene composites compared with the value of the damping factor of pure polyester. The maximum of the damping factor for polyester-graphene oxide composites are obtained for higher temperatures comparing with the maximum of the damping factor of pure polyester. This is also influenced by the decrease of the polyester-graphene oxide composites compared with that of pure polyester. Graphene oxide has the tendency to agglomerate and thus

decreases the molecular movement of the polyester chain. The maximum values are obtained for the polyester with 0.15 wt% graphene oxide composite.

Fig. 7 shows that the damping factor decreases in the polyester-graphite composites and the maximum values of the damping factor for each composite is obtained at smaller temperatures compared with the values of the damping factor of pure polyester. Stiffness of the polyester-graphite composites is higher than the stiffness of pure polyester. The smaller values of the maximum of the damping factor are due to the possible higher amplitude of the molecular movement of the polyester chain. Figure 8 shows theoretical and experimental curves for the damping factor of the polyester with 0.05 wt% graphene oxide composite. The theoretical values are identical with experimental values in case of polyester-graphene composites while negligible small differences are present into the polyester-graphite composites. These diagrams confirm the validity of Nielsen's law applied to polyester/graphite and polyester/graphene oxide composite.

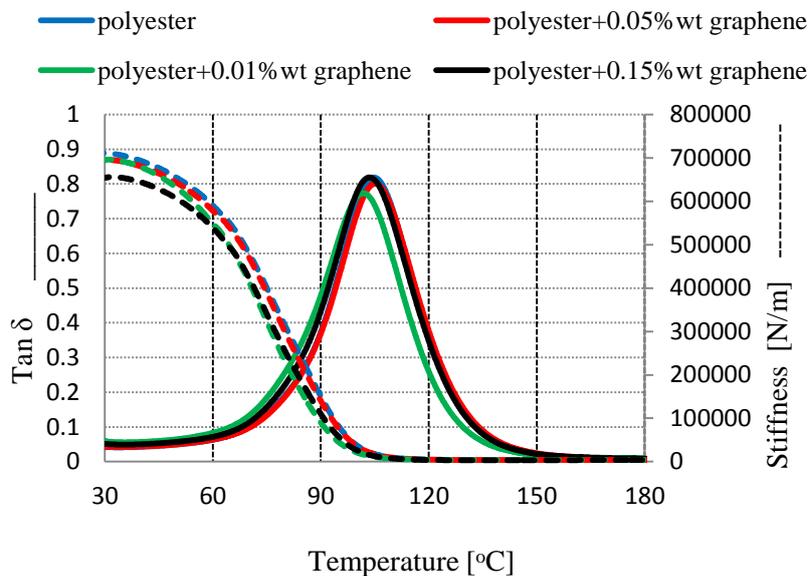


Fig. 6. Damping factor and stiffness vs temperature for polyester/graphene composites

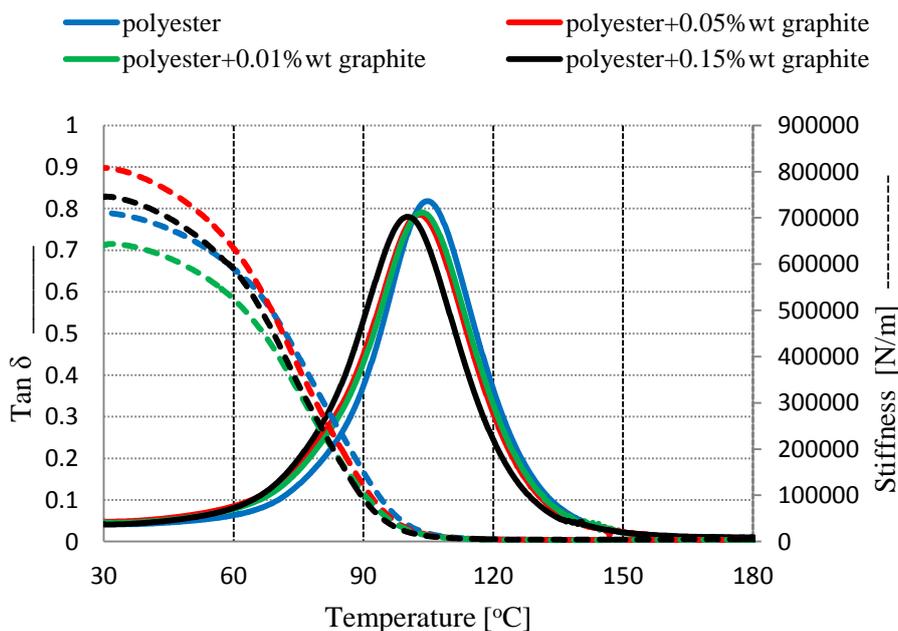


Fig. 7. Damping factor and stiffness vs temperature for polyester/graphite composites

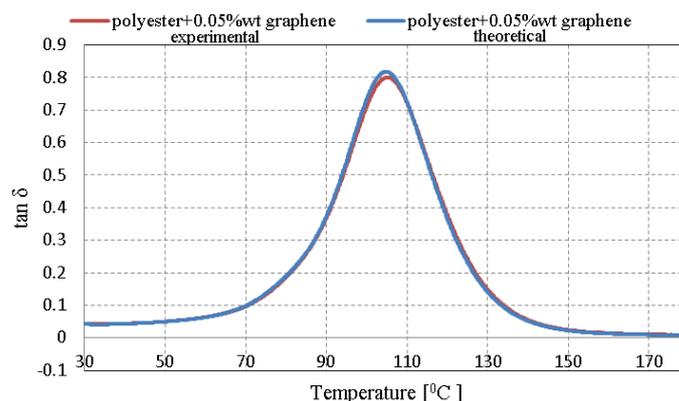


Fig. 8. Comparison between experimental and theoretical damping factor vs temperature for polyester-graphene composites

3.1.5. Glass transition temperature measurement by DMA

The analysis of the DMA tests allows determining the glass transition temperature, T_g . In ASTM E1640 there are shown several methods for determining T_g using DMA [44]: intersection of tangent to curve E' before T_g and tangent to curve E' when this starts to decrease suddenly, “peak” on the loss modulus curve and “peak” on the damping factor curve.

In case of the polyester, the real values of T_g are the temperature obtained by using the first method which is shown in Fig.9. Decreasing the T_g for higher concentrations can be caused by the break in hydrogen bond [40] or by the effect of blocking the molecular movement of the graphene composite [25,45]. Table 1 shows an increase of T_g polyester composites with graphene oxide and graphite. This is due to the limiting effect of the molecular movement of polyester by graphene oxide and graphite. Due to the higher thermal conductivity of the graphene oxide, the values of the T_g are higher for the polyester-graphene oxide composites compared with the values obtained for the polyester-graphite composites.

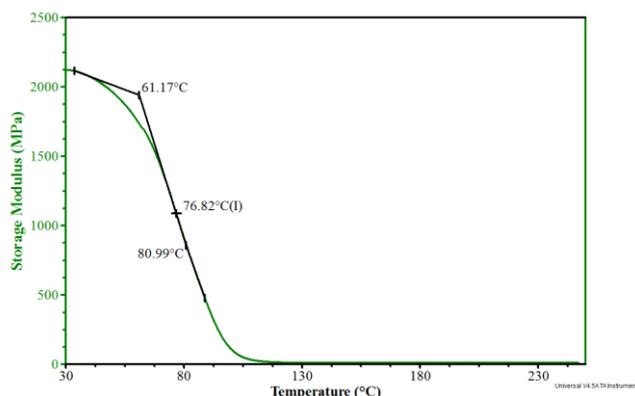


Fig. 9. T_g determined by storage modulus curve of polyester+0.05 wt% graphene oxide

Table 1: T_g for polyester with graphene oxide and polyester with graphite composites

T_g [°C]			
Polyester	55.91	Polyester	55.91
Polyester+0.05 wt % graphite	56.51	Polyester+0.05 wt % graphene oxide	61.17
Polyester+0.10 wt % graphite	58.95	Polyester+0.10 wt% graphene oxide	58.11
Polyester+0.15 wt % graphite	57.75	Polyester+0.15 wt % graphene oxide	59.46

3.2. Thermogravimetric analysis

Graphene oxide influence on polymers during TGA tests result in a charred layer which covers the surface of the polymer, thus interrupting the absorption of the oxygen necessary for the burning process [23]. When the thermal degradation of the polymer leads to the cleavage of polymer chains and the forming of the radical starts, the carbon surface of graphene oxide behaves as a thermal protective material, which leads to delaying the start of the thermal degradation [38]. Polymer macromolecules attach themselves to the surface of the graphene oxide, thus decreasing the amplitude of the molecules moving under the temperature influence [24].

Derivative thermogravimetry (DTG) is the derivative curve which indicates the starting temperatures of thermal degradation, the temperature of the maximum of degradation rate, the temperature of the end of thermal degradation, the number and content of the steps involved in the thermal degradation of the samples.

Thermal degradation of the graphene oxide represents a massive weight loss around 220°C, because of functional groups degradation which contain oxygen, hydroxyl and carboxyl group. This phenomenon happens both in air and nitrogen atmosphere [38, 46].

Graphite has a very good thermal stability when heating up to 900°C, while graphene oxide are not thermally stable and start losing mass during heating below 100°C. The severe mass loss it suffers at 190°C-200°C is because of the oxygen pyrolysis from hydroxyl, carboxyl and carbonyl groups as well as because the humidity loss, which results in a rapid thermal expansion of the material, which generates gases such as CO, CO₂, H₂O [25,47].

Figure 10 shows that for the polyester with 0.1 wt% graphite composite mass loss accentuates when the temperature is 307°C and when the mass loss is of 50 % reaches 385°C, having a residue of 1.5 % at 600°C.

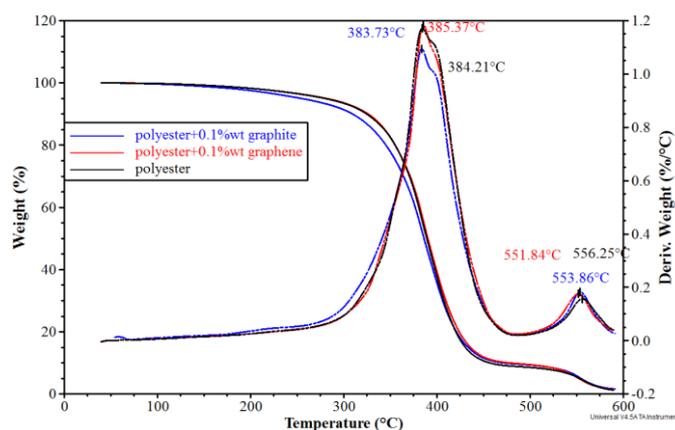


Fig. 10. TGA and DTG diagrams for polyester composite with graphene and graphite

For polyester with 0.1 wt% oxide graphene composite the temperature when mass loss accentuates is 320°C, and mass loss reaches 50% for temperatures of 390°C, having a residue of 1.5% at 600°C. For pure polyester the temperature when mass loss accentuates is 320°C, and mass loss reaches 50% for the temperature of 388°C, having a residue of 1.5% at 600°C. The graphs show that graphite decreases the temperature when polyester/graphite composite degradation takes place at 307°C comparing with the starting temperature of degradation for the pure polyester at 320°C. Graphite also influences the temperature when mass loss reaches 50%, this decreasing from 390°C for pure polyester to 385°C for polyester with 0.1 wt graphite composite. Graphene oxides at small concentrations, of 0.1wt, do not have a significant influence on the thermal decomposition process of polyester/oxide graphene composites.

3.3. SEM investigation

Fig. 11 shows SEM images for polyester/graphene oxide and polyester/graphite composite. In the marked square area on Fig. 11a, a layered bundle of graphene oxide can be seen. Otherwise, a uniform dispersion of smaller graphene oxide sheets intruded in the polyester matrix can be noticed. The increase in graphene oxide content leads to the clusters occurrence which causes a lower dispersion (Fig. 11b). Graphite particles tend to agglomerate even at low content, as shown in the Figure 11c. Increased content of graphite results in a enlarged clusters (Fig. 11d). Anyway, at the same content, graphene oxide has a better dispersion than graphite.

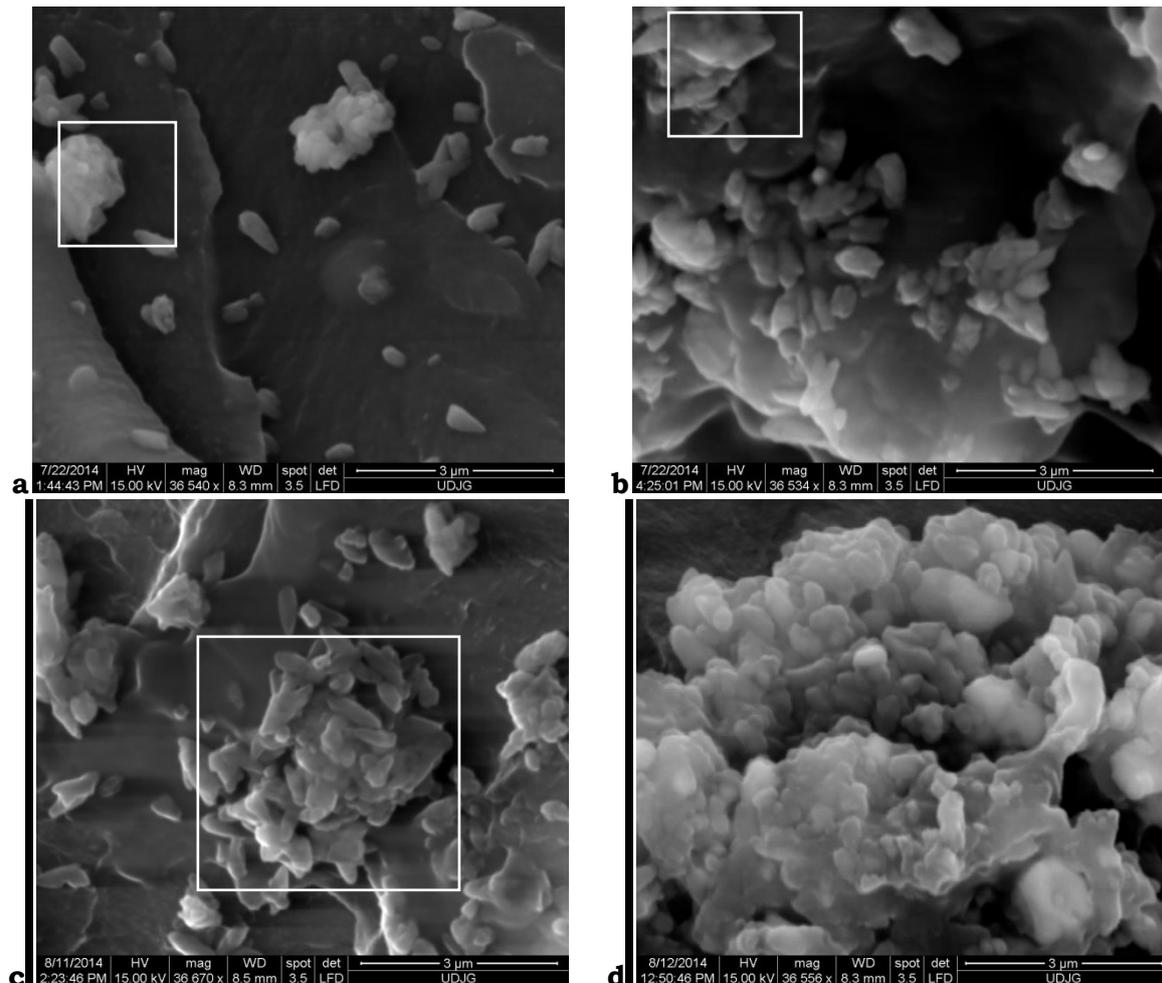


Fig. 11. SEM images for a) polyester+0.08%wt graphene oxide; b) polyester+0.1%wt graphene oxide; c) polyester+0.08%wt graphite; d) polyester+0.01%wt graphite

4. Conclusions

This work was focused on the influence of graphene oxide and graphite on mechanical and thermal properties of composites with polyester matrix. DMA and TGA tests allowed emphasizing following findings:

- storage modulus doesn't have a strong dependence on the graphene oxide content, while the graphite increases storage modulus, up to 65 °C;
- in case of polyester/graphene and polyester/graphite composites, loss modulus increases and takes higher values compared to neat polyester, up to 80 °C;

- for polyester/graphene composites, damping factor values are higher than those of neat polyester, up to 110 °C, whereas the stiffness does not record significant differences beside polyester;
- it can be noticed that both graphene and graphite have increased in glass transition temperature;
- graphite decreased the temperature when polyester/graphite composite degradation takes place (at 307°C) comparing with the starting temperature of degradation for the neat polyester (at 320°C);
- graphene oxide at small content (0.1 wt%), does not have a significant influence on thermal degradation of polyester composites;
- SEM microscopy revealed the presence of graphene flakes, graphite particles and dispersion degree.

Further investigations are needed to study thermo-mechanical properties of polyester composites enhanced by higher content of graphene oxide flakes.

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