THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2013, ISSN 1453 – 083X

EFFECT OF SINGLE-WALL CARBON NANOTUBES ON THERMAL PROPERTIES OF POLYESTER COMPOSITES

Luminita CIUPAGEA, Virgil ILIUTA, Gabriel ANDREI
"Dunarea de Jos" University of Galati, Romania
email: luminitacotet@yahoo.com

ABSTRACT

This paper presents the effect of different contents of single-wall carbon nanotubes (SWCNT) on the specific heat and coefficient of thermal expansion of polyester composites. By adding small content of SWCNT in the matrix of the polyester, the specific heat increase compared to pure polyester. For a content higher than 0.15 wt% SWCNT, the coefficient of thermal expansion increases compared with pure polyester on cooling curve.

KEYWORDS: polyester, nanocomposites, SWCNT, thermal properties

1. Introduction

Unsaturated polyester is a polymer used in industrial applications as matrix for different type of composites. In recent years, nanomaterials have become the subject of intensive research. As for nanomaterials manifold, carbon nanotubes (CNT) attracted the attention of researchers because of their properties such as: low density, good stiffness, uncommon strength, exceptive electrical properties, excellent optical and thermal properties. By adding CNT into polymer matrix, a composite with better mechanical, thermal and electrical properties may be obtained.

In their study, Kucukyildirim et al added 1% wt multi-wall carbon nanotube (MWCNT) into polyester/glass fiber composite and they reported better mechanical properties such as tensile strength and toughness [1].

Other researchers used carbon nanofibers (CNF) into polyester matrix. Even small content of CNF, between 0.1 and 0.3 % wt, may increase the strength at flexural tests [2]. As regards thermal approach, a content between 1 and 3%wt MWCNT into polyester matrix improves thermal conductivity of the composite [3]. The biggest challenge regarding carbon nanotubes or nanofibers is the manufacture of an homogeneous composite by getting a good dispersion of the nanomaterial into polymer matrix. Mechanical stirring or ultrasonic methods are the most used techniques in order to obtain an homogeneous mixture. As for mechanical mixing, the more energy is higher, the dispersion is better. [4].

Scientific literature reveals other techniques which provide a suitable dispersion of CNT into polymer, such as: *in situ* polymerization or chemical functionalization [5].

2. Experimental results

2.1. Materials

The composites samples were prepared with commercial orthophtalic unsaturated polyester resin with 40% styrene (Norsodyne H 13271 TA). The main features of the resin are: density at 20^{o}C is 1.1g/cm^3, viscosity at 23^{o}C is 4.5 dPas, solid ranges between 56 – 60%, the working temperature was 23^{o}C and gel time was 12 min.

The methyl ethyl ketone peroxide was used as catalyst in order to initiate the polymerization reaction.

Single-wall carbon nanotubes, purchased from the company Cheap Tubes Inc., have a purity of over 90%, external diameter between 1 and 2 nm, internal diameter between 0.8 and 1.6nm, length between 5 and 30μm, specific surface 407m^2/g and density 2.1g/cm^3.

2.2. Preparation of the composites materials

Preparation of the composites materials was made using mechanical stirring technique. A short description of the procedure is related in this paragraph.

After weighting, the resin and single-walled nanotubes were placed into mortar for homogenization. Dispersion was performed by progressive addition of the polyester over SWCNT. After adding the entire amount of polymer, the

mixture was stirred by a magnetic stirrer for 1 hour, at 600rpm. Next step was degassing the mixture to remove bubbles air using a vacuum pump for 1 minute. The catalyst was introduced for starting the polymerization process. Homogenization of the catalyst inside the mixture mass was done using the stirring solution for 5 minute at 600 rpm, followed by a second degassing. Molding was performed using a vacuum pump to avoid the formation of the voids into composite. Finally, the polymerization was completed by placing the materials into oven for 8 hours, at 70^{o}C.

The following samples were prepared:

- polyester composite with 0.10% wt SWCNT;
- polyester composite with 0.15% wt SWCNT;
- polyester composite with 0.20% wt SWCNT.

These composites and pure polyester were tested for determination of specific heat and coefficient of thermal expansion.

2.3. Method for determining the specific heat

The **specific heat** of the materials was determined based on differential scanning calorimetry data recorded with a (DSC) instrument, type DSC1 Star System Mettler Toledo.

The testing method for all the samples consisted of following steps:

1. Keeping the sample at 30^{o}C for 5 minutes;
2. Heating the sample from 30^{o}C to 130^{o}C with a rate of 10^{o}C/min.
3. Keeping the sample at 130^{o}C for 5 minutes;
4. Cooling the sample from 130^{o}C to 30^{o}C with a rate of 10^{o}C/min.

The specific heat value was calculated by the relation:

$$c = \frac{Q}{m \cdot (T_2 - T_1)}$$

where c is the specific heat (J xg^{-1}×^{o}C^{-1}), Q is the heat flow (J), m is specimen mass, (g), T_1, T_2 are heating temperatures from start and end points (^{o}C).

The specific heat values for all tested materials was calculated in the range of 70 - 110^{o}C for both heating and cooling curves. In this range, the material behaviour can be considerated rather liniar, as shown figure 1.

The determination of the **thermal expansion coefficient** was done using a thermo mechanical analyzer (TMA) type TMA – SDTA 840, Mettler Toledo.

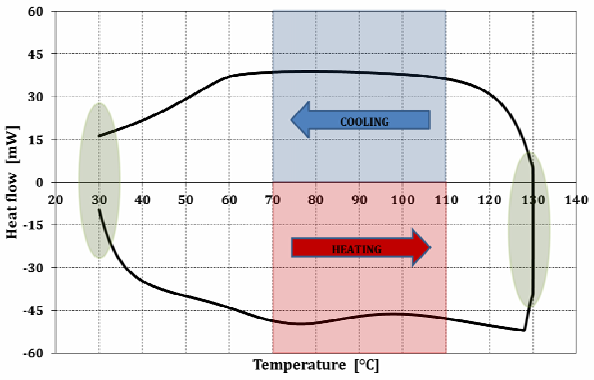

***Fig. 1.** Graph of the heat flow depending on the temperature for tested materials*

Testing method consist of following steps:

1. Keeping at 30^{o}C for 5 minute;
2. Heating from 30^{o}C to 130^{o}C with a thermal rate of 10^{o}C/min under a 0.02N loading;
3. Keeping at 130^{o}C for 5 minute;
4. Cooling from 130^{o}C to 30^{o}C with a thermal rate of 10^{o}C/min under a 0.02N loading.

Linear thermal expansion coefficient was calculated using the formula:

$$\alpha = \frac{L}{\Delta L \times \Delta T}$$

where α thermal expansion coefficient, (10^{-6}/^{o}C), L is initial length of the sample (mm), ΔL is the difference between final and initial length of the sample (mm); ΔT is the difference between final and initial temperature of the sample (^{o}C).

The values of the coefficient of thermal expansion were calculated into the interval 70 – 110^{o}C.

3. Results and discussion

3.1. Specific heat

The experimental results for specific heat of the polyester nanocomposite and pure polyester, on the heating curve, are shown in the Figure 2. From the graph it can be seen that the polyester nanocomposites with SWCNT have greater values for specific heat. This means that small amounts of well dispersed SWCNTs could improve the specific heat of the composite. From the graphs presented in the Figures 2 and 3 it can be seen that all the nanocomposites shown better values for specific heat as compared to pure polyester. The value of specific heat increases with 63%, in case of 0.10% wt SWCNT, with 69% for 0.20% wt SWCNT and with 76% for 0.15% wt SWCNT, all values compared with the specific heat of polyester.

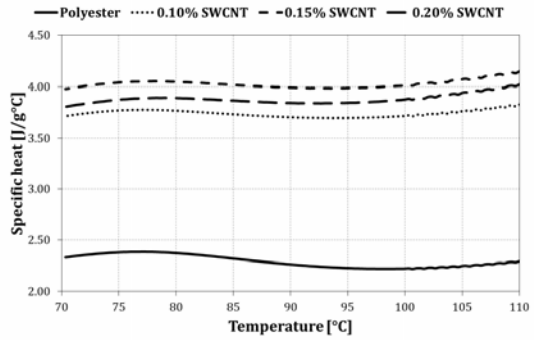

Fig. 2. *Variation of the specific heat for polyester and polyester nanocomposite with different content of SWCNT on heating curve*

The figures 4 and 5 show the specific heat values on cooling curve. All values for nanocomposites are bigger compared with specific heat of pure polyester.

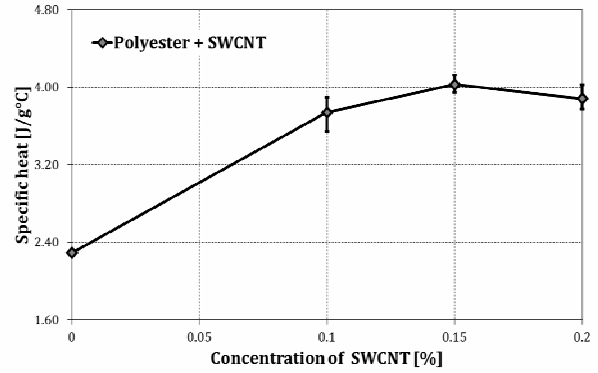

Fig. 3. *Variation of the specific heat depending on the content of SWCNT added into polyester, on heating curves*

On cooling curve, the polyester nanocomposite with 0.15% wt SWCNT has the higer value from all tested materials as is shown in figure 4.

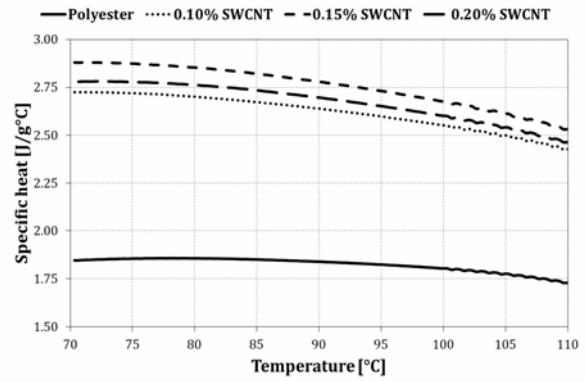

Fig. 4. *Variation of the specific heat for polyester and polyester nanocomposite with different contents of SWCNT on cooling curve*

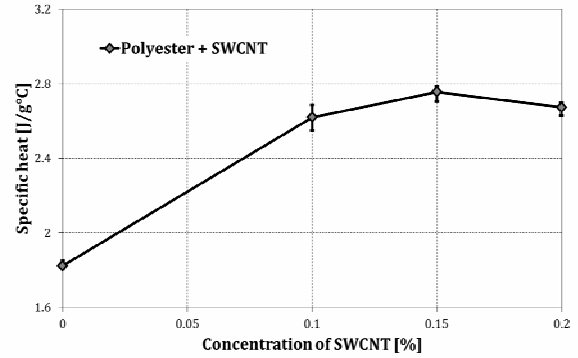

Fig. 5. *Variation of the specific heat depending on content of SWCNT added into polyester, on cooling curves*

As for nanocomposite with 0.10% wt SWCNT, specific heat increase with 44%, for 0.15% wt SWCNT, with 51% and for 0.20% increase with 47%, all values were compared with specific heat of polyester.

3.2. Coefficient of thermal expansion

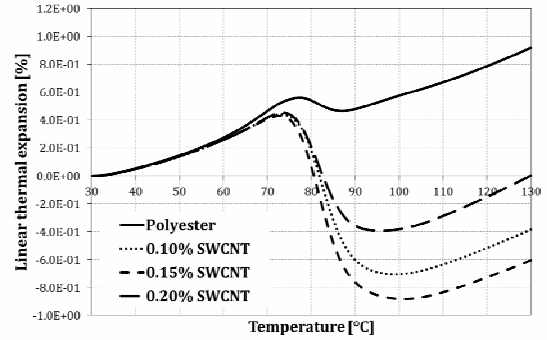

Fig. 6. *Evolution of linear thermal expansion with temperature for polyester and SWCNT composites on heating curve*

Regarding the linear thermal expansion on heating and cooling curves, the experimental results reveled different situation as shown in Figures 6 and 7.

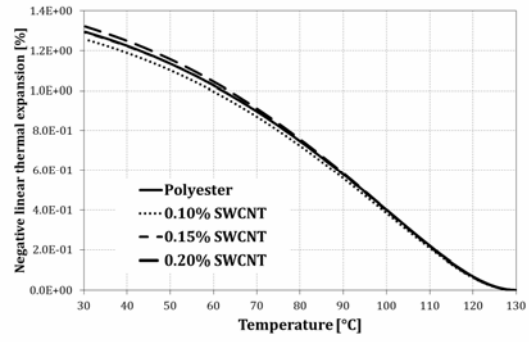

Fig. 7. *Evolution of linear thermal expansion with temperature for polyester and SWCNT composites on cooling curve*

On heating curves (Figure 6) all of nanocomposites have an increasing trend for linear expansion until the glass transition temperature (Tg) value is achieved. After this point, practically between 70 and 100^{o}C, the curve has a descending trend, reaching negative values for thermal expansion. The neat polyester has a small decrease after Tg, in the interval 75-90^{o}C, over this range, thermal linear expansion increase. It can be concluded that in case of nanocomposite beyond Tg there is a rearrangement of molecules within material.

On cooling curves, negative linear thermal expansion, for all of tested materials, has a almost similar evolution, with small differences, as is shown in Figure 7.

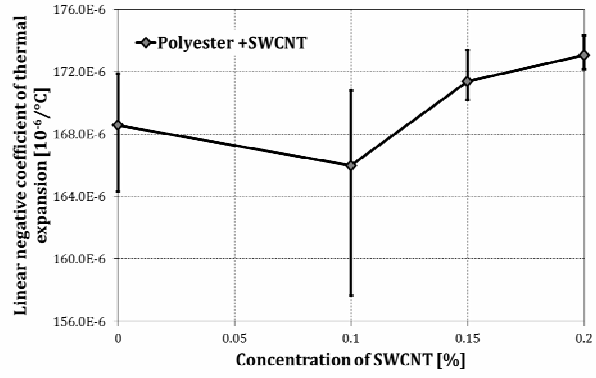

Fig. 8. *Variation of linear negative coefficient of thermal expansion depending on the content of SWCNT added into polyester, on cooling curves*

Figure 8, shows that, except polyester composite with 0.10% wt, all of nanocomposites have increasing values for linear negative coefficient of thermal expansion, compared with neat polyester. The biggest value was obtained for polyester nanocomposite with 0.2%wt SWCNT.

4. Conclusion

The aim of this work was to determine the important thermal properties of polyester and polyester composites with small contents of SWCNT.

The experimental results shown that the specific heat of nanocomposite increase for both heating and cooling curves. The biggest value for specific heat was obtained for nanocomposite with 0.15 wt % SWCNT on heating curves, the increasing was 76% compared with polyester value.

Concerning the coefficient on thermal expansion calculated on cooling curves, the polyester nanocomposites with 0.15 wt % and 0.20 wt % shown increased values compared with polyester value.

Acknowledgement

This work was carried out with the support of the Project POSDRU - 76822 TOP ACADEMIC.

References

[1]. Kucukyildirim, B.O. et al - Mechanical Behavior of Industial Grade MWCNT and Glass Fiber Reinforced Polyester Hybrid Nanocomposites, *International Journal of Arts and Sciences* 3 (9), (2010), pp.252-257.

[2]. Hossain, M.K. et al. - Flexural and Compression Response of Woven E-glass/Polyester-CNF Nanophased Composites, *Composites: Part A42*, (2011), pp. 1774-1782.

[3]. Wang, S. et al. - Enhancing Thermal Conductivity of Glass Fiber/Polymer Composites Through Nanotubes Incorporation; *Composites Part B: Engineering, Vol. 41, Issue 7*, (2010), pp. 533-536.

[4]. Agullo, J-Vera et al. - Comparative Study of the Dispersion and Functional Properties of Multiwall Carbon Nanotubes and Helical – Ribbon Carbon Nanofibers in Polyester Nanocomposites, *Composites Science and Technology 69*, (2009), pp. 1521 – 1532.

[5]. Xie, X-L et al. - Dispersion and Alignment of Carbon Nanotubes in Polymer Matrix: A Review, *Materials Science and Engineering* R 49, (2005), pp 89-112.

[6]. Alsina, O. L.S. et al, 2005, Thermal properties of hybrid lignocellulosic fabric-reinforced polyester matrix composites, *Polymer Testing* 24, Issue, pp.81-85.

[7]. Ashby, M. - *Materials Selection in Mechanical Design*, Second Edition, Ed. Elsevier Butterworth – Heinemann, pp. 22 -28.

[8]. Crawford, R. J., 1998, *Plastics Engineering*, Third Edition, Ed. Elsevier Butterworth – Heinemann, (1999), p.7.

[9]. Morgan, P.- *Carbon Fibers and Their Composites*, Ed Taylor and Francis Group, (2005), p 537.

[10]. Moreira, D.C. - Experimental investigation of heat conduction in polyester – Al2O3 and polyester – CuO nanocomposites; *Experimental Thermal and Fluid Science*, Vol.35, Issue 7, (2011), pp. 1458-1462.

[11]. Ruban, Y. J. V. et al. - Mechanical and Thermal Studies of Unsaturated Polyester – Toughened Epoxy Composites Filled with Amine-Functionalized Nanosilica; Appl. Nanosci, (2011).