THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
Nº. 2 - 2015, ISSN 1453 – 083X

DETERMINATION OF GLASS TRANSITION TEMPERATURE FOR POLYESTER / GRAPHENE OXIDE AND POLYESTER / GRAPHITE COMPOSITE BY TMA AND DSC

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ABSTRACT

The influences of oxide grapheme and grapheme in thermosetting polymer composites are complex and they very much depend on the chemical bonds formed between the additives and the polymer matrix. This study has used polyester as polymeric matrix and oxide grapheme and graphite as additives. Determination of glass transition temperature (Tg) is important for practical uses of polyester composites due to the changes of characteristics triggered by transition, thus the polymer passes from elastic to plastic state. In order to determine the Tg we used TMA, DSC, DMA tests. The differences in determined Tg values for the same composite are due to different measurements as resulted from each test.

KEYWORDS: polyester, graphene oxide, graphite, Tg, TMA, DSC, DMA

1. Introduction

The glass transition temperature (Tg), of amorphous polyester is one of the most important parameters for industrial applications. At temperatures above Tg, polyester behaves rubbery, below the Tg, polyester is described as a glass state. The rubbery state of polyester may be described as the situations in which the entanglements restricted the motion of polyester chains, will be resolved and polyester will behave like viscous fluid. Polyester is one of the most used rigid polymer raisins; it is mainly used as matrix for composites used in almost all industries due to excellent mechanical properties, improved processability, good thermal, electrical, chemical and dimensional stabilities. Polymer matrix composites with grapheme oxide or graphite will improve mechanic and thermal characteristics of polyester [1-5]. Graphite is an allotropic form of carbon, which is naturally abundant. In graphite, carbon atoms are covalently bonded in hexagonal manner, forming individual graphene sheets, and these sheets are bound together by Van der Waals forces. Graphite has been used in many industrial applications such as lubricant and additives in composite. It has received attention lately due to its superior in-plane properties. There are two types of graphene structures mainly used as additives in composites namely, the graphene oxide and reduced graphenes. Graphene oxide consist of oxygen based groups such as carbonyl, hydroxile or oxygen, these being bonded to the graphenes [6] in order to make graphene oxide more functional, as well as their better dispersion into the polymers, more methods have been discovered/found. [7-9]. The difficulty in treating the glass transition is caused by almost undetectable changes in the structure despite of qualitative changes in characteristic and extremely large change in the time scale [10]. For that reason, it used to determine Tg, different test and physics parameters. The values of Tg depends on functional groups of the polymer, as carbonyl, carboxyl [11].

2. Methods and materials

2.1. Thermo-mechanical analysis (TMA)

Thermomechanical analysis (TMA) is a method used in order to determine the size changes of the material, according to the temperature. This change can be used to determine the coefficient of linear thermal expansion and temperature of glass transition. For testing we used TMA/SDTA 840 device from METTLER TOLEDO. The samples were measured before testing. A 0.02 N force has been applied on the sample, which was necessary in order to keep the sample still during heating. The thickness of the sample was 4 mm. There have been tested five samples for each concentration. The TMA test only determines the beginning the glass transition temperature, which takes place during a temperature interval. The test was made according to ASTM E831 standard.

2.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a method used in order to determine heat quantity needed by the tested material in order to change its temperature. Measurements are made according to a reference material. Thus, the specific heat and the glass transition temperature of the material can be determined. Tester DSC1 Mettler Toledo was used for testing.

The tube mass was measured by weighing them on the analytic scales *Mettler Toledo AB204—S/FACT* 0.1mg precision. The testing process consists of the following steps: 3 min maintaining at 30 °C, heat speed 10 °C/min up to 190 °C, maintaining for 3 min at 190 °C, cold speed 10 °C/min up to 30 °C, maintaining for 3 min at 30 °C. For each concentration there have been tested five samples. DSC test determines both the temperature beginning of the glass transition on the curve temperature or “midpoint”. In order to compare them, only the the beginning of the glass transition temperature will be used. The tests have been made according to ASTM E 1269 standard.

2.3. Materials

The analysis has been made on non-saturated polyester raisin samples added at five concentrations: 0.02 wt.%; 0.04 wt.%; 0.06 wt.%; 0.08 wt.%; 0.10 wt.% by using two additives: graphene oxide and graphite. In a 500 ml beaker was placed graphite (Graphite Crystalline PMM 11/99.9 KOH-I-NOOR GRAFI s.r.o Netolice, CZ). Then it was added perchloric acid 70%, (Merck) and solutions was mixed in a magnetic stirring for 30 minutes (2500 rpm). After that the mixture was cooled in ice bath. When solution reached 25 °C potassium permanganate (achieved from Fluka) was added. This reaction is highly exothermic, and for that the permanganate was incorporated in four steps. The temperature of solution during the process increased from 25 °C to 35 °C. In order to maintain the temperature below 35 °C, the beaker was introduced in ice bath. All reaction time was 20 hours. In this cooled solution was introduced the hydrogen peroxide 30% in ten steps, during 4h. When reaction is completed (CO_2 emission ceased), the final suspension was spinned at 19,000 rpm. The clear phase was removed, the solid phase was washed in distilled water in 5 stages; the amount of distilled water was 2500 ml. Aqueous reached the pH value of 6.5 (identical with distilled water one). Aqueous was mixed twice using absolute ethanol (volume of 700 ml) and was spinned. The residue obtained was introduced into a crystallizer vessel as a thin film and dried in an oven at 115 °C for 12 h.

First step to achieved polyester/graphite and polyester/graphene oxide nanocomposite respectively, it was to introduce the proper quantities of graphite, graphene oxide into polyester resin, achieving finally a total amount of 100 g of nanocomposite. Following the concentrations fixed for the experiment, it was weighed at the analytical balance % grams of graphite and graphene oxide respectively and it was placed in a mortar. A dry grinding stage was set for 60 minutes. After that it was introduced 5-6 g of polyester resin and followed a "wet grinding" stage for another 60 minutes. The polyester composite was obtained by a "washing" procedure, using small quantities of resin until the final amount of 100 g. Polyester composite was introduced in a 300 ml stirred tank and it was stirred for 2h using a magnetic stirrer (2500 rpm). After this step, the dispersion of the particles into the polyester resin by sonication was split in two stages of 15 minutes. In order to maintain the temperature under control during the reaction process at 45 °C, the mixture was placed in an ice bath. The composite was then degassed under vacuum (4-5 torr) for 4 minute. In next step, the catalyst (2% PMEK) was introduced under continuously stirring. This step was followed by a mechanical homogenization for another 12 minute. The composite was poured into rubber molds. The solidification time was 77 minutes. After two hours the nanocomposite was extracted from the mold and placed in the oven to complete the reaction at 70 °C for 7 h.

3. Results

3.1. Glass transition temperature determined by TMA

Determination of Tg by using TMA method is made on the samples heating curve as can be seen in Figure 1.

Figure 1 shows the composite variation of samples dimension versus the temperature for the polyester 0.02 wt.% graphene oxide composite. It has been noticed an increase of Tg for all the concentrations tested. The biggest values have been obtained for polyester+0.1 wt.% graphene oxide composite and polyester+0.1 wt.% graphite. The values obtained are showed in Table 1. For all the concentrations studied the maximum values have been obtained for polyester/graphene oxide composites.

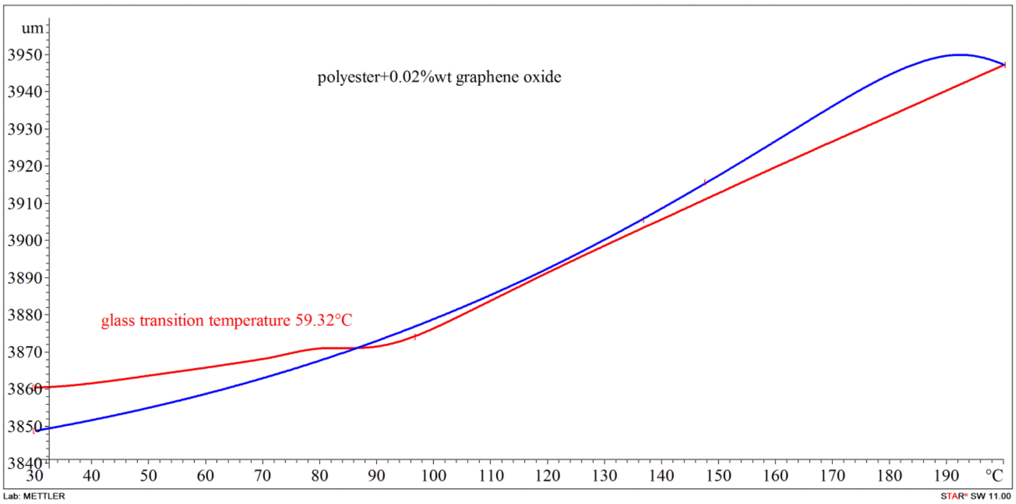

Fig. 1. *Change length vs temperature for polyester+0.02 wt.% graphene oxide*

3.2. Glass transitions temperature determined by DSC

The test DSC can determine Tg both on the heating and the cooling stage. In order to compare the values obtained by this test with the values obtained by the TMA tests, only the value determined on the heating stage of heat flow or specific heat will be used. The best Tg values have been obtained for polyester+0.1 wt.% graphene oxide composites and polyester+0.1 wt.% graphite composites. For all the concentrations studied, the maximum values have been obtained in polyester/graphene oxide composites. Fig. 2 shows the thermal curve flux according to the temperature for the polyester+0.02 wt.% graphene oxide composites on which the glass transition temperature has been determined both in the heating and cooling process. The differences between Tg determined on heating stage and cooling stage could be determined by the generates gases such as CO, CO_2, H_2O in heating stage [12, 13]. Table 1 shows us a small difference between Tg determined by DSC and TMA test.

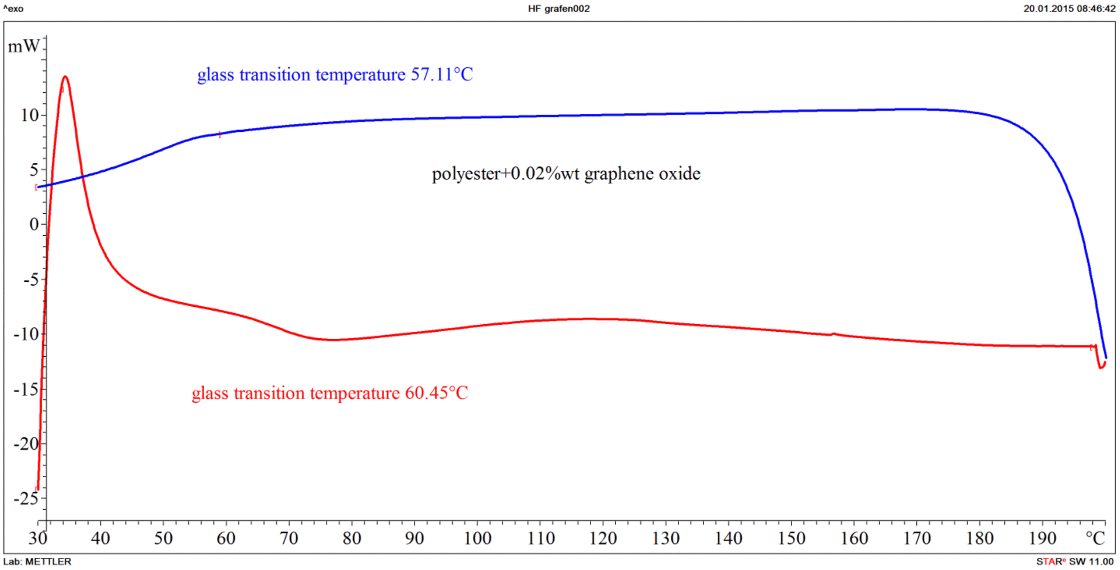

Fig. 2. *Tg for polyester+0.02 wt.% graphene oxide determined by DSC*

Table 1. *Glass transition temperature determined by DSC and TMA tests*

	Tg	
	DSC	TMA
	[^{0}C]	[^{0}C]
polyester	55.27	54.14
polyester+0.02%wt graphene oxide	60.45	59.32
polyester+0.04%wt graphene oxide	63.45	61.86
polyester+0.06%wt graphene oxide	65.98	63.25
polyester+0.08%wt graphene oxide	68.41	65
polyester+0.1%wt graphene oxide	68.98	65.8
polyester+0.02%wt graphite	58.02	56.92
polyester+0.04%wt graphite	59.95	57.9
polyester+0.06%wt graphite	61.83	59.26
polyester+0.08%wt graphite	63.05	60.45
polyester+0.1%wt graphite	65.06	63.45

Each test uses different physics parameters to determine glass transition temperature. In DSC test it used heat flow or specific heat curves and in TMA test it used change length curve. In the literature, have been reports differences of values up to 13 ºC. In both test the glass transition temperatures determined are on-set temperatures for glass transition, glass transitions extended over a range of temperature.

4. Conclusions

For all the composites studied, there has been observed a rise in glass transition temperature according to the rise of the additives concentration. The biggest increase in temperature has been observed for polyester/graphene oxide composites. This can be the result of both the nature and the number of the chemical bonds formed between the graphene oxide and the polyester matrix. In polyester/graphite composites only Van der Waals bonds appear while in polyester/graphen oxide composites there also appear hydrogen bonds which are much stronger than Van der Waals bonds. These are formed between esther groups from the polyester matrix with carbonyl and carboxyl groups which are formed during the process of obtaining the graphene oxide. The number of hydrogen bonds is smaller than Van der Waals bonds but much stronger than that. For the same concentration of additives, the number of chemical bonds formed between grapheme layer and the polyester matrix is much bigger than for polyester/graphite composites due to the graphite exfoliations into graphene layers, which have a specific surface much bigger comparing it with that of graphite they come/derive from. Graphene oxide involves molecular movement of the polyester chains during heating, thus the process of glass transition will start at a higher temperature comparing it with that of pure polyester. The differences obtained for the same concentrations, is due to different physical parameters used in DMA and TMA test.

Acknowledgement

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132397 ExcelDOC.

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