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CORRELATION BETWEEN GRAPHENE OXIDE / GRAPHITE CONTENT AND THERMAL PROPERTIES OF POLYESTER COMPOSITES

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Dynamic mechanical analysis (DMA), thermo-mechanical analysis (TMA) and differential scanning calorimetry (DSC) were used in order to assess the thermal behaviour of polyester composites with graphene oxide and graphite. Heat flow, specific heat, glass transition temperature (Tg) and mass loss were determined on heating and cooling stages, for neat polyester and its composites, depending on filler (graphene oxide/graphite) content. Coefficient of thermal expansion (CTE) and Tg were inferred based on measurement of the specimen thickness versus test temperature, in the range of 30…220 °C. Results obtained from DMA, such as storage modulus, were used to estimate mechanical properties and Tg. A comparative analysis was done as regards glass transition temperature determined through three different methods (DSC, TMA and DMA), for polyester composites, on heating and cooling stages, depending on filler content. The careful observation of the test results, revealed that polyester composites exhibit a better thermal behaviour as compared to that of neat polyester.

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1. Introduction

Polymer with graphene nanofillers has as a result an improvement in mechanical and thermal characteristics in comparison with carbon nanotubes[1][2][3]. At room temperature, specific heat of graphite is Cs=0.7J/g^{0}C [4,5]. For graphene, it has been measured the specific heat on the two axes of the basal plane of graphene as follows: for "armchair" direction it has been measured the value 0.65 J/g^{0}C and, for the "zigzag" direction it has been measured the value 0.64 J/g^{0}C [6]. Some other tests compared the specific heat of the graphene, graphite and carbon nanotubes, where the values of the specific heat at the room temperature being very close, oscillating around the value of 0.7 J/ g^{0}C [7–11] For pure polyester it has been measured the specific heat value of 1,4 J/g^{0}C [12], 1,5 J/g^{0}C [13], 1.3 J/g^{0}C [14] at the room temperature. The influence of carbon nanotubes in polyester composites formed on the specific heat is manifested through its increase up to 40% [15] or 60% [2]. Graphene oxide or graphite addition have a positive influence on specific heat of thee polyester composites, thus reaching increases up to 30% of the specific heat of the composites formed by polyester with oxide graphenes [16].

The measurement of the linear coefficient of thermal expansion (CTE) by using TMA is necessary in order to know the dimensional stability of polyester with graphene oxide or polyester with graphite composites. In order to determine CTE of graphene oxide, that was heated until 150^{0}C, and having value -67μm/m ^{0}C, above this CTE decreases to -1028 μm/m ^{0}C[17]. For graphite CTE values are presented in Table 1.

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Table 1. CTE values for graphite

CTE [µm/m ^{0}C]		References
“armchair” direction	“zigzag” direction	
-1.6	6.9	[18]
-1.5	8	[19], [20]
-1.3	3.5	[21]
-1.4	5	[22]
-0.5	8.5	[23]

Using graphene oxide as additives, CTE decreases with 40% for epoxy/graphene oxide composites [24]. TMA showed that the addition of graphene in the nanocomposites with polyethylene increased its dimensional stability due to the increased material hardness. The CTE values of the nanocomposites was decreased significantly with the addition of small quantities of graphene [25].

The glass transition temperature (Tg) is one of the most important properties of any polymer and is the temperature range where the polymer transitions from a hard, glassy material to a soft, rubbery material. For polyester Tg is determined at 52^{0}C [26].

Results of DMA test of polymer with graphene oxide composites indicated that a higher graphene oxide content further increases E' values for the nanocomposites. The stiffening effect (higher E' values) is more evident at low temperatures. The enhancements believed to be associated with the fine dispersion of graphene oxide within the polyamide matrix [27].

Storage modulus of the composites increases with increasing graphene content. The homogeneous dispersion of graphene in the ethylene vinyl acetate matrix restricts the chain mobility, resulting in the improvement of E' values [28]. The incorporation of graphite into poly(vinylidene fluoride) has a good reinforcing effect, which may originate from both the stiff graphite particles and a graphite-induced increase in the degree of crystallinity of poly(vinylidene fluoride) [29].

It was found that the polylactide composites loaded with graphite, exhibit superior thermomechanical properties, as storage modulus, within a wide temperature range [30].
Different values for Tg in polymer with graphene composites are mentioned in Table 2.

Table. 2 The increase of Tg values for polymer with graphene composites

Tg [^{0}C]	Polymer	References
15	polyester	[16]
2.5	polyester	[31]
15.1	epoxy	[32]
15	polyester	[33]
4.4	PMMA	[34]
8	STS	[35]
3-5	epoxy	[36]
4	polystyrene	[37]
40	poly(acrylonitrile)	[38]
30	poly(methyl methacrylate)	[38]
8	polyester	[39]
19	epoxy	[40]
20	tetraethylenepentamine	[41]

2. Materials and methods

Graphite was purchased from Koh-I-Noor, unsaturated orthophthalic polyester (P) resin commercially knows as Norsodyne H 13 271 TA, was purchased from Rompolimer. Graphene oxide was obtained from graphite by using Staudenmaier method. Concentrations of graphite and oxide graphene were as follows: 0.05 wt%, 0.1 wt%, 0.15 wt %. The materials will be abbreviated as follows:

- GO 0.05, GO 0.1 and GO 0.15 – composite with polyester matrix and 0.05 wt% graphene oxide, 0.1 wt % graphene oxide or 0.15 wt % graphene oxide;
- G 0.05, G 0.1 and G 0.15 – composite with polyester matrix and 0.05 wt% graphite, 0.1 wt% graphite or 0.15 wt % graphite;
- P – pure polyester.

Differential Scanning Calorimetry (DSC)

DSC method was used in order to measure the specific heat and glass transition temperature (Tg). Using the DSC test, Tg can be measured on both heating and cooling stages. The apparatus used for testing is DSC1 from Mettler Toledo. The samples were weighted, before and after testing, by the analytical balance AB204-S/FACT from Mettler Toledo. The software for data interpretation was Star^e from Mettler Toledo. The test was made according to the ASTM1269 standard. The samples were kept at 30℃ for 3 minutes, then heated from 30℃ to 220℃ with the heated rates of 10℃/min, then kept for 3 minutes at 220℃, cooled from 220℃ to 30℃ with cooling rates of 10℃/min. The mass of samples was of 103 mg.

Thermomechanical Analysis (TMA)

TMA method was used to measure the linear coefficient of thermal expansion and Tg. For testing it has been used TMA/SDTA 840 tester from METTLER TOLEDO**.** The samples were measured before testing. A 0.02 N load has been applied on the sample. The samples thickness was of 4 mm. For each concentration five samples were tested. The TMA test only measures the beginning temperature of the glass transition, as glass transition was carried on a time interval. The test was done according to ASTM E831 standard. It can also be calculated the coefficient of linear thermal expansion as average value in the studied temperature range, or it can be studied the thermal expansion coefficient in the temperature range below Tg and in the temperature range above Tg. Tg can also be measured on the cooling curve.

Dynamic Mechanical Analysis (DMA)

The DMA method was used to measure storage modulus E’, as Tg would be measured there. During DMA test, Tg can be measured only on the heating curve as there was no cooling curve. Dynamic mechanical properties of samples were measured using a tester called "Dynamic Mechanical Analyzer" DMA Q800 from TA Instruments. Measurement results were interpreted using Universal Analysis 2000 software. The test was done in dual cantilever bending. Oscillation frequency was 1 Hz and amplitude deformation was 20 μm. Temperature range was 25 – 250ºC and heating rates was 3°C/min. Samples dimensions were as follows: lenght = 60 mm, width =11 mm, thickness = 5 mm.

3. Results and Discussion

Differential Scanning Calorimetry

Specific heat was measured for both heating and cooling stage of the test. The specific heat was inferred by the relation (1):

$$c = \frac{Q}{m \times \Delta T} \text{ [J/g ℃]} \tag{1}$$

where *c*- specific heat of the material, Q- amount of heat absorbed by sample, *m* – sample mass, ΔT – temperature difference between maximum and minimum value of temperature the specific heat is studied. There have been measured the values of the specific heat during the whole interval 30-220℃. Tables 3 and 4 show specific heat values for 38℃ and 60℃, for both heating and cooling stage.

Figure 1 shows that the specific heat, for all the polyester composites with graphene oxide is higher than the values obtained for polyester. The higher values have been obtained for GO 0.15 composite. Figure 2 shows the values of specific heat for polyester with graphite composites. In all the cases the specific heat is higher than that of polyester. The highest values have been obtained for G 0.15 composite. Figure 3 shows the values of the specific heat for GO 0.15 and G 0.15 composites. For all the composites studied, the values of the specific heat are higher for polyester with graphene oxide composites comparing with polyester with graphite composites. This is due to the bonds between graphene oxide/graphite and polyester matrix. Van der Waals and hydrogen links can be formed between graphene oxide and polyester, while between graphite and polyester only Van der Waals bonds can be formed. Hydrogen bonds are formed between carbonyl and carboxyl groups of the graphene oxide and the ester groups of polyester. Hydrogen bonds are stronger than Van der Waals bonds but less numerous.

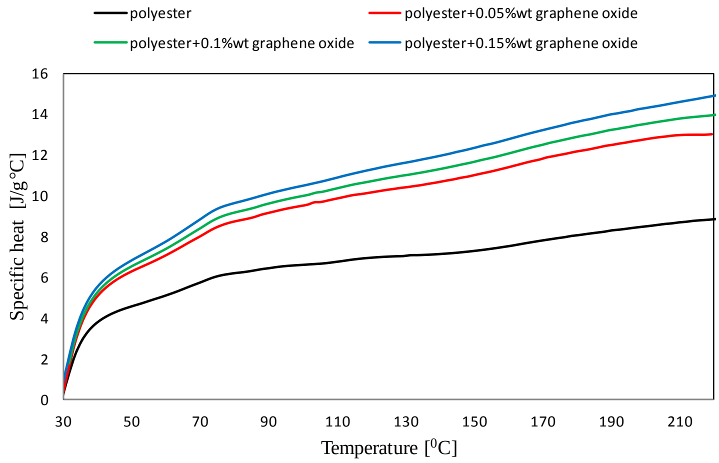

Fig.1 Specific heat vs. temperature for polyester with graphene oxide composite, on heating stage

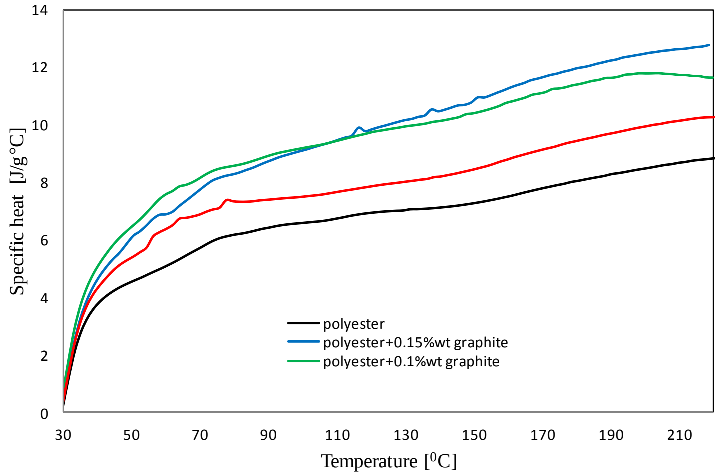

Fig.2 Specific heat vs. temperature for polyester with graphite composite, on heating stage

Figures 4 and 5 show that heat flow is directly proportional to the specific heat and it can be observed the glass transition for GO 0.15 composite. Figure 5 shows T_g values on both curves, for heating and cooling stage.

Tables 3 and 4 show T_g values for polyester with graphene oxide and polyester with graphite composites which are higher comparing with those of polyester. It can be noticed that for the same concentration, Tg values are higher for polyester with graphene oxide composites comparing with those of polyester with graphite composites, both during the heating and the cooling stage. Comparing the values of the specific heat in Tables 3 and 4 with values measured for the polyester with MWNT composites, it is observed that the influence of the graphene oxide and graphite is stronger [15].

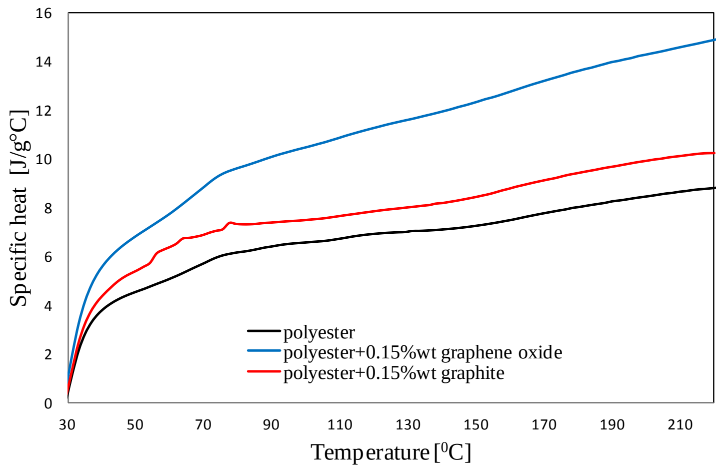

Fig. 3 Specific heat vs. temperature for GO 0.15 oxide and G 0.15

The differences between the Tg values for heating and the cooling stage is due to the fact that during the heating process it takes place oxygen pyrolysis from hydroxyl, carboxyl, carbonyl groups and of humidity loss, thus generating gases such as CO, CO_2, H_2O [36,40]. The gas removal leads to breakage of some hydrogen bonds which were formed between graphene oxide and polyester and Van der Waals bonds which were formed between graphite and graphene oxide with polyester. The chemical bonds between graphene oxide or graphite and polyester matrix decrease molecular movements of the polyester chain during heating process. Gas removal during heating is shown in Table 5. It can be noticed that graphene oxide and graphite lead to the effect of strengthening they induce to polyester composites and thus leading to mass loss during heating process.

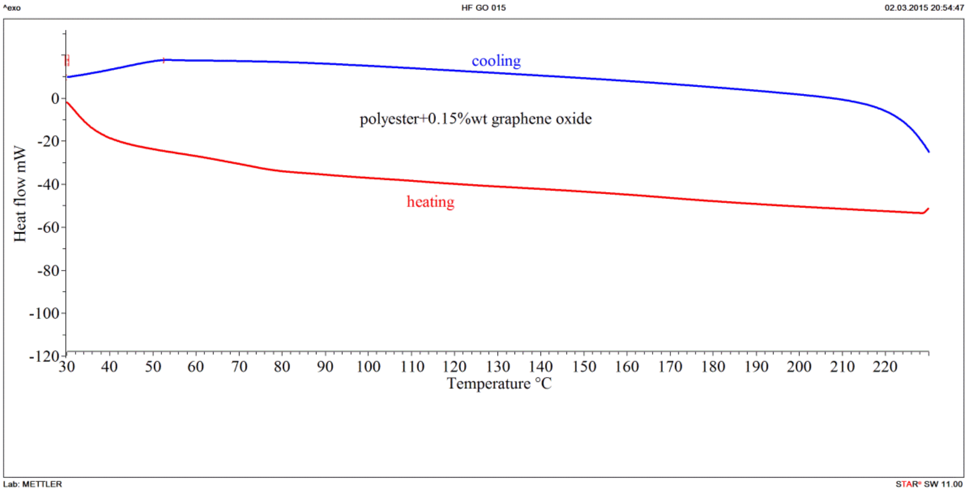

Fig. 4 Heat flow vs temperature for GO 0.15

Table 3 Specific heat for polyester with graphene oxide and polyester with graphite composite at 33℃

	c [J/g °C]			c [J/g °C]	
	Heating	Cooling		Heating	Cooling
P	2.15	1.38			
GO 0.05	2.74	2.2	G 0.05	2.5	1.7
GO 0.1	2.98	2.43	G 0.1	2.77	1.9
GO 0.15	3.22	2.73	G 0.15	2.94	2.31
Polyester with 0.02 wt % MWCNT [15]				2,7	

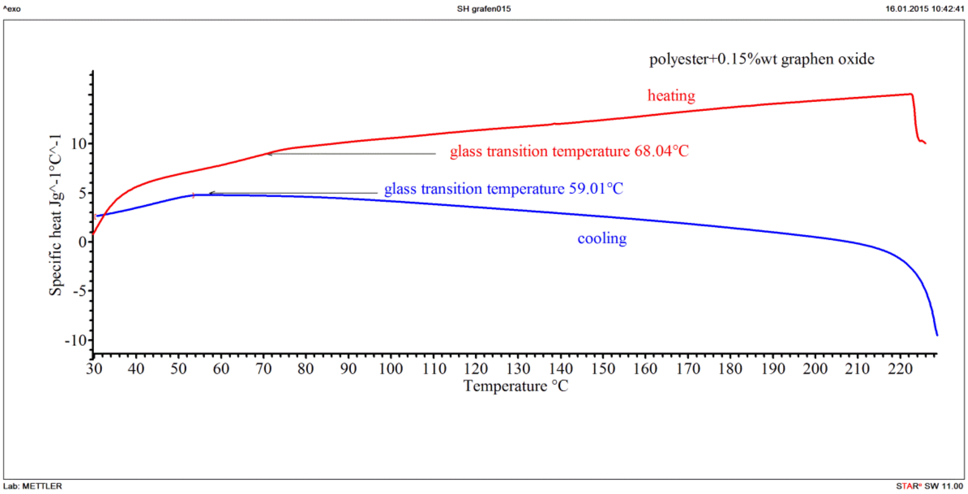

Fig. 5 Determinaton of Tg for GO 0.15 by DSC

Table 4 Specific heat for polyester with graphene oxide and polyester with graphite composite at 60℃

	c [J/g °C]			c [J/g °C]	
	Heating	Cooling		Heating	Cooling
P	5.11	2.57			
GO 0.05	7.1	3.7	G 0.05	6.21	2.81
GO 0.1	7.78	4.31	G 0.1	7.06	3.54
GO 0.15	9.78	4.42	G 0.15	7.37	3.83
Polyester with 2 wt % MWCNT [2]				1.7	

Table 5 Mass loss as a function of additives content in polyester with graphene oxide and polyester with graphite composite (DSC)

	Mass loss		Mass loss
P	2.9%		
GO 0.05	2.6%	G 0.05	2.6 %
GO 0.1	2%	G 0.1	2.3%
GO 0.15	1.1%	G 0.15	2.1%

Because the start temperature for the test was 30℃, it was choosen to show in Table 3 the values for specific heat at 33℃. Comparing the values obtained for polyester+0.1 wt % MWCNTs, 1.4 J/g ℃ [13] with the values obtained for GO 0.1, as 7.78 J/g ℃, and G 0.1, as 7.06 J/g ℃, it can be noticed that the first are smaller than last ones. The smallest mass loss is observed for GO 0.15 composite.

The much bigger number of chemical bonds the graphene oxide forms with polyester matrix, compared with the bonds graphite makes with polyester matrix, lead to a much better dimensional thermal stability of these composites.

Thermomechanical Analysis (TMA)

It was measured the average of the CTE for the temperature range below Tg, for the temperature range above Tg and for the whole range of studied temperatures. In order to clearly delimitate the measurement intervals of the CTE in the temperature range below and above Tg, Tg had to be measured for each composite. The measured values can be seen in Table 6.

Taking into account that, in case of polyester composites, the temperature range for Tg was between 53℃ and 69℃, the coefficient of thermal expansion was measured along the intervals of 30-50℃ and 70-230℃ (Table 7). From the table, it can be seen that CTE decrease directly proportional with the increase in additives concentration. The highest decrease is to be seen at polyester with graphene oxide composites. Both graphene oxide and graphite have a positive influence on dimensional stability of the polyester composites. This fact emphasizes the strengthening effect these additives have in the polyester matrix through the chemical bonds they form with polyester matrix and due to high thermal conductivity these additives have thus leading the composite to remove the heat. CTE values are smaller for the temperature interval below Tg comparing with the values identified for the temperatures above Tg.

Figure 6 shows the samples thickness variation according to the temperature, for the GO 0.15 composite and CTE values, on temperature intervals below and above Tg.

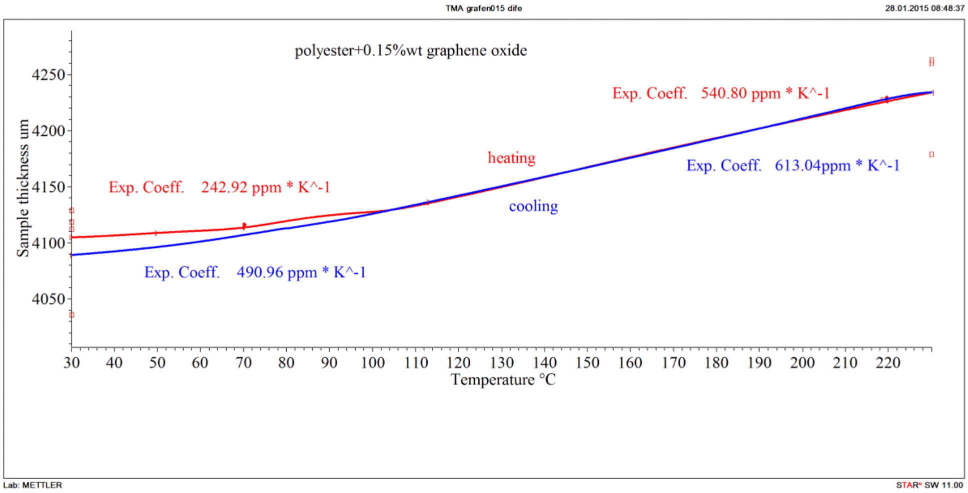

Fig.6 Sample thickness vs temperature for GO 0.15

Table 6. Tg for polyester with graphene oxide and polyester with graphite composite determined by DMA, DSC and TMA

	DMA	DSC		TMA
	[^{0}C]	Heating stage [^{0}C]	Cooling stage [^{0}C]	Heating stage [^{0}C]
P	55.91	53.31	55.15	54.47
GO 0.05	61.17	64.28	56.41	57.3
GO 0.1	58.11	67.42	58.36	59.3
GO 0.15	59.46	68.04	59.01	63.4
G 0.05	56.51	54.62	57.99	56.1
G 0.1	58.95	55.45	57.53	57.23
G 0.15	57.75	60.71	57.7	59.4

Table 7. Coefficient of linear thermal expansion for polyester with graphene oxide and polyester/graphite

	Linear coefficient of thermal expansion					
	heating			cooling		
	30-50^{0}C	70-230^{0}C	30-230^{0}C	30-50^{0}C	70-230^{0}C	30-230^{0}C
P	279.69	596.19	509.13	538.31	655.63	648.93
GO 0.05	268.38	582.44	500.58	526	644.95	642.93
GO 0.1	262.84	555.53	436.49	520.94	630.97	633.25
GO 0.15	242.92	540.8	424.61	490.96	613.04	625.49
G 0.05	271.77	591.54	502.58	528.41	651.62	646.54
G 0.1	266.69	573.27	464.7	528.5	648.39	645.28
G 0.15	243.4	550.51	445.12	501.54	644.24	635.08

Dynamic Mechanical Analysis

Tg was measured on the storage modulus curve of polyester with graphene oxide or graphite composites. Figure 7 shows the storage modulus values for GO 0.15 and G 0.15. The tests revealed that both graphite and graphene oxide have a significant influence on the storage modulus. Measured values for Tg reflect the strengthening effect of the additives, and at the same concentration the higher values are obtained for polyester/graphite composites. The highest Tg value can be noticed for the GO 0.15 composite. Figure 8 shows the Tg measuring method on the storage modulus curve. The value of Tg determined by DMA was used in other paper work [42].

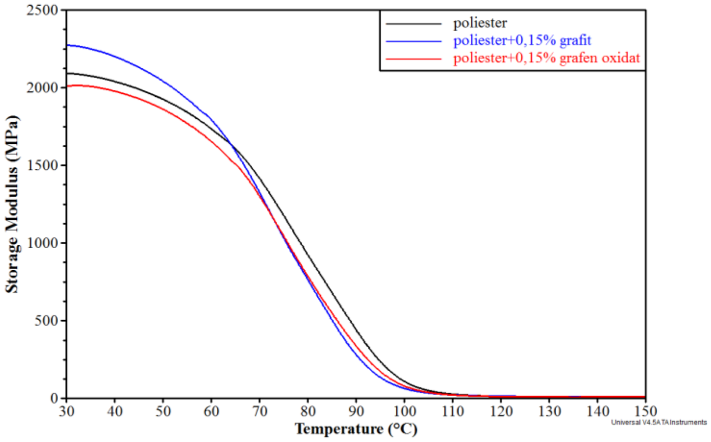

Fig.7 Storage modulus vs temperature for polyester+0.15 wt % graphene oxide and polyester+0.15 wt % graphite

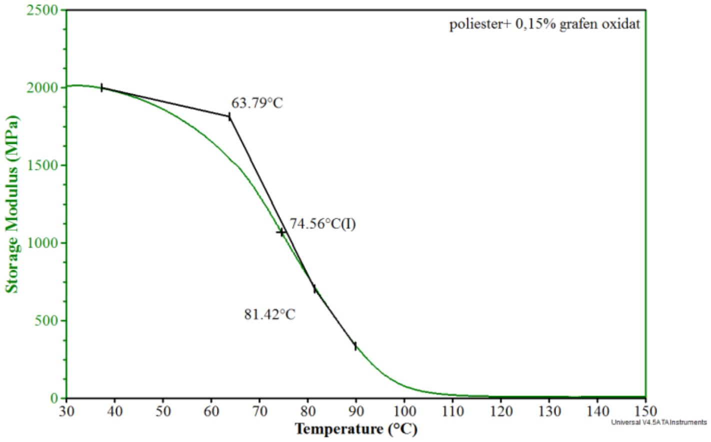

Fig. 8 Determination of Tg for polyester+0.15%wt graphene oxide

4. Conclusions

The results of TMA, DSC and DMA tests carried out on polyester with graphene oxide/graphite composites were discussed according to temperature range and filler content.

The specific heat measured for the polyester with graphene oxide is higher than the values measured for polyester with graphite composites for the same content of fillers. For the temperature value of 33^0C, the specific heat of GO 0.15 was higher with 9% compared with that of G 0.15, and with 49% higher than that of polyester. For the temperature value of 60^0C the specific heat of GO 0.15 was higher with 32% compared with that of G 0.15, and with 91% higher than that of polyester.

Mass loss measured for the studied composites decrease directly proportional to the increase of the concentration of additives. The smallest mass loss can be noticed in case of polyester with graphene oxide composites. The value of mass loss for GO 0.15 was with 61% smallest than that of polyester and with 50% than that of G 0.15.

The value of Tg increases with 2.55-7.4 ^{0}C for G 0.15 compared to the value of Tg for polyester, depending on the test method was used. For GO 0.15, the value of Tg increases with 4-13^0C than the values of polyester. Tg values measured for composites in all tests show their increase directly proportional with the increase in additives concentration The values measured for Tg at the same concentration of fillers through the three test methods (DSC, TMA and DMA) are comparable.

The CTE calculated for temperature interval below Tg is smaller than CTE calculated for temperature interval above Tg. Also, CTE is smaller for polyester with graphene oxide composites comparing with those measured for polyester with graphite, for the same content of fillers. For GO 0.15, the values of CTE was with 10% smaller than the values for polyester, and for G 0.15 was with 9% smaller than values of polyester.

All results obtained in TMA, DSC, DMA tests emphasize the significant influence the graphene oxide has on thermal characteristics of the composites with polyester matrix.

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