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RESEARCH

Determination of Specific Heat of Polyester Composite with Graphene and Graphite by Differential Scanning Calorimetry

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A B S T R A C T

Some polymers show low thermal properties which can be improved by adding various types of materials. Using nanoparticles, an enhancement of thermal properties can be obtained, even for small contents of additives. The evaluation of thermal properties of polymer composites with graphene can be achieved relying on Differential Scanning Calorimetry tests (DSC). This work presents a few conclusions resulting from DSC tests of the polyester composites with graphene and graphite.

1. INTRODUCTION

Graphene has aroused great interest among the scientists lately, due to their special physical properties which are supposed to be transferred to composite materials [1,2]. Polyester is widely used in industry in the form of fabric, film, recipient, etc. Due to its widely spread usage, many polyester based composites have been tested in order to improve the tribological [3], mechanical [4-6], thermal, electrical [7] and chemical properties of polyester. Besides, a good dispersion of fillers into the polyester matrix could enhance the overall properties of the composite [8]. There has also been tested the change of specific heat of different polyester based composites. The specific heat was measured by means of Differential Scanning Calorimetry [9]. Using the same method to measure the specific heat of polyester, other researchers measured the following values for the specific heat 1.93 J/g °C [10], 1.4 J/g °C [11]. Thus the polyester–sansevieria composite specific heat increases from 0.9 J/g °C la 1.46 J/g °C for the 30 °C – 90 °C. It was further noticed that there is a decreasing trend in the temperature range of 90 °C – 20 °C, which is attributed to decrease of phonons mean free path [12]. For the polyester leaf fiber composite specific heat has the value of 0.97 J/g °C [11]. For the polyester composite with 0.15 %wt SWCNT specific heat was established with the value of 4 J/g °C, and for the polyester composites with 0.2 %wt MWCNT specific heat value was measured as having the value of 2.7 J/g °C [13]. For the polyester sisal/cotton composite specific heat increases at 1.23 J/g°C, for ramie/cotton composite value of specific heat was established at 0.89J/g °C, and for jute/cotton composite specific heat was 1.017 J/g °C, compared with the value of specific heat 0.987 J/g °C for pure polyester [14].

There has been measured the variation of temperature for polyester palmyra composite and it has been observed an increase during the interval 30 °C – 80 °C, the phenomenon being explained by means of better storage heat. Specific heat is decrease beyond 80 °C that is heat storing capacity decreases [15]. In our study we used orthophthalic unsaturated polyester resin with 40 % styrene. The resin was added with graphite or graphene. We have also studied its influence on the specific heat of the composite in its exothermic stage, where during the cooling stage the composite gives away heat as well as in its endothermic stage where the composite retains heat.

2. MATERIALS AND METHODS

The research was carried out on two types of composite materials, made of polyester with graphene 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. Graphenes were obtained through chemical reactions as a version of Staudenmaier method from graphite. In a beaker was placed graphite (purchased from Koh-I-Noor). Then it was added perchloric acid 70 %, and the obtained mixture was homogenized using a magnetic stirrer. Afterwards, the mixture was cooled in an ice bath before the addition of potassium permanganate. The temperature during the chemical reaction increased from 25 °C to 35 °C. In order to keep the temperature below 35 °C, a cooling procedure was applied on the entire reaction mass, using an ice bath. Next, the hydrogen peroxide 30 % was added to the mixture. Upon reaction completion (CO_2 emission ceased), the resulting suspension was centrifuged at 18,000 rpm. The clear phase was separated and washed five times with distilled water.

In order to obtain polyester composites with graphene and graphite, respectively, the measured quantities of graphite or graphene were introduced into polyester resin. Then, polyester resin was added, followed by a wet grinding stage.

a)

b)

Fig. 1. a) Samples and b) DSC tester.

The mixture was sampled by a washing procedure. The mixture was poured in a tank and it was stirred for 1h using a magnetic stirrer (1500 rpm). Next, the dispersion of the particles into the matrix was improved by ultrasonication, two times, successively. The reaction mass was then degassed under vacuum (1-2 torr) for 1 minute. After that, the catalyst (2 % P-MEK) was added under continuously stirring. After an hour the composite specimens were removed from the mold and placed into the oven to complete the reaction at 60 °C for 4h. Concentrations chosen were 0.02 wt%, 0.04 wt%, 0.06 wt%, 0.08 wt% and 0.1 wt% respectively, for both graphene and graphite. Samples have been weighed with AB204-S/FACT balance from Mettler and tested according to ASTM 1269 on tester DSC1 using STAR^e software, both made by Mettler Toledo, Fig. 1b. Tests were performed using a speed of heating or cooling of 10 °C/min between 30 °C and 200 °C for five specimens of each composite.

In order to obtain more precise results, the measurements of the specific heat values were performed between intervals of 0.3 °C. The ASTM 1269 standard does not impose the size or shape of tubes, as these are shown in Fig. 1 a).

3. RESULTS AND DISCUSSIONS

3.1 Specific heat

We measured separately the specific heat for pure polyester, for graphene oxide, graphite and for each concentration of polyester with graphene, polyester with graphite composites, both during heating stage from 30 °C to 200 °C and during the cooling stage from 200 °C to 30 °C.

The specific heat at constant pressure was calculated using the following relation:

$$c = \frac{Q}{m \times \Delta T}, \text{ [J/g °C]} \quad (1)$$

where c is the specified heat at constant pressure, Q - is the absorbed or released heat [J], m- represents the mass [g], and ΔT- temperature rise of specimen [°C].

As shown in Figure 2, the specific heat of oxidized graphene is smaller than the specific heat of the polyester, but all their composites have a much higher specific heat than the specific heat of the pure polyester. Graphene influence on the specific heat of the composites is more stronger in polyester composite with 0.1 %wt graphene. Thus, at the temperature of 38 °C, we measured the specific heat of the pure polyester 1.87 J/g °C , the specific heat of the oxidized graphenes 1.08 J/g °C and the specific heat of the polyester with 0.1 %wt graphene composite 6.26 J/g°C. The value of the specific heat of the polyester with 0.1 %wt graphene composites is 334 % higher, which shows a very big influence of graphene in increasing the specific heat of the composite.

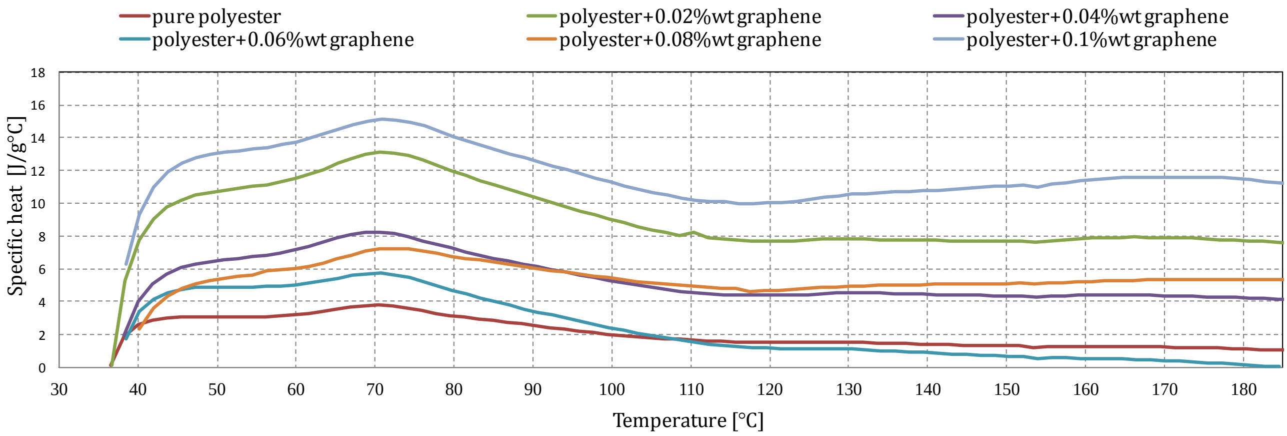

Fig. 2. Specific heat depending on temperature during heating stage for polyester with graphene composite.

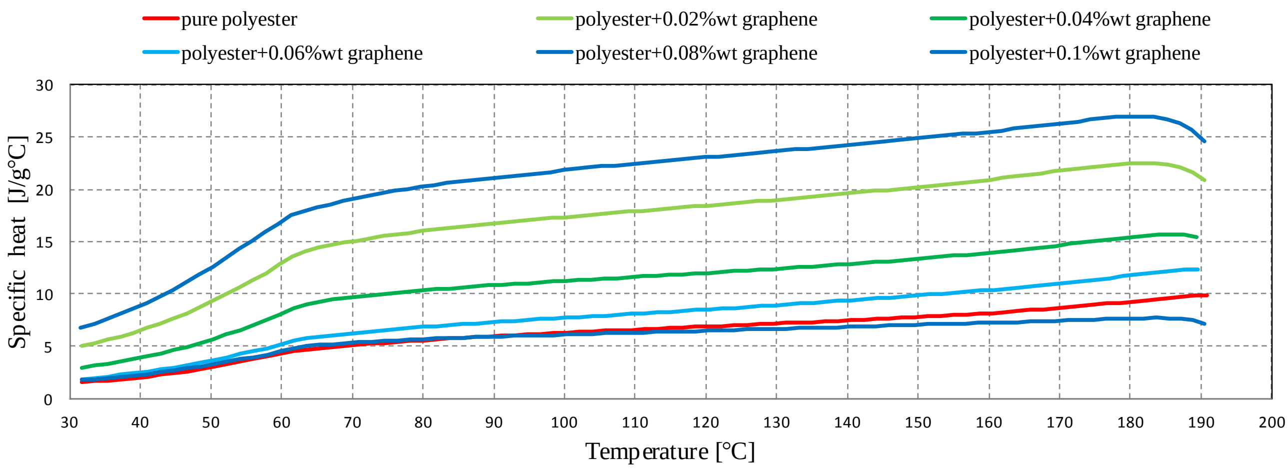

Fig. 3. Specific heat depending on temperature for polyester-graphene composite on cooling stage.

All the composites keep the tendency of increasing the specific heat by temperature increase during the interval 30 °C – 70 °C and its decrease after the temperature of 70 °C. In Fig. 3 is shown the influence of graphene on the specific heat of the polyester with graphene composites during the cooling test.

The highest temperature values of the specific heat are measured for polyester with 0.01 %wt graphene composite. For pure polyester we measured the maximum value 9.81 J/g °C, for polyester with 0.01 %wt graphene 25.74 J/g °C, for graphene oxide 9.43 J/g °C.

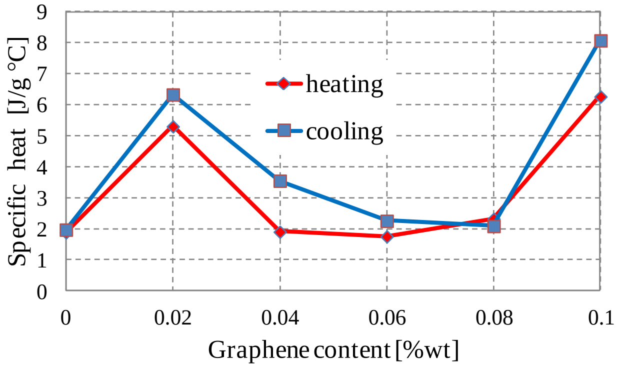

Fig. 4. Specific heat depending on graphene content.

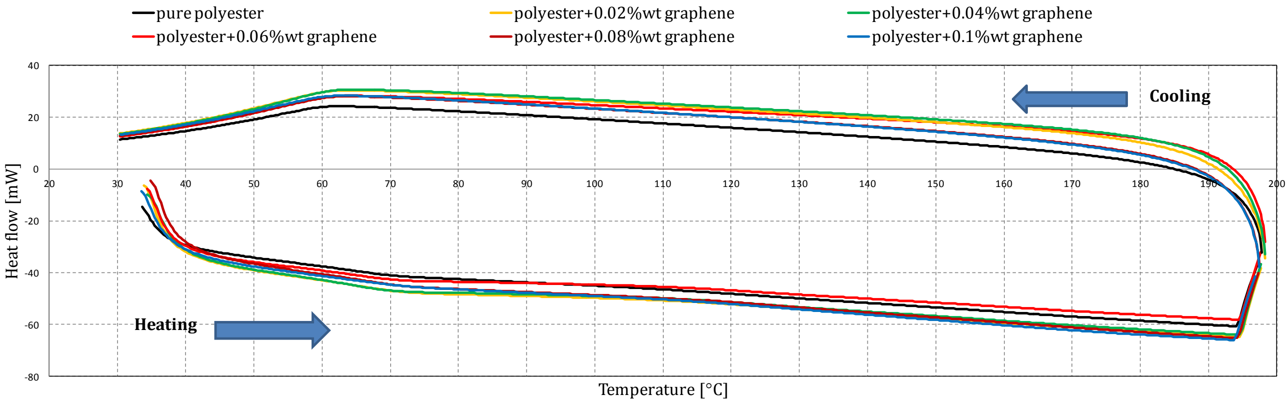

Fig. 5. Heat flow depending on temperature for polyester with graphene composites.

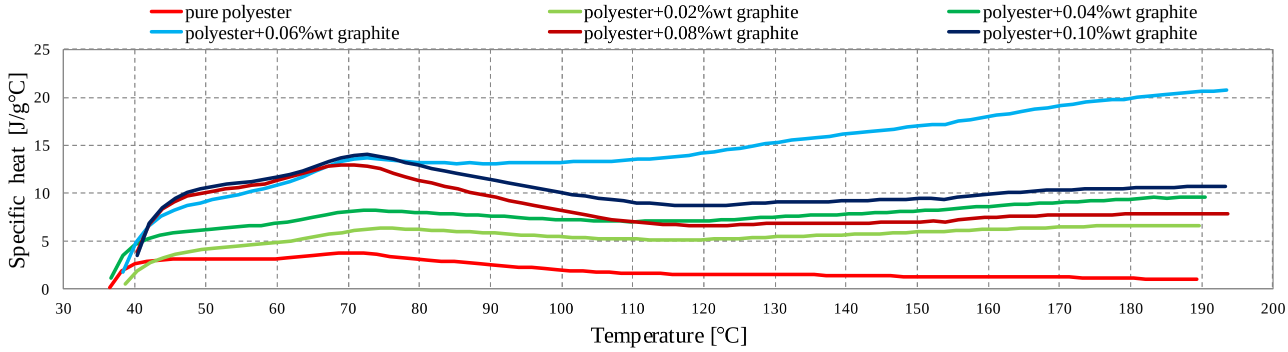

Fig. 6. Specific heat depending on temperature for polyester with graphite composite on heating stage.

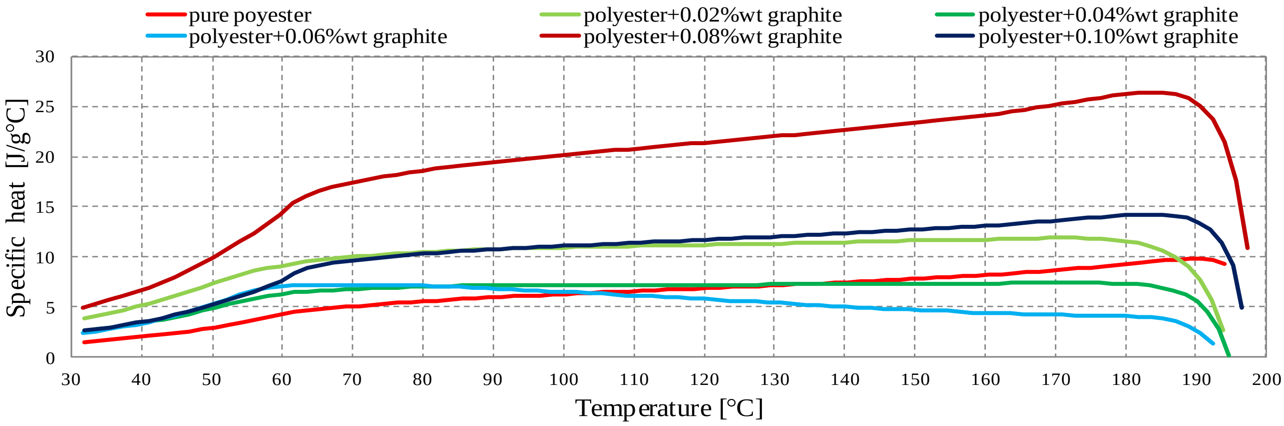

Fig. 7. Specifc heat depending on temperature for polyester-graphite composite on cooling stage.

The value of specific heat of polyester with 0.1 %wt graphene is 262 % higher. It can also be noticed a higher increase of specific heat of the polyester with graphene under the influence of the graphene. The maximum values for the specific heat have been measured for the temperatures of 189 °C.

Variation of specific heat due to graphene concentration both during the heating process as well as during the cooling process is shown in Fig. 4. The values have been measured for the temperature of 38 °C. It can be noticed in this figure that higher values for the specific heat of the polyester with graphene composites can be obtained during the cooling cycle, as the composites have to release more heat in order to decrease their temperature with one degree compared with how much they need to absorb in order to increase their temperature with one degree. Variation of the heat flux in accordance with the temperature is shown in Fig. 5. Comparing the variations of heat flux with variations of specific heat it can be noticed that they are directly proportional.

Figure 6 shows the variation of specific heat of the polyester-graphite composites during the heating process. The specific heat curve shows a maximum point for the temperature of 72 °C. Maximum values of the specific heat can be obtained for the polyester with 0.01 %wt graphite composite at the temperature smaller below 78 °C, while for the temperatures higher than 78 °C can be obtained higher values for the specific heat of polyester with 0.06 %wt graphite composite. For the temperature of 38 °C we measured the following values of the specific heat: for pure polyester1.87 J/g °C, for graphite 0.1 J/g °C, for polyester with 0.01%wt graphite 3.49 J/g °C, which is a 186 % increase of the value of the specific heat. Figure 7 shows that, during the cooling process, the highest values of the specific heat can be obtained for the polyester with 0.08 %wt graphite composite. For the temperature of 188 °C the measured values are: 9.74 J/g °C for pure polyester and 25.82 J/g °C for polyester with 0.08 %wt graphite composite, which is a 265 % increase. In Figure 8 we compared the values of the specific heat measured at 38 °C both during the heating process and during the cooling process of polyester with graphite composites. As in the case of polyester with graphene composites, it can be observed higher values of the specific heat during the cooling process.

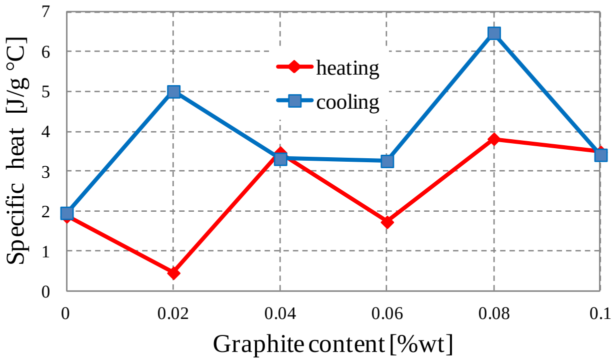

Fig. 8. Specific heat depending on graphite content.

In Fig. 9 we compared the values of the specific heat during the heating process for the polyester with graphene and the polyester with graphite composites. It can be observed that for the concentrations of polyester with 0.02 %wt graphene and the polyester with 0.1 % wt graphene, the values of the specific heat are higher than those of the polyester with graphite composites. Thus, for the polyester with 0.02 %wt graphene composite, the specific heat is 5.29 J/g °C, while for the polyester with 0.02 %wt graphite , the specific heat is 0.46 J/g °C, thus the values of the polyester with 0.02 %wt graphene composite being 1150 % higher than those of the polyester with 0.02 %wt graphite composite. For the polyester with 0.1 %wt graphene composite, the specific heat is 6.26 J/g °C, and for the polyester with 0.1 % wt graphite composite the specific heat is 3.49 J/g °C, the value of the polyester with 0.1 %wt graphene composite thus being 79 % higher than those of the polyester with 0.1 %wt graphite composite.

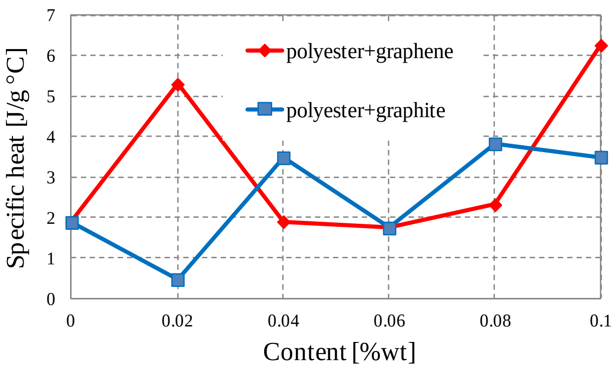

Fig. 9. Specific heat depending on content for polyester with graphene and polyester with graphite composite on heating stage

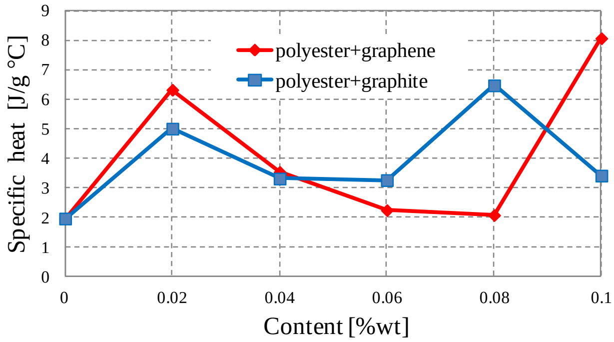

Fig. 10. Specific heat depending on content for polyester with graphene and polyester with graphite composite on cooling stage.

In Fig. 10 we compared the values of the specific heat during the cooling process for the polyester with graphene and polyester with graphite composites. It can be observed that for the concentrations of polyester with 0.02 %wt graphene and polyester with 0.1 %wt graphene composites, the values of the specific heat are higher than those of the polyester with graphite composites. Thus, for the polyester with 0.02 %wt graphene composite the specific heat is 6.32 J/g °C, while for the polyester with 0.02 %wt graphite composite, the specific heat is 5.01 J/g °C, thus the values of the polyester with 0.02 %wt graphene composite being 26 % higher than those of the polyester with 0.02 %wt graphite composite.

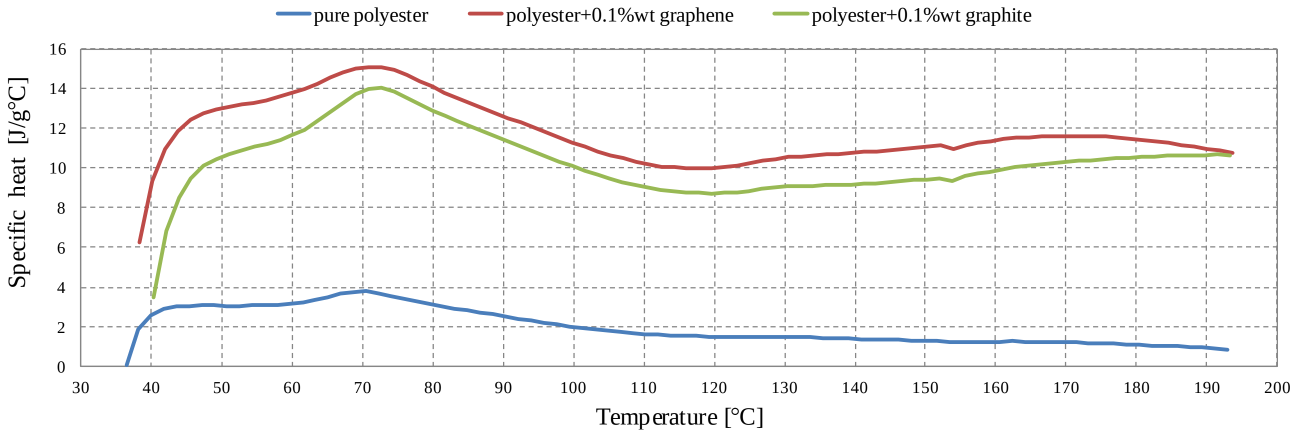

Fig. 11. Specific heat depending on temperature for polyester with 0.1%wt graphene and polyester with 0.1 %wt graphite composite on heating stage.

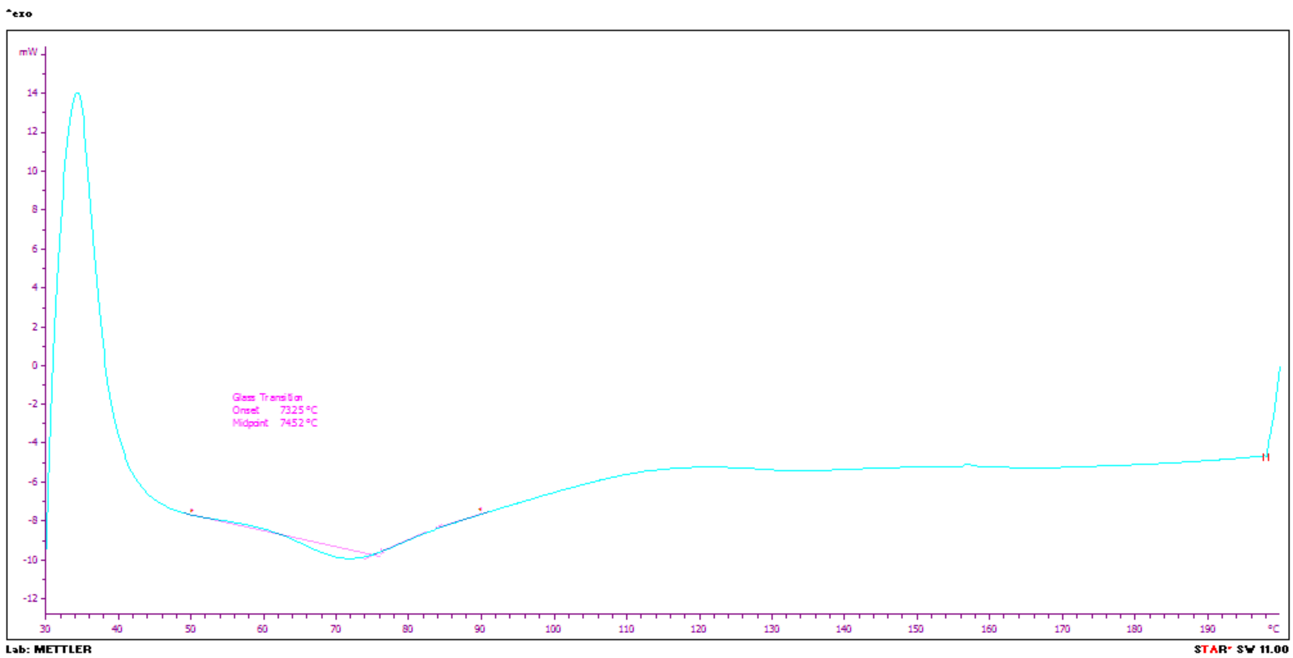

Fig. 12. Determination of glass transition temperature for polyester with 0.04%wt graphene composite.

For the polyester with 0.1 %wt graphene composite, the specific heat is 8.07 J/g °C and for the polyester with 0.1 % wt graphite composite the specific heat is 3.42 J/g °C, thus the values of the polyester with 0.1 %wt graphene composite being 135 % higher than those of the polyester with 0.1 % wt graphite composite.

Figure 11 shows the variation of the specific heat polyester with 0.1 %wt graphene and polyester with 0.1 %wt graphite composites. It can be observed that the values of the specific heat of the i polyester with 0.1 %wt graphene composite are 10 % higher than those of the polyester with0.1 %wt graphite composite. This is due to higher specific heat of the graphenes than the specific heat of the graphite.

3.2 Glass transition temperature

The glass–liquid transition (or glass transition for short) is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state [16]. The glass transition temperature (*T*g), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. *T*g constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured. We used for determination of *T*g, Star^e software from Mettler Toledo. In Fig. 12 we showed a diagram from Star^e software, which present us the method to determine *T*g.

Table 1. Glass transition temperature for polyester based composite.

Glass transition temperature, *T*g [°C]	
pure polyester	55.27
Polyester + 0.02 %wt graphene	62.64
Polyester + 0.04 %wt graphene	73.25
Polyester + 0.06 %wt graphene	76.41
Polyester + 0.08 %wt graphene	56.64
Polyester + 0.1 %wt graphene	70.82
Polyester + 0.02 %wt graphite	65.06
Polyester + 0.04 %wt graphite	62.67
Polyester + 0.06 %wt graphite	61.83
Polyester + 0.08 %wt graphite	74.33
Polyester + 0.1 %wt graphite	61.05

As can be seen in Table 1, polyester with graphene or graphite composites have temperature *T*g greater than pure polyester. The largest increase in *T*g was measured in polyester composites with graphene. This increase can be attributed to carbon-links that form between polymer and graphene/graphite [17] or can be attributed to the reinforcing effect of rGO which reduces segmental motion of the polymer chain [18-28]. The highest value of *T*g=76.41 °C is obtained for polyester with graphene composites for graphene concentration of 0.06 % wt. Polyester composites with graphite have maximum value of *T*g=74.33 °C is obtained for the concentration of 0.08 wt% graphite.

4. CONCLUSIONS

The specific heat of the polyester with graphene and polyester with graphite composites has been studied both during the heating stage and during the cooling stage. For all the composites it has been observed an increase in the specific heat value compared with that of the pure polyester. For polyester with graphene composites, the highest value of the specific heat was obtained for the polyester with 0.1 %wt graphene composite, both during the heating stage and during the cooling stage. During the heating stage the specific heat of the polyester with 0.01 %wt graphene composite is 334 % higher than that of the pure polyester. During the cooling stage, the specific heat of the polyester with 0.01 %wt graphene composite is 264 % higher than that of the pure polyester. For polyester with graphite composites, the highest value of the specific heat can be obtained for the polyester with 0.1 %wt graphite composite up to the temperature of 72 °C. Beyond this temperature the values of the specific heat are higher for the polyester with 0.06 % graphite composite. During the heating stage the specific heat of the polyester with 0.01 %wt graphite composite is 186 % higher than those of the pure polyester. During the cooling stage, the specific heat of the polyester with 0.08 %wt graphite composite is 265 % higher than those of the pure polyester.

Comparing the values of the specific heat for the polyester with graphene and polyester with graphite composites, it can be observed that the values of the specific heat are 10 % higher for the polyester with graphene composites compared with the values of the specific heat for the polyester with graphite composites.

A further research study will aim at studying the variation of the specific heat for composites with concentrations higher than 0.1 %wt both for graphenes and for graphite.

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