Preparation and characterization of nanocomposites based on COOH functionalized multi-walled carbon nanotubes and on poly(trimethylene terephthalate)

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Abstract. Poly(trimethylene terephthalate) nanocomposites containing COOH functionalized multi-walled nanotubes were synthesized with *in situ* polymerization method. The microstructure of the nanocomposites was studied by SEM, in terms of the dispersion state of the nanotubes and the polymer–nanotube interface. The thermal behaviour, mechanical properties and conductivity of these resultant PTT/MWCNTs nanocomposites were studied. The effect of the presence of MWCNTs on cold crystallization of PTT was monitored by dielectric spectroscopy. From thermal analysis study, it is found that the melting temperature and glass transition temperature are not significantly affected by the addition of MWCNTs. The crystallization temperature of PTT matrix is affected by the presence of CNTs. Nanocomposites have slightly higher degree of crystallinity than neat PTT and their thermo-oxidative stability is not significantly affected by the addition of MWCNTs. The study of the isothermal cold crystallization of amorphous PTT and its nanocomposites monitored by dielectric spectroscopy reveals that the presence of MWCNTs have influence on crystallization rate, especially at higher concentration (0.3 wt%). In comparison with neat PTT, the MWCNTs reinforced nanocomposites possess higher tensile strength and Young's modulus at low MWCNTs loading (0.05–0.3 wt%). In addition, all nanocomposites show reduction of brittleness as compared to the neat PTT. The electrical percolation threshold was found between 0.3 and 0.4 wt% loading of MWCNTs.

Keywords: polymer nanocomposites, poly(trimethylene terephthalate), carbon nanotubes

1. Introduction

Poly(trimethylene terephthalate) PTT is relatively recently commercialized polyester under trade names Corterra and bio-based Sorrona produced by Shell Chemicals and DuPont respectively [1–3]. PTT is produced by the polycondensation reaction of 1,3-propanediol (PDO) with terephthalic acid or dimethyl terephthalate. The main problem in com-

mercialization of PTT was the high cost of PDO production, which was solved by Shell, which developed the low cost method of producing (petrochemical) PDO from ethylene oxide. At present the 1,3-propanediol used for the polymerization can be prepared either chemically or biologically. DuPont Tate & Lyle recently developed a biological process for the large-scale production of PDO using corn

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sugar as the raw material in place of petroleum [2–5]. DuPont's PTT Sorrona fibers are made from PDO derived from renewable corn sugar and fossil fuel derived terephthalic acid.

PTT is a semicrystalline polymer which combines the advantageous properties of polyesters and polyamides with main application field in textile industry. Many research groups [3, 6–8] have shown that the structure of PTT is very different from that of commercially well known aromatic linear polyesters poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), although their chemical composition is very similar. Owing to unusual properties such as excellent elastic recovery, high thermal and chemical resistance and dyeability, PTT is now a potential competitor of PBT and PET in textile, packing and engineering thermoplastic markets. Review of literature concerning recent advances in the field of PTT based copolymers [9–11], blends [12–14] and composites [15–17] shows a evident trend toward the development of such materials.

PTT is an important candidate for being compounded with various nanoparticles to further broaden its utility. Significant improvements in ultimate properties have been observed after incorporation of various types of nanoparticles into engineering polymers [18, 19]. In particular, carbon nanotubes (CNTs) due to their relatively high surface to volume and aspect ratios, extraordinary mechanical properties, low density and their superior thermal and electrical properties [20–22] are recognized as an ideal nanofiller material in structural and functional polymer composites. Introduction of small quantities of CNTs into a polymer matrix can lead to obtain structural composites with high elastic modulus, high tensile and compressive strength and stiffness. The mechanical properties combined with electrical, thermal, optical and many other properties have been extensively investigated by many research groups for wide range of applications [22–30].

In this work, poly(trimethylene terephthalate)/multi-walled carbon nanotubes nanocomposites were prepared by *in situ* polymerization method. The effect of carboxy-functionalized multi-walled nanotubes (MWCNTs) concentration on thermal, mechanical, and electric properties of the obtained composites was studied. Here we show that at low loading of MWCNTs it is possible to obtain electrical conduc-

tive PTT nanocomposites with improved mechanical properties, and the presence of carbon nanotubes have effect on cold crystallization rate of nanocomposites.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT, Elana S.A., Torun, Poland), 1,3-propanediol (PDO, Shell Chemicals Europe B.V., The Netherlands), anhydrous N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich), COOH-functionalized multi-walled carbon nanotubes (MWCNTs, Nanocyl S. A., Belgium) with diameter $\cong 9.5$ nm, length < 1.5 μm , and COOH functionalization < 4 wt%, were applied to prepare PTT nanocomposites. Purity of MWCNTs as received was $> 97\%$. PDO was distilled before using. As catalyst the tetrabutyl orthotitanate ($\text{Ti}(\text{OBu})_4$, Fluka), and as antioxidant the tetrakis(methylene(3,5-dit-butyl-4-hydroxyphenyl)hydro-cinnamate)methane (Irganox 1010, Ciba-Geigy, Basel, Switzerland) were used as received.

2.2. Preparation of PTT/MWCNTs nanocomposites

Nanocomposites containing 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 wt% of COOH functionalized MWCNTs were prepared by polycondensation in the molten state. The polymerizations were carried out in a 1L high pressure reactor (Autoclave Engineers Pennsylvania, USA) equipped with a vacuum pump, condenser, and cold trap for collecting the by-products. Before introduction to the reaction mixture the MWCNTs were dispersed in 300 ml of N-methyl-2-pyrrolidone (NMP) using ultra-high speed stirrer and then ultrasound (Homogenizator HD 2200, Sonopuls, Bandelin, Berlin, Germany). Completed time of dispersing was 30 min. During the last 10 min of dispersing time the PDO was introduced into MWCNTs dispersion in NMP. Then the dispersion was introduced into reactor containing melted DMT. The first step of polycondensation, the transesterification reaction, was carried out under a constant flow of nitrogen at 165°C in the presence of catalyst (0.15 wt%) for one and half hour. During the reaction, methanol was distilled off. The conversion of the transesterification reaction was calculated by monitoring the amount of effluent methanol. When the reaction was completed, the

thermal stabilizer Irganox 1010 (0.5 wt%) and the second portion of catalyst (0.1 wt%) were introduced to the reactor. Then the reaction temperature was increased slowly to 220°C and the pressure was reduced slowly. When the NMP was distilled off, the reaction temperature was increased to 260°C and pressure reduced below 25 Pa for the 2nd step of the polycondensation reaction. The stirring torque change was monitored in order to estimate the melt viscosity of the product. All syntheses were finished when melt reach the same value of viscosity at 260°C. The molten composite was extruded from reactor into water cooling bath, and then granulated and dried before processing. At the same conditions the neat PTT was synthesized as reference.

2.3. Sample preparation

Dumbbell shape samples of nanocomposites for tensile and DMTA tests were obtained by injection moulding at a pressure of around 50 MPa and at temperature 250°C, into a mould at temperature 40°C. Before tests samples were annealed at 80°C for 8 hours. Amorphous films of about 280 µm thickness for conductivity and dielectric properties studies were prepared by press moulding (Collin P 200E) at 245°C and 15 bar for 2 min and subsequently quenched (250°C/min). Subsequently, circular gold electrodes 2 cm in diameter were deposited onto the surface of the film sample.

2.4. Characterization methods

The limiting viscosity number (intrinsic viscosity) $[\eta]$ of PTT and PTT/MWCNTs nanocomposites was measured 30°C on Ubbelohde viscometer with capillary Ic ($K = 0.03294$) using a polymer solution of 0.5 g/dl in phenol/trichloroethylene (60/40 by weight). The limiting viscosity number is related to the molecular weight, M_v , through the Mark-Houwink equation (Equation (1)):

$$[\eta] = K \cdot M_v^\alpha \quad (1)$$

where K and α are constants specific to the solvent and temperature. The viscosity average molecular weight (M_v) of PTT and its nanocomposites was calculated by using constants: $K = 5.36 \cdot 10^{-4}$ dl/g and $\alpha = 0.69$ available in literature [31]. The measurements of $[\eta]$ were repeated for some samples, which have been earlier purified by means of the following procedure: PTT/MWCNTs (or PTT) was

dissolved in phenol/trichloroethylene (60/40 w/w), then filtered to separate the CNTs. The sample was precipitated by adding methanol and recovered by filtration and again dissolved and re-precipitated twice. Finally, the precipitated solid was dried in vacuum at 60°C for 24 hours. The aim of this procedure was to eliminate the influence of MWCNTs presence on measured $[\eta]$ values.

The melt flow rate (MFR) of all the samples was determined using a melt flow tester (CEAST, Italy) according to ISO 1133 specification, under 21.18 N load, orifice diameter 2.095 mm and at temperature 230°C. The samples before measurements were dried in a vacuum dryer at 60°C for 24 hours.

The melt viscosity (η) of the nanocomposites were measured at 240°C on an ARES rheometer (Rheometric Scientific Inc., USA) at frequency of 1 Hz during 10 min, in a parallel-plate fixture ($d = 25$ mm) with a gap distance of 2 mm.

The calorimetric measurements were carried out by means of a TA Instruments DSC Q-100 (New Castle, DE, USA). Indium was employed for the temperature and heat flow calibration. The heat capacity at each temperature was evaluated with respect to sapphire standard. Weighed (10 ± 0.2 mg) and encapsulated in aluminum pans samples were heated from 20 to 250°C, and kept at 250°C for five minutes and cooled back down to -25 °C, and then measurements were taken over a temperature range of -25÷250°C at a heating rate of 10°C/min, and under nitrogen flow. The glass transition temperature (T_g) was taken as the midpoint of the change of heat capacity increment ($\Delta C_p/2$) associated with the glass-rubber transition. The specific heat increment ΔC_p associated with T_g of amorphous phase of semicrystalline PTT, was calculated from the vertical distance between two extrapolated baselines at the glass transition temperature according to the literature [32]. The nominal melting temperature (T_m) was defined as the of peak of the melting endotherm during heating from 25 to 250°C, and the nominal crystallization temperature (T_c) was defined as the peak of the crystallization exotherm upon cooling from 250 to -25°C. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) of the crystal phase were calculated from the area of the DSC endo- and exotherm, respectively. The degree of crystallinity, x_c , (i.e. the weight fraction crystallinity) was determined according to Equation (2) as the ratio of the

integrated heat of fusion ΔH_m value of the sample over the heat of fusion of fully crystalline PTT, i.e. $\Delta H_m^0 = 145.6 \text{ J/g}$ [3, 33]:

$$x_c [\%] = \frac{\Delta H_m}{\Delta H_m^0} \quad (2)$$

The thermogravimetric analysis (TGA) was carried out on a SETARAM TGA 92-16 apparatus. Samples ($5 \pm 0.1 \text{ mg}$) were placed in alumina crucibles and heated from ambient to 700°C at heating rate of 10°C/min in a 20 ml/min flow of argon or dry air. Dynamic mechanical thermal properties were measured by DMTA Mk-II apparatus (Polymer Laboratories, Church Stretton UK.) using the bending mode at a frequency of 1 Hz , and at a heating rate of 3°C/min from -100 to 250°C . The glass transition temperature was taken as the temperature at the maximum α -relaxation peak of the loss modulus E'' and $\tan \delta$ curves [32].

The tensile tests were performed on an Instron 1112 tensile testing machine (Norwood, MA, USA) at room temperature. Tensile examinations were measured on dumbbell samples at a constant crosshead speed of 5 mm/min . Young's modulus, yield strength, stress and elongation at break, were calculated from the stress-strain curves on an average of twelve specimens for each kind of materials according to DIN 53455 standards.

The morphology of the fracture surface of composite samples was examined by a JEOL JSM-610 scanning electron microscope (SEM). Samples were fractured at liquid nitrogen and gold sputtered prior to observation.

Measurements of the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' represents the permittivity and ε'' the dielectric loss, of the nanocomposites were performed in the frequency range of $10^{-1} \text{ Hz} < f < 10^7 \text{ Hz}$, using a Novocontrol system (Hundsangen, Germany) integrating an ALPHA dielectric interface. Sputtered gold electrodes, 2 cm diameter, were employed to prepare a sandwich type capacitor. The temperature was controlled by means of a Novocontrol Quatro Cryosystem nitrogen gas jet, leading to isothermal conditions within an error of 0.1°C during every single sweep. The dielectric relaxations were empirically described in terms of the Havriliak-Negami (HN) Equation (3) [34]:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau_{\text{HN}})^b]^c} \quad (3)$$

where $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the dielectric strength; ε_0 , ε_∞ are the relaxed and unrelaxed dielectric constant value, respectively; $\omega = 2\pi f$ is the frequency; τ_{HN} is the central relaxation time; b and c are parameters that describe the shape of the relaxation time distribution function (symmetric and asymmetric broadening). Obtained values of $\varepsilon''(\omega)$ $\varepsilon'(\omega)$ were fitted to approximated with Equation (1). HN curve fits were performed using the WinFit v.2.9 software program from Novocontrol.

Alternating current (ac) electrical conductivity measured at room temperature was derived by $\sigma(\omega) = \varepsilon_0 2\pi f \varepsilon''$, where f and ε_0 are frequency and vacuum permittivity respectively.

3. Results and discussion

3.1. Dispersion of PTT/MWCNTs nanocomposites

Nanocomposites were prepared by using *in situ* polycondensation method. The control of the degree of dispersion of the nanotubes in a polymer matrix is difficult because of the strong intramolecular forces that exist between carbon nanotubes which are responsible for the formation of $10\text{--}50 \text{ nm}$ nanotube bundles. These bundles are difficult to exfoliate since the nanotubes may be hundreds to thousands of nanometers long, disturbing the uniform dispersion of the nanotubes in a polymer matrix [24, 20]. In order to obtain a homogenous distribution of MWCNTs in the whole composite system, the CNTs were mechanically and sonically dispersed in solvent (NMP) and then introduced to the reaction mixture. The presence of dispersing solvent which was distilled off during the synthesis and the presence of COOH functionalized MWCNTs had a slight influence on the syntheses of PTT nanocomposites. In comparison to the neat polymer the reaction of polymer chain growth monitored by increase of reactive mixture viscosity proceeded slower and the reaction time lasted about one hour. The highest content of CNTs achieved in the prepared nanocomposites was $0.5 \text{ weight\%}$. The introduction of higher content of CNTs was not possible because, the melt does not flow.

In Table 1 the physical properties of obtained nanocomposites are listed. The average molecular weight ($\overline{M}_v$) of neat PTT and PTT in the nanocomposites determined from limiting viscosity number measurements is range from $44\,000$ to $37\,000 \text{ g/mol}$. The

Table 1. Characteristic of PTT and PTT/MWCNTs nanocomposites

Sample	w _{CNT} [wt%]	[η] [dl/g]	$\bar{M}_v \cdot 10^4$ [g/mol]	MFR [g/10 min]	η Pa·s
PTT	0	0.82; 0.83 ^A	4.2 ^A	16.8	210
PTT/0.05	0.05	0.84	4.3	15.7	—
PTT/0.1	0.1	0.82; 0.82 ^A	4.1 ^A	16.1	330
PTT/0.2	0.2	0.78; 0.80 ^A	4.0	15.9	372
PTT/0.3	0.3	0.78; 0.76 ^A	3.7 ^A	15.2	359
PTT/0.4	0.4	0.77	3.8	14.4	343
PTT/0.5	0.5	0.78; 0.76 ^A	3.7 ^A	13.7	342

w_{CNT} – weight fraction of MWCNTs; [η] – limiting viscosity number; $\bar{M}_v$ – viscosity average molecular weight determined from [η]; MFR – melt flow rate at 230°C; η – melt viscosity of polymer at 240°C and frequency of 1 Hz.

values of the melt flow rate of nanocomposites are lower than for neat PTT suggesting their higher melt viscosity. Measurements of the viscosity (η) of the nanocomposites determined on ARES-rheometer have confirmed that nanocomposites have higher viscosity 240°C than the neat PTT. Moreover, the increase in viscosity does not change appreciably with the CNTs content. Higher melt viscosity of nanocomposites in comparison to the neat PTT suggest the existence of interconnected or network structures formed as a result of CNT-CNT and CNT-polymer interactions. The COOH functional groups

at the surface of MWCNTs can interact in the PTT/MWCNTs composite with ester groups of PTT molecules through hydrogen bonding. The presence of hydrogen bond interaction between functional groups of CNT and polyester molecules has been confirmed in PEN/CNTs composites [35].

3.2. Thermal stability

The mass loss (TG) and its derivative (DTG) curves of PTT and PTT/MWCNTs composites with different weight content of CNTs in argon and air atmosphere are shown in Figures 1a–d. The values of the

Figure 1. The mass loss (TG) and its derivative (DTG) curves as a function temperature for PTT nanocomposites in argon (a, c) and in air atmosphere (b, d)

Table 2. The characteristic temperatures of the decomposition of the PTT and PTT/MWCNTs nanocomposites in argon and air

	MWCNT content [wt%]						
	0	0.05	0.1	0.2	0.3	0.4	0.5
in argon							
$T_{2\%}$ [°C]	358	360	364	360	361	362	360
$T_{10\%}$ [°C]	383	384	384	384	384	385	384
T_{DTG} [°C]	405	405	405	407	405	407	406
in air							
$T_{2\%}$ [°C]	354	360	358	360	365	365	353
$T_{10\%}$ [°C]	382	382	379	381	383	383	382
T_{DTG1} [°C]	404	405	403	406	406	407	406
T_{DTG2} [°C]	503	511	506	530	538	540	528

$T_{2\%}$, $T_{10\%}$ – temperature of 2 and 10% weight loss respectively; T_{DTG} – temperature at the maximum weight loss rate

characteristic temperatures, including the temperature of 2 and 10% weight loss ($T_{2\%}$, $T_{10\%}$) and the temperature at the maximum weight loss rate (T_{DTG}) of neat PTT and MWCNTs-filled nanocomposites are presented in Table 2. It is evident that neat PTT and its nanocomposites exhibit one decomposition step in argon and two decomposition steps in air. The study of the thermal decomposition kinetics of PTT [36] have shown that the first step of the decomposition of PTT in both argon and air atmospheres is an overlapping of two decomposition processes. The first process is caused by degradation of the polymer chain implying an end group initiation mechanism affected by the molecular weight of PTT. The second degradation process is mainly caused by the thermal degradation of the products formed during the first decomposition process and it is not affected by the molecular weight (end groups) of PTT. Wang *et al.* [37] have shown that the first small weight-loss process (weight loss 2–4%) in argon is highly sensitive to molecular weight and the weight loss during this step decreased steadily with increasing molecular weight. These effect is a result of relatively poor thermal stability of hydroxyl terminal groups in PTT which initiate thermal degradation of PTT (especially ester groups). Additionally, Kelsey *et al.* [38] have shown that the predominant thermal degradation mechanism of PTT and other commercially important aromatic polyesters as PET and PBT is consistent with concerted, electrocyclic oxo retro-ene reaction [39–41], sometimes referred to as the McLafferty (ML) rearrangement. Hence, during thermal degradation of PTT one of the two ester groups between benzene rings forms hexatomic ring, and then after ML

rearrangement some chain fragments with end-COO group and end-allyl ester group are formed, which are easy to decarboxylation and latter to de-esterification under high-temperature condition. In these processes products of thermal degradation of PTT, among others, CO₂, CO, acrylaldehyde and some fragments such as phenyl-containing chain were indentified [42].

Studies by Wang *et al.* [36] indicated a three overlapping weight-loss stages for the degradation of PTT in air. During the first process the PTT chains are degraded into smaller fragments by an initial end chain scission. These small fragments during the second processes are oxidized into volatile products. Decomposition of initially stable structures formed in first and second processes forming probably crosslinked residues take place during the third stage of the thermo-oxidative degradation of PTT. According to the Figures 1c–d, neat PTT and all the nanocomposites starts with a first main degradation stage in air at around 335°C independent of the content of MWCNTs. The weak second degradation step in the temperature range 450–600°C (Figure 1d) is due to the decomposition of some thermostable species formed during first degradation step. These may include decomposition of cross-linked carbonaceous structures and also carbon nanotubes. For nanocomposites, the temperature of the maximum weight loss rate (T_{DTG2}) at this post-major/second weight loss step is shifted to higher temperatures. The obtained results show that the thermal and oxidative stability of PTT is independent of the COOH functionalized MWCNT content. These results are in agreement in other researchers [43] observed for PET/CNT nanocomposites which have

confirmed also that functionalization of CNTs and concentration have no influence of thermal stability of polyester nanocomposites.

3.3. Microstructure of the PTT nanocomposites

Morphology of PTT nanocomposites containing short thin COOH functionalized MWCNTs was investigated by using SEM analysis. Figures 2a–d shows SEM micrographs of fracture surfaces of PTT nanocomposites with MWCNTs. As mentioned above, CNTs often tend to bundle together by van der Waals interaction between the individual nanotubes with high aspect ratio and large surface area and lead to some agglomerations, which prevent efficient load transfer to nanotube. Moreover, most of the nanotubes show pulling out and sliding at the surface of nanocomposite, suggesting a limitation of load transfer [44–45]. SEM analysis of the fracture surfaces of PTT/MWCNTs nanocomposites indicate rather homogenous distribution of carbon nanotubes in the PTT matrix. Individual nanotubes, some entanglements or bundles of CNTs, apparently pulled out from the matrix during fracturing are observed on the surface.

3.4. Effect of MWCNTs addition on the thermal transition of PTT

Carbon nanotube functionalization inducing interactions between polymeric matrix and carbon nanotubes can cause changes in the crystallization and melting behavior of the semicrystalline polymer. In many polymer systems after introduction of carbon nanotubes the increase in crystallization temperature, enhancing in nucleation density and in some cases reduction of crystallization time was observed [35, 43, 46–50]. The effect of the presence of COOH functionalized MWCNT in PTT matrix on the melting and crystallization processes was studied by DSC. Table 3 summarizes data obtained from heating and cooling DSC scans for PTT and PTT/MWCNTs nanocomposites which are presented on Figure 3. PTT/MWCNTs nanocomposites exhibit a negligible decrease (1–2°C) in the glass transition compared to pure PTT. Nanocomposites with different amount of MWCNTs have very slightly lower values of ΔC_p at T_g than neat PTT. Introduction of CNTs can separates the long polymer chain into shorter cooperatively rearranging (CRR) segments [51]. The shift of T_g toward lower temperatures can be a result of the higher mobility of these shorter CRR

Figure 2. SEM images of cryofractured PTT nanocomposites with 0.3 wt% (a–b) and 0.5 wt% (c–d) of MWCNTs

Table 3. Thermal properties of PTT and PTT/MWCNTs nanocomposites

Sample	T_g [°C]	ΔC_p [J/(g·°C)]	T_m [°C]	ΔH_m [J/g]	$T_{c,on}$ [°C]	T_c [°C]	ΔH_c [J/g]	ΔT [°C]	x_c [%]
PTT	52	0.18	229	50.7	180	170	50.3	59	34.8
PTT/0.05	50	0.15	229	53.7	186	168	53.7	61	36.9
PTT/0.1	51	0.16	229	54.4	186	166	53.5	63	37.4
PTT/0.2	50	0.16	229	54.1	190	166	54.0	63	37.1
PTT/0.3	51	0.16	230	54.3	186	167	54.4	63	37.2
PTT/0.4	51	0.15	230	53.9	187	168	53.5	62	37.0
PTT/0.5	51	0.16	230	54.2	186	168	53.7	62	37.2

T_g – glass transition temperature; T_m , ΔH_m – temperature and enthalpy of melting respectively; ΔC_p – change of heat capacity; $T_{c,on}$ – onset temperature of crystallization; T_c , ΔH_c – temperature and enthalpy of crystallization respectively; x_c – degree of crystallinity of the sample; $\Delta T = T_m - T_c$ – degree of supercooling

Figure 3. DSC heating and cooling curves for PTT nanocomposites; where:
1 – PTT, 2 – PTT/0.05, 3 – PTT/0.1, 4 – PTT/0.2,
5 – PTT/0.3, 6 – PTT/0.4, 7 – PTT/0.5

segments. Recently, for semicrystalline polymers such PTT, PET, PEEK [51–53], a three phase model consisting of crystalline, mobile amorphous phase (MAP) and rigid amorphous phase (RAP) was used to describe the structural formation of PTT at various conditions. The RAP exists at the interface of crystal and amorphous phase as a result of the immobilization of a polymer chain due to the crystal. In semicrystalline nanocomposites, the RAP fraction sometimes exists at the surface of nanofillers in the polymer nanocomposites material. Ma and Cebe [53] have used these model in to explain lowering the T_g and decreasing degree of crystallinity with the CNTs loading for PTT/MWCNTs (with aspect ratio 36) fibers prepared by electrospinning. They have established that addition of CNTs results in increase in the RAP, which indicates an enhancement in the constrains on the polymer chains in PTT composites nanofibers due to the decrease of chain mobility. Here, the melting temperature and degree of crystallinity of the PTT/MWCNTs nanocomposites (Table 3) are not significantly affected

by the presence on the MWCNTs. The degree of crystallinity of nanocomposites increase very slightly around 2–2.6%. Nanocomposites have wider crystallization peak than those of neat PTT, indicating the heterogenous nucleation effect of the CNTs for the PTT matrix. In PTT/MWCNTs nanocomposites, the onset crystallization temperature ($T_{c,on}$) increase by about 6–10°C, whereas the crystallization peak temperature (T_c) decreases by about 2–4°C. Usually the lower degree of supercooling reflects higher nucleation and crystallization rates. The PTT/MWCNTs nanocomposites have a little higher degree of supercooling ($\Delta T = 61$ – 63°C , Table 3) with the introduction of the MWCNTs in comparison with pure PTT ($\Delta T = 59^\circ\text{C}$). Crystallization of polymer occurs from the alignment of mobile polymer chains. The addition of filler in polymer composites changes the thermal properties of the materials due to the formation of interfacial connections between the filler surfaces and polymer. The connections, which may be physical adsorption or chemical bonding, or a combination of both, restrict the mobility of the polymer chains. Here, the introduced short and thin MWCNTs into PTT matrix are not effective nucleating agent caused the increase of the degree of supercooling. These can be a result of their low aspect ratio or their strong interactions with PTT chains. The topological confinement of macromolecular chains at their interfaces and strong interactions between them can increase of supercooling. Recent study on crystallization behaviour of nanocomposites based on high density polyethylene and CNTs performed by Müller and coworkers [54, 55] have shown that in nanocomposites a competition between super-nucleation and confinement occur. At low contents the nucleation effect dominates. The confinement increases as the nano-filler

content increases. In consequence of confinement the reduction of both crystallization and melting temperatures, a strong reduction of the crystallinity degree, an increase in the supercooling needed for isothermal crystallization and a depression of the overall crystallization rate were observed.

The effect of the presence of MWCNT on non-isothermal crystallization behavior of PTT nanocomposites observed here, is in contrast to the results reported in literature for aromatic polyester/CNT nanocomposites. For example, poly(ethylene 2,6-naphthalate) (PEN) nanocomposites [35, 47] have shown the increase in the crystallization temperature of PEN by incorporating pristine MWCNTs and COOH functionalized MWCNTs. Moreover, PEN nanocomposites have a lower degree of supercooling for crystallization with the introduction of the MWCNTs. This behavior has suggested that nanotubes act as effective nucleating agents in the PEN matrix, resulting in the enhancement of the crystallization of the PEN nanocomposites. The increase in the crystallization temperature and degree of crystallinity was observed for poly(butylene terephthalate) nanocomposites containing of 0.2 wt% of pristine MWCNTs and NH₂ functionalized MWCNTs [44] and for poly(ethylene terephthalate) (PET) nanocomposites containing acid treated MWCNTs [43, 48–49]. Correlation of spectroscopic measurements with DSC have shown that acid treated MWCNTs present in PET nanocomposites not only enhanced crystallinity but also lead to a much better polymer crystalline order [49]. The presence of MWCNTs in PET matrix transforms trans conformers of the noncrystalline phase into crystalline domains with the nanotubes acting as moderate nucleation agents. Xu *et al.* [50] have studied the crystallization behaviour of PTT/MWCNTs nanocomposites, which were prepared by solution blending. They report that for such PTT nanocomposites the melting temperature and crystallinity were not affected by the presence on the MWCNTs. However, an increase of crystallization temperature and a decrease of the degree of supercooling was observed with increasing nanotube concentration. Comparison of the results obtained for PTT nanocomposites prepared by solvent blending [50] and those studied here for PTT nanocomposites prepared by *in situ* polymerization seems to indicate that the preparation method in addition to the type

of carbon nanotube can affect the crystallization behavior of PTT.

3.5. Effect of MWCNTs on cold crystallization of PTT nanocomposites

In situ real time dielectric isothermal crystallization of amorphous PTT and PTT/MWCNTs nanocomposites at 50°C was monitored by dielectric spectroscopy. Figure 4 shows dielectric loss ε'' and dielectric permittivity ε' at different crystallization times (t_c) of amorphous neat PTT (a–b) and PTT nanocomposites containing 0.05 wt% (c–d) and 0.3 wt% (e–f) of MWCNTs. The obtained spectra recorded in each sweep (4 min) are representative of an isostructure at a given stage of crystallization because the time scale for a sweep is short in comparison with time scale for crystallization. The initial dielectric spectrum for amorphous neat PTT and PTT nanocomposites shows the typical α -relaxation associated with the segmental motions of the amorphous chains above the glass transition. Regarding the analysis of the dynamics of the amorphous phase during isothermal crystallization, the segmental motions of the amorphous polymer chains are confined between the crystalline regions thus modifying the main α -relaxation. It was established for many polymers, that the occurrence of crystallinity in a polymer affects the segmental dynamics, as characterized by DS, in the following way: i) a decrease of the dielectric strength, ii) a shift of the relaxation rate to lower values and iii) a considerable broadening of the relation function [34, 55–58]. The dielectric strength of a relaxation process is, in a first approach, proportional to the total amount of relaxing units participating in the process. The decrease of the dielectric strength (reduction of the relaxing material) is caused by crystal formation due to the progressive transfer of the amorphous material to the growing crystalline phase [34, 56–58]. For neat PTT and PTT/MWCNTs nanocomposites it is observed a decrease in the intensity of the α -relaxation process, characterized by the value of the dielectric loss at the maximum ($\varepsilon''_{\max}$) and a positional shift of the maximum of the α -relaxation towards lower frequencies with increasing crystallization time in agreement with previous results [55–58]. Figure 5 represents the variation of $\varepsilon''_{\max}$ and $f_{\max}$ with crystallization time. Analysis of the changes of $\varepsilon''_{\max}$ and $f_{\max}$ indicates that the presence

Figure 4. Real time evolution of the dielectric loss (a, c, e) and the dielectric constant (b, d, f) during isothermal crystallization at 50°C as a function of frequency at different crystallization times

of MWCNTs has an effect on cold crystallization of PTT, especially at higher content of MWCNTs (0.3 wt%). As crystallization time increases, for nanocomposite containing 0.3 wt% of MWCNTs the faster shift of $f_{\max}$ in the direction of low frequencies and a higher decrease in the intensity of $\epsilon''_{\max}$ than for PTT and PTT with 0.05 wt% of MWCNTs was observed. The changes of the values of the dielectric parameters: $\Delta\epsilon$, τ_{HN} , b , c obtained after fitting the Equation (1) are presented in Figure 6 as a function of crystallization time. After $t_c =$

40 min a 92, 74 and 82% reduction of the dielectric strength (Figure 6a) for PTT/0.3 and PTT/0.05 and neat PTT, respectively was observed. These results indicate that PTT/0.3 nanocomposite crystallizes faster than PTT and PTT/0.05 nanocomposite. PTT and its nanocomposites show a slight increase of the relaxation time τ_{HN} values (calculated by Equation (1), Figure 6b). For neat PTT, the relaxation time τ_{HN} of the α process tends to be slower with crystallization time in a linear fashion with time during the whole crystallization period. The same

Figure 5. Variation of the maximum dielectric loss values $\epsilon''_{\max}$ (a) and frequency of the maximum loss $f_{\max}$ (b) as a function of crystallization time at 50°C. (Dotted lines are to guide the eyes).

Figure 6. Real time evolution of the HN parameters: $\Delta\epsilon$ (a), τ_{HN} (b), b (c), c (d) during isothermal crystallization processes of net PTT and PTT/MWCNTs nanocomposites at 50°C. (Dotted lines are to guide the eyes).

behaviour of relaxation time was detected for cold crystallization of PTT by A. Sanz *et al.* [58]. This effect is a result of the restricted mobility by crystals. As crystallization time increase, the segmental dynamics in the amorphous phase slows down due to an increase of the crystalline phase. PTT nanocomposites containing: 0.3 and 0.05 wt% of MWCNTs shows higher initial ($t_c = 0$) values of

their relaxation times than that of unfilled PTT. This effect could be due to a restricted mobility of the polymer chains at the polymer/nanofiller interface where the interactions between PTT chains and CNTs surface can play role. Obviously, this interaction is not present for unfilled PTT. As shown in Figure 6b–c, a continuous change of b and c shape parameters with crystallinity is observed. For neat

PTT, the increase of the c parameter towards the highest possible value of $c = 1$ after $t_c = 40$ min indicates a decrease of the asymmetry of the relaxation upon crystallization. For PTT nanocomposite with 0.05 wt% at the beginning of crystallization time ($t_c < 32$ min) an increase of the value of c parameter is found. Then, independent on the crystallization time, remains constant ($c \approx 0.5$ – 0.6). Also a gradual increase with crystallization time of the c parameter is observed for PTT with 0.3 wt% of MWCNTs. During crystallization of neat PTT, a decrease of the b parameter (Figure 6b) with crystallization time is found. This indicates that the relaxation curve become broader. Broader curves, higher b values, are observed for PTT nanocomposites around 0.5 and 0.8 for PTT/0.05 and PTT/0.05 nanocomposites respectively, and then his decrease with crystallization time is observed. This study of the isothermal cold crystallization of amorphous PTT and its nanocomposites reveals that the presence of MWCNTs have influence on crystallization rate, especially at higher concentration (0.3 wt%) of CNTs.

3.6. Dynamic mechanical thermal analysis

The storage and loss modulus and the loss factor $\tan \delta$, determined by DMTA measurements for the pure PTT matrix and nanocomposites filled with MWCNTs, are plotted versus the temperature in Figures 7a, 7b and 7c respectively. It can be seen that magnitudes of the storage modulus and location of the loss peak change significantly for nanocomposites. The addition of MWCNTs to PTT matrix show an influence of the nanotube content on the storage modulus in the glassy region and also in some samples in the rubbery region above the glass transition. For convenience of comparison, data of E' modulus at 25°C are presented in Table 4. All nanocomposites have higher values of E' modulus compared to pure PTT. The highest increase by about of 55% of E' modulus at 25°C was observed for the sample containing 0.3 wt% of MWCNTs. These changes of the E' modulus can be attributed to cohesive interactions between the large surface area of nanotubes and PTT [59]. On loss modulus E'' and $\tan \delta$ curves (Figure 7b–c), the two relaxation peaks β and α are observed. The β -relaxation peak at about -75°C is attributed to the reorientation of the hydroxyl groups and the local motions of the carboxyl groups in the

Figure 7. The storage and loss modulus and normalized $\tan \delta$ as a function of temperature for PTT and PTT/MWCNTs nanocomposites

amorphous phase. The α -relaxation peak corresponds to the glass transition of amorphous PTT. Usually for semicrystalline polymers the increasing of the T_α and decreasing intensity of α -relaxation peak is observed with the increase of crystallinity. $\tan \delta$ is sensitive to all molecular movements occurring in polymer. For nanocomposites, the molecular movement at the interface contribute to the value of the $\tan \delta$ that enables to estimate the bonding

Table 4. DMTA properties of PTT and PTT/MWCNTs nanocomposites

Sample	E' at 25°C [MPa]	T _α (E'') [°C]	T _α (tan δ) [°C]
PTT	2136	59	70
PTT/0.05	2683	70	85
PTT/0.1	2524	70	85
PTT/0.2	3081	70	85
PTT/0.3	3316	70	84
PTT/0.4	2971	70	85
PTT/0.5	2716	70	84

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

between the interphase of the matrix and the CNTs. The normalized tan δ peak of nanocomposites (except 0.5 wt%) was narrower than for neat PTT, which can be indicative of changes in the molecular dynamics for the polymer nanocomposites. Independent on the MWCNTs content, the T_α is shifted on tan δ curves from 70°C for the neat PTT to 85°C for PTT/ MWCNTs nanocomposites. This can be due to reduction of the mobility of the PTT chains around the nanotubes by interfacial interactions between CNTs and polymer matrix. The values of T_g determined from the peak maximum of tan δ or E'' curves are found to be higher than from DSC data because of the different frequency of perturbation involved in their measurements and sample preparation. Samples studied by DMTA were prepared by injection molding and then annealed at 80°C. As the MWCNTs content increases, the increase of the intensity of β-relaxation peak is observed for nanocomposites. As mentioned above this peak is associated with the motions of the short chain-segments of PTT and is cooperatively related to the glass transition, the increase of these peak associated with this transition can be regarded as evidence for partial activation of PTT chains by the COOH functionalized MWCNTs.

3.7. Mechanical properties of nanocomposites

The tensile properties of the synthesized PTT/MWCNTs nanocomposites are listed in Table 5 and representative stress-strain curves are shown in Figure 8. The variation of tensile strength and tensile modulus of the nanocomposites are shown in Figure 9. As the content of the MWCNTs increase to 0.3 wt%, the nanocomposites tensile strength and

Table 5. Tensile properties and brittleness of PTT/MWCNTs nanocomposites

Sample	E [GPa]	σ _b [MPa]	ε _b [%]	B [10 ¹⁰ ·(%·Pa)]
PTT	2.10±0.03	69.1±2.6	4.3±0.3	1.089
PTT/0.05	2.20±0.04	70.5±2.2	4.4±0.5	0.847
PTT/0.1	2.21±0.05	72.4±2.9	4.6±0.6	0.861
PTT/0.2	2.22±0.04	73.4±2.7	4.2±0.5	0.773
PTT/0.3	2.25±0.04	74.5±1.5	4.7±0.4	0.641
PTT/0.4	2.25±0.03	69.2±2.9	4.2±0.5	0.801
PTT/0.5	2.24±0.05	69.7±3.3	4.4±0.4	0.836

E – tensile modulus; σ_b – stress at break; ε_b – elongation at break; B (=1/(ε_b·E')) – brittleness [61]

Figure 8. Representative stress strain curves of nanocomposites **Figure 9.** Stress at break and Young's modulus of nanocomposites as a function of MWCNTs weight fraction

Young's modulus increases. However, further addition of MWCNTs (0.4–0.5 wt%) lowers tensile strength and Young's modulus, but their values are still comparable or higher (modulus) to neat PTT. The values of elongation at break are higher or comparable to the neat PTT. SEM analysis (Figure 2) have shown that the CNTs are well distributed in the polymer matrix for all concentrations, note that the increase of CNT content does not lead

to formation of visible agglomerates (except small entangled CNTs structures) in the bulk volume of the polymer. When two immiscible phases such PTT and MWCNTs meet, the interaction between them occurs at their interfaces. At the interface, the net internal force of each phase is not zero and will lead to the appearance of a tension called interfacial tension. Interfacial tension is somewhat similar to surface tension in that cohesive forces are also involved [60]. However, the main forces involved in interfacial tension are adhesive forces, i.e., tension between phases. The interphase in PTT nanocomposites is influenced by the Van der Waals forces between MWCNTs and PTT matrix. Additional effect can rise from the interactions of the COOH functional groups at the surface of MWCNTs with ester groups of PTT molecules (hydrogen bonds) and from the interactions between the graphene rings of the MWCNTs and benzene rings of terephthalate moiety. The increase of the tensile strength can be attributed to strong interphase interaction between the matrix and the CNTs. The lower values of tensile strength of nanocomposites compared with neat PTT could be explained by the lower molecular weight (Table 1) of PTT. The molecular weight strongly affects the cohesion of polymer. It was mentioned earlier, that the syntheses of PTT/MWCNTs nanocomposites was carried out to the define viscosity of the reaction mixture at established temperature, which was controlled by the stirrer torque. The presence of CNTs strongly influence on the melt viscosity of polymer and hence the molecular weight of polymer in composites (0.3–0.5 wt%) have lower values of molecular weight compared with neat PTT. Brittleness of the nanocomposites was calculated by Equation (4) [61]:

$$B = \frac{1}{\varepsilon_b \cdot E'} \quad (4)$$

where ε_b is the tensile elongation at break and E' is the storage modulus determined at 1 Hz and 25°C by DMTA. It can be seen (Table 5) that addition of CNTs reduces the brittleness of the nanocomposites. Brittleness of nanocomposites shows opposite tendency to the tensile strength, i.e. brittleness was found to decrease with the CNTs loading until 0.3 wt%, while at CNTs loading above 0.3 wt% increase.

In recent years, many studies with different focuses on mechanical properties of polymer/CNTs composites have been published. Due to the extraordinary mechanical properties, high aspect ratio and low density, the outstanding potential of CNTs as reinforcements in many polymer composites is evident. For example, the mechanical properties improvement was observed for the polyacrylonitrile/CNTs [62] composite fibers containing single wall carbon nanotubes (SWCNTs), double wall carbon nanotubes (DWCNTs) and multiwall carbon nanotubes (MWCNTs). The low-strain properties (modulus and thermal shrinkage) were most improved by SWNT, while the high-strain properties were most improved by MWCNTs. Gao *et al.* [63] have studied the nylon 6/CNTs composites fibers, which were prepared by *in situ* ring-opening polymerization of caprolactam in the presence of carboxylated SWCNTs. These composites containing 1 wt% of SWCNTs show a 153% increase in Young's modulus and 103% increase in tensile strength. Reinforcement effects were also observed by adding of CNTs in polystyrene [64], epoxy resin [65], poly(ethylene oxide) [66]. Nevertheless, for many polymer/CNTs nanocomposites a critical CNTs content in the matrix could be found when the CNT reinforcement effect on randomly oriented polymer/CNTs composites was studied. Below this content, the reinforcement effect for polymer/CNTs composites increases with increasing CNT content. Above this content, the strength of the polymer/CNTs composites decreases, and in some cases, even lower than that of the polymer matrix. For example, the epoxy/CNT [67] and polypropylene/CNT [68] composites shows the critical CNTs content at about 0.5 wt%. At higher CNTs content, the extent of improvement in mechanical properties might be limited by the high viscosity of the composite and by poor load transfer between CNTs and polymer matrix resulted from imperfect dispersion and not completely covered some surface of the CNTs by polymer matrix due to the large specific area of CNTs. As will be noted in many reports, most of randomly oriented polymer/CNTs composites show only a moderate or no strength enhancement, especially for composites containing untreated CNTs, mainly attributed to poor load transfer between polymer matrix and CNTs.

3.8. Electrical properties

When electrically conducting particles such as carbon nanotubes are randomly distributed within an insulating polymer matrix, the sample is non-conducting, before a critical volume fraction of the conducting phase is reached. This critical value is known as the percolation threshold. In addition, close to the percolation threshold, the electrical properties show a nonlinear (critical) behaviour characterized by small variations in the physical parameters, such as temperature, composition or voltage, result in large variations of electrical properties [69]. The percolation threshold for the electrical conductivity in polymer/CNTs nanocomposites shows the complex dependence on a variety of factors, including nanotube characteristics (aspect ratio, single- or multi-wall), and fabrication/processing conditions, which affect the filler's distribution and orientation and the filler-matrix interactions [70]. Figures 10 and 11 show the alternating current conductivity, at room temperature, as a function of frequency and the conductivity measured at 0.1 Hz respectively, for PTT nanocomposites with different MWCNTs content. At loadings below 0.26 vol%, the PTT nanocomposites exhibit a strong frequency dependence of the conductivity, which is typical for insulating materials. At loadings in excess of 0.20 vol% (percolation threshold), the composites exhibited a conductive behaviour which is nearly independent of frequency.

The critical concentration of MWCNTs dispersed in PTT matrix can be estimated on the concept of excluded volume for a system of randomly oriented, nanotubes as capped cylinders by using Equation (5) [71]:

$$\varphi_c = 1 - \exp \left[- \frac{V_{ex} \left(\frac{\pi}{4} D^2 L + \frac{\pi}{6} D^3 \right)}{\frac{4\pi}{3} D^3 + 2\pi D^2 L + \frac{\pi}{2} D L^2} \right] \quad (5)$$

where V_{ex} ($= 1.4$) is total excluded volumes for continuum, randomly infinitely thin rods. The nanotubes were modeled as capped cylinders of radius $r = D/2$ and length L , in the limit of very high aspect ratio ($r/L \ll 1$) [71]. The critical volume percentage of nanotubes was predicted to be 0.434 vol%, which is about one half higher than of the experimental value (0.262 vol%). This results indicate that con-

Figure 10. Frequency dependence of ac conductivity at room temperature of PTT/MWCNTs nanocomposites with different MWCNTs content

Figure 11. Electrical conductivity of PTT/MWCNTs nanocomposites at frequency of 0.1 Hz and at room temperature as a function of MWCNTs volume fraction

ductive pathways due to the content between adjacent nanotube are formed at lower content of nanotubes than was predicted. It can be also a result of well-dispersion of short-thin MWCNTs in PTT matrix, because the presence of aggregates usually increase the conductivity percolation threshold.

4. Conclusions

In situ polycondensation of PDO and dimethyl terephthalate in the presence of carboxylated MWCNTs (with aspect ratio around 158) was carried to obtain the PTT/MWCNTs nanocomposites. The poly (timethylene terephthalates) (PTT), with average molecular weight in range $4.3\text{--}3.7 \cdot 10^4$ g/mol were obtained. The melting and glass transition temperatures of nanocomposites obtained by non-isothermal crystallization (DSC results) were not significantly affected by the presence of CNTs. Nanocomposites have slightly higher degree of crystallinity

than pure PTT. The study of the isothermal cold crystallization of amorphous PTT and its nanocomposites monitored by dielectric spectroscopy reveals that the presence of MWCNTs have influence on crystallization rate, especially at higher concentration (0.3 wt%). Dynamic mechanical analysis studies revealed an enhancement of the storage modulus, in the glassy state, up to 55% at an CNTs loading of 0.3 wt%, and for nanocomposites the increase the glass transition temperature about 10–15°C. With increasing of MWCNTs loading from 0.05 to 0.3 wt%, the increase of tensile strength and Young's modulus of nanocomposites was found. All nanocomposites show reduction of brittleness in comparison to as compared to the neat PTT. The electrical percolation threshold was found at an loading between 0.3 and 0.4 wt% of MWCNTs.

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References

- [1] Liu H., Xu Y., Zheng Z., Liu D.: 1,3-Propanediol and its copolymers: Research, development and industrialization. *Biotechnology Journal*, **5**, 1137–1148 (2010). DOI: [10.1002/biot.201000140](https://doi.org/10.1002/biot.201000140)
- [2] Kurian J. V.: A new polymer platform for the future – Sorona® from corn derived 1,3-propanediol. *Journal of Polymers and the Environment*, **13**, 159–167 (2005). DOI: [10.1007/s10924-005-2947-7](https://doi.org/10.1007/s10924-005-2947-7)
- [3] Chuah H. H.: Synthesis, properties and applications of poly(trimethylene terephthalate). in 'Modern polyester: Chemistry and technology of polyesters and copolyesters' (eds.: Scheirs J., Long T. E.) Wiley, Chichester, 361–397 (2004). DOI: [10.1002/0470090685.ch11](https://doi.org/10.1002/0470090685.ch11)
- [4] Patel M. K., Crank M.: Projections for the production of bulk volume bio-based polymers in Europe and environmental implications. *Journal of Biobased Materials and Bioenergy*, **1**, 437–453 (2007). DOI: [10.1166/jbmb.2007.020](https://doi.org/10.1166/jbmb.2007.020)
- [5] Wolfson W.: Spinning corncocks into socks farming plastics with 'green' chemistry. *Chemistry and Biology*, **13**, 109–111 (2006).
- [6] Frisk S., Ikeda R. M., Chase D. B., Kennedy A., Rabolt J. F.: Structural analysis of poly(trimethylene terephthalate) fibers and films using polarized raman spectroscopy. *Macromolecules*, **37**, 6027–6036 (2004). DOI: [10.1021/ma049234j](https://doi.org/10.1021/ma049234j)
- [7] Desborough I. J., Hall I. H., Neisser J. Z.: The structure of poly(trimethylene terephthalate). *Polymer*, **20**, 545–552 (1979). DOI: [10.1016/0032-3861\(79\)90163-0](https://doi.org/10.1016/0032-3861(79)90163-0)
- [8] Ho R-M., Ke K-Z., Chen M.: Crystal structure and banded spherulite of poly(trimethylene terephthalate). *Macromolecules*, **33**, 7529–7537 (2000). DOI: [10.1021/ma000210w](https://doi.org/10.1021/ma000210w)
- [9] Shyr T-W., Lo C-M., Ye S-R.: Sequence distribution and crystal structure of poly(ethylene/trimethylene terephthalate) copolyesters. *Polymer*, **46**, 5284–5298 (2005). DOI: [10.1016/j.polymer.2005.04.030](https://doi.org/10.1016/j.polymer.2005.04.030)
- [10] Szymczyk A., Senderek E., Nastalczyk J., Roslaniec Z.: New multiblock poly(ether-ester)s based on poly(trimethylene terephthalate) as rigid segments. *European Polymer Journal*, **44**, 436–443 (2008). DOI: [10.1016/j.eurpolymj.2007.11.005](https://doi.org/10.1016/j.eurpolymj.2007.11.005)
- [11] Szymczyk A.: Structure and properties of new polyester elastomers composed of poly(trimethylene terephthalate) and poly(ethylene oxide). *European Polymer Journal*, **45**, 2653–2664 (2009). DOI: [10.1016/j.eurpolymj.2009.05.032](https://doi.org/10.1016/j.eurpolymj.2009.05.032)
- [12] Krutphun P., Supaphol P.: Thermal and crystallization characteristics of poly(trimethylene terephthalate)/poly(ethylene naphthalate) blends. *European Polymer Journal*, **41**, 1561–1568 (2005). DOI: [10.1016/j.eurpolymj.2005.01.023](https://doi.org/10.1016/j.eurpolymj.2005.01.023)
- [13] Huang J-M.: Polymer blends of poly(trimethylene terephthalate) and polystyrene compatibilized by styrene-glycidyl methacrylate copolymers. *Journal of Applied Polymer Science*, **88**, 2247–2252 (2003). DOI: [10.1002/app.11945](https://doi.org/10.1002/app.11945)
- [14] Lee L-T., Woo E-M.: Miscible blends of poly(4-vinyl phenol)/poly(trimethylene terephthalate). *Polymer International*, **53**, 1813–1820 (2004). DOI: [10.1002/pi.1588](https://doi.org/10.1002/pi.1588)
- [15] Liu Z., Chen K., Yan D.: Crystallization, morphology, and dynamic mechanical properties of poly(trimethylene terephthalate)/clay nanocomposites. *European Polymer Journal*, **39**, 2359–2366 (2003). DOI: [10.1016/S0014-3057\(03\)00166-6](https://doi.org/10.1016/S0014-3057(03)00166-6)
- [16] Mishra J. K., Chang Y-W., Choi N. S.: Preparation and characterization of rubber-toughened poly(trimethylene terephthalate)/organoclay nanocomposite. *Polymer Engineering and Science*, **47**, 863–870 (2007). DOI: [10.1002/pen.20770](https://doi.org/10.1002/pen.20770)
- [17] Xu Y., Jia H-B., Piao J-N., Ye S-R., Huang J.: Crystallization behavior of poly(trimethylene terephthalate)/multi-walled carbon nanotube composites. *Journal of Materials Science*, **43**, 417–421 (2008). DOI: [10.1007/s10853-007-2161-1](https://doi.org/10.1007/s10853-007-2161-1)
- [18] Paul D. R., Robeson L. M.: Polymer nanotechnology: Nanocomposites. *Polymer*, **49**, 3187–3204 (2008). DOI: [10.1016/j.polymer.2008.04.017](https://doi.org/10.1016/j.polymer.2008.04.017)

- [19] Coleman J. N., Khan U., Gun'ko Y. K.: Mechanical reinforcement of polymers using carbon nanotubes. *Advanced Materials*, **18**, 689–706 (2006). DOI: [10.1002/adma.200501851](https://doi.org/10.1002/adma.200501851)
- [20] Jorio A., Dresselhaus G., Dresselhaus M. S.: Carbon nanotubes: Advanced topics in the synthesis, structure, properties and applications. Springer, Berlin (2008).
- [21] Yu M-F., Lourie O., Dyer M. J., Moloni K., Kelly T. F., Ruoff R. S.: Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science*, **287**, 637–640 (2000). DOI: [10.1126/science.287.5453.637](https://doi.org/10.1126/science.287.5453.637)
- [22] Szleifer I., Yerushalmi-Rozen R.: Polymers and carbon nanotubes – Dimensionality, interactions and nanotechnology. *Polymer*, **46**, 7803–7818 (2005). DOI: [10.1016/j.polymer.2005.05.104](https://doi.org/10.1016/j.polymer.2005.05.104)
- [23] Lau A. K-T., Hui D.: The revolutionary creation of new advanced materials – Carbon nanotube composites. *Composites Part B: Engineering*, **33**, 263–277 (2002). DOI: [10.1016/S1359-8368\(02\)00012-4](https://doi.org/10.1016/S1359-8368(02)00012-4)
- [24] Moniruzzaman M., Winey K. I.: Polymer nanocomposites containing carbon nanotubes. *Macromolecules*, **39**, 5194–5205 (2006). DOI: [10.1021/ma060733p](https://doi.org/10.1021/ma060733p)
- [25] Eitan A., Fisher F. T., Andrews R., Brinson L. C., Schadler L. S.: Reinforcement mechanisms in MWCNT-filled polycarbonate. *Composites Science and Technology*, **66**, 1162–1173 (2006). DOI: [10.1016/j.compscitech.2005.10.004](https://doi.org/10.1016/j.compscitech.2005.10.004)
- [26] García-Gutiérrez M. C., Hernández J. J., Nogales A., Panine P., Rueda D. R., Ezquerro T. A.: Influence of shear on the templated crystallization of poly(butylene terephthalate)/single wall carbon nanotube nanocomposites. *Macromolecules*, **41**, 844–851 (2008). DOI: [10.1021/ma0713512](https://doi.org/10.1021/ma0713512)
- [27] Nogales A., Broza G., Roslaniec Z., Schulte K., Šics I., Hsiao B. S., Sanz A., García-Gutiérrez M. C., Rueda D. R., Domingo C., Ezquerro T. A.: Low percolation threshold in nanocomposites based on oxidized single wall carbon nanotubes and poly(butylene terephthalate). *Macromolecules*, **37**, 7669–7672 (2004). DOI: [10.1021/ma049440r](https://doi.org/10.1021/ma049440r)
- [28] Giraldo L. F., Brostow W., Devaux E., López B. L., Pérez L. D.: Scratch and wear resistance of polyamide 6 reinforced with multiwall carbon nanotubes. *Journal of Nanoscience and Nanotechnology*, **8**, 3176–3183 (2008). DOI: [10.1166/jnn.2008.092](https://doi.org/10.1166/jnn.2008.092)
- [29] Giraldo L. F., López B. L., Brostow W.: Effect of the type of carbon nanotubes on tribological properties of polyamide 6. *Polymer Engineering Science*, **49**, 896–902 (2009). DOI: [10.1002/pen.21386](https://doi.org/10.1002/pen.21386)
- [30] Glenis S., Likodimos V., Guskos N., Yarmis D., Zolnierkiewicz G., Szymczyk A., Lin C. L.: Magnetic properties of carbon nanotube poly(ether-ester) nanocomposites. *Journal of Applied Physics*, **108**, 054314/1–054314/4 (2010). DOI: [10.1063/1.3481688](https://doi.org/10.1063/1.3481688)
- [31] Chuah H. H., Lin-Vien D., Soni U.: Poly(trimethylene terephthalate) molecular weight and Mark–Houwink equation. *Polymer*, **42**, 7137–7139 (2001). DOI: [10.1016/S0032-3861\(01\)00043-X](https://doi.org/10.1016/S0032-3861(01)00043-X)
- [32] Brostow W.: Performance of plastics. Hanser, Munich (2001).
- [33] Pyda M., Boller A., Grebowicz J., Chuah H., Lebedev B. V., Wunderlich B.: Heat capacity of poly(trimethylene terephthalate). *Journal of Polymer Science Part B: Polymer Physics*, **36**, 2499–2511 (1998). DOI: [10.1002/\(SICI\)1099-0488\(199810\)36:14<2499::AID-POLB4>3.0.CO;2-O](https://doi.org/10.1002/(SICI)1099-0488(199810)36:14<2499::AID-POLB4>3.0.CO;2-O)
- [34] Kremer F., Schönhals A.: Broadband dielectric spectroscopy. Springer, Berlin (2000).
- [35] Kim J. Y., Han S. I., Hong S.: Effect of modified carbon nanotube on the properties of aromatic polyester nanocomposites. *Polymer*, **49**, 3335–3345 (2008). DOI: [10.1016/j.polymer.2008.05.024](https://doi.org/10.1016/j.polymer.2008.05.024)
- [36] Wang X-S., Li X-G., Yan D.: Thermal decomposition kinetics of poly(trimethylene terephthalate). *Polymer Degradation and Stability*, **69**, 361–372 (2000). DOI: [10.1016/S0141-3910\(00\)00083-5](https://doi.org/10.1016/S0141-3910(00)00083-5)
- [37] Wang X-S., Li X-G., Yan D.: High-resolution thermogravimetric analysis of poly(trimethylene terephthalate) with different molecular weights. *Polymer Testing*, **20**, 491–502 (2001). DOI: [10.1016/S0142-9418\(00\)00064-7](https://doi.org/10.1016/S0142-9418(00)00064-7)
- [38] Kelsey D. R., Kiibler K. S., Tutunjian P. N.: Thermal stability of poly(trimethylene terephthalate). *Polymer*, **46**, 8937–8946 (2005). DOI: [10.1016/j.polymer.2005.07.015](https://doi.org/10.1016/j.polymer.2005.07.015)
- [39] McNeill I. C., Bounekhel M.: Thermal degradation studies of terephthalate polyesters: 1. Poly(alkylene terephthalates). *Polymer Degradation and Stability*, **34**, 187–204 (1991). DOI: [10.1016/0141-3910\(91\)90119-C](https://doi.org/10.1016/0141-3910(91)90119-C)
- [40] McLafferty F. W.: Mass spectrometric analysis. Molecular rearrangements. *Analytical Chemistry*, **31**, 82–87 (1959). DOI: [10.1021/ac60145a015](https://doi.org/10.1021/ac60145a015)
- [41] Botelho G., Queirós A., Liberal S., Gijsman P.: Studies on thermal and thermo-oxidative degradation of poly(ethylene terephthalate) and poly(butylene terephthalate). *Polymer Degradation and Stability*, **74**, 39–48 (2001). DOI: [10.1016/S0141-3910\(01\)00088-X](https://doi.org/10.1016/S0141-3910(01)00088-X)

- [42] Liu J., Bian S. G., Xiao M., Wang S. J., Meng Y. Z.: Thermal degradation and isothermal crystalline behavior of poly(trimethylene terephthalate). *Chinese Chemical Letters*, **20**, 487–491 (2009). DOI: [10.1016/j.cclet.2008.11.035](https://doi.org/10.1016/j.cclet.2008.11.035)
- [43] Yoo H. J., Jung Y. C., Cho J. W.: Effect of interaction between poly(ethylene terephthalate) and carbon nanotubes on the morphology and properties of their nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, **46**, 900–910 (2008). DOI: [10.1002/polb.21424](https://doi.org/10.1002/polb.21424)
- [44] Kwiatkowska M., Broza G., Schulte K., Roslaniec Z.: The in-situ synthesis of poly(butylene terephthalate)/carbon nanotubes composites. *Reviews on Advanced Materials Science*, **12**, 154–159 (2006).
- [45] Broza G.: Thermoplastic elastomers with multi-walled carbon nanotubes: Influence of dispersion methods on morphology. *Composites Science and Technology*, **70**, 1006–1010 (2010). DOI: [10.1016/j.compscitech.2010.02.021](https://doi.org/10.1016/j.compscitech.2010.02.021)
- [46] Lu K., Grossiord N., Koning C. E., Miltner H. E., Van Mele B., Loos J.: Carbon nanotube/isotactic polypropylene composites prepared by latex technology: Morphology analysis of CNT-induced nucleation. *Macromolecules*, **41**, 8081–8085 (2008). DOI: [10.1021/ma8008299](https://doi.org/10.1021/ma8008299)
- [47] Kim J. Y., Han S. I., Kim D. K., Kim S. H.: Mechanical reinforcement and crystallization behavior of poly(ethylene 2,6-naphthalate) nanocomposites induced by modified carbon nanotube. *Composites Part A: Applied Science and Manufacturing*, **40**, 45–53 (2009). DOI: [10.1016/j.compositesa.2008.10.002](https://doi.org/10.1016/j.compositesa.2008.10.002)
- [48] Wang Y., Deng J., Wang K., Zhang Q., Fu Q.: Morphology, crystallization, and mechanical properties of poly(ethylene terephthalate)/multiwall carbon nanotube nanocomposites via *in situ* polymerization with very low content of multiwall carbon nanotubes. *Journal of Applied Polymer Science*, **104**, 3695–3701 (2007). DOI: [10.1002/app.25677](https://doi.org/10.1002/app.25677)
- [49] Tzavalas S., Drakonakis V., Mouzakis D. E., Fischer D., Gregoriou V. G.: Effect of carboxy-functionalized multiwall nanotubes (MWNT–COOH) on the crystallization and chain conformations of poly(ethylene terephthalate) PET in PET–MWNT nanocomposites. *Macromolecules*, **39**, 9150–9156 (2006). DOI: [10.1021/ma0613584](https://doi.org/10.1021/ma0613584)
- [50] Xu Y., Jia H.-B., Piao J.-N., Ye S.-R., Huang J.: Crystallization behavior of poly(trimethylene terephthalate)/multi-walled carbon nanotube composites. *Journal of Materials Science*, **43**, 417–421 (2008). DOI: [10.1007/s10853-007-2161-1](https://doi.org/10.1007/s10853-007-2161-1)
- [51] Hong P.-D., Chuang W.-T., Yeh W.-J., Lin T.-L.: Effect of rigid amorphous phase on glass transition behavior of poly(trimethylene terephthalate). *Polymer*, **43**, 6879–6886 (2002). DOI: [10.1016/S0032-3861\(02\)00617-1](https://doi.org/10.1016/S0032-3861(02)00617-1)
- [52] Wundrelich B.: Reversible crystallization and the rigid–amorphous phase in semicrystalline macromolecules. *Progress in Polymer Science*, **28**, 383–450 (2003). DOI: [10.1016/S0079-6700\(02\)00085-0](https://doi.org/10.1016/S0079-6700(02)00085-0)
- [53] Ma Q., Cebe P.: Phase structure of electrospun poly(trimethylene terephthalate) composite nanofibers containing carbon nanotubes. *Journal of Thermal Analysis and Calorimetry*, **102**, 425–434 (2010). DOI: [10.1007/s10973-010-0977-4](https://doi.org/10.1007/s10973-010-0977-4)
- [54] Müller A. J., Arnal M. L., Trujillo M., Lorenzo A. T.: Super-nucleation in nanocomposites and confinement effects on the crystallizable components within block copolymers, miktoarm star copolymers and nanocomposites. *European Polymer Journal*, **47**, 614–629 (2011). DOI: [10.1016/j.eurpolymj.2010.09.027](https://doi.org/10.1016/j.eurpolymj.2010.09.027)
- [55] Trujillo M., Arnal M. L., Müller A. J., Bredeau S., Bonduel D., Dubois P., Hamley I. W., Castelletto V.: Thermal fractionation and isothermal crystallization of polyethylene nanocomposites prepared by *in situ* polymerization. *Macromolecules*, **41**, 2087–2095 (2008). DOI: [10.1021/ma702272e](https://doi.org/10.1021/ma702272e)
- [56] Napolitano S., Wübbenhorst M.: Deviation from bulk behaviour in the cold crystallization kinetics of ultra-thin films of poly(3-hydroxybutyrate). *Journal of Physics: Condensed Matter*, **19**, 205121/1–205121/9 (2007). DOI: [10.1088/0953-8984/19/20/205121](https://doi.org/10.1088/0953-8984/19/20/205121)
- [57] Šics I., Ezquerro T. A., Nogales A., Denchev Z., Alvarez C., Funari S. S.: Cold crystallization of poly(ethylene naphthalene-2,6-dicarboxylate) by simultaneous measurements of X-ray scattering and dielectric spectroscopy. *Polymer*, **44**, 1045–1049 (2003). DOI: [10.1016/S0032-3861\(02\)00742-5](https://doi.org/10.1016/S0032-3861(02)00742-5)
- [58] Nogales A., Ezquerro T. A., Denchev Z., Šics I., Baltá-Calleja F. J., Hsiao B. S.: Molecular dynamics and microstructure development during cold crystallization in poly(ether-ether-ketone) as revealed by real time dielectric and X-ray methods. *Journal of Chemical Physics*, **115**, 3804–3813 (2001). DOI: [10.1063/1.1388627](https://doi.org/10.1063/1.1388627)
- [59] Sanz A., Nogales A., Ezquerro A. T., Soccio M., Munari A., Lotti N.: Cold crystallization of poly(trimethylene terephthalate) as revealed by simultaneous WAXS, SAXS, and dielectric spectroscopy. *Macromolecules*, **43**, 617–679 (2010). DOI: [10.1021/ma902188c](https://doi.org/10.1021/ma902188c)
- [60] Kopeczynska A., Ehrenstein G. W.: Polymeric surfaces and their true surface tension in solids and melts. *Journal of Materials Education*, **29**, 325–340 (2007).
- [61] Brostow W., Hagg Lobland H. E., Narkis M.: Sliding wear, viscoelasticity, and brittleness of polymers. *Journal of Materials Research*, **21**, 2422–2428 (2006). DOI: [10.1557/jmr.2006.0300](https://doi.org/10.1557/jmr.2006.0300)
- [62] Chae H. G., Liu J., Kumar S.: Carbon nanotubes-enabled materials. in ‘Carbon nanotubes properties and applications’ (ed.: O’Connell M. J.) CRC Press Taylor and Francis Group, Boca Raton, 213–253 (2006).

- [63] Gao J., Zhao B., Itkis M. E., Bekyarova E., Hu H., Kranak V., Yu A., Haddon R. C.: Chemical engineering of the single-walled carbon nanotube–nylon 6 interface. *Journal of the American Chemical Society*, **128**, 7492–7496 (2006).
DOI: [10.1021/ja057484p](https://doi.org/10.1021/ja057484p)
- [64] Qian D., Dickey E. C., Andrews R., Rantell T.: Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Applied Physics Letters*, **76**, 2868–2870 (2000).
DOI: [10.1063/1.126500](https://doi.org/10.1063/1.126500)
- [65] Allaoui A., Bai S., Cheng H. M., Bai J. B.: Mechanical and electrical properties of a MWNT/epoxy composite. *Composites Science and Technology*, **62**, 1993–1998 (2002).
DOI: [10.1016/S0266-3538\(02\)00129-X](https://doi.org/10.1016/S0266-3538(02)00129-X)
- [66] Geng H. Z., Rosen R., Zheng B., Shimoda H., Fleming L., Liu J., Zhou O.: Fabrication and properties of composites of poly(ethylene oxide) and functionalized carbon nanotubes. *Advanced Materials*, **14**, 1387–1390 (2002).
DOI: [10.1002/1521-4095\(20021002\)14:19<1387::AID-ADMA1387>3.0.CO;2-Q](https://doi.org/10.1002/1521-4095(20021002)14:19<1387::AID-ADMA1387>3.0.CO;2-Q)
- [67] Bai J. B., Allaoui A.: Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites – Experimental investigation. *Composites Part A: Applied Science and Manufacturing*, **34**, 689–694 (2003).
DOI: [10.1016/S1359-835X\(03\)00140-4](https://doi.org/10.1016/S1359-835X(03)00140-4)
- [68] Koval'chuk A. A., Shchegolikhin A. N., Shevchenko V. G., Nedorezova P. M., Klyamkina A. N., Alsdyshev A. M.: Synthesis and properties of polypropylene/multiwall carbon nanotube composites. *Macromolecules*, **41**, 3149–3156 (2008).
DOI: [10.1021/ma800297e](https://doi.org/10.1021/ma800297e)
- [69] Foulger S. H.: Electrical properties of composites in the vicinity of the percolation threshold. *Journal of Applied Polymer Science*, **72**, 1573–1582 (1999).
DOI: [10.1002/\(SICI\)1097-4628\(19990620\)72:12<1573::AID-APP10>3.0.CO;2-6](https://doi.org/10.1002/(SICI)1097-4628(19990620)72:12<1573::AID-APP10>3.0.CO;2-6)
- [70] Kalaitzidou K., Fukushima H., Drzal L. T.: A route for polymer nanocomposites with engineered electrical conductivity and percolation threshold. *Materials*, **3**, 1089–1103 (2010).
DOI: [10.3390/ma3021089](https://doi.org/10.3390/ma3021089)
- [71] Celzard A., McRae E., Deleuze C., Dufort M., Furdin G., Marêché J. F.: Critical concentration in percolating systems containing a high-aspect-ratio filler. *Physical Review*, **53**, 6209–6214 (1996).
DOI: [10.1103/PhysRevB.53.6209](https://doi.org/10.1103/PhysRevB.53.6209)