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Thermal Properties of Polyester/Graphene Oxide and Polyester/Graphite Determined by TMA

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Abstract -In this article we are going to study the influence graphene oxide and graphite have on thermal characteristics of polyester composites with the previously mentioned additives. By using the TMA method we managed to determine the coefficient of linear thermal expansion (CLTE) as well as the Tg of polyester composites with graphene oxide and graphite. We also calculated the average value of CLTE for the entire temperature interval studied, for temperatures below Tg in the 30-50^{0}C interval and temperatures higher than Tg, in 70-190^{0}C interval. For each of these values it has been noticed a significant decrease of CLET. The influence of the additives on Tg of the polyester composites additivated with graphene oxide and graphite has resulted in its increase

***Keywords*:** graphene oxide, graphite, polyester, TMA, coefficient of linear thermal expansion

1. Introduction

The study of thermal characteristics of polyester is important in order to find out the behavior of polyester in usage. Polyester is one of the most utilized polymers in industry, as the spare parts manufactured from polyester are subjected to a wide temperature interval during their functioning. That is why it is of utmost importance to know the coefficient of linear thermal expansion. By means of additivated those with various nanoparticles it is meant to decrease CLTE, so that the resulted composite should be more thermally stable. We are going to study the composites formed between polyester and graphene oxide or graphite, in order to better observe the influence of these additives on CLTE.

If heated at a 50^{0}C temperature, graphene oxide have a CLTE of -67μm/m ^{0}C, while above this temperature, the CLTE decreases suddenly and it reaches the value of de -1028 μm/m ^{0}C (Su et al. 2012). Graphite also has negative values of CLTE, from -1.6 to -0.7 μm/m ^{0}C in longitudinal direction and an average value of 6,9 μm/m ^{0}C (Rupnowski et al. 2005), -1,5 μm/m ^{0}C in longitudinal direction and an average value of 8 μm/m ^{0}C (Zhou et al. 2011), -1.5 μm/m ^{0}C in longitudinal direction and an average value of 8 μm/m ^{0}C(Preston & Marsden 2006), -1.3 μm/m ^{0}C in longitudinal direction and an average value of 3.5 μm/m ^{0}C (Tsang et al. 2005) , -1.4 μm/m ^{0}C in longitudinal direction and an average value of 5 μm/m ^{0}C (Morgan 1972), -0.5 μm/m ^{0}C in longitudinal direction and an average value of 8.5 μm/m ^{0}C (Martin & Entwisle 1963). The influence of the grapheme oxide on coefficient of linear thermal expansion has been studied in many polymer composites. It has been measured the CLTE 5,51 μm/m ^{0}C(Gao & Huang 2014) for the graphene oxide heated up to 700 ^{0}C. Thus it has been observed a decrease of CLTE cu 33% (Wu & Drzal 2014) in composites with polyetherimide. The addition of graphene oxide decreases the CLTE value in epoxy matrix composites with almost 40% (Shiu & Tsai 2014).

TMA is used so as to determine the dimension changes of the materials subjected to temperature changes. By using TMA we determine the coefficient of linear thermal expansion as well as glass transition temperature. It is important to determine these values so as to know if aparts subjected to temperature changes will not change the integrity of the structure it is part of. The aim of the graphene oxide or graphite is to reduce the coefficient of linear thermal expansion and to increase the value of glass transition temperature.

2. Materials and Methods

The analyses have been made on samples of nonsaturated polyester raisins additivated to five concentrations: 0,02%; 0,04%; 0.06%;0.08%;0,10% by using two additives: graphene oxide, graphite. The graphite has been purchased from KOH-I-NOOR and the graphene oxides have been obtained by using a version of Staudenmayer method. Polyester has been purchased from Rompolymer. Composites have been made by mixing and pouring into the mould. For testing was used TMA/SDTA 840 device from METTLER TOLEDO. The samples were measured before testing. A force of 0.02 N was applied on the samples. The thickness of the samples was of 4mm. For each concentration there were five samples used. The TMA test only determines the beginning temperature of the glass transition, which takes place on one interval. The test was made according to the ASTM E831 standard.

3. Results and Discussions

The coefficient of thermal expansion is determined using the equation:

$$\bar{\alpha}(\Delta T)=\frac{\Delta L}{L_0\,\Delta T} \qquad \left[\frac{\mu m}{m\,{}^{\circ}\mathrm{C}}\right] \tag{1}$$

Where ΔL is the tridimensional change of the sample, L_0 is the initial dimension of the sample, ΔT is the difference between the initial temperature of the sample and the final temperature to which the linear coefficient is determined.

The average values of the coefficient of linear thermal expansion are smaller in the temperature interval below the glass transition temperature comparing with the average values obtained for temperatures above Tg. These differences are also confirmed by tests made on polyester composites with some other additives (Foix et al. 2010) and they are considered the result of high mobility of the polyester chains at high temperatures.

The temperature interval chosen in order to determine the average values of the coefficient of linear thermal expansion was 25°C-190°C, the heating/cooling speed of 10°C/min. Determinations are made on the heating and cooling curve. It will also be determined the coefficient of linear thermal expansion for the temperature interval below Tg, for temperature interval above Tg as well as for the entire temperature interval studied. Fig.1 shows the method to determine Tg for the polyester +0.1% graphene oxide composite.

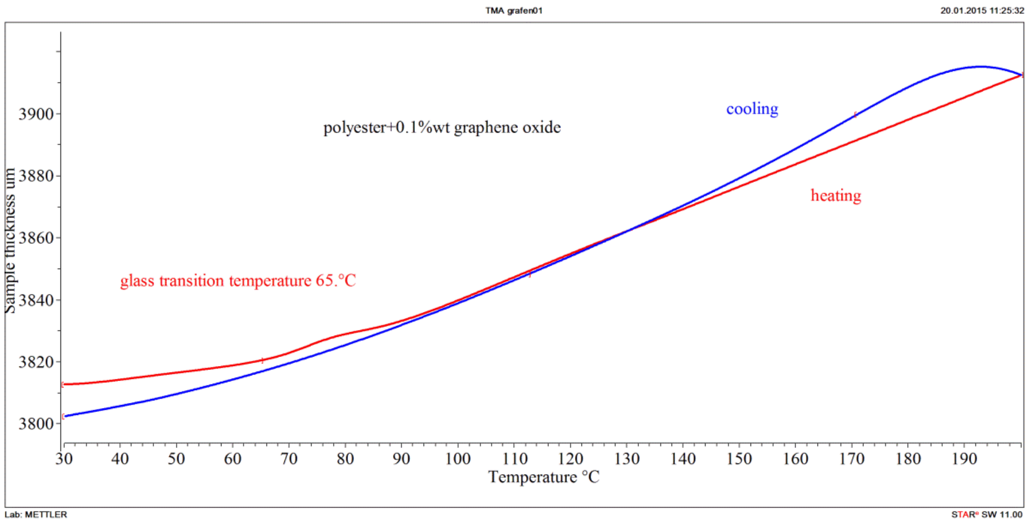

Fig. 1. Determination of Tg for polyester+0.1%wt graphene oxide on samples thickness curves

In order to clearly delimitate the measurement intervals of the coefficient of linear thermal expansion in temperature interval below Tg and above it, we determined the Tg for each composite. The determined values are shown in Tab.1.

In order to determine the average values of the coefficient of linear thermal expansion below and above Tg, we chose the 30-50℃ and 70-190℃ intervals. Their values are shown in Tab. 2.

The strongest influence on Tg has graphene oxide, which increases the value of the Tg with almost 11^0C comparing it with the value of the polyester Tg. Graphite has a smaller influence on Tg, and manages to increase the value of the Tg for polyester+0.1%wt graphite composites with 9^0C.

Table. 1. Tg values for polyester/graphene oxide and polyester/graphite composite.

	Tg [^{0}C]		Tg [^{0}C]
polyester	54.14		
polyester+0.02%wt graphene oxide	59.32	polyester+0.02%wt graphite	56.92
polyester+0.04%wt graphene oxide	61.86	polyester+0.04%wt graphite	57.9
polyester+0.06%wt graphene oxide	63.25	polyester+0.06%wt graphite	59.26
polyester+0.08%wt graphene oxide	65	polyester+0.08%wt graphite	60.45
polyester+0.1%wt graphene oxide	65.8	polyester+0.1%wt graphite	63.45

Table. 2. Values of coefficient of linear thermal expansion for polyester/graphene oxide and polyester/graphite composite.

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	30-50^{0}C	mediu	70-190^{0}C	30-50^{0}C	mediu	70-190^{0}C
polyester	591.01	804.24	856.32	981.16	1028.33	1051.1
polyester+0.02%wt graphene oxide	541.16	728.98	765.16	954.31	1007.81	1028.17
polyester+0.04%wt graphene oxide	505.31	677.05	731.22	908.38	997.08	1007.19
polyester+0.06%wt graphene oxide	470.94	663.67	711.18	903.41	947.33	1005.58
polyester+0.08%wt graphene oxide	423.63	627.86	704.74	884.5	929.32	992.23
polyester+0.1%wt graphene oxide	347.02	606.29	698.39	868.84	920.63	968.21
polyester+0.02%wt graphite	561.61	766.03	821.36	977.38	1017.9	1043.96
polyester+0.04%wt graphite	545.2	736.83	804.55	947.86	1009.83	1035.62
polyester+0.06%wt graphite	497.19	721.33	796.74	919.37	991.25	1027.8
polyester+0.08%wt graphite	452.93	708.37	784.15	909.24	969.01	1013.09
polyester+0.1%wt graphite	393.97	678.09	763.6	887.63	941.56	1003.44

For the heating cycle there has been observed the highest decrease, with 25% of the average CLT and for the cooling cycle it has been observed a 10% decrease for polyester+0.1%wt graphene oxide composites. For polyester/graphite composites, the decrease of the average CLET was of 16% for the heating cycle and of 13% for the cooling cycle. The table shows that the highest decrease of CLTE is made for polyester/graphene oxide composites.

If we study CLTE on 30-50^{0}C and 70-190^{0}C temperature intervals, the highest influence in decreasing has the graphene oxide composites. In the 30-50^{0}C temperature interval, for polyester+0.15%wt graphene oxide composites, the decrease was of 42% for heating cycle and of 11% for the cooling cycle. For the same temperature interval, in case of graphite composites, the highest decrease is shown for the polyester+0.1%wt graphite composite, while for the heating cycle the decrease of CLTE is of 34% and for the cooling cycle of 9%. For the 70-190^{0}C temperature interval there have been recorded the biggest decrease for the polyester/graphene oxide composites also. For the heating cycle the decrease of CLET was of 18% for polyester+0.1%wt graphene oxide composite, for the cooling cycle recording a decrease of 8% for the same composite. For the same temperature interval, in case of graphite composite, the biggest decrease is shown by polyester+0.1%wt graphite composite, for the heating cycle the CLET is of 11% and for the cooling cycle it is of 4%. The bigger influence of graphene oxide on Tg as well as the CLET, at the same concentrations with graphite, is due to the bigger specific surface of the graphene oxide comparing it with graphite it is part of and, as well as of the chemical bondages between graphene oxide and the polyester matrix. Chemical bondages established between graphite and polyester are of Van der Waals type. Between graphene oxide and polyester, besides Van der Waals bondages established between the graphene and polyester layer, there are also hydrogen bondages among carbonyl and carboxyl groups of the graphene oxide and polyester. The hydrogen bondages are stronger than Van der Waals bondages, but less numerous than the latter.

4. Conclusions

In this article there have been studied the influences of the graphene oxide and of graphite on thermal characteristics of composites they form with polyester. The biggest influence on CLTE have polyester/graphene oxide composites, both during the heating process as well as during the cooling process. In the case of increasing the Tg, the biggest influence have polyester/graphene oxide composites. Graphene oxide has a bigger influence on thermal characteristics of the composites formed with polyester comparing it with the influence of the graphite.

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