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# Investigation of Carbon Nanotube Particles Addition Effect on the Dispersed Composite Structure Thermal Diffusivity

Łukasz Omen[1*], Robert Szczepaniak[2], Andrzej J. Panas[1]

[1] Military University of Technology, Faculty of Mechatronics, Armament and Aerospace, Gen. Sylwestra Kaliskiego Street No 2, 00-908 Warsaw, Poland

[2] Polish Air Force University, Faculty of Aviation, Dywizjonu 303 Street No 35, 08-521 Dęblin, Poland

* Corresponding author's e-mail: lukasz.omen@wat.edu.pl

## ABSTRACT

The article addresses the issue of the possibility of improving the thermal transport parameters of an epoxy resin, such as thermal diffusivity (TD) and thermal conductivity (TC), by the addition of carbon nanotubes (CNT) as a high thermal conductivity filler. In the case presented here, the effect of the addition of high TC carbon nanotubes to commercial epoxy resin LH145 cured with H147 hardener was investigated experimentally. The main parameter studied was thermal diffusivity. Measurements were carried out for samples of epoxy resin and epoxy resin matrix composites with dispersed CNTs with a volume fraction of carbon nanotubes ranging from 1% to 6%. A modified Ångström temperature oscillation method was used to obtain TD. Basic measurements were performed in the temperature range from −20 ºC to 80 ºC while maintaining high temperature resolution that allows to observe the TD changes with the temperature change. During complementary microcalorimetric studies focussed on specific heat determination effects of matrix resin postcuring were also characterized. The studies were performed within extended up to 80 ºC temperature range. As a result, the temperature dependence of thermal conductivity was determined and data for determining thermal diffusivity was obtained. However, the analysis of the obtained results did not show a significant dependence of the studied parameters on the amount of CNT additive for the studied compositions.

**Keywords:** epoxy resin matrix composites, carbon nanotubes filler, disperdes composite structures, thermal diffusivity, thermal conductivity, Ångström method.

## INTRODUCTION

Composite materials are a significant group of structural materials that are widely used in various industries e.g. aerospace [1]. Due to their high strength with relatively low weight [2], these materials can successfully replace metal alloys, for example in aeronautical structures. Among them, carbon composites in an epoxy resin matrix occupy an important place [3]. Further expansion of their field of application can be achieved by modifying the existing structures or fabricating new ones [3]. Any modification of the structure requires material testing, including studies of the thermophysical properties that determine, among other things, the permissible thermo-mechanical stresses of the structure [4]. Previous work on this type of modification has partly confirmed the possibility of modifying the properties of the already existing composites by introducing carbon inclusions. For one such structure, a fivefold increase in the diffusivity value was observed after the introduction of the carbon additive compared to its baseline value obtained for the pure resin which constitutes matrix material [5]. However, this example relates to long carbon fibre infill. Confirmation of the expected effect of the addition of long fibers other than carbon is also documented in [6] where natural sizal fibers were analysed. However, these examples relate to long fibre filling – reinforcement or ordered filler structure. Still, at least two problems are

still drawing attention of researches in view of a possible application of carbon nanotubes (CNT), a nanostructure known for its very high thermal conductivity, for thermal transport enhancement within composite structures [7]. The first issue concerns effects of a disordered configuration of relatively short inclusions on the resultant composite structure properties. The second problem considered is the influence of the much smaller characteristic dimension on these properties and difficulties of the sample preparation technology. The effect of the addition of short inclusions, as well as the effect of inclusion shares on selected thermophysical properties is significant. Currently, there are many publications on the impact of nano additives on mechanical properties, strength, or lubricity [8, 9] and heat transfer [10], but papers on thermal conductivity, or interchangeably thermal diffusivity, are less common. If papers on the study of these parameters are published, the published data relate mainly to classical thermal analysis [11] or the reported results are characterized by low temperature resolution [12]. There are also theoretical works in the field of analytical or numerical modeling of the phenomena of heat accumulation and transport in structures with nanoadditives [13]. The need to supplement the literature data, both in order to verify the experimental data and to provide data for theoretical analyses, motivated the research of this study.

In this context, the aim of the study was to check the possibility of shaping selected thermophysical properties of the composite by introducing a nano-dispersion additive in the form of multi-walled carbon nanotubes (manufacturer: 3D-nano). The motivation for selecting the type of inclusion was based on literature reports highlighting significant thermal conductivity values of carbon nanotubes [14]. The matrix of the composite was LH145 resin with H147 hardener (manufacturer: Havel Composites).

The authors investigated to test the possibility of shaping the thermal properties by determining possible changes in thermal diffusivity due to the presence of the nanotube additive. The rationale for choosing this parameter stems from its universal nature expressing the reciprocal relationship between the transport and storage properties of heat [15].

The experimental data set was complemented by the results of specific heat measurement of the selected samples of the investigated series.

## MEASUREMENT METHOD AND PROCEDURES

A modified Ångström method [16] was used to determine the thermal diffusivity. In relation to the original method [17], the solution is sought in the form of a superposition of solutions of a one-dimensional heat conduction problem in a flat infinite plate of thickness $l$. The transformation of the solution of the problem for the regular heating range condition of the III-rd kind [18, 19] leads to two non-linear equations:

$$\psi(x) = \sqrt{\frac{\cosh 2kx + \cos 2kx}{\sinh\ 2kl + \cos 2kl}} \tag{1}$$

$$\varphi(x) = \arg\left[\frac{\cosh kx(1+i)}{\cosh kl(1+i)}\right] \tag{2}$$

describing the reduction in amplitude $\psi$ and the phase shift $\varphi$ of the response signal relative to the forcing signal, respectively, with $x$ representing a linear coordinate along the thickness of the plate. Thermal diffusivity $a$ is included in the parameter $k$:

$$k = \sqrt{\frac{\pi f}{a}} = \sqrt{\frac{\pi}{a\tau_\Omega}} \tag{3}$$

where: $f$ – the oscillation frequency [Hz].

Solving equations (1) and (2) in turn enables the amplitude $a_\psi$ and phase $a_\varphi$ values of thermal diffusivity to be determined, respectively. These values should coincide, provided the model assumptions of the method have been met [18].

The implementation of the method consists of generating and measuring sinusoidal temperature variations in the forcing plane and the thermal response plane, respectively, under the above-mentioned orderly heat transfer (OHT) conditions. For periodic temperature excitation, these are the so-called regular heating regime conditions of the third type [19].

The adopted measurement procedures assumed testing for symmetrical thermal forcing, which is schematically presented in Figure 1. The requirement was to use external double sided symmetrical excitation, of identical temperature oscillations, with measurement of the response in the plane of symmetry. In practice it means that two identical specimens comprising a tested sample must be used.

Complementary studies of specific heat by the three-curve method [20] were carried out using scanning microcalorimetry (DSC) with dedicated

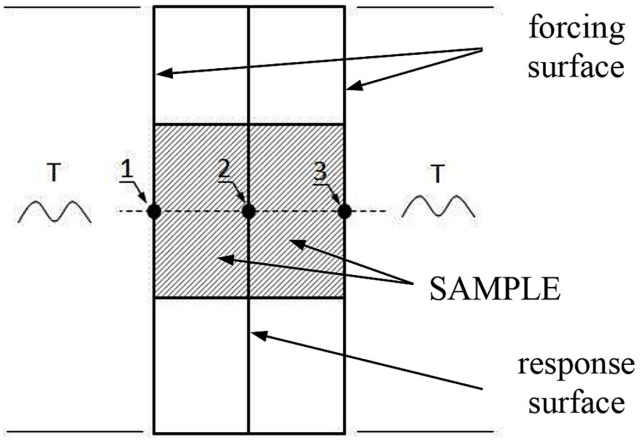


**Fig. 1.** Diagram of bilateral thermal forcing (b), 1,3 – readout points of the forcing signal, 2 – readout points of the response signal

measurement procedures in order to determine the specific heat for both heating and cooling stages of the sample [21, 22].

## EXPERIMENTAL STUDIES

### Research stand

Performing thermal diffusivity tests required the setup of a test stand, whose diagram is presented in Figure 2. The main component of the test rig is the measurement cell, which allows for the installation of the sample under bilateral thermal excitation, the linear and oscillatory thermal excitation of the test sample, as well as the recording of time-varying temperatures at selected points in the sample (Figure 1). Linear temperature variation at a preset heating/cooling rate was provided by thermostat blocks fed with water from a programmable low-temperature thermostat (Lauda RL 6CP). Temperature oscillations were generated by a set of Peltier elements, powered with a DC power supply (Amrel PPS 1322). In order to obtain uniform side surface temperature distribution of the generated thermal excitation copper plate spacers placed between the surface of the thermal excitation and the Peltier element were used.

The data acquisition system consisted of a set of thermocouple cards (NI SCXI 1000) and a set of type K thermocouples (TCs). Two thermocouples recording the outside – temperature

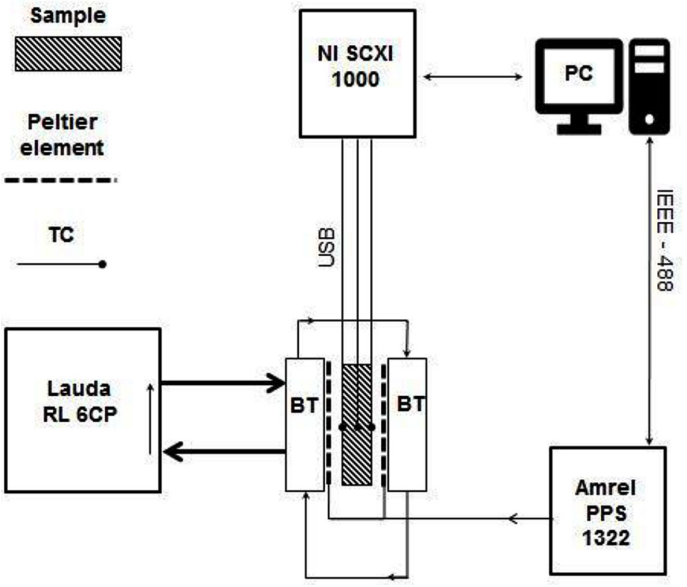


**Fig. 2.** Scheme of the test stand for thermal diffusivity tests using the modified Ångström method. Head in a configuration for bilateral forcing tests, BT - thermostatic blocks

excitation - signal and one thermocouple recording the response signal were used. The position of the measurement junctions was guaranteed at the stage of measuring head assembly. The controller for the whole station was a computer with LabView software installed. LabView software was used to record temperature signals and in part also for data processing.

### Samples

The authors tested five samples created from LH145 epoxy resin with H147 hardener. Four samples contained nano-dispersion reinforcement in the form of multi-walled carbon nanotubes. They were mixed with the resin and evenly distributed by ultrasonic spreading. The series of samples prepared for testing included 0%, 1%, 2%, 4% and 5% nano-dispersion volume filling, respectively. It was not possible to make samples with a higher filling volume proportion due to the technological difficulties of the used ultrasonic mixing method, caused by the low bulk density of the nanotubes at 0.06 g/cm$^3$ (manufacturer's data: 3D-nano). The adopted test procedures involved the preparation of 5 pairs of disc samples for bilateral forcing tests, each 35 mm in diameter and 3 mm thick. The sample preparation consisted of casting the liquid into a silicon mould and leaving it to solidify. The prepared samples for bilateral testing were placed in 2 square-shaped frame spacers, each with a side length of 55 mm and a thickness of 3 mm, allowing the sample to be mounted in the measuring head. The prepared test samples are presented in Figure 3.

The samples for complementary microcalorimetric testing were obtained from the overflow of samples used for thermal diffusivity testing or from witness samples. In the preparatory stage, the samples were cut each time to ensure a mass of 20 mg and a shape that allowed the sample to be encapsulated in the aluminium vessel. A view of an exemplary sample, in this case with 4 per cent volume of the nanotube content, is presented in Figure 4.

## RESEARCH FINDINGS

As a result of the conducted thermal diffusivity measurements, a set of measurement data was obtained for each sample of the tested series. The tests were performed in measurement cycles, in which a single cycle comprises one heating segment and one cooling segment. Obtaining the test result, in the form of a temperature characteristics of thermal diffusivity, required the processing of the obtained experimental data. Due to the change in the base dimension - thickness - of the tested samples in the bilateral forcing regime after the

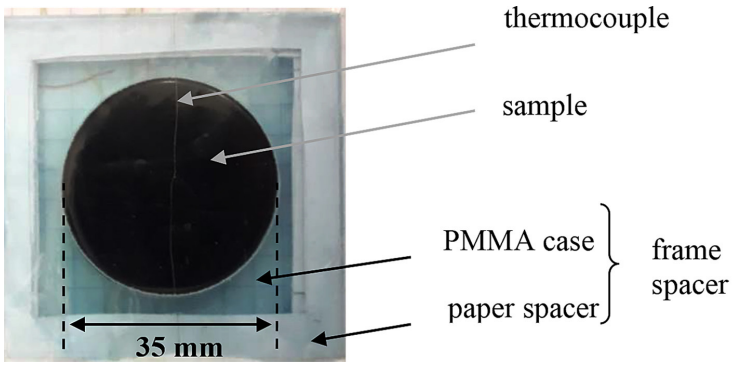


**Fig. 3.** Test specimen in bilateral forcing configuration

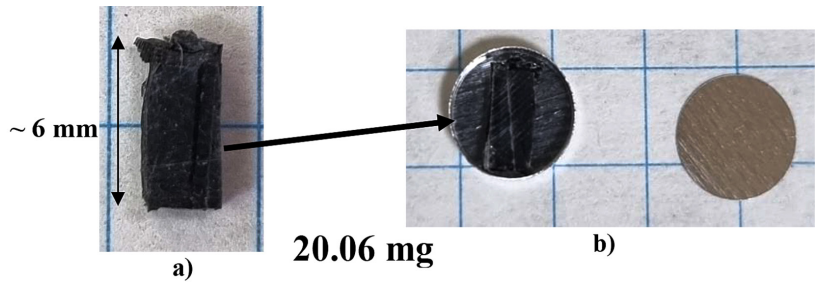


**Fig. 4.** DSC test sample in the initial state (a) and place to the sample pan (b; sample pan lid on the right)

softening temperature had been exceeded, a dilatation correction had to be introduced in addition to the standard methodology for developing the experimental data. Figure 5 presents the results of the first measurement cycle obtained for the resin sample without dispersion filling with an apparent change in the value of the tested parameter (Fig. 5a), and the results after dilatation correction (Fig. 5b).

A comparison of the test results obtained from the first and second measurement cycles of the resin sample without carbon nanotubes (Fig. 6) shows a stabilisation of the thermal properties after the first measurement cycle. This is indicated by the overlap of the calculated diffusivity values of the two compared characteristics in the common temperature range of measurement from 20 ºC to 80 ºC. In addition, the results of the second measurement cycle (carried out between 20 ºC and 100 ºC) reveal a characteristic decrease in the thermal diffusivity value once the temperature exceeds approximately 80 ºC. The overlapping effects of residual polymerisation and resin glass transition are most likely responsible for the observed effect of decreasing diffusivity values.

Qualitatively, similar effects were observed in the results obtained for the other samples investigated in the bilateral forcing regime. A comparison of all thermal diffusivity test results is presented in Figure 7. The comparative analysis revealed that there was no significant effect of the nano-dispersion additive in the form of carbon nanotubes at an inclusion rate not exceeding 5 per cent of the volume. The maximum observed relative difference in the geometric mean thermal diffusivity value (calculated according to a standard procedure as the square root of the product of the amplitude and phase diffusivity values) for a temperature of 25 ºC, occurring for samples with 4% and 5% nanotube additives, does not exceed 6% (Figure 8). The dominant error factor in the described thermal diffusivity measurements is the uncertainty in determining the characteristic dimension. In this case, this dimension is the thickness of the sample, and more precisely, the distance between the measuring thermocouples. For the 0.1 mm in diameter thermocouple wires of and 0.02 mm uncertainty of measuring the thickness of samples, the uncertainty of determining the characteristic dimension does not exceed 5% of relative values. This value is shown in Figure 8. The dispersion of measurement data, which is a feature of research with high temperature resolution, can be characterized by the standard deviation for the determined approximation characteristics. The values of the standard deviation

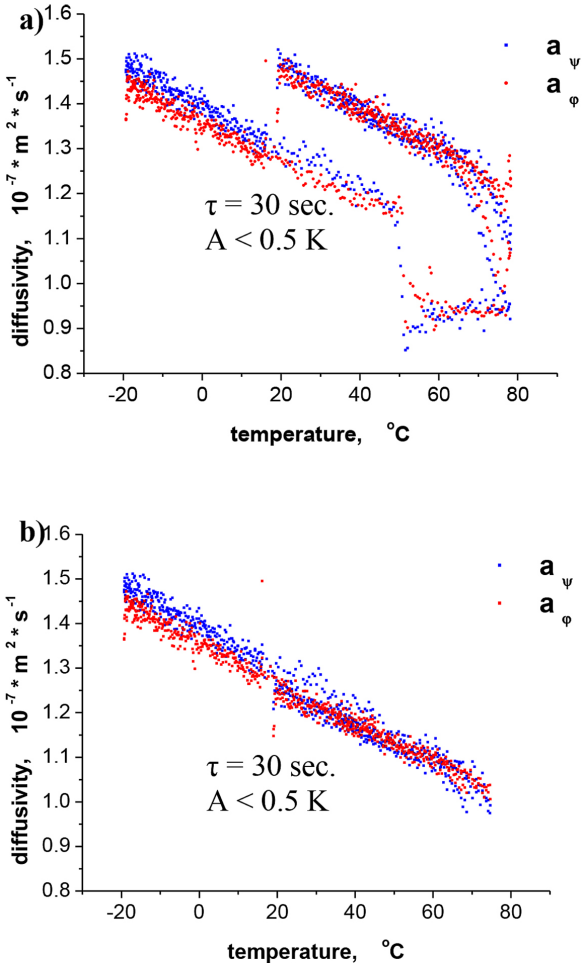


**Fig. 5.** Results of thermal diffusivity tests from the first measurement cycle for a resin sample with 0% nano-dispersion filling before (a), and after (b) dilatation correction

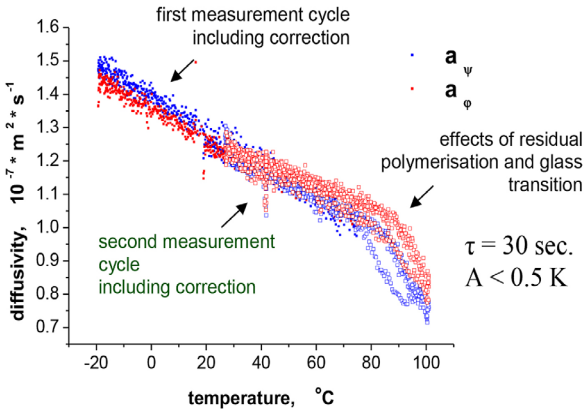


**Fig. 6.** Comparison of the results of the first and second thermal diffusivity tests for a resin sample with 0% nano-dispersion filling

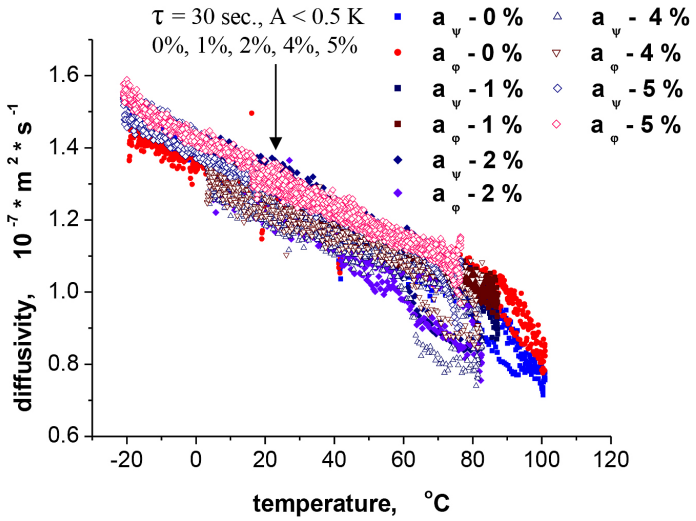


**Fig. 7.** Comparison of thermal diffusivity test results for the entire range of samples from 0% to 5% nano-dispersion addition

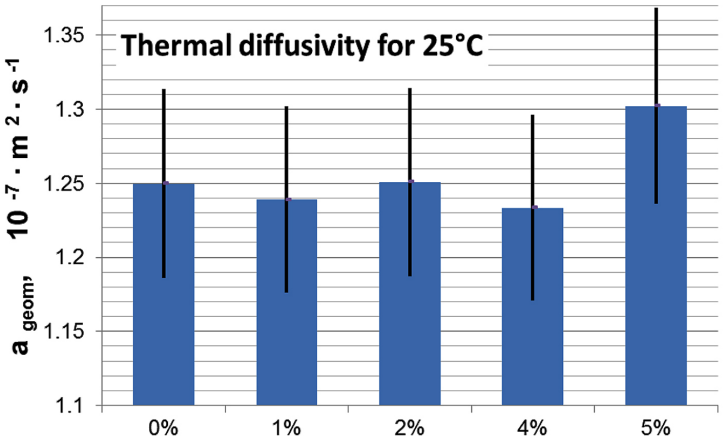


**Fig. 8.** Comparison of the geometric mean value of the thermal diffusivity at 25 ºC of the entire range of 0% to 5% nano-dispersion additives

(STD) of the linear regression of all measurement data – for the entire temperature range of the tests – are presented in Table 1. Numeric data has also been converted to relative values (relative deviation - RD). To complete the data, the Table 1 also presents the value of the directional coefficient (slope) *b* of the straight line, describing the relationship:

$$a(T) = a_{geom} + b \cdot T \qquad (4)$$

On this basis, it is possible to reconstruct the approximation characteristics of thermal diffusivity to the onset temperature of phase transition.

Supplementary DSC measurements were each time carried out in two heating and cooling cycles for all samples of the tested series. As a result of the performed tests, a set of temperature-specific heat characteristics was obtained in the range from -25 to 130 °C.

Figure 9 presents the results of testing the specific heat of the LH145H147 resin in the delivery condition. The course of the specific heat values resulting from the development of the first heating results for the composite in the delivery state revealed the existence of a heat effect related to the post-curing of the material of the examined material. It justifies a lack of similar effects in the development results of the subsequent cooling and heating segments. This effect with varying intensity, yet for a similar temperature range, was also observed for the other samples of the tested series.

Representative specific heat characteristics of the heat-stabilised state, obtained in the examination of the resin sample and the sample with 5% volume of nano-additives, have been presented in Figure 10. In each case, the results revealed the occurrence of a sigmoidal change

**Table 1.** The values of the standard deviation

| Sample | $a_{geom}$ | STD | RD | $b$ |
|---|---|---|---|---|
| | $[10^{-7}\cdot m^2\cdot s^{-1}]$ | $[10^{-7}\cdot m^2\cdot s^{-1}]$ | % | $[m^2\cdot s^{-1}\cdot K^{-1}]$ |
| 0% | 1.2498 | 0.143 | 11.4 | -0.00481 |
| 1% | 1.2390 | 0.074 | 6.0 | -0.00404 |
| 2% | 1.2508 | 0.140 | 11.2 | -0.00597 |
| 4% | 1.2335 | 0.116 | 9.5 | -0.00466 |
| 5% | 1.3023 | 0.134 | 10.3 | -0.00471 |

in the characteristics curve of the identified parameter in the range from approximately 85 °C to approx. 100 °C. The relative difference in specific heat $\Delta c_p$ (Figure 10) calculated from the specific heat values for the extreme values of the indicated temperature range did not exceed 30%. These features are typical and characteristic of a glass transition with applied residual polymerisation effects. An aggregate analysis of the obtained results did not reveal any significant differences in the qualitative course of the characteristics, including the repeatability of the temperature range of the occurrence of glass transition effects. However, approximately 3–4% relative difference in specific heat values for the extreme samples of the range were observed. Such a difference is within the uncertainty of the used research method.

When discussing the determined values of parameters: thermal diffusivity and specific heat, it should be noted that with a very low effective density of the nanotube bed, their mass share in the tested composite is small. The 5% by volume content of nanotubes, while the volume is referred to the nanotube bed volume, means about 0.2% mass filler content. Concerning the specific heat of a mixture, for which the mass fraction weighted mixture rule is widely used [23], the small contribution of low mass CNTs explains the DSC results. As far as

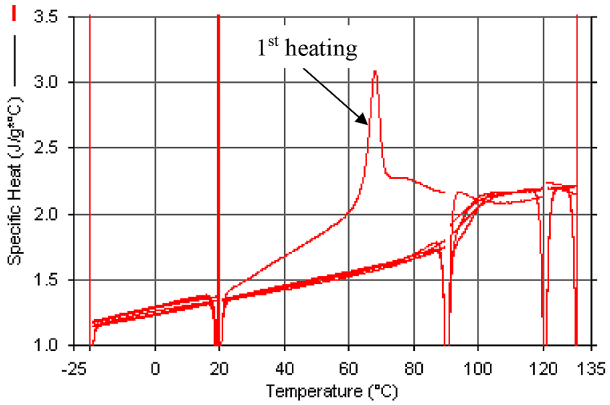


**Fig. 9.** Temperature characteristics of the specific heat of the resin (LH145H147) obtained for 1 and 2 heating/cooling cycles

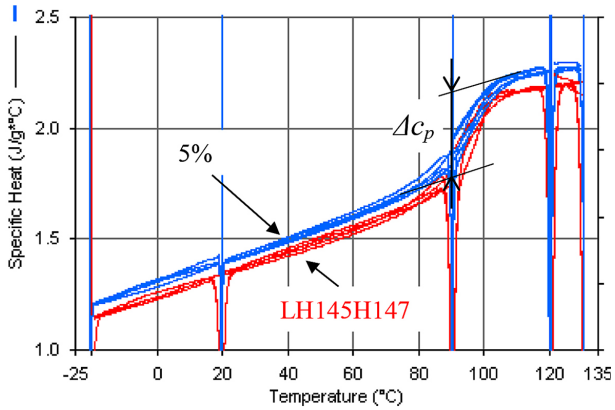


**Fig. 10.** Temperature characteristics of the specific heat of the resin (LH145H147) and the composite structure with 5% volume of nanotubes (5%) obtained for the heat-stabilized state – 1 cooling and 2 heatings and coolings

thermal diffusivity is concerned, a clear influence of the additive on the improvement of heat transfer parameters was expected during the research. In the case of the tests described in [24] the addition of 0.1% wt. of multiwall CNT increased the thermal diffusivity of a high density polypropylene by about 30%. 0.1% wt. share corresponds to about 2.5% vol. content in the present research. So, the lack of the filler influence can only be justified by configurational phenomena. The lack of contact between individual tubes is not conducive to the formation of percolating paths. This phenomenon should continue to be studied.

The thermal diffusivity data processing were concluded with calculation of the thermal conductivity by applying a standard recalculation procedure [23]. The minimum and maximum values of diffusivity (from Table 1), an average density of 1151 kg/m$^3$, from Archimedes law weightings, and a specific heat of 1375 J/kg/K were used for the calculation. As a result, the calculated value of thermal conductivity for 2 5°C is in the range from 0.196 to 0.206 W/m/K.

## CONCLUSIONS

The paper presents the results of thermal diffusivity tests. At the stage of developing the obtained measurement data, the necessity of applying a dilation correction to the test results was demonstrated, in the case of examining the thermal diffusivity test using the temperature oscillation method in the regime of bilateral thermal forcing. The results confirmed the occurrence of a property stabilisation effect in the subsequent cycle with a maximum temperature no greater than that of the first cycle. In addition, the results of the second measurement cycle showed the occurrence of overlapping effects of residual polymerisation and material glass transition. On the basis of the analysis of the results, no significant effect of addition of stochastically disoriented carbon nanotubes, up to a volume share of 5% of the examined structure, was observed in the shaping of the thermal diffusivity values. Conclusions drawn from the diffusivity test results were confirmed by microcalorimetric results.

The result of the work confirmed the effectiveness of the employed measurement procedures, which enabled high-resolution and reliable thermal diffusivity results to be obtained by using the temperature oscillation method to complement the range of thermal analysis methods and techniques. Concerning quantitative aspects of the experimental results the calculated values of the thermal conductivity revealed insulating properties of all the investigated specimens.

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