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Preparation and characterization of *in situ* polymerized cyclic butylene terephthalate/graphene nanocomposites

Gábor Balogh[1], Sándor Hajba[1], József Karger-Kocsis[1,2] and Tibor Czigány[1,2*]

1 – Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3., H-1111

2 – MTA–BME Research Group for Composite Science and Technology, Muegyetem rkp. 3., H-1111 Budapest, Hungary

Corresponding author: Tibor Czigány

Department of Polymer Engineering, Budapest University of Technology and Economics, Műegyetemrkp.3 T/305, H-1111 Budapest, Hungary

Phone: +36-1-463-2003

Fax: +36-1-463-1527

Email: czigany@eik.bme.hu

url: www.pt.bme.hu

Abstract

Graphene reinforced cyclic butylene terephthalate (CBT) matrix nanocomposites were prepared and characterized by mechanical and thermal methods. These nanocomposites containing different amounts of graphene (up to 5 wt%) were prepared by melt mixing with CBT that was polymerized in situ during a subsequent hot pressing. The nanocomposites and the neat polymerized CBT (pCBT) as reference material were subjected to differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), thermogravimetrical analysis (TGA) and heat conductivity measurements. The dispersion of the grapheme nanoplatelets was characterized by transmission electron microscopy (TEM). It was established that the partly exfoliated graphene worked as nucleating agent for crystallization, acted as very efficient reinforcing agent (the storage modulus at room temperature was increased by 39 and 89% by incorporating 1 and 5 wt.% graphene, respectively). Graphene incorporation markedly enhanced the heat conductivity but did not influence the TGA behaviour due to the not proper exfoliation except the ash content.

Keywords: graphene; cyclic butylene terephthalate (CBT); nanocomposite;, dynamic-mechanical analysis (DMA); crystallization; heat conductivity

Introduction

Nowadays a new generation of low melt viscosity, reactively polymerizing thermoplastics became available on the market. These materials polymerize through ring opening polymerization (ROP) and are typically polyesters and polyamides. One of them is the cyclic butylene terephthalate (CBT) which exhibits very low (10^{-2} Pas) melt viscosity [1,2]. This is one of the properties which makes CBT a promising matrix material for composites. This aspect has already addressed by researchers (e.g. [3]). Another interesting property is the *in situ* ROP, which means that CBT oligomers polymerize inside the mould directly within the timeframe of processing. ROP offers also a unique possibility to produce nanocomposites which is now in the spotlight of research.

Graphene is a recently explored form of carbon and is a one-atom-thin layer of carbon atoms [4]. It is described as a carbon monolayer with outstanding mechanical and electrical properties [5]. Graphene may also be considered as a building material of all other carbon structures [6]. It may be used as reinforcement for nanocomposites [7] as well as additive to modify given properties (e.g. for increasing the heat conductivity [8,9]).

CBT is a special reactive oligomer which polymerizes into pCBT (which is chemically identical to polybutylene terephthalate, PBT) both below and above the melting temperature of the resulting pCBT. CBT is manufactured by Cyclics Corp. (Schenectady, NY, USA). The cyclic oligomers contain 2-7 monomer units which are opened by heat and polymerize in presence of suitable catalysts. CBT grades are available with and without polymerization catalysts. The polymerization is entropically driven, no by-product is made and CBT has water-like melt viscosity prior this ROP process [10,11].

The above possibility was already used by several researchers and nanocomposites were prepared and investigated via several methods:

Lanciano *et al.* [12] prepared nanocomposites of CBT and montmorillonite (MMT) and followed the polymerization by DSC and studied the crystalline structure by wide angle X-ray scattering (WAXS). It was found that CBT polymerizes and crystallizes below its equilibrium melting point, but if CBT and MMT were premixed, polymerization takes place above the melting point and the material crystallizes during the cooling stage. Further results showed that if CBT polymerizes and crystallizes below its melting point then the resulting crystals have higher lamellar thickness values than those samples which were polymerized above the melting range.

Berti *et al.* [13] polymerized CBT at 205°C and used MMT to prepare nanocomposites. Results were promising since the low viscosity of molten CBT ensures good nanoclay dispersion. Beside this, the nanocomposites showed better thermomechanical properties and higher molecular weights than those without MMT.

Clay-nanocomposites were also prepared with pCBT matrix by Tripathy *et al.* [14]. They used Cloisite 20A montmorillonite (MMT) and CBT. According to their WAXS studies most of the MMT was exfoliated but some agglomerates were still present in the pCBT which was also supported by transmission electron microscopy (TEM). Thermogravimetrical analysis in nitrogen atmosphere showed an increased thermal stability.

Multiwall carbon nanotubes (MWCNT) were incorporated in pCBT making use of high energy ball milling of CBT powder and MWCNT prior to the polymerization of the former. This technique resulted in excellent dispersion of MWCNT however at cost of its aspect ratio. The authors concluded an optimum amount of MWCNT (ca. 0.3 wt%) with respect to the mechanical performance [15].

Hybrid composites with MWCNT and unidirectional E-glass fabric were produced by Baets [16]. He adapted a vacuum-assisted resin transfer moulding (VARTM) process and the amount of MWCNT was varied between 0 – 0.1 wt%. During production a faster polymerization reaction was experienced so a lower catalyst amount (0.2 wt%) than the conventional one (0.45 wt% corresponds to 3 mol‰) was used. The lower catalyst amount did not affect final conversion but led to a slightly tougher material. Mixing was ‘rotational mixing’ of the molten CBT for 5 minutes which resulted in a good dispersion according to TEM pictures. For unreinforced samples, 0.05 wt% of CNTs caused an increase in stiffness and strength, but their presence decrease failure strain and had no effect on crystallinity. In case of the hybrid systems, the glass fibres acted as filters and thus the MWCNT dispersion was not satisfactory.

The above survey indicates that nanoparticle reinforced pCBT matrix-based composites have been already studied, however, graphene as a reinforcing agent was not yet incoporated this matrix system. So the aim of our work is to produce and characterize graphene-pCBT nanocomposites and discuss the effects of this additive on the morphological, thermal, dynamic mechanical and heat conductivity properties.

Materials and methods

As matrix material CBT160 powder (Lot# 000071-25S-01) supplied by Cyclics Europe GmbH (Schwarzheide, Germany) was used. CBT160 contains 0.3 mol% Fascat 4101 (butylchlorotin dihydroxide) [16] by Arkema Inc. (PA, USA) [18] as catalyst. Before usage the CBT160 powder was dried in an oven at 80°C for 8 h in order to remove residual moisture [1].

Grade H graphene from XG Sciences Inc. (Lansing, Miami, USA) containing OH groups [19] was used with an approximate layer thickness of 15 nm, specific surface area of 50-80 m^2/g and an electrical conductivity of 10^7 Siemens/m. The graphene nanoplatelets were used as received.

Sample preparation

Graphene and CBT were melt mixed in a PlastiCorder PL 2000 type mixer (Brabender, Duisburg, Germany) at 200°C, 180 revolution/min for 2 minutes. Then this mix was fine-grinded in a mortar. The powder obtained via this method was used for sample processing and was also dried (80°C, 8h) prior to hot pressing.

Samples were produced via hot pressing in a Collin P200E type (Ebersberg, Germany) hot press at 240°C. Polymerization time was 10 min at 2 MPa pressure and 1 mm thick sheets were obtained by this method.

Testing methods

Differential scanning calorimetry (DSC) tests were performed using a Mettler Toledo DSC821 (Greifensee, Switzerland) device. For the DSC tests 6-8 mg samples were used and subjected to a heating-cooling-heating cycle between 20-270°C. The crystallization enthalpy ($\Delta H_{c,sample}$) was determined from the area under the melting peak of the second heating cycle. The degree of crystallinity (χ_c) was calculated by assuming 142 J/g for the heat of fusion of the 100% crystalline PBT.

Dynamical mechanical analysis (DMA) was performed on a TA Instruments Q800 device (New Castle, Delaware, USA). The applied temperature range was 0 to 150°C with a heating range of 2°C/min. Tensile arrangement was applied due to sample thickness (~1 mm) with a fixed strain of 5 μm at a frequency of 10 Hz.

Thermogravimetrical analysis (TGA) was performed on a Shimadzu DTG60 device (Kyoto, Japan) in a temperature range of room temperature to 600°C in order to examine the decomposition in oxygen atmosphere. For these measurements aluminum pans were used with an approximate sample weight of 20 mg.

Thermal conductivity was studied via guarded heat plate method: A sheet specimen was introduced between two known-temperature reference sheets. Thermal power was calculated on the basis of the input electrical heating power at the higher temperature side. Based on this the coefficient of thermal conductivity was determined.

Dispersion of the graphene nanoplatelets in the pCBT matrix was studied by TEM. The TEM device (Zeiss LEO 912 Omega, Oberkochen, Germany) was working at an acceleration voltage of 120 kV. Thin specimens (50 nm) were prepared by an ultramicrotome (Leica EM UC6, Wetzlar, Germany) cut with a diamond knife (Diatome, Biel, Switzerland), and were subjected to TEM investigations without any staining.

Results and discussion

Differential Scanning Calorimetry

Calorimetrical analyses were performed in order to study the nucleating effect of graphene and other effects on crystallization properties. Results obtained from graphene modified pCBT are listed in Table 1. Data in Table 1 clearly confirm the nucleating effect of grapheme through the increase of the crystallization peak temperature with increasing graphene content. Accordingly, during cooling the graphene nanoplatelets serve as nucleation points from where crystallization can start. Due to the hydroxyl groups on the nanoplatelets [18] chemical and hydrogen bonds may also be formed between graphene and pCBT.

The more graphene is in the system the earlier the crystallization starts. At 3 and 5 wt% graphene content the crystallization starts already above 210°C.

In case of melting an interesting phenomenon was found. Unmodified pCBT has double melting characteristic based on the appearance of peak doubling in the related melting traces (206 and 220°C, respectively, in Figure 1). Explanation for this is simultaneous melting and recrystallization. This phenomenon is discussed extensively in [20]. What is surprising after adding different amounts of graphene is that the lower temperature peak starts growing before its declination at high grapheme content (Figure 1). This occurs due to the nucleating effect of graphene – the more graphene is in the system, the more perfect crystalline structure is formed. So recrystallization requires more energy so it starts at higher temperatures.

Graphene content	Melting		Crystallization
[wt%]	Peak 1 [°C]	Peak 2 [°C]	Peak [°C]
0	209.3	223.9	198.9
0,25	216.9	224.2	198.2
0,5	217.4	224.4	201.1
0,75	217.5	224.4	201.7
1	217.3	224.3	200.5
3	216.9	223.7	212.1
5	216.0	222.9	202.7

Table 1 Melting and crystallization peak temperatures of graphene modified pCBT samples

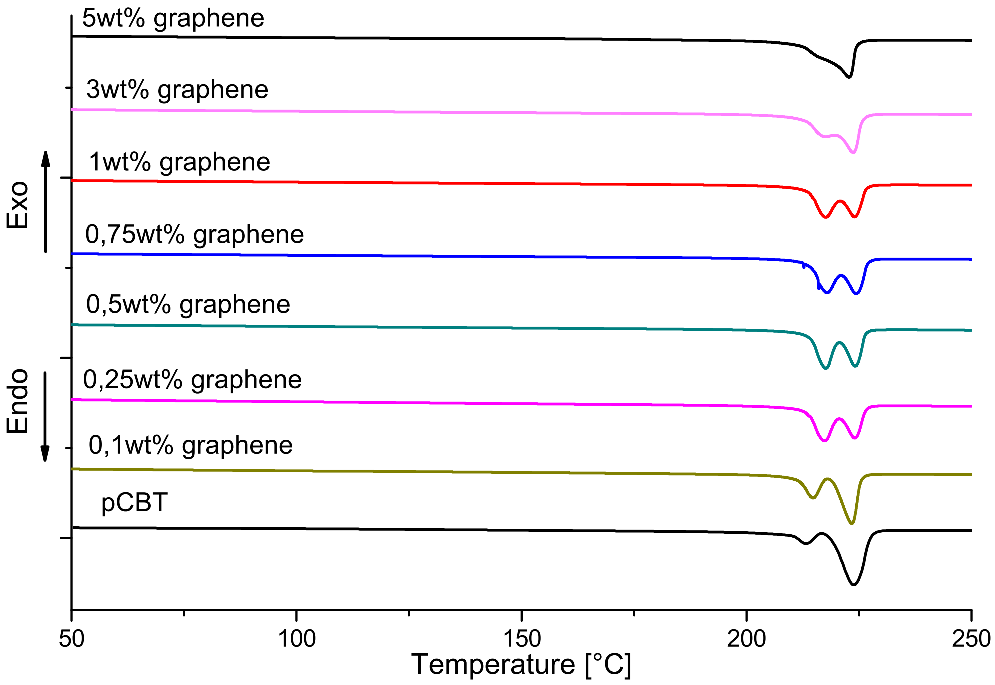


Figure 1 Melting DSC scans of graphene containing pCBT samples

Based on the melting and crystallization enthalpies, the corresponding crystalline fractions were determined. Results are depicted in Figure 2. One can note that the melting-based crystallinity values are somewhat higher than the cooling-based ones. This can be ascribed to the remelting/recrystallization phenomena occurring during heating. Note that the crystallinity goes through a maximum as a function of the graphene content. This may suggest a strong adhesion of the pCBT molecules on the abundantly present graphene sheets strongly reduces their mobility which is essential for the crystallization. Through this “immobilization” effect the crystalline fraction is reduced at high graphene contents.

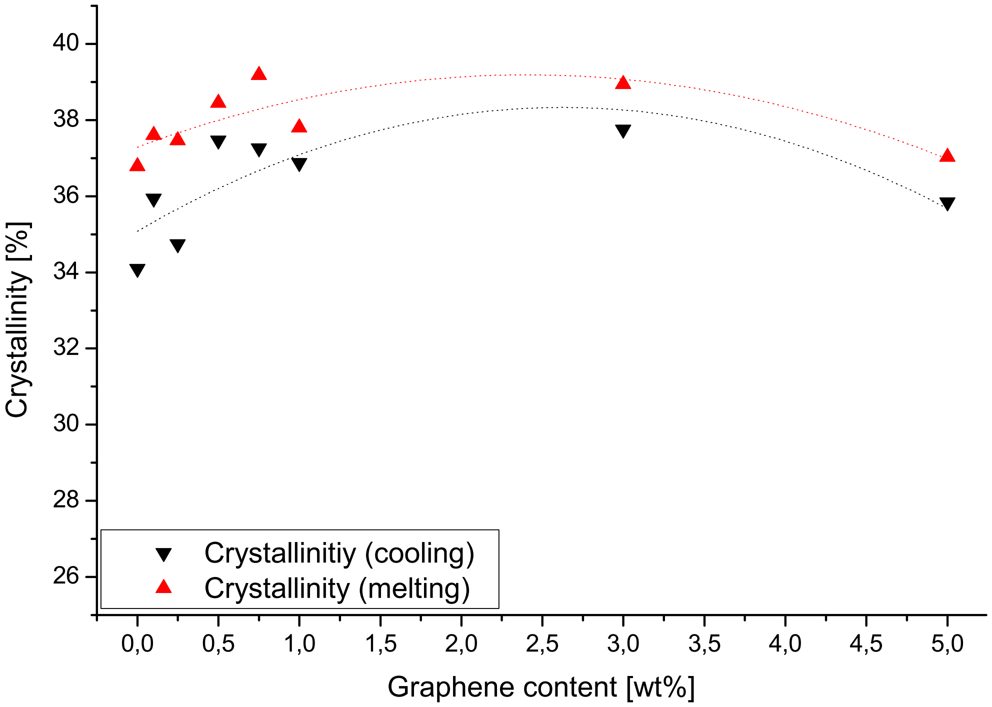


Figure 2 Crystallinity in function of graphene content

Dynamical Mechanical Analysis

DMA was utilized to examine the effect of graphene content on the glass transition temperature and storage modulus of the nanocomposites. According to Figure 3 there is some change in the peak temperature of the tangent delta vs. temperature curves. Though the glass transition temperature (T_g) is in the range of 60±5°C the appearance of the related traces may suggest the formation of a more and a less mobile amorphous fractions. To clarify this issue further investigations are, however, needed.

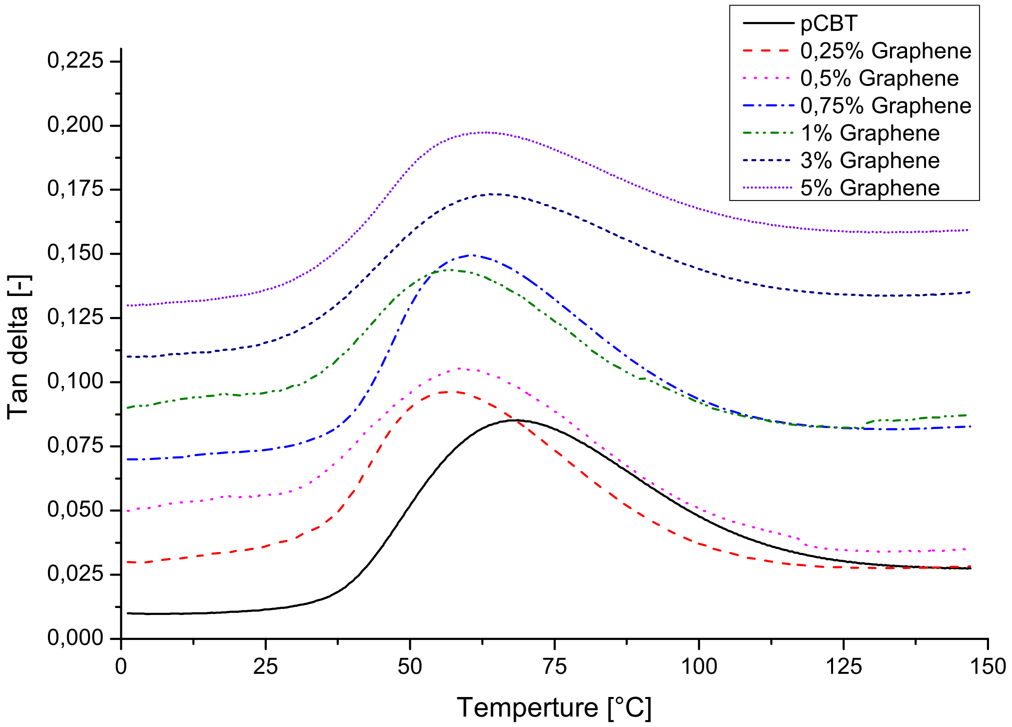


Figure 3 Tangent delta vs. temperature curves of pCBT samples containing different graphene amount (curves shifted along the y axis for better visibility

According to the storage modulus vs. temperature traces of the nanocomposites at different graphene contents (Figure 4) a significant reinforcing effect can be resolved. Graphene incorporation prominently increased the storage modulus. Around the T_g range a pronounced decrease is seen, but above even above T_g the graphene nanoplatelets still work as very efficient reinforcements, especially in case of 5 wt% graphene. Interestingly the nanocomposite with 0.75 wt% graphene has much storage modulus in the entire temperature range than all other composites up to 3 wt% graphene. This finding should be linked with the dispersion stage of the graphene that is most probably optimal for the nanocomposites with 0.75 wt% graphene.

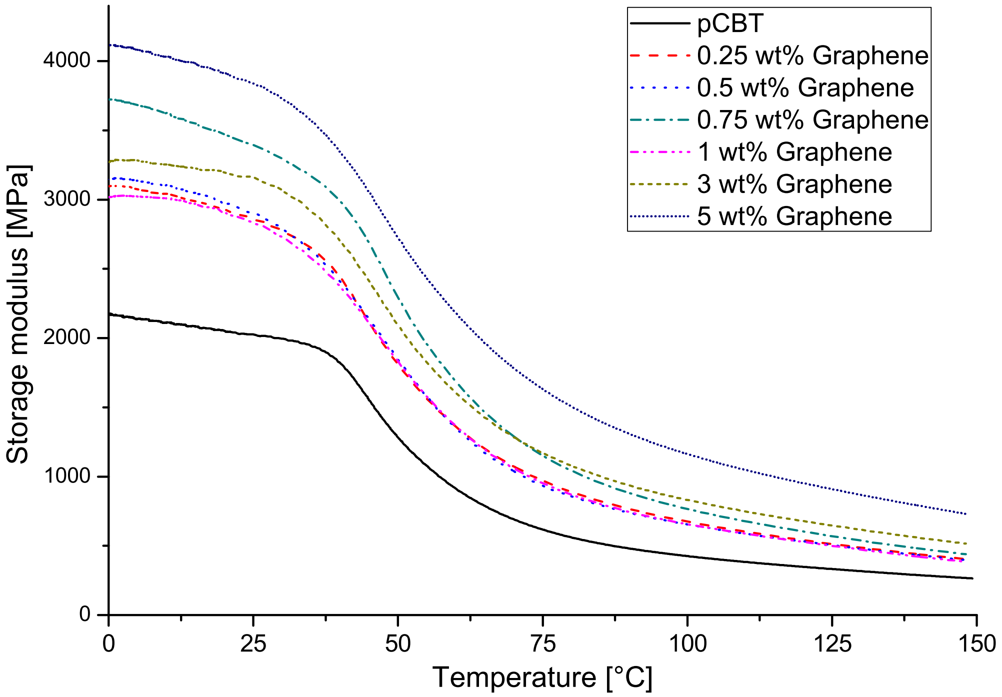


Figure 4 Storage modulus vs. temperature curves of pCBT and pCBT nanocomposites containing different amounts of graphene

Thermogravimetrical Analysis

Weight vs. temperature curves of graphene-modified pCBT (Figure 5) allows us to study the thermal decomposing properties of the nanocomposites produced. Temperatures indicating the 5 wt% loss, maximum weight loss and residual char are depicted in Figure 6. The char yield tends to increase with increasing amount of graphene. By contrast, the thermal stability of the nanocomposites based on the temperatures at 5wt% loss maximum rate of weight loss (read as the temperature of the corresponding derivate curves) did not alter significantly with increasing graphene content. This finding is at odds with the literature, where increased thermal stability was reported for polyesters filled with graphene owing to the enhanced barrier properties [21,9]. On the other hand, a moderate increase in thermal stability was reported for PBT-CNT nanocomposites [22,23], which is close to our results.

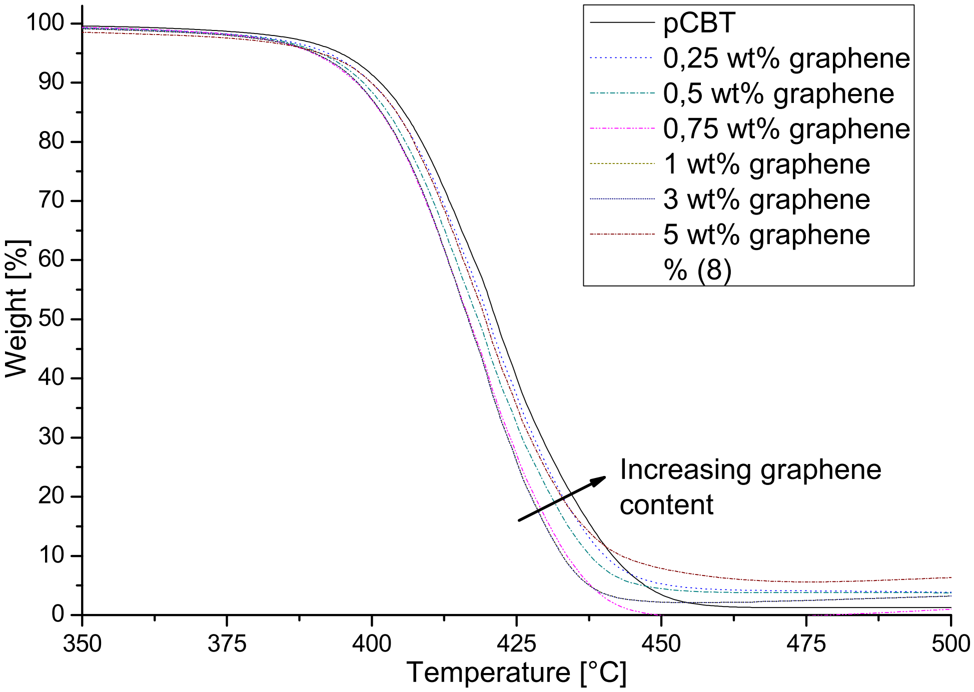


Figure 5 Thermogravimetrcical curves of graphene-modified pCBT samples

It is obvious that the dispersion (exfoliation) stage of graphene should have a strong effect on the TGA behavior. Our finding suggests that the initial and maximum decomposition rate temperatures are not affected opposed to the ash content. The strong increase in the latter above 3 wt% graphene may be an indicator for the supposed strong molecular adsorption affecting the charring process itself.

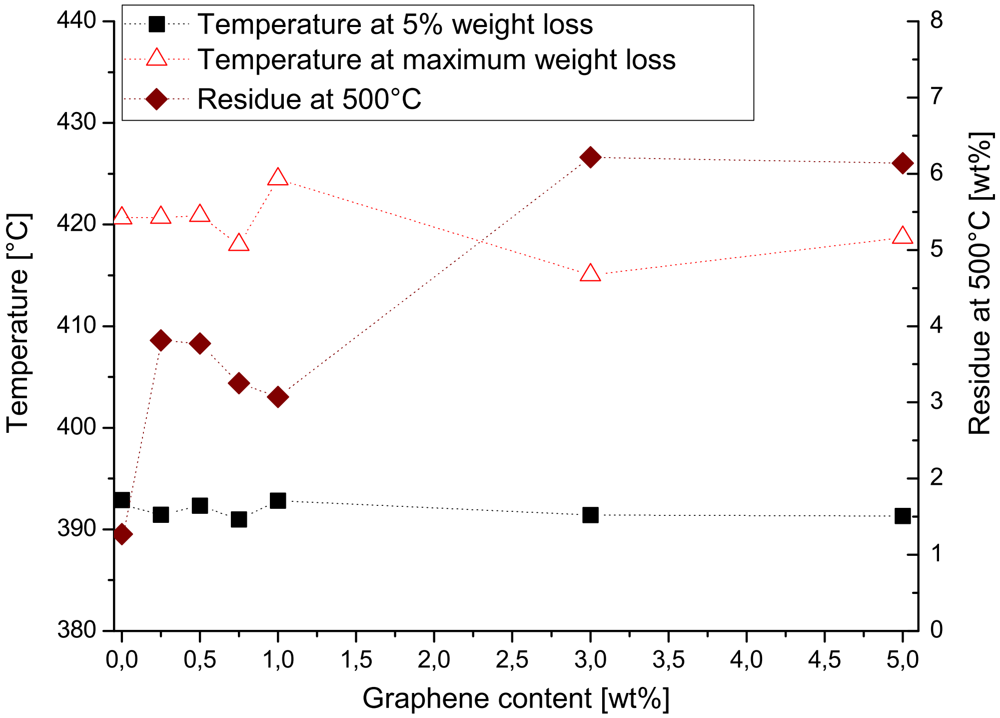


Figure 6 Thermal decomposing properties of graphene-modified pCBT samples

Heat conductivity

Adding graphene to pCBT increases its heat conductivity as it is seen in Figure 7. Heat is transferred by lattice vibration. To transfer heat proper coupling has to be present at the vibration nodes between the nanoparticle and the polymer. Usually this coupling is poor and so it is responsible for the low thermal conductivity of filled polymers. In the present case even 0.25 wt% graphene increases heat conductivity from 0.115 to 0.16 W/mK which means a 40% increase. Higher amounts of graphene do not yield such a pronounced increase. This finding may suggest that between pCBT and graphene a covalent bond was formed due to the functional groups available on the nanoplatelets and through this the phonon scattering was successfully reduced.

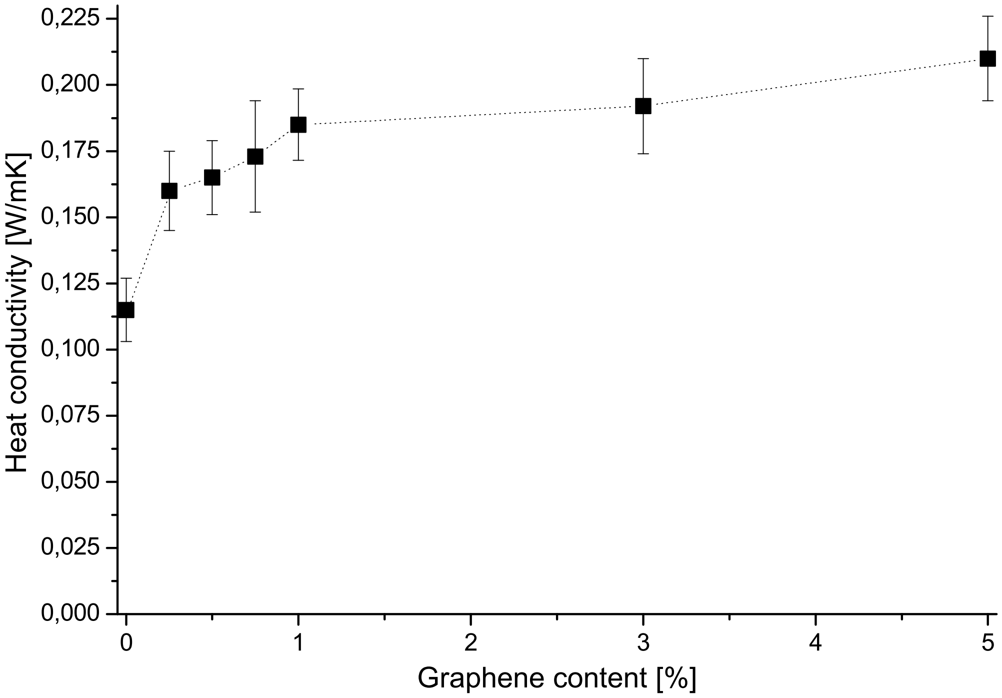
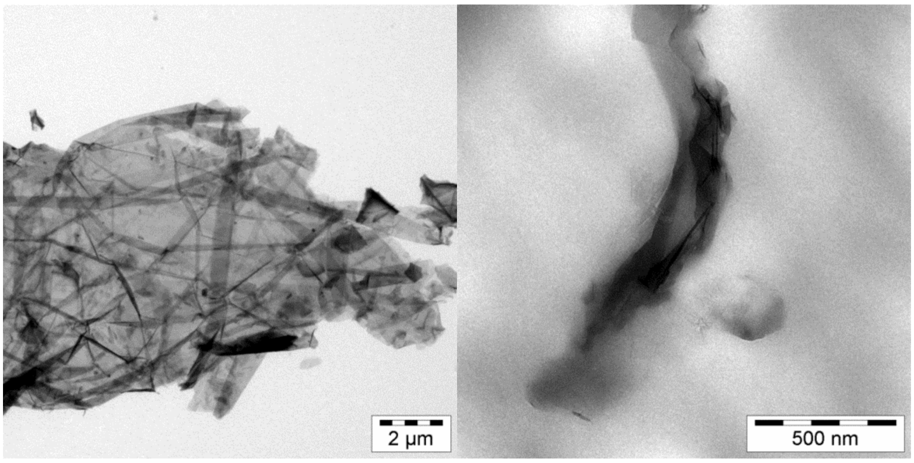


Figure 7 Effect of graphene content on the heat conductivity of pCBT

Transmission electron microscopy

Dispersion of graphene nanoplatelets were studied by TEM. The TEM image in Figure 8a shows that graphene is initially present in agglomerates. Though they are broken up in the nanocomposites but remain still agglomerated (Figure 8b). Figure 8b confirms that the exfoliation of graphene could not be achieved. This result supports the former speculation on the changes of the storage modulus and heat conductivity data as function of the graphene content of the nanocomposites.



a) *b)*

Figure 8 TEM images of graphene nanoplatelets (a) and graphene-pCBT nanocomposites

Conclusion

Cyclic butylene terephthalate (CBT) – graphene nanocomposites were prepared via melt mixing and a subsequent hot pressing. The melting/crystallization, dynamical mechanical, thermogravimetrical and heat conductivity properties of these nanocomposites along with neat polymerized CBT (pCBT), as reference material, were characterized.

DSC studies proved the nucleating effect of graphene on the pCBT crystallization. It was also revealed that crystalline fraction goes through a maximum as a function of graphene content (at ca. 3 wt%). This was ascribed to the sorption reduced molecular mobility of the pCBT chains via which the crystallization was hindered. It turned out from DMA measurements that graphene has a prominent reinforcing effect in the pCBT matrix. The reinforcing efficiency of graphene depended on its dispersion stage. TGA studies showed that the thermal stability based on the temperatures linked to the 5wt% weight loss and maximum decomposition rate, respectively, do not change. This suggests that supposed beneficial effects of graphene (thermal barrier, adsorption of volatile gaseous products) were not at work probably due to the poor dispersion of the graphene sheets. This was confirmed by TEM resolving large agglomerates. This dispersion was traced to the moderate increase in heat conductivity as a function of the graphene content.

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