SPECIFIC HEAT AND THERMAL EXPANSION OF POLYESTER COMPOSITES CONTAINING SINGLEWALL -, MULTIWALL - AND FUNCTIONALIZED CARBON NANOTUBES

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The influence of carbon nanotubes (CNT) on thermal properties of polyester composites was examined tacking into account the type and the content of CNT. Polyester nanocomposites have been obtained by adding a small content of different types of carbon nanotubes, i.e. multi-wall carbon nanotubes (MWCNT), functionalized multi-wall carbon nanotubes (MWCNT–COOH) and single-wall carbon nanotubes (SWCNT). Specific heat and linear coefficient of thermal expansion have been measured and comparatively discussed for all the nanocomposites samples.

1. Introduction

Unsaturated polyester is a material with easy fabrication technique, light weight, good resistance into corrosive media, and low cost [1, 2]. Moreover, unsaturated polyester is part of the thermosetting materials which, after complete polymerization, prove good thermal stability, excellent dimensional steadiness and good creep resistance [2]. The major advantage of thermosetting materials is that the mechanical properties are not influenced by temperature [3].

One of the industrial applications for unsaturated polyester concerns the matrix of polymer composites. As for thermal behavior, researchers identified new materials in order to improve specific heat, thermal diffusivity and thermal conductivity. Alsina et al. increase thermal properties such as thermal conductivity, thermal diffusivity and specific heat of polyester composites by adding jute/cotton, sisal/cotton and ramie/cotton in polyester matrix. Also, by determining thermal properties in a plane perpendicular and parallel to the fabric plane, it have been reported better values for measurement in parallel plane [4].

Nanomaterials are considered an advanced class of materials with unique properties related to their dimensions. The most important properties for industrial applications are: very good mechanical properties, electrical conductivity, thermal conductivity (carbon nanotubes), fire resistance (nano-clay) or antimicrobial features (nano-silver) [5, 6]. As regards nanomaterials added into polymer matrix, there are a lot of studies which show increase in thermal properties of final composites even for small content of nanomaterial [7-17]. It is important to perform a very good dispersion of the nanomaterials into polymer matrix, since only in this way the properties of the nanomaterials are transferred to final composite. Different techniques for obtaining a homogeneous nanocomposite are highlighted in the scientific literature [18, 19]. Wang et al. studied thermal conductivity of the polyester composites with multiwall carbon nanotubes and glass fibers. The experimental results and theoretical model demostrate improving of the thermal conductivity of the composites [20].

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Values of thermal conductivity of the polyester nanocomposites with different content of aluminum oxide and copper oxide increase with content of nanoparticles, as obtained Moreira et al. [21]. Into unsaturated polyester matrix, Seghar et al., introduced different content of clay nanoparticules.

The results show an increasing of glass transition temperature of final composites and a decrease of the coefficient of thermal expansion [22]. A good thermal stability was obtained by Thanh et al. in their study, by adding modified clay into polyester matrix [23]. Various methods have been used in order to improve the dispersion of carbon nanotubes into polymer matrix [19] with effect on mechanical and electrical properties [24-26]. Different types of polymer composites have been developed and investigated as regards wear resistance as possible substitute of metallic parts and structures [27]. The purpose of this study is to analyze the influence of different types of carbon nanotubes added into unsaturated polyester matrix in small weight content.

2. Experimental

2.1 Materials

In order to obtain polyester nanocomposites, the following materials were used:
- unsaturated polyester resin with 40 % stiren, trade name Norsodyne H 13271 TA, with main physical and chemical features: density at 20°C is 1.1 g/cm^3, viscosity at 23°C is 4.5 dPas, solid content 56 – 60%, working temperature 23°C and gel time 12 min;
- methyl ethyl ketone peroxide was used as catalyst;
- carbon nanotubes supplied by the company Cheap Tubes Inc., with features presented in Table 1. In this work, three types of carbon nanotubes were used: multi-wall carbon nanotubes (MWCNT), multi-wall carbon nanotubes COOH functionalized (MWCNT –COOH) and single-wall carbon nanotubes (SWCNT).

Table 1. Main features of carbon nanotubes.

Carbon nanotubes type	Purity %	Outer diameter [nm]	Inner diameter [nm]	Length [μm]	Specific surface [m^2/g]	Density [g/cm^3]	Functionalization
MWCNT	> 95	8 - 15	3 - 5	10 - 50	233	2.1	-
MWCNT-COOH	> 95	8 - 15	3 - 5	10 - 50	233	2.1	2.5 % COOH
SWCNT	> 90	1 - 2	0.8 – 1.6	5 - 30	407	2.1	-

2.2   Preparation of the composites materials

Using the materials listed above, polyester nanocomposites were obtained by mechanical stirring technique. A short description of the procedure is presented in Figure 1. Small contents of carbon nanotubes were added into polyester matrix, as follows: 0.10 % wt, 0.15 % wt and 0.20 % wt. As it is shown in Figure 1, the procedure involve, a progressive dispersion of carbon nanotubes into polyester matrix and homogenization of the mixture by stirring one hour at 600 rpm. In order to eliminate air bubbles from the mixture, a vacuum pump for degassing was used. Once the polymerization process started by adding the catalyst, the mixture was homogenized for 5 minute at 600 rpm followed by another degassing. The mixture was molded under the action of vacuum pump. The polymerization process was completed by placing all composites into an oven for 8 hours at 70°C. The content and types of obtained composites are listed in Table 2.

2.3 Experimental procedure

Specific heat. The specific heat for neat polyester and all nanocomposites was determined using a DSC instrument type DSC1 Star System (Mettler Toledo) and following test method: sample was kept for 5 minutes at 30°C then was heated from 30°C to 130°C with 10°C/min, where was kept 5 minute at 130°C and then was cooled from 130°C to 30°C with 10°C/min. All values for specific heat were calculated in the range where the behavior of all materials can be considered linear, that means between 70 and 110°C, both for heating and cooling curves.

Coefficient of thermal expansion. The coefficient of thermal expansion for neat polyester and all nanocomposites was determined using a TMA instrument, type TMA – SDTA 840 (Mettler Toledo).
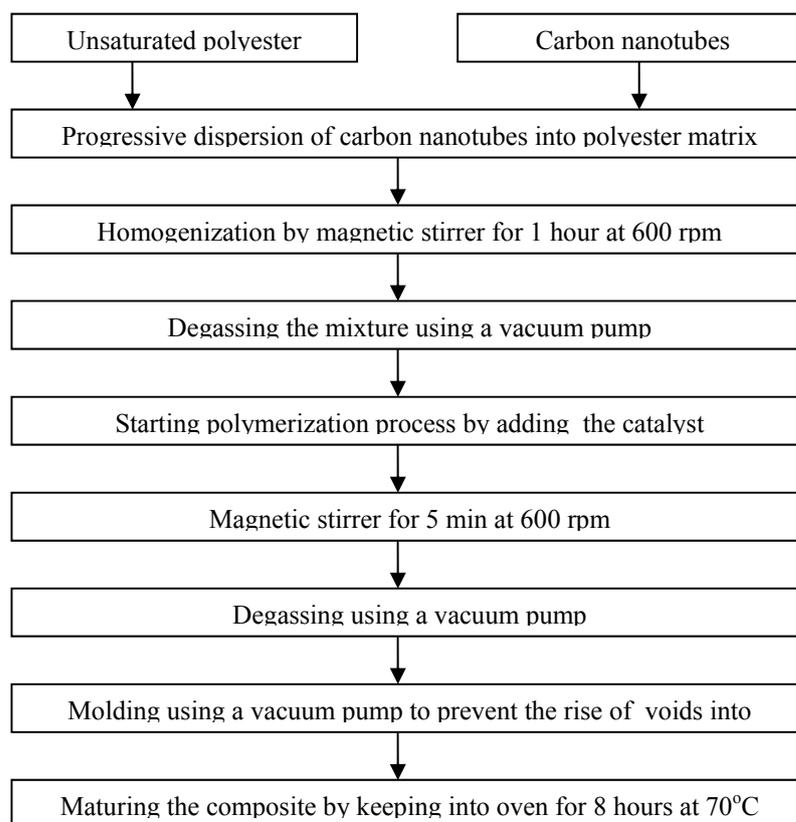

Fig. 1 A brief description of the procedure for obtaining polyester nanocomposites

Table 2: Obtained nanocomposites

No.	Nanocomposite types and contents
1	Unsaturated polyester + 0.10% wt MWCNT
2	Unsaturated polyester + 0.15% wt MWCNT
3	Unsaturated polyester + 0.20% wt MWCNT
4	Unsaturated polyester + 0.10% wt MWCNT - COOH
5	Unsaturated polyester + 0.15% wt MWCNT - COOH
6	Unsaturated polyester + 0.20% wt MWCNT - COOH
7	Unsaturated polyester + 0.10% wt SWCNT
8	Unsaturated polyester + 0.15% wt SWCNT
9	Unsaturated polyester + 0.20% wt SWCNT

The test method consists of the following steps: maintaining the sample for 5 minutes at 30°C, then heating from 30°C to 130°C with 10°C/min, followed by keeping for 5 minute at 130°C and cooling from 130°C to 30°C with 10°C/min. Given the same reasons discussed above for determining the specific heat, the range of calculation of the coefficient of thermal expansion was chosen between 70 and 110°C.

3. Results and discussions

3.1 Specific heat evaluation

According to described procedure for specific heat tests, values for all the polyester composites were compared to those of neat polyester. The specific heat values were discussed firstly, by influence of the additive concentration and secondly, by influence of the additive type.
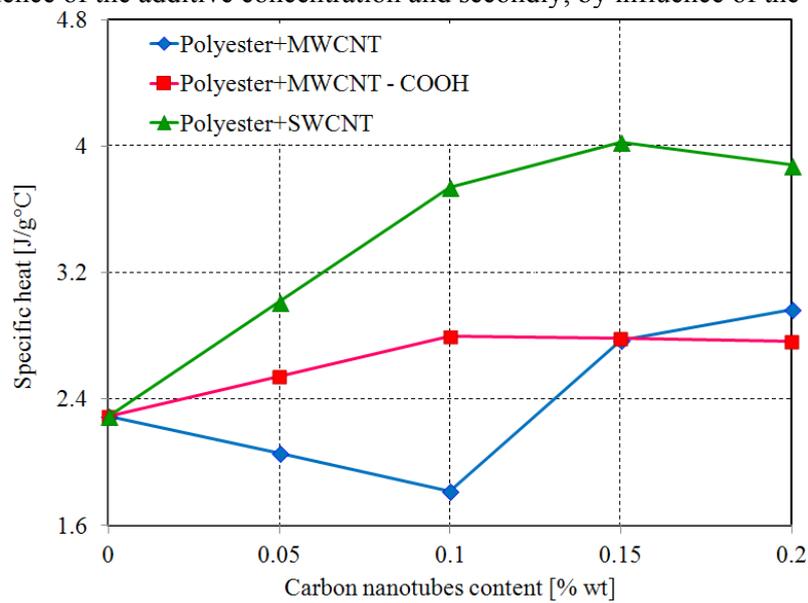

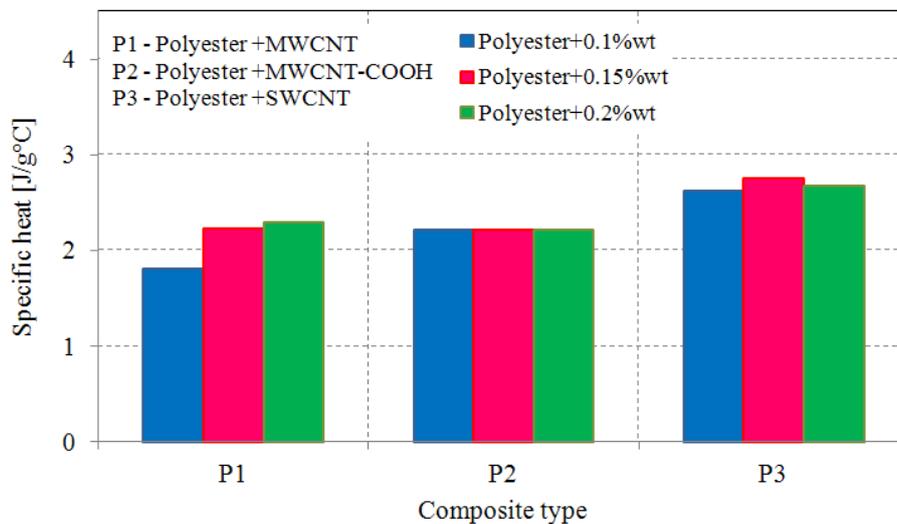*Fig.2 Specific heat depending on the content of nanomaterial added into polyester, measured on heating curve*

Fig. 3 Specific heat depending on the type of nanomaterial added into polyester, measured on heating curves

Measurements on heating curve. Experimental values for specific heat depending on additive concentration for all types of polyester nanocomposites are shown in Figure 2. The first graph in the Figure 2 represents variation of specific heat with additive content for polyester composite with MWCNT.

In this case, except for the content of 0.10 % wt MWCNT, for 0.15 % wt and 0.20 % wt MWCNT the composites show increasing trend for specific heat. Compared with specific heat of neat polyester which is 2.292 J/gºC on heating curve, the specific heat values increase with 21% when the content is 0.15 % wt MWCNT and with 29 % when the content is 0.20 % wt MWCNT. The maximum value is noticed for 0.2% MWCNT.

Evolution of specific heat in the case of polyester composites with MWCNT – COOH is depicted in the second graph of Figure 2. It can be seen that all the composites samples show increasing values compared with those of neat polyester. Small differences between specific heat values are recorded for the composites samples with additives, as follows: specific heat increase with 22 % for 0.10 % wt MWCNT – COOH, with 21.5 % wt for 0.15 % wt MWCNT – COOH and with 21 % wt for 0.20 % wt MWCNT – COOH. The third graph in Figure 2 reveals experimental results for polyester nanocomposites with SWCNT. The measurements clearly state increasing values of specific heat, for all the nanocomposites in comparison with those of neat polyester. Highest increase, with 76 %, was noticed in case of composite with 0.15 % wt SWCNT, next 69 % for composite with 0.20 % wt and 63 % for composite with 0.10 % wt SWCNT. As for the effect of CNT type, Figure 3 illustrates how carbon nanotube sort may influence the value of specific heat. From the first graph of Figure 3, it can be noticed that at the same content of nanomaterial, 0.10 % wt, the bigger increasing for specific heat is given by single-wall carbon nanotubes type. Specific heat value for polyester nanocomposite with 0.10 % wt SWCNT is higher with 33 % compared with nanocomposite with 0.10 % MWCNT – COOH.

The second graph on Figure 3 shows specific heat for composites with 0.15 % wt nanomaterial. In this case, specific heat of composites with MWCNT – COOH and MWCNT are almost equal. Regarding polyester nanocomposite with SWCNT, experimental results shown the best values for specific heat. Practically, SWCNT nanocomposite shows value with 45 % over than that of MWCNT composite and with 44.6 % over that of MWCNT–COOH composite. The third graph of Figure 3 presents variation of specific heat for composites with 0.20 % wt carbon nanotubes. For this case polyester nanocomposite with SWCNT presents the highest value for specific heat, with 31 % over than that of composite with MWCNT and with 40 % higher than that of composite with MWCNT – COOH. It can be seen that specific heat for nanocomposite with MWCNT is higher with 7 % than that of nanocomposite with MWCNT – COOH.

Measurements on cooling curve. Figures 4 and 5 show results concerning specific heat for polyester nanocomposites compared with neat polyester, also the influence of additive content and type. The first graph from Figure 4 depicts the same trend on cooling curve like as for heating curve. Thus, except for polyester composite with 0.10 % wt MWCNT, specific heat exhibits higher values compared with neat polyester. Taking into account the specific heat of neat polyester on cooling curve which is 1.823 J/gºC, specific heat increase with 22 % for composite with 0.15 % wt MWCNT and with 25 % for composite with 0.20 % wt MWCNT.

The second graph on Figure 4 shows the uniformity of specific heat values for polyester composite with functionalized nanotubes. The specific heat values of nanocomposites are with 21 % higher than specific heat of polyester. Polyester nanocomposite with SWCNT reveals experimental values for specific heat higher than those of polyester, as shown in Figure 4, third graph. The highest increase was recorded for nanocomposite with 0.15 % wt SWCNT, which displays a 51 % rise compared with polyester. Specific heat is higher with 46 % and 43 %, for polyester composite with 0.20 % wt and 0.10 % wt, respectively, than specific heat of neat polyester. The graphs from Figure 5 show the influence of carbon nanotubes type on specific heat.
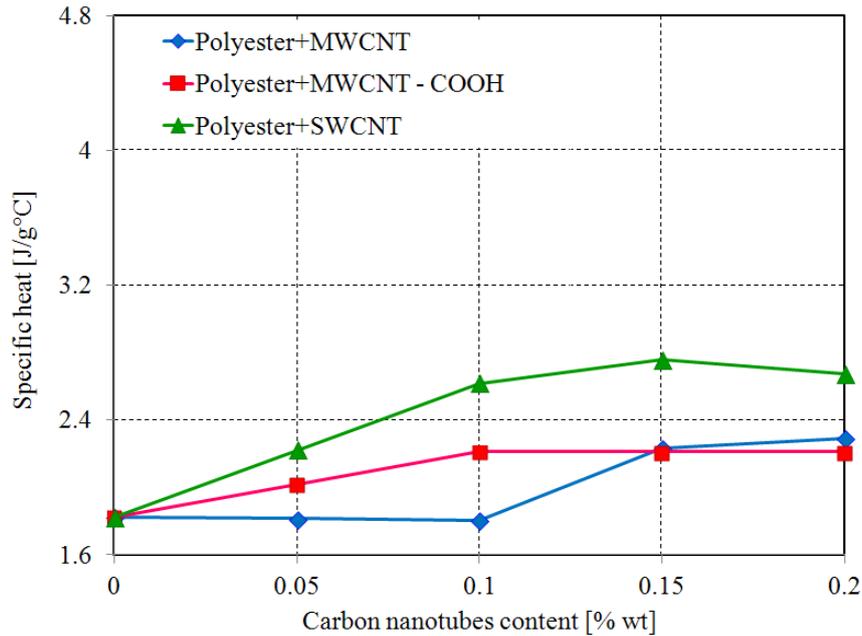
Fig. 4 Specific heat depending on the content of nanomaterial added into polyester, measured on cooling curve
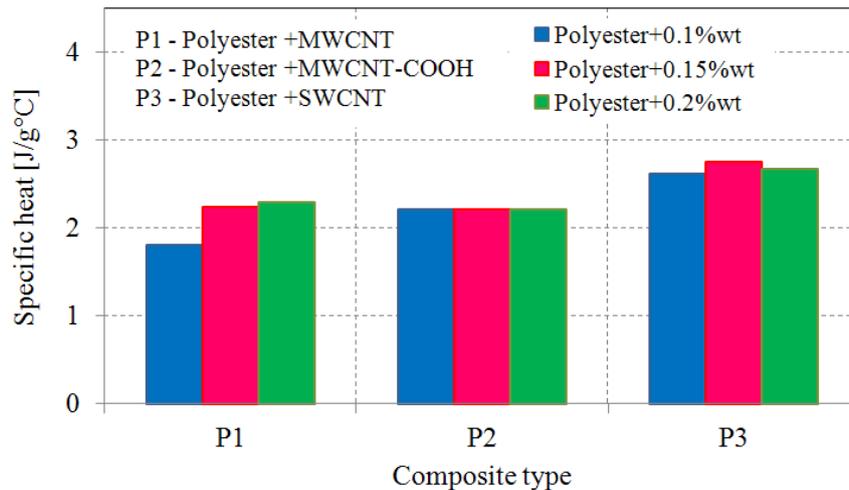

Fig. 5 Specific heat depending on the type of nanomaterial added into polyester, measured on cooling curves

When 0.10 % wt carbon nanotubes have been added into polyester matrix, the highest value for specific heat was recorded for polyester with SWCNT, higher than specific heat for composite with MWCNT –COOH. When adding 0.15 % wt carbon nanotubes, as Figure 5 shown, the composite with SWCNT also recorded the higher value for specific heat, practically with 23 % over that of composite MWCNT and with 25 % higher than that of composite based on MWCNT – COOH. Figure 5 shows the case when 0.20 % wt nanomaterial was incorporated into polyester. By adding SWCNT, specific heat had the highest value, with 16 % over than that of polyester composite with MWCNT and with 21 % higher than that of composite with MWCNT –COOH.

3.2 Coefficient of thermal expansion

Coefficient of thermal expansion (CTE) was calculated only on cooling curve, for all composites. On heating curve, after reaching glass transition temperature (Tg), for all tested samples a descending trend to negative values has been noticed. Over Tg value, a rearrangement of molecules within nanocomposite might occur. Results concerning the coefficient of thermal expansion are presented in Figures 6 and 7. In the first graph of Figure 6 it is shown the linear negative coefficient of thermal expansion in case of polyester composites with MWCNT. There are very small differences between nanocomposites and neat polyester concerning coefficient of thermal expansion. The highest value was recorded for polyester composite with 0.20 % wt which is higher than neat polyester value. The coefficient of thermal expansion for composites with 0.10 % wt and 0.15 % wt shows closer values and higher than coefficient value for polyester. In case of polyester nanocomposites enriched with MWCNT – COOH, (second graph of Figure 6), all composites prove higher values for coefficient of thermal expansion compared with neat polyester. In these cases, the nanocomposites with different content of MWCNT-COOH point out a higher coefficient of thermal expansion compared with that of polyester.

The result exposed in the third graph of Figure 6 refers to the test of nanocomposite made from polyester and SWCNT. One can be noticed that, except for composite with 0.10 % wt SWCNT, all composites demonstrate higher values for coefficient of thermal expansion. Actually, composite with 0.20 % wt SWCNT prove higher CTE compared with that of neat polyester. Figure 7 depicts the tendency of linear negative coefficient of thermal expansion for different types of nanomaterials. As for 0.10 % wt carbon nanotubes into polyester matrix, as Figure 7 shows, the highest value of CTE is obtained for MWCNT-COOH, which is higher than the other two. When 0.15 % wt carbon nanotubes have been added into polyester matrix, (Figure 7), the composite with SWCNT proves the highest value, which is higher than those of the other two. As regards 0.20 % wt carbon nanotubes added into polyester, (Figure 7) the highest value of CTE was obtained for MWCNT–COOH.
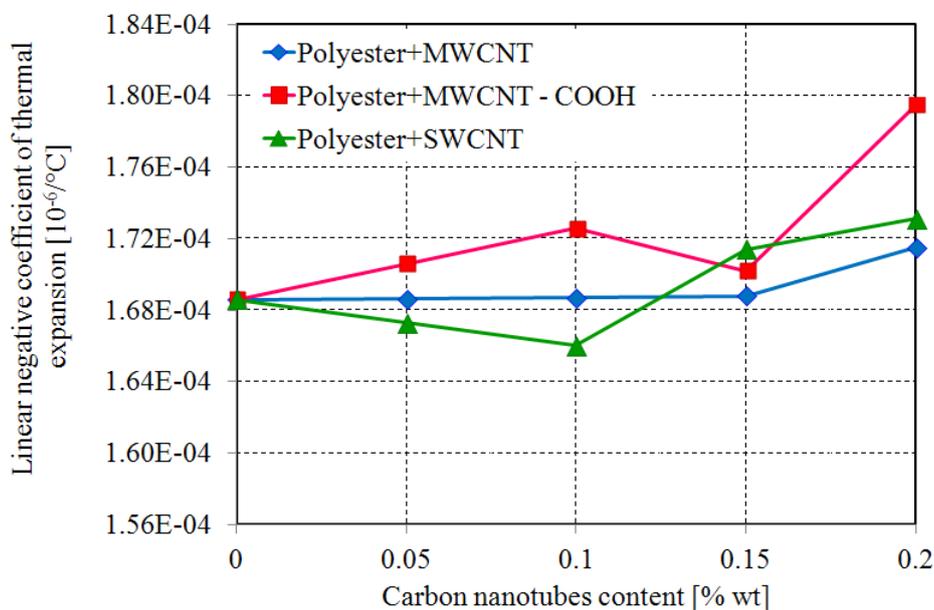

*Fig. 6 Linear negative coefficient of thermal expansion depending on content
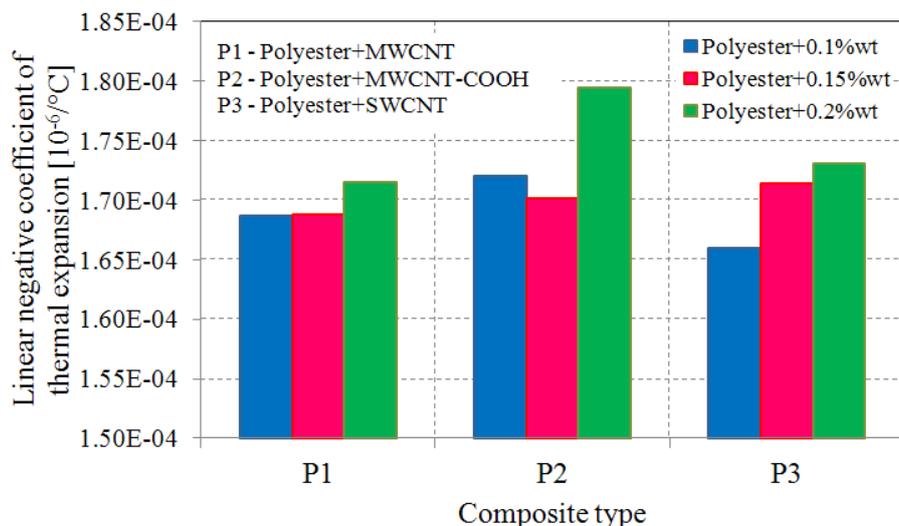of nanomaterial added into polyester, measured on cooling curves*

Fig. 7 Linear negative coefficient of thermal expansion depending on the type of nanomaterial added into polyester, measured on cooling curves

4. Conclusions

The specific heat of polyester nanocomposites with carbon nanotubes has been assessed through measurements on heating and cooling curves. The nanocomposites (except for polyester composite with 0.1 % wt MWCNT) have shown increasing values for specific heat compared with neat polyester.

For both heating and cooling curves, nanocomposites with SWCNT proved higher values for specific heat, with a maximum in case of content 0.15 % wt. On heating and cooling curves, the increase in specific heat was 76 % and 51 %, respectively, compared to that of neat polyester.

The nanocomposites with functionalized nanotubes (MWCNT – COOH), revealed similar values of specific heat, on heating and cooling curves. One can conclude that functionalization of MWCNT provides a good compatibility with polyester matrix and improves the homogeneity of nanocomposites. On cooling curves, the specific heat of nanocomposites has demonstrate smaller values than those obtained on heating curves.

The linear negative coefficient of thermal expansion has been measured on cooling curves. The coefficient of thermal expansion shown slight increased values compared to those of neat polyester, for all the nanocomposites thermally tested. A maximum increase of CTE (6.5%) has been recorded for the nanocomposite with 0.20 % wt MWCNT–COOH compared with that obtained for the neat polyester. Under 0.2 %wt content, irrespective of the carbon nanotubes type, CTE measurements have pointed out a dimensional steadiness of all the samples.

Acknowledgement

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