Comparative study on the properties of poly(trimethylene terephthalate) based nanocomposites containing multi-walled carbon (MWCNT) and tungsten disulfide (INT-WS₂) nanotubes

S. Paszkiewicz¹*, A. Szymczyk², I. Janowska³, R. Jedrzejewski¹, A. Linares⁴, T. A. Ezquerra⁴, H.D. Wagner⁵, R. Tenne⁵, Z. Rosłaniec¹

¹West Pomeranian University of Technology, Institute of Material Science and Engineering, Piastow Av. 19, 70310 Szczecin, Poland
²West Pomeranian University of Technology, Institute of Physics, Piastow Av. 48, 70311 Szczecin, Poland
³Institute of Chemical and Processes for Energy, Environmental and Health (ICPEES), CNRS and University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
⁴Instituto de Estructura de la Materia, IEM-CSIC, Serrano 119-121, 28006 Madrid, Spain
⁵Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovot, Israel

*Corresponding author: spaszkiewicz@zut.edu.pl, tel.:+48 91 449 45 89; fax: +48 91 449 43 56

Abstract

Multi-walled carbon (MWCNT) and tungsten disulfide (INT-WS₂) nanotubes are materials with excellent mechanical properties, high electrical and thermal conductivity. These special properties make them excellent candidates for high strength and electrically conductive polymer nanocomposite applications. In this work, the possibility of the improvement of mechanical, thermal and electrical properties of poly(trimethylene terephthalate) (PTT) by the introduction of multi-walled carbon (MWCNT) and tungsten disulfide (INT-WS₂) nanotubes was investigated. The PTT nanocomposites with low loading of nanotubes were prepared by
in situ polymerization method. Analysis of the nanocomposites’ morphology carried out by SEM and TEM have confirmed that well-dispersed nanotubes in the PTT matrix were obtained at low loading (< 0.5 wt %). Thermal and thermo-oxidative stability of nanocomposites was not affected by the presence of nanotubes in PTT matrix. Loading with INT-WS₂ up to 0.5 wt % was insufficient to ensure electrical conductivity of PTT nanocomposite films. In the case of nanocomposites filled with MWCNT, it was found that nanotubes incorporation leads to increase of electrical conductivity of PTT films by 10 orders of magnitude, approaching a value of 10⁻³ S/cm at loading of 0.3 wt %. Tensile properties of amorphous and semicrystalline (annealed samples) nanocomposites were affected by the presence of nanotubes. Moreover, the increase in the brittleness of semicrystalline nanocomposites with the increase in MWCNT loading was observed, while the nanocomposites filled with INT-WS₂ were less brittle than neat PTT.

**Keywords:** poly(trimethylene terephthalate); multi-walled carbon nanotubes, tungsten disulphide nanotubes; in situ polymerization; electrical conductivity; mechanical properties

1. **Introduction**

Polymer nanocomposites (PNC) for over two decades represent a radical alternative to the conventional polymer composites and thus find wide applications in aerospace, automotive industry, packaging, electronics, biotechnology and many others. They offer the possibility of developing new class of materials with tailor-made structure-property relationship. These materials can be easily formed to near-final shape being lighter than conventional composites. Furthermore, depending on the type of nanofiller, they can exhibit outstanding combination of mechanical, thermal and barrier properties along with electrical and thermal conductivity. Research on nanocomposites based on aromatic polyesters, such as poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT) is still an open topic for many research groups. Among them, with regards to the advantageous features, poly(trimethylene
terephthalate) (PTT) manifests itself as an interesting candidate to be examined as a potential matrix for nanocomposites with tailor-made performance. Due to the odd number of methylene glycol groups, PTT exhibits unique crystal structure and has an intermediate crystallization rate [1] compared to slowly crystallization of PET and relatively fast crystallization of PBT and can be processed by injection moulding, film casting and fiber spinning [2]. PTT exhibits an outstanding combination of strength and modulus, high heat deflection temperature, impact strength, suitable crystallization rate, while preserving dimensional stability, electrical insulation and chemical resistance [3] [4] [5]. In comparison to PET and PBT, PTT has good potentials at serving both processing and property requirements for applications where the choice of neat polymer is of primary significance. It is also of great importance to notice, that the product of DuPont™ Sorona® EP PTT contains 20% to 37% renewable material from non-food biomass [6]. Moreover, DuPont™ Sorona® EP PTT delivers moulding characteristics comparable to high-performance PBT, including good strength and stiffness and consequently good dimensional stability and finishing qualities, making it an excellent choice for uses from automotive parts to furniture and mobile phone housings, and both industrial and consumer products. Additionally, PTT may be further reinforced with surface-modified fillers to manufacture high-strength composites and can be nanoprocessed by laser techniques [7].

One can find carbon nanotubes (CNT) as interesting candidates with potentially unique properties [8] [9] [10]. They exhibit exceptionally high stiffness and strength [11] [12] [13], a diameter dependent specific surface area of up to 1300 m²/g [14], as well as an aspect ratio in the range of several thousands. Accordingly to their graphitic structure, CNT possess high thermal and electrical conductivity and can behave like semi-conducting or metal materials, depending on the chiral angle of the graphene sheet. The combination of the aforementioned properties makes CNT highly desirable candidates to improve the properties of polymers.
Besides, the development of CNT/polymer nanocomposites enables to obtain multi-functional materials, e.g., conductive polymers with improved mechanical and thermal properties.

Another highly promising new systems are polymer nanocomposites containing inorganic fullerene-like nanoparticles (IFN) and inorganic nanotubes (INT) [15] [16] [17]. The synthesis of layered metal dichalcogenide, i.e. tungsten disulphide (WS$_2$) and molybdenum disulphide (MoS$_2$) nanophases was first reported by R. Tenne et al. [18] [19]. Hence, the methods and technology of the synthesis process have been improved up to the point where nearly pure (>99%) materials are already accessible at an industrial scale [20]. The process does not require any catalysts, while the precursors (tungsten oxide and H$_2$S or sulphur) are relatively inexpensive. Additionally, great attention has been paid to these layered metal dichalcogenide nanophases due to their surprising properties such as high impact resistance and superior tribological behaviour, which wind down a wide range of opportunities for applications in rechargeable batteries, catalysis, solar cells, drug delivery and electronics and, increasingly, the field of polymer nanocomposites [15] [16] [17] [21]. WS$_2$ nanotubes (INT-WS$_2$) have been used as reinforcing agents to improve the mechanical and tribological properties of epoxy composites [22], electrospun poly(methyl methacrylate) fibers [17], poly(propylene fumarate) (PPF) [23] nanocomposites, as well as nucleating agents, for instance of poly(3-hydroxybutyrate) (PHB) nanocomposites [24]. However, as far as we know no one has studied how the addition of INT-WS$_2$ affects the physical properties and crystallization behaviour of semicrystalline thermoplastic polyesters, more particularly PTT, which is partially obtained by our research group from renewable raw materials (bio-based glycol).

The present study deals with preparation and characterization of PTT based nanocomposites containing two types of nanotubes. We produced nanocomposites via in situ polymerization method using identical processing conditions, by varying nanotubes-type and
content. All results have been compared to the ones obtained for reference material, i.e. neat PTT. Keeping most variables constant, the aim of this study was to compare the influence of two different types of multi-walled nanotubes, carbon (MWCNT) and tungsten disulfide (INT-WS₂), on the mechanical, thermal and electrical properties and to evaluate their potential in obtaining multifunctional material based on bio polyester matrix. Furthermore, structural and morphological characterization of the samples gave us an explicit insight into the sample behavior and allows us to understand the properties’ improvement.

2. Experimental part

2.1. Materials

2.1.1. Preparation of polymer nanocomposites

Dimethyl terephthalate (DMT) (Sigma-Aldrich), Susterra®1,3-propanediol (bio-PDO™, DuPont Tate & Lyle BioProducts, Loudon USA), catalyst: tetrabutyl orthotitanate (Ti(OBu)₄, Fluka) and antioxidant: Irganox 1010 (Ciba-Geigy, Basel, Switzerland) were used to prepare both, neat PTT and PTT-based nanocomposites via in situ polymerization, following the same procedure as described elsewhere [25] [26] [27] [28] [29]. Briefly, appropriate amounts of nanotubes were dispersed in 200 ml of bio-PDO using ultra-high speed stirrer (Ultra-Turax T25) for 15 min, and subsequently an ultrasonicator (Homogenizer HD 2200, Sonoplus, with frequency of 20 kHz and power 200 W) for 15 min. The prepared dispersion of carbon nanofillers in bio-PDO was introduced into the reaction mixture. The polymerization was carried out in a 1 dm³ high pressure reactor (Autoclave Engineers Pennsylvania, USA) in two stages: transesterification under a constant flow of nitrogen in temperature range of 165 °C, in the presence of catalyst for ca. two hour. When the amount of methanol was at about 90 % of the stoichiometric calculated value, the second stage begins. Then the stabilizer and second portion of catalyst were added along with the slow increase of the temperature of the reaction up to 265 °C and decrease of the pressure. At this stage, the stirring torque change was
monitored in order to estimate the melt viscosity of the product. All syntheses were finished when viscosity of the melt reached the same established value at 265°C. The molten nanocomposite was extruded from reactor into water bath, then granulated and dried before processing. The same conditions were applied to prepare the reference sample, i.e. the neat PTT.

2.1.2. Multi-walled nanotubes

(a) Multi-walled carbon nanotubes (MWCNT)

The MWCNT were purchased from Nanocyl S.A. (Belgium). According to provider’s data sheet, MWCNT exhibit the average length of 1.5 μm and average diameter of 9.5 nm. Moreover, they were distinguished by the carbon purity of 90 %, transition metal oxide of < 1 % and the surface area of 250-300 m²/g.

(b) Inorganic WS₂ nanotubes (INT-WS₂)

INT-WS₂ nanotubes with the length of 2–20 mm, diameter of 40–120 nm and an aspect ratio of up to 500 were provided by prof. R. Tenne group. These nanotubes were characterized in detail in [30] and the synthesis process was described in [31]. Briefly, part of the nanotubes had open tip, while others were close-ended. The INT-WS₂ nanotubes preferably had large amount of layers (10–40) and relatively small core. It was shown that the INT-WS₂ nanotubes generally exhibit a high degree of structural perfection and uniformity with respect to the stacking order and chirality. However some structural defects, like local expansion of the interlayer spacing (c-axis); non-planar triple layers, and dislocations were observed mainly within the outer walls of the WS₂ nanotubes.

2.2. Testing samples preparation

Dumb-bell shape samples of both series nanocomposites for DMTA and tensile tests were obtained by injection moulding at a pressure of around 50 MPa and at temperature of 250 °C. Before tests, samples were annealed at 80 °C for 4 hours. However, the tensile tests
were also conducted on the amorphous samples, for comparison purpose. The structure of both, amorphous and semicrystalline specimens (annealed) was confirmed by WAXS analysis.

Amorphous films of about 200±10 \( \mu \)m thickness for electrical conductivity measurements were prepared by press moulding using Collin P 200E moulding press at 245°C and 15 bar for 2 min and subsequently quenched in ice water (250°C/min). In the case of dielectric measurements, the obtained films were covered by circular gold electrodes with 20 mm in diameter, while the specimens for volume resistivity with the diameter of 65 mm and were covered with silver paste before the test.

2.3. Characterization methods

The dispersion state of MWCNT and INT-WS\(_2\) in the PTT nanocomposites was investigated using scanning electron microscopy (SEM, JEOL JSM 6100). Cryogenically fracture surfaces of the samples, subsequently vacuum coated with a thin gold film, were used for the analysis. The dispersion of nanotubes in the polymer matrix analysis was further expanded upon transmission electron microscopy (TEM) using JEOL JEM-2100 microscope with 120 kV accelerating voltage. Microtomed sample sections with 100 nm thickness were used for the observation.

The basic physicochemical properties along with rheological characterization of the PTT based nanocomposites were characterized via intrinsic viscosity, melt viscosity and melt flow index measurements. The intrinsic viscosity \([\eta]\) of the samples was determined at 30 °C in the mixture of phenol/1,1,2,2-tetrachloroethane (60/40 by weight) following the same procedure as described elsewhere [28]. Employing Mark-Houwink equation that relates the limiting viscosity number with molecular weight, the viscosity average molecular mass (M\(\nu\)) has been calculated using the formula: \([\eta] = K \cdot M_\nu^\alpha\), where \(K\) and \(\alpha\) are specific constants for a given solute-solvent-temperature system. In our case, for PTT/phenol/1,1,2,2-
tetrachloroethane (60/40) mixture/30 °C, the following constants: K=5.36·10^{-4} \text{ dl/g} and α=0.69 [32] were applied. The melt flow index (MFI) of the obtained nanocomposites was determined using a melt flow tester (CEAST, Italy) according to ISO 1133 standard, under 21.18 N load, orifice diameter of 2.095 mm and at temperature of 230°C. All samples were dried in a vacuum dryer at 60°C for 24 hours before the measurement. The melt viscosity ($\eta^M$) of the specimens was measured using ARES rheometer (Rheometric Scientific Inc., USA). The measurements were performed at 240 °C in the frequency range of 0.1-50 Hz, in a parallel-plate fixture (diameter = 25 mm) with a gap distance of 2 mm.

The calorimetric measurements were performed by means of differential scanning calorimetry (DSC) using a differential calorimeter Q-100 (TA Instruments, USA, 2004) following the same procedure as described in [25]. Therefore, the specimens of about 10 mg weight were subjected to the cycle of heating-cooling- 2nd heating in the temperature range of 25 to 250 °C at the heating rate of 10 °C/min. The values of temperatures of physical transitions, i.e. glass-transition temperature ($T_g$), crystallization temperature ($T_c$) and melting temperature ($T_m$) were designated. The $T_g$ was taken as the midpoint of the change in heat capacity. Additionally, the degree of crystallinity was calculated using the following equation:

$$X_c(\%) = \frac{\Delta H_m^c}{\Delta H_m^p},$$

where $\Delta H_m^c$ is the ideal melting enthalpy of 100 % crystalline sample, for PTT equals to 146 J/g [4] and $\Delta H_m$ is derived from melting peak area on DSC thermograms.

The dynamic mechanical thermal analysis (DMTA) was carried out using a Polymer Laboratories MK II device working in a bending mode at a frequency of 1 Hz in a temperature range from –100 °C to the polymer melt temperature and heating rate of 3 °C/min. The values of storage modulus ($E'$) at 25 °C and 1 Hz and values of temperature of α-relaxation ($T_\alpha$) corresponding to the glass transition determined from the maximum of loss modulus ($E''$) and tan δ curves were designated.
In order to study the electrical properties two complementary measurements were performed. Firstly, the complex permittivity \( \varepsilon^* = \varepsilon' - i\varepsilon'' \) (where \( \varepsilon' \) represents the permittivity and \( \varepsilon'' \) the dielectric loss) was measured as a function of frequency \( (10^{-2} \text{ Hz} < F < 10^7 \text{ Hz}, \text{where} \ F \text{ is the frequency of the applied electric field}) \) using a Novocontrol broadband dielectric spectrometer. The measurements were carried out at room temperature and the electrical conductivity was derived by \( \sigma(F) = \varepsilon_0 \Re \varepsilon'' \) where \( \varepsilon_0 \) is the vacuum permittivity. Secondly, the volume resistivity measurements were performed using Electrometer 6517A (Keithley Instruments, Inc.) device together with a set of Keithley 8009. Resistivity measurement was performed according to the standards: IEC 93:1980, PN – 88/E-04405 and ASTM D 257-99.

The tensile tests were carried out using Instron 1112 tensile testing machine at room temperature. Tensile examinations were measured on two series of dumb-bell samples, amorphous and semicrystalline (annealed) at a constant crosshead speed of 5 mm/min. Young’s modulus, yield strength and strain, stress and elongation at break, were calculated from the stress–strain curves. Ten specimens for each kind of materials were studied according to DIN 53455 standard, and the average value calculated.

The structure of amorphous and semicrystalline (annealed) dumb-bell shape samples was confirmed by wide angle X-ray scattering (WAXS) measurements that were performed at Seifert XRD 3000 0/0 diffractometer using Ni-filtered Cu K\( \alpha \) radiation (\( \lambda = 0.154 \text{ nm} \)) at a scanning speed of 0.02 \( \text{o} \text{/s} \).

Thermal and thermo-oxidative stability of the obtained 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 (argon) and oxidizing atmosphere i.e. dry, synthetic air \( (N_2 : O_2 = 80 : 20 \text{ vol. %}) \). The study was conducted in the temperature range of 20 – 700 \( \text{ C} \) at the heating rate of 10 \( \text{o} \text{/C/min} \). Measurements were performed in accordance with the principles of PN-EN ISO 11358:2004.
3. Results and discussion

3.1. Morphological characterization

PTT-based nanocomposites were prepared via \textit{in situ} polymerization method preceded by an additional stage of dispersion preparation. The high shear forces along with alternately applied ultrasounds introduced by high-speed mechanical stirring and sonication were sufficient to disperse the MWCNT and INT-WS$_2$ uniformly in PTT matrix (Fig. 1). Despite the fact that control over the dispersion degree of nanotubes in a polymer matrix is difficult due to strong intramolecular forces that exist between nanoparticles, we were able to obtain well-dispersed both types of nanotubes in the whole volume of polymer matrix. Only in the case of PTT/0.3MWCNT (Fig. 1b) several areas with higher concentration of carbon nanotubes were visible. However, generally MWCNT at both concentration were well-distributed in the nanocomposite and individual nanotubes were seen. On the other hand, in the case of INT-WS$_2$, even at the concentration of 0.5 wt % of nanotubes a proper dispersion was observed. The INT-WS$_2$ do not require exfoliation or modification in order to obtain nanocomposites with homogenously distributed nanoparticles, thus avoiding the complexity and processing costs associated with such treatments [33]. In turn, the functionalization of CNT is an effective, common way to prevent nanotube aggregation helping better dispersion and stabilization of the CNT within a polymer matrix [34]. However, herein the dispersion of non-functionalized MWCNT was comparable to the dispersion level obtained previously in [28] for PTT/MWCNT-COOH nanocomposites.
Presently, TEM is the only method to attain qualitative information concerning a distribution of nanoparticles in a polymer matrix. Therefore, we investigated the obtained composites by TEM. In Fig. 2a-d representative TEM micrographs of the achieved dispersion for the investigated both types of multi-walled nanotubes at the highest concentration, i.e. 0.3
and 0.5 wt % for MWCNT (Fig. 2 a, b) and INT-WS2 (Fig. 2 c, d), respectively, are shown. As it can be seen both types of nanoparticles exhibit a high degree of dispersion in the PTT matrix. This clearly indicates that in situ polymerization allows obtaining proper dispersion of organic and inorganic nanoparticles in the whole volume of polymer matrix.

Fig. 2 TEM micrographs of PTT/0.3MWCNT (a, b) and PTT/0.5INT-WS2 (c, d) nanocomposites.

3.2 Physicochemical properties

For both series of nanocomposites the study on their physicochemical properties along with rheological behaviour was conducted. Table 1 summarizes the collected data. The average viscosity molecular masses (Mₐ), determined from intrinsic viscosity [η] range from 38 200, 45 400 and 24 500 g/mol for neat PTT, PTT/0.1MWCNT and PTT/0.3MWCNT, respectively. Comparing the reaction of polymer chain growth for neat polymer and CNT-
filled nanocomposite a decrease of time of the second stage of the polymerization was observed. Especially in the case of PTT/0.3MWCNT nanocomposite the reactive mixture reached high melt viscosity in almost half of the time if compared to reference sample (PTT). Therefore, the strong decrease in the intrinsic viscosity value was observed for this concentration of MWCNT. Probably, it was due to the fact that CNT on polymer melt show typical thixotropic behaviour [35] [36], so when the stirring was stopped (before extrusion from the reactor), the nanocomposite melt almost completely covered the stirrer and it was almost impossible to extruded it from the reactor. Therefore, the highest content of CNT achieved in the prepared nanocomposites was 0.3 wt % and thus introduction of higher content of MWCNT was not possible because the melt does not flow. Similar behaviour was observed previously for PTT/MWCNT-COOH nanocomposites [28]. However, the functionalization of MWCNT allows obtaining nanocomposites with 0.5 wt % of nanotubes. On the other hand, INT-WS₂ nanotubes affect the reaction mixture in different manner. The values of intrinsic viscosity and the average viscosity molecular mass, for the series of nanocomposites were comparable to one another and higher than those obtained for neat PTT. This indicates the INT-WS₂ affect the rheological behaviour of PTT matrix in completely different way in comparison of MWCNT. Measurements of the melt viscosity (\(\eta^M\)) (Fig. 3) and MFI confirmed that almost all nanocomposites exhibit higher values of viscosity than the neat PTT. Higher melt viscosity of nanocomposites if compared to the neat PTT suggest the existence of interconnected or network structures formed as a result of nanotube-nanotubes and nanotubes-polymer interactions (Fig. 3, Table 1). The melt viscosity decrement observed with increasing INT-WS₂ nanotubes content can be due to the lubricating effect of these nanotubes. The addition of inorganic nanofillers to thermoplastic polymers generally leads to an improvement in the tribological properties. Naffakh et al. [33] explained that the improved tribological properties of the poly(3-hydroxybutyrate) (PHB) films with INT-WS₂ can be
attributed to strengthening of the film by the inorganic nanotubes and their possible exfoliation during friction and wear tests, which provided a lubricating layer on the rubbed surfaces. Similar observations were made for PEEK/INT-WS₂ nanotubes obtained by traditional melt processing [37].

Table 1 Characteristics of PTT-based nanocomposites containing MWCNT and INT-WS₂ nanotubes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[η] dl/g</th>
<th>Mᵥ x10⁴ g/mol</th>
<th>MFI g/10 min</th>
<th>η⁰ M Pa·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>0.779</td>
<td>3.82</td>
<td>6.33</td>
<td>59.36±0.31</td>
</tr>
<tr>
<td>PTT/0.1MWCNT</td>
<td>0.876</td>
<td>4.54</td>
<td>8.07</td>
<td>108.56±1.21</td>
</tr>
<tr>
<td>PTT/0.3MWCNT</td>
<td>0.572</td>
<td>2.45</td>
<td>15.92</td>
<td>157.34±0.62</td>
</tr>
<tr>
<td>PTT/0.1INT-WS₂</td>
<td>0.851</td>
<td>4.35</td>
<td>10.42</td>
<td>175.43±1.20</td>
</tr>
<tr>
<td>PTT/0.3INT-WS₂</td>
<td>0.783</td>
<td>3.85</td>
<td>11.55</td>
<td>169.47±1.51</td>
</tr>
<tr>
<td>PTT/0.5INT-WS₂</td>
<td>0.834</td>
<td>4.22</td>
<td>6.33</td>
<td>116.59±0.80</td>
</tr>
</tbody>
</table>

[η] - intrinsic viscosity; Mᵥ, viscosity average molecular weight, MFI – melt flow index at 235 °C; η⁰ M – melt viscosity of polymer at 240°C and frequency of 1 Hz

![Melt viscosity as a function of frequency](image)

Fig. 3. Melt viscosity as a function of frequency of the prepared nanocomposites.

3.3 Structural characterization of PTT nanocomposites

The incorporation of organic and inorganic nanotubes into polymer systems may cause an increase in crystallization temperature, enhancement in nucleation density and in some cases
reduction of crystallization time [38] [39] [40] [41] [42] [43] [24] [44]. The influence of the addition of two types of multi-walled nanotubes in PTT matrix on the melting and crystallization behaviour was studied by DSC. Table 2 summarizes the data obtained from DSC scans during cooling and 2nd heating and data are presented in Fig. 4 a and b. One can find that the addition of both, organic and inorganic nanotubes didn’t affect the glass transition temperature ($T_g$) of PTT matrix. Nanocomposites exhibit also only negligible changes in $\Delta C_p$ at $T_g$ if compared to neat PTT ($\approx 0.02$ J/g·°C). It might suggest that in this case the MWCNT and INT-WS$_2$ don’t affect the chain mobility and don’t cause the formation of shorter cooperatively rearranging (CRR) segments [45]. Previously in [28], it was observed that COOH functionalized MWCNT caused a slight decrease (1-2 °C) in the glass transition temperature. Herein, the melting temperature was not affected by the presence of MWCNT and INT-WS$_2$ nanotubes, while, a slight increase in the degree of crystallinity (1.1-3.6 %) was observed along with the addition of nanoparticles. A seven-degree increase in $T_c$ was observed for PTT/0.1MWCNT, whereas for PTT/0.3MWCNT no effect was seen. On the other hand, along with the increasing content of INT-WS$_2$ an increase in $T_c$ was observed. Moreover, almost all nanocomposites exhibited lower values of degree of supercooling in comparison to neat PTT. Only in the case of PTT/0.3MWCNT no effect was seen. Generally, organic and inorganic nanotubes affect the nucleation of wide range of polymer matrices, due to the formation of interfacial connections between the filler’s surface and polymer’s chain. Polymers’ crystallization results from the alignment of mobile polymer chains. Such interactions that may be physical adsorption or chemical bonding, or a combination of both, restrict the mobility of the polymer chains. Herein, the introduction of MWCNT and INT-WS$_2$ caused no significant effect on the crystallization behaviour and even a slight decrease in degree of supercooling was seen. This can result from the low aspect ratio of tubes or their inconsiderable/week interactions with PTT chain, especially in the case of MWCNT. The
topological confinement of macromolecular chains at the interfaces (nanotubes-polymer chain) and strong interactions between them can increase the degree of supercooling. Previously [28] functionalized MWCNT caused a shift of $T_c$ of about 2-4 °C toward lower temperatures. Xu et al. [43] reported that for PTT/MWCNT nanocomposites the melting temperature and degree of crystallinity were not affected by the presence of MWCNT. However, an increase of crystallization temperature and a decrease of the degree of supercooling were observed with increasing nanotube concentration.

Table 2. Thermal properties of PTT and PTT/MWCNT and PTT/INT-WS$_2$ nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ [°C]</th>
<th>$\Delta C_p$ [J/g·°C]</th>
<th>$T_m$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
<th>$T_c$ [°C]</th>
<th>$\Delta H_c$ [J/g]</th>
<th>$\Delta T$ [°C]</th>
<th>$\Delta x_c$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>53</td>
<td>0.17</td>
<td>229</td>
<td>44.0</td>
<td>171</td>
<td>46.7</td>
<td>58</td>
<td>30.1</td>
</tr>
<tr>
<td>PTT/0.1 MWCNT</td>
<td>53</td>
<td>0.16</td>
<td>228</td>
<td>46.9</td>
<td>177</td>
<td>50.1</td>
<td>51</td>
<td>32.1</td>
</tr>
<tr>
<td>PTT/0.3 MWCNT</td>
<td>53</td>
<td>0.16</td>
<td>228</td>
<td>49.3</td>
<td>170</td>
<td>53.3</td>
<td>58</td>
<td>33.7</td>
</tr>
<tr>
<td>PTT/0.1 INT-WS$_2$</td>
<td>53</td>
<td>0.15</td>
<td>228</td>
<td>46.8</td>
<td>174</td>
<td>51.7</td>
<td>54</td>
<td>32.1</td>
</tr>
<tr>
<td>PTT/0.3 INT-WS$_2$</td>
<td>53</td>
<td>0.17</td>
<td>228</td>
<td>45.2</td>
<td>178</td>
<td>48.8</td>
<td>50</td>
<td>31.2</td>
</tr>
<tr>
<td>PTT/0.5 INT-WS$_2$</td>
<td>53</td>
<td>0.16</td>
<td>228</td>
<td>46.7</td>
<td>177</td>
<td>49.8</td>
<td>51</td>
<td>32.1</td>
</tr>
</tbody>
</table>

$T_g$ - glass transition temperature; $\Delta C_p$ - change of heat capacity; $T_m$ - melting temperature; $T_c$ - crystallization temperature $\Delta H_m, \Delta H_c$ - enthalpy of melting and crystallization; $\Delta T = T_m - T_c$ - degree of supercooling; $x_c$ - mass fraction of crystallinity determined from DSC.

Fig. 4 DSC thermograms obtained during cooling and second heating for the series of nanocomposites containing: a) MWCNT and b) INT-WS$_2$ nanotubes.
DMTA analysis for the series of PTT based nanocomposites containing MWCNT and INT-WS<sub>2</sub> was carried out. The storage and loss modulus and the tan δ, for neat PTT matrix and nanocomposites filled with MWCNT and INT-WS<sub>2</sub> nanotubes are plotted as a function of the temperature in Figure 5. One can observe that magnitudes of storage modulus and location of the loss peak change more pronounced for nanocomposites with MWCNT. No significant changes are observed for nanocomposites with INT-WS<sub>2</sub>. The incorporation of MWCNT into PTT matrix causes an effect on the storage modulus values in the glassy region. In order to better illustrate the changes of the E' modulus at 25 °C the data were summarized in Table 3. All nanocomposites exhibit lower or comparable values of storage modulus if compared to neat PTT. The lowest value (decrease of about 17 %) was observed for the sample with 0.1 wt % of MWCNT. In our previous work with PTT/MWCNT-COOH [28] nanocomposites an increase of E' at 25 °C was observed (even of 55 % for PTT/0.3MWCNT-COOH), which was ascribed to the cohesive interactions between the large surface area of nanotubes and PTT. Herein we can infer that such interactions do not occur in the systems under study. For both series of nanocomposites, on loss modulus (E''') (Fig. 5 a and c) and tan δ curves (Fig. 5 b and d), two relaxation peaks α and β are seen. The α-relaxation peak corresponds to the glass transition of amorphous PTT. Whereas, the β-relaxation peak, observed at about −75 °C, is attributed to the reorientation of the hydroxyl groups and the local movements of carboxyl groups in the amorphous phase. Tan δ is sensitive to any molecular movements in the polymer chain. Thus, in nanocomposites, from the changes in tan δ one can estimate the interactions’ alterations in the interphase between polymer matrix and nanofiller. Along with an increase in MWCNT concentration the T<sub>α</sub> is shifted on tan δ curves from 85°C for neat PTT to 93 °C for PTT/0.3MWCNT nanocomposite. However, the addition of INT-WS<sub>2</sub> caused no effect on the temperature of α-relaxation. Similar observations were made for the changes in temperature of α-relaxation corresponding the glass transition determined from maximum of loss modulus.
(E). For PTT/MWCNT nanocomposites one can presume that these changes in T_g (shown by shift in the tan δ maximum) can be generated by the restriction of the polymer segment mobility, due to the presence of the nanoparticles which act as anchors. Moreover, for nanocomposites containing MWCNT an increase of the intensity of β-relaxation peak is observed (Fig. 5b). This peak is strictly related to the glass transition temperature and its increase may indicate for partial activation of PTT chains by the presence of MWCNT. This was previously observed in [28] for PTT/MWCNT-COOH nanocomposites. Thus, on the basis of the aforementioned observations and literature data, similarly as in the case of crystallization behaviour, both the preparation method of nanocomposites and the type of nanoparticles and polymer matrix may strongly determine the structural characterization of nanocomposites.

Fig. 5 The storage and loss modulus (a, c) and tan δ (b, d) as a function of temperature for neat PTT and PTT based nanocomposites.
Table 3 DMTA properties for neat PTT and PTT based nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>E' at 25°C [MPa]</th>
<th>Tα (E’') [°C]</th>
<th>Tα (tan δ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>3265</td>
<td>70</td>
<td>85</td>
</tr>
<tr>
<td>PTT/0.1 MWCNT</td>
<td>2741</td>
<td>75</td>
<td>88</td>
</tr>
<tr>
<td>PTT/0.3MWCNT</td>
<td>3043</td>
<td>79</td>
<td>93</td>
</tr>
<tr>
<td>PTT/ 0.1INT-WS2</td>
<td>3022</td>
<td>71</td>
<td>86</td>
</tr>
<tr>
<td>PTT/0.3INT-WS2</td>
<td>3113</td>
<td>73</td>
<td>86</td>
</tr>
<tr>
<td>PTT/0.5INT-WS2</td>
<td>2953</td>
<td>73</td>
<td>85</td>
</tr>
</tbody>
</table>

E' – storage modulus at 25°C and 1 Hz; Tα – temperature of α-relaxation corresponding the glass transition determined from maximum of loss modulus (E’’). 4.

4. Electrical conductivity of PTT based nanocomposites

Figure 6 presents the experimentally determined ac electrical conductivity (σ) of PTT/MWCNT and PTT/INT-WS2 nanocomposites as a function of frequency. PTT exhibits a typical insulating behaviour with conductivity of 10⁻¹⁴ S/cm (at 0.1 Hz), but by the addition of MWCNT the conductivity of nanocomposites increases by 10 orders of magnitude, approaching a value of 10⁻³ S/cm for PTT/0.3 MWCNT. The percolation threshold, a critical volume/weight fraction when conducting phase is reached, for PTT/MWCNT is below 0.1 wt % of nanotubes’ concentration. In turn, the series of nanocomposites containing INT-WS₂ exhibit a purely insulating behaviour, as indicated by the frequency-dependent increase in conductivity with a slope of unity on the log-log plot of conductivity against the frequency. In our former paper [28] the PTT/MWCNT-COOH nanocomposites at concentration below 0.2 vol % (0.4 wt %) exhibited strong frequency dependence of the conductivity. However, at loadings in excess of 0.262 vol % (experimental percolation threshold (PT)), the nanocomposites exhibited a conductive behaviour which was nearly independent of frequency. On the other hand, the critical volume percentage of nanotubes was predicted to be 0.434 vol % (0.657 wt %), which was about one half higher than of the experimental value.
This fact was attributed to the well-dispersion of short-thin MWCNTs in PTT matrix, because the presence of aggregates usually increases the conductivity percolation threshold. Since, the MWCNT which were used in this study exhibited similar characteristics (diameter and length) one can assume that proper dispersion of MWCNT allows obtaining such a low percolation threshold. Moreover, lack of functionalized groups on their surfaces enabled to reduce the PT, since they act as obstacles for current flow. In the case of PTT/INT-WS₂ nanocomposites, there is still no study on the improvement of electrical conductivity of thermoplastic polyesters with inorganic tungsten disulphide nanotubes. There are some studies on applying WS₂ in transistors [46] and solar cells [47], thus one can conclude that the introduction of INT-WS₂ might allow obtaining electrically conductive polymer nanocomposites. However, herein the concentration of 0.5 wt % of inorganic nanotubes was not high enough to create the conductive paths.

![Figure 6](image.png)

**Fig. 6** Broadband electrical conductivity as function of frequency at room temperature for neat PTT and PTT-based nanocomposites.

Additionally, for the whole series of nanocomposites dc volume electrical conductivity measurements were conducted to confirm the observations on ac electrical conductivity. It is
clearly visible that the observations from both experiments carried out by two different methods and for samples that differ in shape coincide with one another.

**Table 4 Volume resistivity of synthesized nanocomposites**

<table>
<thead>
<tr>
<th>Sample</th>
<th>dc volume electrical conductivity [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Voltage U=1V</td>
</tr>
<tr>
<td>PTT</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.1MWCNT</td>
<td>4.2E-11</td>
</tr>
<tr>
<td>PTT/0.3MWCNT</td>
<td>13.2E-9</td>
</tr>
<tr>
<td>PTT/0.1INT-WS2</td>
<td>--</td>
</tr>
<tr>
<td>PTT/0.3INT-WS2</td>
<td>--</td>
</tr>
<tr>
<td>PTT/0.5INT-WS2</td>
<td>--</td>
</tr>
</tbody>
</table>

5. **Mechanical properties of PTT/MWCNT and PTT/INT-WS₂ nanocomposites**

The potential reinforcement of the organic and inorganic nanotubes can only be acquired if an effective load transfer from the surrounding polymer matrix into the nanotube and inversely is possible. Thus, good impregnation with the polymer matrix along with strong interfacial adhesion needs to be ensured. Due to the fact that a stress transfer can only occur via the outermost layer of a nanotube, it can be concluded that SWCNT can act as potentially greatest reinforcing agents in composites. However, the larger the provided interface, the more crucial the dispersion conditions, resulting in disruption of the impregnation [48]. Thus multi-walled nanotubes with smaller specific surface area might provide better dispersibility.

The tensile properties of PTT-based nanocomposites are summarized in Tables 5 and 6, for amorphous and semicrystalline (annealed) dumb-bell shape samples, respectively. The representative stress-strain curves are presented in Fig. 7. In the case of amorphous samples, the addition of both types of nanotubes, except the sample containing 0.1 wt% of INT-WS₂, caused an increase in the value of Young’s modulus. The addition of both types of nanotubes
caused a decrease in the value of yield stress. The lowest value of \( \sigma_y \) was noticed for PTT/0.3MWCNT. However, at this concentration of nanotubes the lowest value of molecular mass was obtained. The values of yield strain decrease along with the increasing concentration of MWCNT. On the other hand, for INT-WS\(_2\) a slight increase was visible for smaller concentration of nanotubes (0.1 wt %), while for PTT/0.5INT-WS\(_2\) a decrease was noticed. Moreover, for almost all nanocomposites a distinctive increase in stress at break was observed, even for over 400 % for PTT/0.5INT-WS\(_2\). Only the addition of 0.1 wt % of INT-WS\(_2\) caused a decrease in \( \sigma_b \). The values of elongation at break are almost twice higher for the lowest concentration of MWCNT (0.1 wt %) as well as for 0.3 and 0.5 wt % of INT-WS\(_2\). In first case, this might be probably due to strong stiffening effect of organic nanotubes on the mechanical properties of PTT matrix, which was also confirmed by DMTA analysis, where MWCNT at the concentration of 0.3 wt % cause the shift of \( \alpha \)-relaxation peak toward higher temperature thus restricting the polymer segment mobility. In the case of INT-WS\(_2\) nanotubes, the increase in the value of elongation at break along with the increasing concentration (from 0.3 to 0.5 wt %) might result from the lubricating properties of INT-WS\(_2\) which were described above. The annealing process stabilized the structure of dumb-bell shape samples and at the same time the stress-strain characteristics change significantly. Herein, the nanocomposites containing 0.1 wt % of MWCNTs and 0.3 wt % of INT-WS\(_2\) exhibited higher values of Young’s modulus when compared to that of neat semicrystalline PTT, while for nanocomposites containing 0.1 and 0.5 wt % of INT-WS\(_2\) and 0.3 wt % of MWCNT the lowest values of modulus were found. In our previous paper [28], one could observe that along with an increasing content of MWCNT-COOH from 0.05 to 0.3 wt %, tensile strength and Young’s modulus of nanocomposites increased. However, further addition of MWCNT (0.4 – 0.5 wt %) lowered the tensile strength and Young’s modulus, but their values were still comparable or higher (modulus) to neat PTT. The changes of yield stress and strain are
comparable to those obtained for amorphous samples. It is worth mentioning that in the case of PTT/0.3MWCNT (an) sample the strong decrease in the values of stress and elongation at break were observed. The calculated value of brittleness (B, Table 6) of this nanocomposite showed that this sample was very brittle and underwent destroying when placed in the holders of the tensile testing machine. This indicates the strong influence of MWCNT (especially at higher content) on the structure and properties of PTT based nanocomposites. An increase in the brittleness of the nanocomposites (Table 6) with the increasing loading of MWCNT was observed, whereas the nanocomposites filled with INT-WS2 exhibited the reduction of brittleness if compared to neat PTT. Additionally, the incorporation of INT-WS2 nanotubes induces an increase in both stress and elongation at break. While the values of stress at break for INT-WS2 nanocomposites were comparable to neat PTT, so the values of elongation at break increased by almost 35 % for 0.1 wt % of inorganic nanotubes. This evidently confirms the lubricating properties of INT-WS2 nanotubes in polymer matrix that affect both rheological and tensile properties on the nanocomposites and decrease the viscosity of the matrix during the melt-blending process, thus promoting a more uniform HA distribution. Moreover, INT–WS2 possess excellent mechanical properties such as a very high Young's modulus in the range of 150–170 GPa and strength of 16 GPa [49] hence a small amount of these rigid and crystalline nanostructures can strongly improve the mechanical performance of the binary composites.

### Table 5 Tensile properties of amorphous PTT/MWCNT and PTT/INT-WS2 nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (GPa)</th>
<th>σy (MPa)</th>
<th>εy (%)</th>
<th>σb (MPa)</th>
<th>εb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>2.09±0.04</td>
<td>58.90±2.62</td>
<td>5.79±0.51</td>
<td>12.10±2.11</td>
<td>189.8±11.2</td>
</tr>
<tr>
<td>PTT/0.1MWCNT</td>
<td>2.20±0.06</td>
<td>50.19±1.80</td>
<td>5.57±0.28</td>
<td>37.00±2.70</td>
<td>362.6±28.1</td>
</tr>
<tr>
<td>PTT/0.3MWCNT</td>
<td>2.37±0.03</td>
<td>26.34±5.22</td>
<td>1.29±0.43</td>
<td>33.70±3.67</td>
<td>3.1±0.21</td>
</tr>
<tr>
<td>PTT/0.1INT-WS2</td>
<td>2.00±0.05</td>
<td>52.54±2.88</td>
<td>3.01±0.28</td>
<td>41.11±0.12</td>
<td>18.6±2.11</td>
</tr>
<tr>
<td>PTT/0.3 INT-WS2</td>
<td>2.30±0.02</td>
<td>50.50±1.78</td>
<td>6.92±0.18</td>
<td>41.51±3.52</td>
<td>342.9±17.9</td>
</tr>
<tr>
<td>PTT/0.5INT-WS2</td>
<td>2.32±0.03</td>
<td>49.20±2.18</td>
<td>4.59±0.09</td>
<td>49.30±5.82</td>
<td>393.9±17.3</td>
</tr>
</tbody>
</table>

E – Young’s modulus; σy - yield-strength; εy – yield strain; σb, εb - stress and strain at break respectively.
Table 6 Tensile properties of semicrystalline (annealed) PTT/MWCNT and PTT/INT-WS₂ nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>E</th>
<th>σ_y</th>
<th>ε_y</th>
<th>σ_b</th>
<th>ε_b</th>
<th>B x10¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>2.48±0.03</td>
<td>57.91±1.35</td>
<td>2.69±0.40</td>
<td>69.21±1.41</td>
<td>4.61±0.11</td>
<td>0.643</td>
</tr>
<tr>
<td>PTT/0.1MWCNT</td>
<td>2.64±0.02</td>
<td>56.43±2.70</td>
<td>2.29±0.24</td>
<td>64.50±3.32</td>
<td>3.28±0.61</td>
<td>1.112</td>
</tr>
<tr>
<td>PTT/0.3MWCNT</td>
<td>2.00±0.03</td>
<td>12.15±3.11</td>
<td>0.65±0.08</td>
<td>13.50±2.31</td>
<td>0.76±0.01</td>
<td>4.323</td>
</tr>
<tr>
<td>PTT/0.1INT-WS₂</td>
<td>1.99±0.04</td>
<td>63.59±1.43</td>
<td>4.56±0.02</td>
<td>70.4±2.01</td>
<td>7.13±0.51</td>
<td>0.464</td>
</tr>
<tr>
<td>PTT/0.3INT-WS₂</td>
<td>2.76±0.03</td>
<td>58.44±1.01</td>
<td>2.61±0.11</td>
<td>73.0±1.62</td>
<td>6.10±0.23</td>
<td>0.526</td>
</tr>
<tr>
<td>PTT/0.5INT-WS₂</td>
<td>2.28±0.01</td>
<td>55.44±1.93</td>
<td>2.61±0.31</td>
<td>72.0±2.92</td>
<td>6.41±0.21</td>
<td>0.583</td>
</tr>
</tbody>
</table>

E – Young’s modulus; σ_y, ε_y - strength and strain at elastic limit respectively; σ_b, ε_b - stress and strain at break respectively; B (=1/(ε_b·E)) – brittleness calculated according to the formula published in [28].

6. Structural characterization

The WAXS patterns for both series of nanocomposites are presented in Fig. 8. WAXS analysis was applied in order to: 1) confirm that indeed amorphous and semicrystalline samples are tested; 2) observe the effect of MWCNT and INT-WS2 on crystal form of PTT. At room temperature for the series of amorphous samples only the characteristic diffraction peaks of PTT are observed.
peaks of INT-WS$_2$ [20] [50] [51] are seen (Fig. 8a). While, WAXS diffractograms of semicrystalline PTT based nanocomposites (Fig. 8b) show characteristic diffraction peaks of PTT [52] [53] and INT-WS$_2$ demonstrating that the nanofillers do not influence the crystal structure of PTT. Similar observations were made for nanocomposites based on different polymer matrices with MWCNT [54] and INT-WS$_2$ [44].

Fig. 8 Wide angle X-ray scattering (WAXS) patterns of PTT based nanocomposites containing MWCNT and WS$_2$ nanotubes for (a) amorphous and (b) semicrystalline samples.

7. Effect of MWCNT and INT-WS2 on the thermal stability of PTT nanocomposites

One can find CNT to be thermally stable and exhibit high thermal conductivity of $\sim$6600 W/m·K for SWCNT [55] and 3000 W/m·K for MWCNT [56]. Moreover, introduction of INT-WS$_2$ into polymer matrix can enhance the thermal stability of the final material, since they have thermally inherent stability in nitrogen up to 800 °C [37] [57] [58] [59]. When the thermally stable nanotubes (organic or inorganic) are dispersed in less stable polymer matrices, the thermal stability of the polymer composites can be improved depending on the concentration of nanoparticles. Another reason for the thermal stability improvement of the composites is that the dispersed nanotubes in polymer matrices help to dissipate the heat more quickly in the composites because of their higher thermal conductivity [37] [60]. The mass loss (TG) and its derivative (DTG) curves of PTT/MWCNT and PTT/INT-WS$_2$ nanocomposites with different weight content of nanotubes in air and atmosphere are shown.
in Figs. 9 a and b. Additionally, the values of the characteristic temperatures, including the temperature of 5, 10 and 50% weight loss (T_{5\%}, T_{10\%}, T_{50\%}) and the temperature at the maximum weight loss rate (T_{DTG}) of neat PTT and both series of nanocomposites are summarized in Table 7. It is clearly visible that both neat PTT and its nanocomposites exhibit two decomposition stages in oxidative atmosphere and one decomposition stage in argon. The details about the decomposition behaviour of PTT were previously described in [28]. The temperatures corresponding to 5, 10 and 50 % weight loss in oxidative and argon atmosphere and for all nanocomposites filled with MWCNT and INT-WS\textsubscript{2} are very close to the value of the neat PTT. No effect was also seen in the case of the temperature at maximum of weight loss rate (T_{DTG1} and T_{DTG2}) when nanotubes were incorporates. Only the sample containing 0.3 wt % of MWCNT exhibited higher (5-6 °C) values of T_{5\%} °C and T_{10\%} °C in argon atmosphere, in comparison to neat PTT. Considering the fact that this composite has lower value of molecular mass of PTT matrix, it can be establish that this sample exhibit enhanced thermal stability. These results are in agreement with our earlier study on the thermal and thermo-oxidative stability of PTT nanocomposites reinforced by COOH functionalized MWCNT. Previously obtained results showed that the thermal and oxidative stability of PTT was independent of the COOH functionalized MWCNT content [28]. These results were in agreement with other researchers [61] who observed for PET based nanocomposites containing functionalized MWCNT no influence on the thermal stability of polyester nanocomposites. Similarly, the thermal stability measurements of neat nylon 11 and its nanocomposites [59] revealed that the INT-WS\textsubscript{2} had no influence on the characteristic degradation temperatures of nylon 11. Thus, the temperature at 10% weight loss (T_{10}) and that corresponding to the maximum rate of weight loss (T_{mr}) appeared at the same temperatures as the neat nylon 11 matrix, approximately 397 °C and 437 °C, respectively. Thus, the enhancing effect of MWCNT in air and INT-WS\textsubscript{2} in argon observed herein is even more noteworthy.
Fig. 9 Weight loss and derivative weight loss versus temperature for the PTT/MWCNT and PTT/INT-WS$_2$ nanocomposites in air (a) and in argon (b) at a heating rate of 10°C/min.

Table 7 Temperatures corresponding to 5, 10 and 50 % weight loss and the temperature at maximum of weight loss rate for the PTT/MWCNT and PTT/INT-WS$_2$ nanocomposites obtained in air and argon atmosphere

<table>
<thead>
<tr>
<th>Symbol</th>
<th>$T_{5%}$, °C</th>
<th>$T_{10%}$, °C</th>
<th>$T_{50%}$, °C</th>
<th>$T_{DTG1}$, °C</th>
<th>$T_{DTG2}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement carried out in an oxidizing atmosphere</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTT</td>
<td>373</td>
<td>381</td>
<td>404</td>
<td>402</td>
<td>495</td>
</tr>
<tr>
<td>PTT/0.1 MWCNT</td>
<td>375</td>
<td>383</td>
<td>406</td>
<td>404</td>
<td>506</td>
</tr>
<tr>
<td>PTT/0.3 MWCNT</td>
<td>374</td>
<td>382</td>
<td>406</td>
<td>409</td>
<td>482 and 524</td>
</tr>
<tr>
<td>PTT/0.1 INT-WS$_2$</td>
<td>371</td>
<td>380</td>
<td>404</td>
<td>402</td>
<td>486</td>
</tr>
<tr>
<td>PTT/0.3 INT-WS$_2$</td>
<td>373</td>
<td>381</td>
<td>404</td>
<td>402</td>
<td>500</td>
</tr>
<tr>
<td>PTT/0.5 INT-WS$_2$</td>
<td>372</td>
<td>381</td>
<td>404</td>
<td>403</td>
<td>507</td>
</tr>
<tr>
<td>Measurement carried out in argon</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTT</td>
<td>376</td>
<td>383</td>
<td>407</td>
<td>405</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.1 MWCNT</td>
<td>377</td>
<td>384</td>
<td>407</td>
<td>406</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.3 MWCNT</td>
<td>382</td>
<td>388</td>
<td>407</td>
<td>408</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.1 INT-WS$_2$</td>
<td>371</td>
<td>378</td>
<td>408</td>
<td>406</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.3 INT-WS$_2$</td>
<td>373</td>
<td>382</td>
<td>407</td>
<td>406</td>
<td>-</td>
</tr>
<tr>
<td>PTT/0.5 INT-WS$_2$</td>
<td>375</td>
<td>383</td>
<td>407</td>
<td>406</td>
<td>-</td>
</tr>
</tbody>
</table>
Conclusions

Nanocomposites with well distributed MWCNT and INT-WS₂ in PTT matrix were prepared by in situ polymerization. A percolation threshold <0.1 wt % was reached for PTT/MWCNT nanocomposite films, while nanocomposites filled with INT-WS₂ were not conducive materials. Mechanical properties of amorphous and semicrystalline (annealed samples) nanocomposites were affected by the presence of nanotubes. For amorphous PTT nanocomposites, the increase of Young’s modulus and tensile strength was observed with the increasing loading of both types of nanotubes. The incorporation of INT-WS₂ nanotubes induces an increase in both stress and elongation at break of semicrystalline PTT/INT-WS₂, while the presence of MWCNT reduces the stress and elongation at break with increasing their content in semicrystalline PTT matrix. Besides, the increase in the brittleness of semicrystalline nanocomposites with the increase in MWCNT loading was observed, while the nanocomposites filled with INT-WS₂ were less brittle than neat PTT. Thermal and thermos-oxidative stability of nanocomposites was not affected by the presence of nanotubes in PTT matrix. Taking into account the above mentioned observations on the effect of MWCNT and INT-WS₂ nanotubes on the mechanical properties of PTT based nanocomposites one can conclude that in situ polymerization has presented a number of advantages and allow obtaining new functional materials with improved properties. This is mainly because it is easier to get strong interactions between polymer and nanotube during the growth stage rather than mixing the constituents by various means.

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