Enhanced thermal and mechanical properties of poly(trimethylene terephthalate-*block*-poly(tetramethylene oxide) segmented copolymer based hybrid nanocomposites prepared by *in situ* polymerization via synergy effect between SWCNTs and graphene nanoplatelets

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Abstract. Graphene nanoplatelets/single walled carbon nanotubes/poly(trimethylene terephthalate-*block*-poly(tetramethylene oxide) segmented copolymer (GNP/SWCNT/PTT-PTMO) hybrid nanocomposites were synthesized via *in situ* polymerization. A remarkable synergistic effect between GNPs and SWCNTs on improving thermal and mechanical properties of nanocomposites based on segmented block copolymers was observed. Heterogeneous structure of the PTT-PTMO allowed for a better and more uniform distribution of both types of nanoparticles and stabilized the structure in question. This enabled us to observe a so-called ‘synergistic effect’, caused by the use of mixture of carbon nanotubes and graphene nanoplatelets, on the enhancement of thermal and mechanical properties of the obtained polymer. In order to ascertain the influence of mentioned carbon nanostructures on the nano-phase-separated structure of the synthesized PTT-PTMO block copolymers, differential scanning calorimetric (DSC) and dynamic mechanical thermoanalysis (DMTA) measurements were performed. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images of the PTT-PTMO nanocomposites displayed that hybrid nanofillers exhibited better distribution and compatibility than SWCNTs and GNPs did individually. The tensile modulus of 0.5SWCNT/0.1GNP/PTT-PTMO composites was 68% higher than that of the PTT-PTMO alone, compared to only a 10 and 28% increase in tensile modulus for 0.3GNP/PTT-PTMO and 0.3SWCNT/PTT-PTMO composites respectively (the highest concentration when single nanofiller was added).

Keywords: nanocomposites, nanomaterials, mechanical properties, thermal properties, material testing

1. Introduction

The field of nanocomposite and polymer nanocomposite research is currently one of the most rapidly developing domains of cognitive work and applied engineering. The materials in question are essentially complex systems with two or more phases (continuous and dispersed) with an explicit separation surface. The studies on interfacial interactions

at the nano level which affect the composite’s properties are among the most important subjects of research and development in the field of material science today [1, 2].

Up to and including now, nanocomposites enriched by an addition of carbon nanotubes have sparked great interest among scientists and innovative research groups [3]. Same has been the case for

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graphene, an allotropic form of carbon discovered in 2004, existence of which was earlier only predicted by complex theoretic models. Graphene itself is a one atom thick, two-dimensional (2D) sheet composed of sp^2 carbon atoms arranged in a honeycomb lattice [4] with a carbon–carbon bond length of 0.142 nm [5, 6]. It has proven to have a variety of exceptional intrinsic characteristics among which high electron mobility at room temperature ($250\,000\text{ cm}^2/(\text{V}\cdot\text{s})$) [7, 8], (where, unlike in the case of CNTs, chirality does not impede its electrical conductivity), exceptional thermal conductivity ($5000\text{ W}/(\text{m}\cdot\text{K})$) [9], and superior mechanical properties with Young's modulus of $\sim 1\text{ TPa}$ and ultimate strength of 130 GPa [8] can be distinguished. Aforementioned characteristics, along with an extremely high surface area (theoretical limit: $2630\text{ m}^2/\text{g}$) and gas impermeability [10], demonstrate graphene's unique potential for improving electrical, mechanical, thermal and gas barrier properties of polymers [11, 12]. Taking all above into consideration, a simultaneous introduction of two types of carbon nanofillers such as graphene (a plate filler – 2D) and CNTs (a fibrous/linear filler – 1D) may seem desirable from the standpoint of their influence on electrical and mechanical qualities.

A controlled distribution of both nanoplatelets and linear nanoparticles throughout a polymer matrix may result in obtaining specified physical characteristics, most important being the enhancement of mechanical properties and obtaining electrically conductive materials. All at a very low total concentration of both nanofillers. This claim is substantiated by several cases i.e. thin polymer films have been fabricated from a mixture of single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes [13, 14] and from a mixture of SWCNTs and carbon fibers [14]. In each mentioned case the examined samples displayed an array of significantly improved properties. Furthermore, another recent research has looked at the mixtures of oxidized nanotubes and graphene oxide [15]. Finally, Khan *et al.* [16] prepared hybrid films comprised of single walled carbon nanotubes and nano-graphite. It has been demonstrated that these hybrids displayed mechanical and electrical properties that were superior to those of either nanotube-only or graphene-only films.

Latest literature on the subject indicates that it was not yet possible to fully utilize the potential of apply-

ing a mixture of carbon nanotubes and graphene to observe a so-called 'synergistic effect' which in theory should result in a significant enhancement of properties of obtained materials. Indeed, a remarkable synergistic effect between multi-graphene platelets (MGPs) and multi walled carbon nanotubes (MWCNTs) causing an improvement of mechanical properties and thermal conductivity in epoxy composites has been studied [17]. However, obtaining similar results for thermoplastic polymer composites remains an unresolved and thus a noteworthy subject, hence it is widely undertaken by many research groups. Therefore, the addition of carbon nanoparticles to segmented block copolymers, composed of both flexible and rigid segments, seems particularly interesting as they demonstrate a behaviour similar to that of thermoplastic elastomers. Due to their excellent mechanical qualities, like strength and elastic properties in a wide temperature range, multiblock poly(ether–esters) (PEEs) have been intensely studied [18, 19]. A recent study on a novel family of polyester thermoplastic elastomers based on poly(trimethylene terephthalate) (PTT) has been conducted [20, 21]. The influence of organoclay [22], carbon nanotubes [23] and graphene oxide [24] on the structure and physical properties of PTT-PTMO copolymers has been previously described. This type of segmented block copolymers, based on poly(trimethylene terephthalate) (PTT) as rigid segments and polyether (PTMO) as flexible segments, displays a variety of remarkable qualities such as low glass transition temperature (T_g), high melting temperature of rigid phase (T_m) and a temperature independent rubbery plateau. An addition of carbon nanoparticles in mentioned block copolymers may influence the phase separation thus changing the elastic properties of the used polymer matrix. It is anticipated that the heterogeneity of the PTT-PTMO structure will allow for its stabilization and a better and more uniform dispersion of nanoparticles. Although the phase size of polyester thermoplastic elastomers is greater than the size of nanoparticles, it is believed that the multiphase structure of block copolymers will significantly improve both thermal and mechanical characteristics. Moreover, it will allow to observe a synergistic effect between carbon nanotubes and graphene nanoplatelets on properties enhancement

This work is a part of a wider project with an objective to fabricate electrically conductive polymer

nanocomposites containing carbon nanoparticles [25]. In this study, PTT-PTMO based nanocomposites with hybrid fillers comprising of SWCNTs and GNPs were developed in order to enhance thermal stability and mechanical characteristics. The thermal and mechanical properties of the obtained nanocomposites were thoroughly evaluated and favourably compared with those of neat block copolymer and those containing either SWCNTs or GNPs alone.

2. Experimental section

2.1. Materials

The single walled carbon nanotubes KNT 95 (SWCNTs) were purchased from Grafen Chemical Industries (Grafen Co., located in Ankara, Turkey) a leader in the field of fabrication and application of carbon nanomaterials. According to manufacturers' data: diameter: <2 nm, electrical conductivity (EC): >100 S/cm, length: $5\text{--}30$ μm , purity: $>95\%$, surface area: 380 m^2/g . Graphene nanoplatelets (<1 nm) was purchased from ANGSTRON Materials (Dayton, Ohio, USA), it was bought in the form of a powder with less than three graphene layers and $x\text{--}y$ dimensions of up to 10 μm . The carbon content is $\sim 97.0\%$, and the oxygen content is $\sim 2.10\%$. Graphene nanoplatelets have a specific surface area of $400\text{--}800$ m^2/g and a true density of ≤ 2.20 g/cm^3 .

The following materials were used in the course of fabrication of the PTT-PTMO block copolymer and PTT-PTMO/carbon nanoparticles nanocomposites: dimethyl terephthalate (DMT, Sigma-Aldrich) and poly(tetramethylene oxide) glycol with molecular mass of 1000 g/mol (PTMG, Terathane 1000, DuPont, USA) were used as received. 1,3-propanediol (PDO, Sigma-Aldrich) was distilled before use. Tetraethyl orthotitanate (TEOT, Fluka) was used as catalyst in transesterification and polycondensation. Irganox 1010 (Ciba-Geigy, Switzerland) was used as antioxidant.

2.2. Synthesis of PTT-PTMO based nanocomposites

Poly(trimethylene terephthalate)-*block*-poly(tetramethylene oxide) (PTT-PTMO) segmented block copolymer based nanocomposites with carbon nanotubes and/or graphene nanoplatelets were prepared by *in situ* polymerization according to a procedure described earlier for nanocomposites with MMT [22] and GO [24]. The PTT-PTMO block copolymer with the content of 50 wt% of PTT rigid segments

and 50 wt% of PTMO soft segments was used as nanocomposite polymer matrix. The process of *in situ* polymerization was preceded by a stage of nanofillers dispersion. For that purpose a specified amount of graphene nanoplatelets was mixed in a liquid substrate (1,3-propylene glycol) during a 30 min period, alternately using a high speed stirrer and vibrations of an ultrasound stirrer. Subsequently, for the purpose of greater separation of graphene sheets an ultrasonic washer was used for a period of 8 hours. To a so prepared mixture of graphene nanoplatelets, in the case of hybrid nanocomposites, a specified amount of carbon nanotubes was added. However, due to the high fragility of nanotubes only an ultra-high speed stirrer high (Ultra-Turrax[®] T25) and ultrasonic homogenizer (Sonopuls HD 2200, Bandelin) were used in order to prepare their dispersion in an appropriate manner. A ready dispersion was then put into a polycondensation reactor (Autoclave Engineers, Pennsylvania, USA), preheated to 80°C , along with dimethyl terephthalate (DMT) and a first portion of catalyst. First stage of the reaction, the transesterification process, was performed in a $160\text{--}185^\circ\text{C}$ temperature range. The course of the reaction was controlled by observing the secretion of its by-product – methanol. When its amount reached about 90% of the quantity computed by means of stoichiometric calculations, the second stage of synthesis, being the polycondensation process, was commenced. For this purpose PTMO mixed with thermal stabilizer (Irganox 1098), along with the second portion of catalyst were inserted. The temperature of the reaction was then gradually increased up to 250°C . However, unlike the first stage which was performed under atmospheric pressure, the polycondensation stage was carried out under reduced pressure (~ 20 Pa). In this case, the course of the reaction was monitored by observing the stirrer's torque. When the polymer/nanocomposite melt reached a high molecular mass, it was then extruded in the form of a thin wire. It was subsequently granulated and subjected to injection moulding procedure.

2.3. Preparation of test samples

The dumbbell shaped samples for density, DMTA, SEM and tensile tests were obtained using a Boy 15 (Dr BOY GmbH&Co., Germany) injection moulding machine with parameters as follows: injection pressure 55 MPa, melt temperature 225°C , mould temperature 30°C , holding down pressure of 20 MPa

for 15 s and cooling time 10 s. Prior to performing the above mentioned measurements, the dumbbell shaped samples were annealed at 80°C for a period of 2 h.

2.4. Methods of characterization

The intrinsic viscosity $[\eta]$ of the obtained samples was determined using a phenol/1,1,2,2-tetrachloroethane mixture (60/40 by weight) at 30°C. The concentration of polymer in the solvent amounted to 0.5 dL/g. The measurement was performed using a capillary viscometer Ubbelohde (type 1c, $K = 0.03294$). In order to remove the influence of the nanofiller on the measured values, a procedure described earlier in [22, 25–27] was used.

Density measurement (d) was performed using a hydrostatic scales (Radwag WPE 600C, Poland), calibrated using working standards of known density. The melt viscosity of the samples was measured using ARES rheometer (Rheometric Scientific Inc., USA). The measurement was performed at 220°C in frequency range 0.1–50 Hz, in a parallel-plate fixture (diameter = 25 mm) with a gap distance of 2 mm.

The structure of nanocomposites was observed using scanning electron microscopes (SEM, JEOL JSM 6100; SEM ULTRA-55 Zeiss and SEM SUPRA-55 VP Zeiss). Prior to testing, the samples were cryofractured in liquid nitrogen, and then vacuum coated with a thin gold film. SEM images were collected with an In-Lens detector at an acceleration voltage of 5 kV and working distance of 5–6 mm. Transmission electron microscopic (TEM) analysis was carried out by a PHILLIPS CM 120 Electron Microscope using an acceleration voltage of 80 kV. The specimens used in TEM examination (thickness about 100–150 nm) were obtained/cut from the central part of the dumbbell shaped sample using Reichert Ultracut R ultramicrotome with a diamond knife. The procedure was carried out only after the sample had been immersed in liquid nitrogen. The direction of the cut was perpendicular to the direction of flow in the mould.

Thermal and thermo-oxidative stability of investigated polymer nanocomposites were evaluated by thermogravimetry (TGA 92-16.18 Setaram) using the system to measure the simultaneous TG-DSC. Measurements were carried out in inert atmosphere (argon) an oxidizing atmosphere i.e. dry, synthetic air ($N_2:O_2 = 80:20$ vol%). The study was conducted at a heating rate of 10°C/min in the temperature range

20–700°C. Measurements were conducted in accordance with the principles contained in the PN-EN ISO 11358:2004.

The dynamic mechanical thermal (DMTA) measurements were performed using a Polymer Laboratories MK II apparatus working in a bending mode at a frequency of 1 Hz in a temperature range from –100°C to polymer melt temperature and heating rate of 3°C/min. Dynamic mechanical thermal analysis comprised of measurements of E' constituents (storage modulus) and E'' (loss modulus) complex elastic modulus and mechanical loss factor $\tan \delta = (E''/E')$. It is one of the relaxation methods, which allows to ascertain the structure and phase transformation of the researched materials. The examined sample is subjected to a sinusoidal alternating causing its' deformation, the properties are determined on the basis of modulus changes and the ability of attenuation as a function of temperature and frequency of load changes. Temperatures of α -relaxation (T_α) and β -relaxation (T_β) were designated from the maximum of the loss modulus change curve (E'') and the loss factor tangent ($\tan \delta$) of temperature curve.

Differential scanning calorimetry (DSC) measurements were carried out using a TA Q100 instrument under a nitrogen atmosphere in a temperature range from –100 to 250°C at the heating and cooling rate of 10°C/min and sample weight of 10 ± 0.2 mg. Each DSC testing cycle consisted of heating, cooling and repeating of the scans. The first cooling and second heating scans were used to determine the melting and crystallization peaks. The heat of fusion has been determined by integration of the normalized area of melting endotherm. The glass transition temperature (T_g) of the polymer samples was taken as the midpoint of the change in heat capacity. The degree of crystallinity of the sample (X_c) was calculated using Equation (1):

$$X_c[\%] = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

where ΔH_m^0 is the enthalpy change of melting for a 100% crystalline sample, for PTT equals to 146 J/g [28] and ΔH_m is derived from melting peak area on DSC thermogram.

Tensile measurements were performed on an Instron 5566 universal tensile testing frame, equipped with a 5 kN Instron load cell, a contact optical long travel extensometer and the Bluehill 2 software. Pneu-

matic 1 kN Instron side action grips were used to clamp the test samples. The measurements were carried out at room temperature using a cross-head speed of 100 mm/min and a grip distance of 20 mm. The tensile properties, being the Young's modulus, yield stress and yield strain, stress and elongation at break, were determined using injection moulded dumbbell-shaped bars (ISO 37 type 3). The results for each polymer are based on data collected from 6 samples (per polymer), for which the mean values and standard deviations were calculated. Moreover, the tensile deformation recovery properties of the samples were investigated. The dumbbell sample was stretched to a predetermined strain at a speed of 100 mm/min at room temperature, and then the imposed strength was released. The residual strain was then measured to calculate the deformation recovery rate. The predetermined strain of 100% was utilized in our testing.

3. Results and discussion

3.1. Rheological properties

A series of hybrid nanocomposites based on multi-block poly(ether-ester) copolymer with PTT as a rigid segment were synthesized via *in situ* polymerization. The values of intrinsic viscosity, melt viscosity and density (Table 1) are dependent on the sample composition. The measured values of intrinsic viscosity for PTT-PTMO copolymer (1.325 dL/g) and PTT-PTMO hybrid nanocomposites (1.299–1.322) [dL/g] (for three hybrids with increasing content of SWCNTs) suggest that molecular weights of studied polymers should be reasonably high. The value of $[\eta]$ decreased slightly along with addition of nanofillers. However, an increase was observed together with a rise in number of SWCNTs and graphene platelets.

It can clearly be seen that the addition of SWCNTs strongly affected the melt viscosity of PTT-PTMO

Figure 1. Melt viscosity versus frequency for neat PTT-PTMO and PTT-PTMO/SWCNTs+GNPs nanocomposites at temperature of 220°C

nanocomposites (Figure 1). On the other hand however, no such behaviour was observed when graphene nanoplatelets were added to the polymer (Table 1). A much stronger effect of the addition of carbon nanotubes on the viscosity of the composition was observed when compared to the hybrid nanocomposite PTT-PTMO/0.1 SWCNTs+0.3 GNPs with the same amount of SWCNTs (0.1 wt%). Same was observed for the nanocomposite with 0.3 wt% of SWCNTs. It can therefore be concluded, that in case of PTT-PTMO hybrid nanocomposites, the mixture of both nanofillers affected the polymer's melt viscosity much stronger than either graphene or nanotubes alone (Figure 1). A similar effect was noticed in the case of nanocomposites based on polycarbonate with carbon black/carbon nanotube systems [29]. It has also been observed that an increase in pure MWCNT/CB content leads to respectively highest/lowest increase rate of melt viscosity. Additionally, the melt viscosity value for composites with mixed filler systems were in between those of pure/singe fillers. In the case described herein, addition of carbon nanoparticles with a 0.5 wt% nanotube content caused a substantial increase in viscos-

Table 1. Intrinsic viscosity, density and melt viscosity of PTT-PTMO/SWCNTs+GNPs nanocomposites

Sample	Nanofiller [wt%]	$[\eta]$ [dL/g]	d [g/cm ³]	Melt viscosity ^M [Pa·s]
PTT-PTMO	0	1.325	1.174	340.02±0.76
PTT-PTMO/0.1 G	0.1	1.315	1.174	124.38±0.93
PTT-PTMO/0.3 G	0.3	1.327	1.175	232.66±0.84
PTT-PTMO/0.1 SWCNT+0.3 G	0.1+0.3	1.299	1.173	428.76±1.22
PTT-PTMO/0.3 SWCNT+0.1 G	0.3+0.1	1.319	1.177	648.65±1.31
PTT-PTMO/0.5 SWCNT+0.1 G	0.5+0.1	1.322	1.176	10 409.07±18.84
PTT-PTMO/0.1 SWCNT	0.1	1.325	1.181	398.52±1.08
PTT-PTMO/0.3 SWCNT	0.3	1.324	1.176	602.11±1.60

$[\eta]$ – intrinsic viscosity; d – density; η – melt viscosity measured at 220°C at 1 Hz

ity value (over a 30 time increase relative to neat copolymer). The aforementioned concentration of nanofillers should be considered as a critical value for the used *in situ* polymerization method. When surpassed, extrusion of polymer from the reactor would be impossible. This indicates that despite an enhancement of mechanical and thermal qualities which is caused by the synergistic effect between SWCNTs and GNPs, the system comprised of 0.5 SWCNTs+0.1 GNPs provides the highest melt viscosity values along with the greatest improvement in tensile properties and thermal stability. However, such a high rise in viscosity may prove unsuitable for processing purposes.

The density of PTT-PTMO hybrid nanocomposites has increased slightly with the addition of nanofillers. Obtained density values depend strongly on the crystallite content as well as on the content of the nanofiller in the polymer matrix. As the obtained hybrid nanocomposites displayed density values comparable to those of nanotubes only, it may be concluded that an addition of nanotubes alone has a greater impact of the density.

3.2. Morphology

Single walled carbon nanotubes and graphene nanoplatelets used in this study were characterized using scanning electron microscopy (SEM), which provided visual information on the ratio of carbon nanofiller to carbonaceous impurities (Figure 2a and 2b). In case of SWCNTs it was presumed that fiber-like areas correspond to bundled SWCNTs, while the other particles and lumps correspond to carbonaceous impurities. Figure 2b displays the photomicrograph of the loose structures of graphene nanoplatelets in sequentially larger magnifications. Obviously, in the case of graphene nanoplatelets loose structures containing multi-pores can be observed. This micrograph also suggests the thickness of the graphene platelet layer is less than 100 nm.

As mentioned in the introduction, the natural tendency of carbon nanostructures to agglomerate (due to van der Waals interactions) is the underlying reason for difficulties in preparation of composites based on thermoplastic matrices, which can be characterized by a high degree of homogeneity of the nanophase. Effectiveness of using the *in situ* polycondensation method, preceded by a dispersion of the carbon nanotubes and/or graphene nanoplatelets in

a substrate, can be assessed qualitatively by means of structure analysis using microscopic techniques. Taking into consideration the development of methods of *in situ* polymer composite preparation, it was assumed that dispersing SWCNTs/GNPs in one of the substrates by means of mechanical forces and vibrations at the ultrasonic frequency, and then carrying out the synthesis of the polymer matrix in the presence of the nanoparticles, would allow to obtain uniform distribution in the mass. The uniform distribution itself is owed to intercalation of growing polymer chains between nanotube bundles and graphene nanoplatelet, causing them to separate even further. One of the main problems encountered during dispersion of CNTs, limiting the effective use of carbon nanotubes as nanofillers in a polymer matrix, is the strong inter-tube attraction between CNTs. Many approaches to overcome this issue have been made, however they mostly result in an excessive modification or even damage to the unique morphology of CNTs. An efficient alternative allowing to tailor the polymer/CNT interface and at the same time preserving the integrity of the tubes is mixing them together with a different shaped nanofiller (i.e. plate-like shape). In the discussed study, it was assumed that application of graphene nanoplatelets might be a suitable solution. A uniform distribution of SWCNTs on graphene's surface should cause a synergistic effect and thus enable them to act together as stronger reinforcing agent for the polymer, resulting in a substantial enhancement of thermal and mechanical properties (Figure 2c–2g). The evenly spaced bright dots and lines are attributed to the ends and edges of the broken SWCNTs/GNPs covered in PTT-PTMO. They are clearly visible due to their high electrical conductivity. A good connection between graphene nanoplatelets, contained in the SWCNTs and GNPs mixture, along with a good compatibility with the polymer matrix were due to residual oxide groups on GNPs' surface [25]. The dual-filler strategy appears to yield a more efficient dispersion of SWCNTs+GNPs/PTT-PTMO. The SEM images of the PTT-PTMO/0.3 SWCNT+0.1 GNPs are shown in Figure 2e–2g. Both the SWCNTs and GNPs show fairly good distribution which can be seen in Figure 2e and 2g. The graphene nanosheets in Figure 2e appear to show better dispersion than those previously observed when only graphene was added to copolymer matrix (incompletely exfoliated structure of nanocomposites based on PTT-PTMO with

Figure 2. (a) and (b) SEM micrographs of SWCNTs and GNPs as received; (c) and (d) SEM micrographs of PTT-PTMO/0.1 SWCNTs+0.3 GNPs hybrid nanocomposites; (e)–(g) SEM micrographs of PTT-PTMO/0.3 SWCNT+0.1 GNPs hybrid nanocomposites

GNP observed in TEM micrographs, Figure 3a, 3b). A detailed study on the influence of GNPs and GO on the morphology of PTT-PTMO matrix was previously described in [25] and [24] respectively. In that particular case this indicates that an addition of

SWCNTs improves the dispersion of graphene nanoplatelets, which agrees with the tensile results which exhibit an improvement in mechanical qualities. However, because of the van der Waals interactions the graphene sheets tend to form irreversible agglom-

Figure 3. (a)–(d) TEM micrographs of PTT-PTMO/GNPs nanocomposites with: (a) 0.1 GNPs, 75 000 $\times$, (b) 0.3 GNPs, 20 000 $\times$, (c) and (d) TEM micrographs of PTT-PTMO/0.1 SWCNT+0.3 GNPs nanocomposites at (c) 100 000 $\times$ and (d) 150 000 $\times$; (e) and (f) TEM micrographs of PTT-PTMO/0.3 SWCNT+0.1 GNPs nanocomposites (e) 150 000 $\times$ and (f) 175 000 $\times$

erates and even restack to form graphite (Figure 2f). Additionally, the SEM images of PTT-PTMO/SWCNT+GNPs in Figures 2g and 2h show that the SWCNTs and graphene nanoplatelets form a kind of network structure. The SWCNTs appear to have a good affinity for GNPs. Aforementioned formation of nanofiller-nanofiller interactions may explain the good thermal stability and mechanical characteristics of PTT-PTMO/0.3 SWCNT+0.3 GNPs. The dispersion state in the composites with hybrid CNTs/graphene particles was further confirmed by transmission microscopy.

The TEM images (Figure 3c and 3d, with two different magnifications of PTT-PTMO/0.1 SWCNTs+0.3 GNPs) display the real distribution of conductive fillers in the respective nanocomposites. They may provide valuable insight into the mechanisms behind the synergy between the hybrid fillers of CNT and graphene platelets in enhancing the conductivity [25] of nanocomposites. Figure 3c depicts both randomly dispersed individual SWCNTs and a round SWCNT agglomerate, also well-dispersed graphene sheets can be seen. In some places carbon nanotubes and graphene plates seem to be connected to one another. This can be better seen in Figure 3d where the dispersion of both nanofillers is even better and only nanotubes attached to graphene planes were observed.

In order to examine the dispersion of SWCNTs/GNPs (with 0.3 wt% of SWCNTs and 0.1 wt% of GNPs) in the polymer hybrids in detail, TEM studies were carried out. They allow a qualitative understanding of the internal structure through direct observation. Typical TEM photographs of hybrids with 0.3 wt% of SWCNT and 0.1 wt% of GNPs are shown in Figure 3e and 3f. They show that both nanofillers were well dispersed in the polymer matrix, meaning that single nanotubes along with homogeneously distributed GNPs were observed. Interestingly, the ‘pull-out’ mechanism of SWCNTs has been also shown as carbon nanotubes counteracted the break of the polymer matrix, which can clearly be seen at a higher magnification. As observed in the figures, the CNT-to-CNT and CNT-to-GNPs interactions by the surface contact (or tunnelling) should increase the mechanical strength of the composite, which will be discussed further.

3.3. Phase structure

An introduction of a carbon nanofiller into the multiphase system (block copolymer) may initiate the formation of a heterophase structure. The newly formed structure stabilizes the distribution of nanoparticles in the polymer matrix. The poly(ether-ester) multiblock copolymer composed of PTT as rigid segment and poly(tetramethylene oxide) PTMO as flexible segment with hardness of 51 Shore D [21, 23], was used as polymer matrix in nanocomposites described herein. During cooling from the melt, mentioned segmented block copolymer’s microphase separated into high melting crystalline PTT hard domains and relatively low glass transition soft PTMO-rich domains. The elastic characteristics of this segmented block copolymer is a consequence of aforementioned microseparated phase structure, which is a result of the chemical nature and incompatibility between the rigid and flexible blocks/segments build into the polymer chains. Here, in order to investigate the effect of the addition of carbon nanostructures, which differ in shape, on the nanoseparated phase structure of the synthesized PTT-PTMO block copolymers, DSC and DMTA measurements were performed.

Forming of above mentioned separation occurs together with the formation of a soft (PTMO-rich) phase and a hard semicrystalline polyester (PTT) phase with characteristic temperatures T_g and T_m , respectively. Existence of such a structure was confirmed by DSC measurement (Figure 4a and 4b). Since the size of domains of the hard phase (few nm, [20]) is comparable to the size of SWCNTs and graphene nanoplatelets which were used to obtain the hybrid nanocomposites, it is difficult to explain the influence of hybrid nanofillers on the microstructure of the resulting nanocomposites. The glass transition temperatures (T_{g1} and T_{g2}) of nanocomposites were not affected by the incorporation of SWCNTs together with graphene nanoplatelets. Both nanofillers, despite good interactions with the polymer matrix (confirmed by SEM analysis), showed no effect on glass transition temperatures of both soft (T_{g1}) and amorphous polyester phase (T_{g2}).

In contrast, the crystallization process was stronger affected in the obtained nanocomposites. A notable rise in the crystallization temperature has been observed along with an increase in content of both

Figure 4. DSC thermograms for PTT-PTMO and PTT-PTMO/SWCNTs+GNPs nanocomposites during the cooling (a) and 2nd heating (b)

SWCNTs and graphene nanoplatelets. The highest shift toward higher T_c temperature was observed in the case of PTT-PTMO/0.5 SWCNT+0.1 GNP, the value in question reached as high as 45°C. Surprisingly, a stronger influence on crystallization behaviour seems to occur in the presence of carbon nanotubes in PTT-PTMO matrix. It can be well observed for hybrid nanocomposites where, with increasing loading of SWCNT (from 0.1 to 0.5), an increase in T_c was observed. However, all values of ΔH_c were comparable to neat PTT-PTMO segmented block copolymer. In addition, the melting temperature remains unchanged for all nanocomposites. Based on the obtained results it can be also concluded that the composition of SWCNT:GNP of 5:1 accelerated the rate of crystallization probably due to larger amount of crystallization agents. It can clearly be seen that the T_c value increased along with an increase in SWCNTs content. The degree of crystallinity of obtained nanocomposites estimated basis DSC changes significantly (1–2%) compared to neat block

copolymer (Table 2). At first slight a decrease can be observed, but with increasing loading of both nanofillers a rise in comparison to neat PTT-PTMO emerges.

The DMTA analysis (Figure 5) has shown that PTT-PTMO based nanocomposites are multiphase systems having one crystalline and two amorphous phases which confirmed the results obtained from DSC measurements. On the storage modulus E' curve at low temperatures an inflection (corresponding to the β_1 maximum in the loss modulus E'') associated with the glass transition of the soft polyether-rich phase can be observed. A decrease and a subsequent rise of the storage modulus value in the temperature range 20–120°C is related to amorphous PTT glass transition which is immediately followed by cold crystallization. (A completely amorphous PTT has a glass transition temperature of 40°C, exceeding that value will cause its crystallization). Above 20°C, the storage modulus depends on the type and content of carbon nanofiller. In the curve presenting the loss

Table 2. Thermal properties of neat PTT-PTMO and PTT-PTMO/SWCNTs+GNPs nanocomposites determined by DSC

Sample	T_{g1} [°C]	T_{g2} [°C]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	x_c [%]	$T_{\beta1}$ [°C]	$T_{\beta2}$ [°C]
PTT-PTMO	-58	53	206	30.9	126	28.3	21.2	-31	43
PTT-PTMO/0.1 G	-61	52	204	28.1	149	27.3	19.2	-35	–
PTT-PTMO/0.3 G	-59	50	205	29.1	149	27.8	19.9	-36	–
PTT-PTMO/0.1 SWCNT+0.3G	-61	51	203	31.1	153	27.8	21.4	-41	70
PTT-PTMO/0.3 SWCNT+0.1G	-62	51	203	31.7	158	28.8	21.7	-41	75
PTT-PTMO/0.5 SWCNT+0.1G	-63	54	206	34.6	171	34.5	23.7	-41	60
PTT-PTMO/0.1 SWCNT	-59	50	208	29.9	155	29.9	20.5	-37	57
PTT-PTMO/0.3 SWCNT	-61	51	204	31.3	157	29.2	21.4	-40	60

T_{g1} – glass transition temperature of soft phase, T_{g2} – glass transition temperature of amorphous polyester phase, T_m – melting temperature of polyester crystalline phase; T_c – crystallization temperature of polyester crystalline phase; ΔH_m , ΔH_c – enthalpy of melting and crystallization of polyester crystals, respectively; x_c – mass fraction of crystallinity, $T_{\beta1}$, $T_{\beta2}$ – temperature of β_1 - and β_2 - relaxations corresponding to the glass transition temperatures determined from maximum of $\tan \delta$

Figure 5. The dependence of storage modulus E' , loss modulus E'' and $\tan \delta$ on temperature for PTT-PTMO/SWCNT+G (a)–(b) and PTT-PTMO/SWCNT and PTT-PTMO/G (c)–(d) nanocomposites

factor tangent of the temperature dependency (Figures 5b, 5c), two relaxations (β_1 , β_2) can clearly be seen. These relaxations are attributed to the glass transition of amorphous polyether-rich phase (β_1) and amorphous polyester phase (β_2). When a hybrid nanofiller in the form of a SWCNTs and GNPs mixture has been added (marked on the plot as G), a clear phase separation occurred. As a result two parts emerged, a PTMO-rich amorphous part (low temperature peak, β_1) and an amorphous PTT part (high temperature peak, β_2). Moreover, the β_1 peak has shifted towards lower temperatures and has become slimmer and narrower than the one corresponding to the neat PTT-PTMO, which proves that the presence of SWCNTs and GNPs influences the phase separation of the examined system. Also, the β_2 peak (max $\tan \delta$) has shifted towards higher temperatures and a change in its intensity can be observed, i.e. in the case of composites containing only graphene nanoplatelets (0.1 and 0.3) or (0.3 CNT, 0.5 CNT+0.1 G) a decrease of β_2 peak's intensity can be seen, which is a clear evidence for a drop in PTT chain mobility.

3.4. Thermal stability

Thermogravimetric analysis (TGA) was used to analyze the effect of the hybrid system of nanofillers (1D+2D) dispersed in PTT-PTMO block copolymer matrix on its thermal and thermo-oxidative stability. The TGA curves for PTT-PTMO/hybrid nanoparticles nanocomposites in air and an inert (argon) atmosphere are presented in Figure 6. No improvement in thermal stability has been observed in an inert atmosphere, as compared to the neat PTT-PTMO block copolymer, but also to PTT-PTMO/SWCNTs and PTT-PTMO/GNPs nanocomposites (Table 3). What is more, a slight decrease in the temperatures of 5 and 10% weight loss ($T_{5\%}$, $T_{10\%}$) was observed. However, in an oxidizing atmosphere for all hybrid nanocomposites the noticeable improvement of thermo-oxidative stability of nanofillers has been found. When comparing the temperature of 5% weight loss for neat PTT-PTMO block copolymer and the hybrid composites, a significant shift of 24°C towards higher temperatures was observed. Interestingly enough, the addition of carbon nanofillers of different shapes and aspect ratios

Figure 6. Weight loss and derivative weight loss versus temperature for the PTT-PTMO/SWCNTs+GNPs nanocomposites in air (a) and in argon (b) at a heating rate of 10°C/min

causes a substantial improvement in the thermo-oxidative stability of the thermoplastic elastomer in question. The thermal stability enhancement does not seem to depend upon a particular shape of the nanofiller as similar results were obtained in the case of SWCNTs and graphene nanosheets individually, as well as for the mixture of both. Apparently, both types of nanoparticles (carbon nanotubes and graphene nanoplatelets) affect the thermal stability of polymers in a similar manner. This can clearly be seen in Figure 6 where all the curves are close each other. Thus, it can be assumed that the morphology differences in PTT-PTMO/SWCNTs+GNPs nanocomposites do not appear to make a noticeable dif-

ference in the thermal stability of the nanocomposites. The possible explanation for such behaviour is that both the SWCNTs and graphene nanoplatelets have high electron affinities and as such seem to be capturing free radicals [30, 31]. Discussed TGA results suggest that by incorporating either SWCNTs or graphene nanoplatelets or the mixture of both into the polymer, its thermo-oxidative stability should be improved.

3.5. Mechanical properties

The use of new carbon nanomaterials with excellent mechanical properties has opened a new and exciting chapter in today's material science. A better understanding of chemistry and the intrinsic properties of both graphene and carbon nanotubes, along with new and innovative approaches to polymer fabrication has led scientists to developing composites with GNPs and SWCNTs and thus creating new materials with substantially enhanced mechanical, electrical, thermal and barrier properties. Similarly to traditional composites, the range of the obtained improvements is referred to using factors such as reinforcement phase concentration, distribution in the host matrix, interface bonding and the reinforcement phase aspect ratio.

The tensile properties of the PTT-PTMO/SWCNTs+GNPs hybrid nanocomposites were examined. Typical stress-strain curves for PTT-PTMO block copolymers were plotted in Figure 7. In order to make the plots more comprehensible, the obtained data is presented in two separate figures where the results obtained for hybrid nanocomposites have been compared to those for graphene (a) and carbon nanotubes (b). A clear tendency for an increase in tensile modulus and a decrease in elongation, caused by a

Table 3. Temperatures corresponding to 5 and 10% weight loss and the temperature at maximum of weight loss rate for the PTT-PTMO/ SWCNT+GNPs (G) nanocomposites obtained in air and argon atmosphere

Symbol	T _{5%} [°C]	T _{10%} [°C]	T _{DTG1} [°C]	T _{DTG2} [°C]
Measurement carried out in an oxidizing atmosphere				
PTT-PTMO	331	352	400	499
PTT-PTMO/0.1 G	322	342	398	500
PTT-PTMO/0.3 G	357	368	397	499
PTT-PTMO/0.1 SWCNT+0.1 G	355	368	399	507
PTT-PTMO/0.3 SWCNT+0.3 G	355	358	401	504
PTT-PTMO/0.5 SWCNT+0.3 G	350	369	403	515
PTT-PTMO/0.1 SWCNT	363	376	402	510
PTT-PTMO/0.3 SWCNT	358	372	406	515
Measurement carried out in argon				
PTT-PTMO	371	382	408	—
PTT-PTMO/0.1 G	366	383	406	—
PTT-PTMO/0.3 G	374	382	408	—
PTT-PTMO/0.1 SWCNT+0.1 G	366	377	406	—
PTT-PTMO/0.3 SWCNT+0.3 G	368	379	407	—
PTT-PTMO/0.5 SWCNT+0.3 G	367	380	409	—
PTT-PTMO/0.1 SWCNT	372	382	408	—
PTT-PTMO/0.3 SWCNT	369	380	408	—

Figure 7. Representative stress-strain curves of PTT-PTMO/SWCNTs+GNPs hybrid nanocomposites (a) in comparison to PTT-PTMO/GNPs and (b) in comparison to PTT-PTMO/SWCNTs nanocomposites

rise in the hybrid system content has been observed (Table 4). Carbon nanofillers (SWCNTs and GNPs) added in small amounts to PTT-PTMO elastomer increase the tension related to deformation, limiting the free length of chains located between physical nodes of the network/matrix (they create additional physical nodes). This effect was significantly stronger when two nanofillers were used. For pristine PTT-PTMO the tensile modulus was 118 MPa. With the incorporation of up to 0.3 wt% of graphene, the tensile modulus decreased to ca. 131 MPa, which is ca. 11% more compared to neat PTT-PTMO block copolymer. However, in the case of PTT-PTMO/SWCNTs a substantial rise up to 162 MPa has been noted. The increase in the modulus was accompanied by lower values of elongation at break for nanocomposites with graphene and with 0.1 wt% of SWCNTs. Only a slight increase in ϵ_b for PTT-PTMO/0.3 SWCNT to 639% was observed. An addition of the hybrid system has further increased the modulus to 149, 178 and 212 MPa, for 0.1 SWCNTs+0.3 G, 0.3 SWCNTs+0.1 GNPs and 0.5 SWCNTs+0.1 GNPs respectively. Hybrid nanocomposite with a concentration of 0.5 wt% of nanotubes and 0.1 wt%

of graphene reached a modulus value which is ca. 68% higher than the pristine elastomer. Thus, the tensile measurements revealed that the effect of hybrid nanofillers system is more pronounced on the tensile modulus. The noticeable increase in the tensile modulus reflects the reinforcement effect attained by the dispersion of the nanotubes and graphene platelets in PTT-PTMO matrix. Calorimetric studies for obtained PTT-PTMO/hybrid nanocomposites (Table 4) showed only minute differences in the polymer melt enthalpy and negligible increase in degree of crystallinity. Therefore, the improvement in the tensile properties at low nanofillers' loading observed herein, cannot be due to a change in crystallinity and is more likely caused by the presence of SWCNTs and graphene nanoplatelets next to PTT hard domains dispersed in PTMO-rich soft phase. Similar results have been also previously observed for PTT-PTMO nanocomposites with graphene oxide (GO) [24] and montmorillonite (MMT) [22].

Elongation at break, on the other hand, decreased significantly for PTT-PTMO/0.5 SWCNTs+0.1 GNPs. At the same time, a rise in the permanent set accom-

Table 4. Tensile properties of PTT-PTMO/SWCNTs+GNPs nanocomposites

Sample	E [MPa]	$\sigma(100\%)$ [MPa]	σ_y [MPa]	ϵ_y [%]	σ_b [MPa]	ϵ_b [%]
PTT-PTMO	118.3±1.5	12.7±0.1	13.6±0.2	44.8±0.9	20.3±0.7	625±12
PTT-PTMO/0.1 GNPs	123.0±1.3	12.8±0.1	13.4±0.2	50.4±1.3	20.3±0.1	594±12
PTT-PTMO/0.3 GNPs	131.7±4.1	13.1±0.1	13.7±0.1	49.6±0.1	19.8±0.2	594±14
PTT-PTMO/0.1 SWCNT+0.3 GNPs	149.2±2.7	13.6±0.1	14.0±0.1	49.8±0.8	19.2±0.3	634±29
PTT-PTMO/0.3 SWCNT+0.1 GNPs	178.3±6.9	13.9±0.1	14.4±0.1	48.1±1.1	20.4±0.2	642±21
PTT-PTMO/0.5 SWCNT+0.1 GNPs	212.2±6.5	14.1±0.1	14.6±0.9	47.6±1.2	18.5±1.2	542±59
PTT-PTMO/0.1 SWCNT	145.1±3.9	13.6±0.3	14.2±0.2	47.8±0.8	20.7±0.6	617±24
PTT-PTMO/0.3 SWCNT	162.5±2.5	13.7±0.1	14.1±0.1	49.7±0.5	19.9±0.2	639±13

E – tensile modulus; $\sigma(100\%)$ – stress at strain of 100%; σ_y , ϵ_y – yield stress and strain respectively, σ_b , ϵ_b – stress and strain at break respectively

Figure 8. Permanent set accompanying the 100% deformation as a function of total content of carbon nanofillers for nanocomposites based on PTT-PTMO

panying the 100% deformation was observed in a limited reversible deformation range. Analysis of the permanent set, created after a 100% deflection for the examined PTT-PTMO composites (Figure 8) proved that content of nanofillers in the amount of up to 0.6 wt% cause only a slight deterioration of elasticity as they cause just a few percent decrease in relaxation from 100% deflection. It can be said however, that nanofillers greatly impede the elasticity, because at 0.6 wt% content an average of the permanent set increased by 20%. The synergistic toughening mechanisms of a combination of SWCNTs and graphene has been observed for PTT-PTMO block copolymer.

4. Conclusions

The present research and experiments focused mainly on the preparation and characterization of polymer composites containing SWCNTs, GNPs and hybrid systems comprising of both SWCNTs/GNPs, in which PTT-PTMO constituted the matrix. The use of *in situ* synthesis allowed to obtain composites with a high degree of homogeneity, which is a key issue for further industrial applications. At the same time, the analysis of the properties of obtained materials showed a strong effect of the addition of carbon nanotubes and graphene nanoplatelets on their structure, physical transitions, thermal stability and mechanical strength. The presence of SWCNTs and GNPs in the polymer melt during cooling substantially speeds up the crystallization process as is evidenced by a shift of the crystallization peak to up to 45°C, which was recorded for PTT-PTMO/0.5 SWCNT+ 0.1 GNP hybrid nanocomposite. The introduction of carbon nanoparticles into the poly-

mer matrix did not have a significant effect on the thermal stability of obtained nanocomposites in an inert atmosphere. However, addition of SWCNTs and graphene nanoplatelets individually, as well as the mixture of both caused substantial enhancement of thermo-oxidative stability, shifting the beginning of the chemical decomposition temperature by 20–25°C. Remarkably, in the case of mechanical properties of presented nanocomposites a synergistic hybrid effect has been observed. The addition of carbon nanotubes together with graphene nanosheets caused an increase in strength of up to 68% for the highest concentration of nanofillers. Results of the experiments contained herein indicate a remarkable potential of the new group of materials, the polymer hybrid nanocomposites, which and might be of extreme importance for further development and possible industrial applications. Determination of the appropriate conditions for obtaining hybrid nanocomposites during the polymer matrix synthesis process is paramount in order to develop new technologies for their production on the pilot and industrial scale. Moreover, the observed positive hybrid effect in the case of segmented block copolymers will allow to lower the final price of the finished product (suitable selection of properties at the optimum price), which can be characterized by good thermal properties with, at the same time, improved mechanical properties.

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