Study on the Heat Transfer in Carbon Nanotube Composites with Polymer Matrix

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Experimental thermal properties on carbon nanotube with polymer matrix composites are analyzed. Increasing of thermal conductivity with carbon nanotube percentages enhancing is obtained and some phenomenological considerations on the heat transfer mechanisms are presented.

Keywords: carbon nanotubes, thermal conductivity, effusivity

Extensive researches have shown that the carbon nanotube (CNT) can considerably enhance the mechanical and conductive properties of polymer and ceramic matrix during last decade [1, 2].

For more than ten years, carbon nanotubes (CNTs) have been extensively studied by many researchers due to their excellent properties and numerous applications [3,4]. Carbon nanotube composite is one of their many applications. In recent years, CNT composites have attracted even increasing attention of many scientists and researchers [5,6]. CNTs are much stronger, have high conductivity and larger aspect ratio as compared to conventional carbon fibers. Many believe that the reinforcement of CNTs in polymer matrix may provide us an entirely new class of materials.

In view of the preceding, there has been an immense effort to establish the most suitable conditions for the transfer of either mechanical load or electrical charge to individual nanotubes in a polymer composite component. A prerequisite for such an endeavour is the efficient dispersion of individual nanotubes and the establishment of a strong chemical affinity (covalent or non-covalent) with the surrounding polymer matrix. Various methods of CNT chemical modification have been proved quite successful in introducing functional moieties which contribute to better nanotube dispersion, and eventually to efficient thermodynamic wetting of nanotubes with polymer matrices [7]. Another area of intense research is the grafting of macromolecules onto the nanotube surface. Indeed, the addition of a whole polymer chain is expected to have greater influence on the nanotube properties and their affinity to polymer matrices as compared to the addition of low molecular weight functionalities.

The modification of CNTs by polymers is separated into two main categories, based on whether the bonding to the nanotube surface is covalent or not. The covalent modification itself involves either “grafting to” or “grafting from” strategies [8]. So far, the majority of the processing methods lead to materials that contain low volume fractions of CNTs that, at least in absolute mechanical property values, cannot seriously compete with commercial polymer composites. For electrical applications, on the other hand, the percolation threshold is so low that large quantities of CNTs are not required and cost-effective composites can be fabricated [6, 9]. In terms of tensile modulus, it has been established by numerous studies [10] that chemically modified nanotubes exhibit a significant increase in modulus as compared to the matrix resin .

Obviously, it is impossible to make a comprehensive overview of all aspects of this large subject in the framework of one article. Therefore, to keep our task manageable, we confine ourselves to discussing the most characteristic and important recent examples, where the homogeneous dispersion of CNTs within polymer matrices plays a crucial role in the fabrication of multifunctional composites. More detailed information is available in topical reviews devoted to particular issues.

In the present paper some thermal properties of carbon nanotube composites with polymer matrix were analyzed with purpose to explain the increasing of thermal conductivity in such structures. Some phenomenological aspects to explain the increasing of thermal conductivity in carbon nanotube composites with polymer matrix are presented.

Experimental part

Preparation method

The samples were prepared in Nanostructured Department of the Ovidius University of Constanta. In such context the rubber samples were worked on BRESTORFF type rolling equipment with the first cylinder rate of 35 rot/min that the second cylinder of 45 rot/min. The distance between those two cylinders was initially 3.5 mm and after reach 5 mm and the cylinders are rolling in opposed directions. The work temperature is around 70^0C ± 4^0C having as components natural rubber, TBBS accelerator, carbon nanotubes and as vulcanization element was used the colloidal sulfur.

The natural rubber has the chemical composition formed by 1.4 polyisoprene concomitant with natural substance nr. CAS: 9006-04-6, Nr. EINECS: 232-689-0 with no dangerous components solid aspect and solid state at 25°C, white color and crystallization under 15°C other properties like density is 930 [kg/mł] at 25°C:, and volume density at 25°C not applicable, insoluble in water but soluble in aliphatic and aromatic hydrocarbons.

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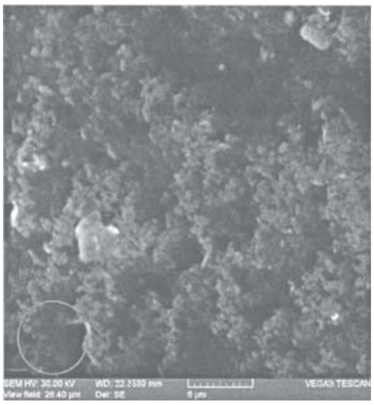

Fig. 1 Scanning electrons microscopy of a polymer matrix composite with 30 % reinforcement carbon nanotubes

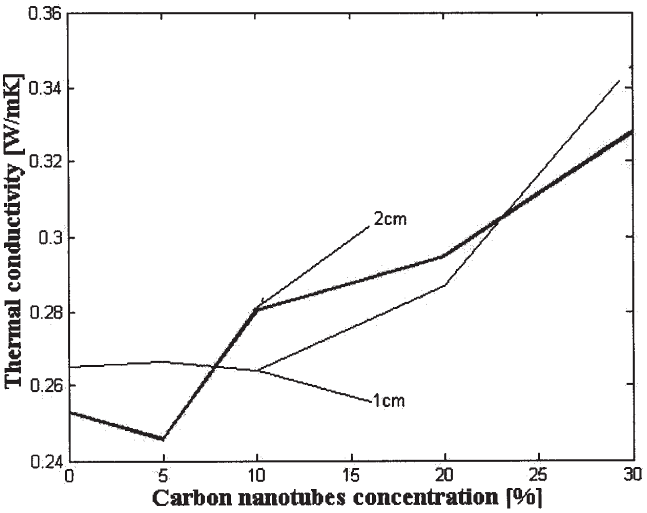

Fig. 2 Thermal conductivity of composite samples with 10 and 20 mm thickness

Table 1
EXPERIMENTAL CONDITIONS AND COEFFICIENTS AT THERMAL CONDUCTIVITY CALCULUS

Sample	1/m	R2	V_0 [mV]	VMax [mV]	ΔV [mV]	T_0 [°C]	ρ [g/cm^3]
MR10mm	90.35481	0.998232	2369.29	2375.676	6.386518	23.59106	0.93
MR5NT10mm	90.57162	0.998231	2369.793	2376.173	6.380939	23.62683	0.95
MR10NT10mm	90.86499	0.998225	2368.242	2374.592	6.349254	24.18131	1
MR20NT10mm	92.68908	0.998473	2369.075	2375.383	6.307888	24.34685	1.1
MR30NT10mm	97.13363	0.998479	2369.257	2375.281	6.024528	24.36233	1.2
MR20mm	89.67938	0.998292	**2368.915**	**2375.374**	**6.459236**	**23.63229**	0.93
MR5NT20mm	89.44073	0.998321	2371.739	2378.228	6.488919	24.6961	0.95
MR10NT20mm	92.15356	0.99829	2371.605	2377.896	6.290603	24.63972	1
MR20NT20mm	93.21179	0.998468	2370.534	2376.798	6.263065	24.3732	1.1
MR30NT20mm	95.70372	0.998474	2370.419	2376.527	6.108022	24.30349	1.2

Used as accelerator material TBBS, N-tert-Butyl-2-benzothiazolesulfenamide, is considered a substance in conformity with EC directives with EC number: 202-409-1 and risk identity R43 R53 with formula C11H14N2S2.

Regarding its physical and chemical properties the aspect is of powder with cream with a reduce amine smell and melting point 109°C. Inflammation point is approximate at 165 °C and the self ignition temperature is about 340 – 380°C, density almost 1290 kg/mł (20°C), water solubility 0.00032 kg/mł (25°C) and partition coefficient n-octanol/water: 4.38.

The carbon nanotubes are type ENF 100 AA- GFE used for reinforcement, graphitized fibers at 3000°C having an 80-150 nm diameter and length >20μm. The thermal conductivity is: >600 W/mK and electrical resistivity smaller than 10^{-3} Ohm/cm, metal contain <0.01% and graphite density 2.17.

As work was done a set of samples with carbon nanotubes in 5, 10, 20 and 30% percentages at 100 g natural rubber. For start were made a set of witness samples by "killing" the natural rubber on rolling equipment at 70 ^{0}C temperature for 3 min with successive cuts during the carbon nanotubes were insert. After 7-10 min of continues milling (function of nanotubes percentages) the rubber became elastic. The TBBS accelerator came in 1.65 g standard value for each sample and with four more minutes of milling. Using 0.8 g colloidal sulfa as vulcanization element also standard value for each sample can be done successive cuts.

The production observations present that carbon nanotubes incorporate twice time faster than other material (like black carbon) and the composite with rubber matrix has a glassy and homogeneous aspect.

After the samples are finished and retained for 24 h they are put on heating press at 150 – 160 atmospheres and kept between 30 and 40 min at 145^{0}C.

Results and discussion

The materials were analyzed using a Scanning Electrons Microscope (SEM) type VegaTescan LMHII for micro-structure investigations and a TCi equipment for thermal conductivity results.

Composite samples with rubber as matrix and carbon nanotubes as reinforcement elements, with 5, 10, 20 or 30 percentages were analyzed.

A 30 % nanotubes composite with natural rubber matrix sample analyzed by microstructure point of view using SEM equipment with the result present in figure 1, reveal the round shape of nanotubes and their dimensions are about of 10 nm diameters and between 700 and 800 nm lengths.

The image from figure 1 was realized at a 20000x magnification power with a secondary electrons detector on a fractured sample marking the area that represents a carbon nanotubes conglomeration. Thermal conductivity experiments were carried out on samples with 10 or 20 mm thickness at free or different carbon nanotubes percentages in rubber matrix. The equipment sensor type was TC92 fully calibrate and the test periods were of 30 s each from 10 measurements made per sample, the average results of the experiment are presented in table 1 and the properties in table 2.

Analyzing the main results, thermal conductivity, of the composite materials for both 10 and 20 mm thickness

Table 2
RESULTS OBTAINED ON THERMAL CONDUCTIVITY TESTS ON SAMPLE OF
1 AND 2 CENTIMETERS THICKNESS AND DIFFERENT CARBON NANOTUBE REINFORCEMENT
ELEMENTS PERCENTAGES (FREE OF NANOTUBES, 5, 10, 20 or 30 %)

Material	Thermal conductivity [k (W/mK)]	Effusivity e [(Ws$^{1/2}$/m^{2}K)]	Diffusivity [(m^2/s)]	Heat Capacity Cp [(J/kg/K)]	Depth Penetration [(m)]	R-Value [(m^{2}K)/W]
MR10mm	0.264975	596.1429	1.9753E-07	1442275	0.004869	0.037756
MR5NT10mm	0.266475	596.5329	2E-07	1405827	0.004893	0.037538
MR10NT10mm	0.264017	594.9078	1.97E-07	1340631	0.004861	0.075792
MR20NT1cm	0.286949	624.1555	2.11E-07	1234232	0.005036	0.034853
MR30NT1cm	0.345724	696.6513	2.46E-07	1170106	0.005434	0.02897
MR20mm	0.252992	580.6785	1.898E-07	1433138	0.004773	0.079059
MR5NT2cm	0.245634	571.0771	1.85E-07	1397823	0.004711	0.081496
MR10NT2cm	0.280215	615.6142	2.07E-07	1454371	0.004986	0.071404
MR20NT2cm	0.294701	633.918	2.16E-07	1239657	0.005092	0.067874
MR30NT2cm	0.32785	675.005	2.36E-07	1158155	0.00532	0.061012

samples and different nanotube percentages, as is graphically represented in figure 2, it is observed a good improvement of thermal conductivity, with 30.56% bigger in composite case with 30% reinforcement nanotube elements, by inserting new elements in rubber matrix.

The density values, represented in table 1, are obtained by experimental investigations on weight and mathematical calculus for each sample presented reduces differences based on nanotube percentages.

Comparing the behaviour of thermal conductivity of composites elements based on their thickness we observed a similar conduit of curves with a little higher values for thinner samples (10 mm) excepting the one with 10 % carbon nanotubes that, based on homogeneity or obtaining process parameters suffer a decrease even comparing with the base free carbon sample MR1, with a smaller value fact observed at sample with 20 mm thickness but for 5% of carbon nanotubes. Both sample types increase as thermal conductivity property for more than 10% of carbon nanotubes reinforcement elements.

Making abstract of small percentages on samples with reduced carbon nano-tubes(5-10%) the thermal conductivity increases at the same time with increasing of carbon nano-tubes. The same behaviour can be observed for effusivity, diffusivity and depth penetration, these results are according with experimental data from [1,5]. Contrariwise the heat capacity and resistivity decrease with increasing of carbon nanotubes percent excepting the materials with (5-10%) percentages.

Conclusions

Increasing the nanotubes percentage in a rubber matrix of a polymer composite will improve the thermal conductivity with at least with 40%. If thermal conductivity, effusivity, diffusivity and depth penetration increase the heat capacity and resistivity decrease at the same time with increase of CNTs percentages, excepting the (5-10%) percentages.

In our opinion the increase of thermal conductivity in carbon nanotube with polymer matrix with the increasing of CNT percentages can be explained based on a new type of conductivity mechanism where collective processes made by self-organizing plays an essential role. In this way ”individual” thermal type conductivity is substituted by self-organizing thermal type conductivity [12-15].

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