Original Article

Effect of multi walled carbon nanotube on mechanical, thermal and rheological properties of polypropylene

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ABSTRACT

In this study, multi-walled carbon nanotube (MWCNT) filled polypropylene (PP) nanocomposites prepared by melt processing methods by employing extruder and injection molding techniques were examined with various characterization methods and test procedures, in detail. Aim and novelty of the work were to merely investigate the effects of amount and dispersion of MWCNTs on mechanical, thermal and rheological properties of PP including no compatibilizer and thus chemical interaction and/or interfacial adhesion effect. The mechanical test results showed that the incorporation of MWCNTs increased the tensile strength (18.4%), flexural strength (35.2%) and modulus of elasticity (45%) while it decreased the impact strength (18%) and elongation at break (690%) values of PP/MWCNT nanocomposites. Thermal analysis data revealed that the MWCNT addition slightly increased the crystallization peak onset and peak maximum temperatures of PP under non-isothermal conditions. Frequency-dependent melt rheological behaviors of nanocomposites in linear viscoelastic regime pointed out that the storage modulus (G'), loss modulus (G''), complex viscosity (η*), and relaxation time of PP increased with the increasing amount of MWCNT. Non-linear rheological tests such as creep and stress relaxation also depicted that nanocomposites exhibited lower creep strain and relaxation rate than PP. Based on the thermal and mechanical test results, 0.3 wt% of MWCNT could be considered as the critical filler amount also called as “percolation threshold” for improving the solid-state physical properties of PP/MWCNT nanocomposites under the circumstances of no compatibilizer.

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1. Introduction

Polymers and polymer composites are extensively used in the industry. In machine design, polymer-based materials are specifically and preferentially employed due to their many advantages such as lightness, chemical resistance, easy processing, and recycling compared to metals and metallic alloys. However, unreinforced polymers possess some disadvantages in terms of their mechanical and thermal properties. In order to enhance some physical properties of polymers various types of fibers such as glass fiber [1], carbon fiber [2], and aramid [3] and particles such as talc [4], calcium carbonate [5], and carbon black [6] having different particle shape and sizes are introduced into polymers. In recent
years, carbon-based nanomaterials (e.g. carbon nanotube-CNT, carbon nanofiber-CNF, and graphene derivatives) have become the most important fillers for improving the physical properties of polymers [7,8]. Superior structural and physical properties of carbon nanotubes such as one-dimensional (1D) geometry, extremely high aspect ratio, modulus of elasticity (200–1000 GPa), and strength (200–900 GPa), electrical and thermal conductivity make them excellent candidates as nanofillers to produce advanced polymer nanocomposites [9–11]. Single-walled or multi-walled carbon nanotube (SWCNT or MWCNT) filled polymer composites can be produced by in-situ polymerization, solution mixture or melt mixing (extrusion and injection) techniques. Among these production methods, melt processing particularly provides a cost-effective process which enables to ensure both fast production and environmental benefits as a solvent-free route [7]. Zou et al. [12] investigated the izod impact strength of MWCNT filled high density polyethylene (HDPE) composites produced by twin-screw extrusion and injection molding methods. Kanagari et al. [13] reported that mechanical properties of HDPE were improved with the addition of CNT in the HDPE/CNT composites produced by injection molding. This was explained with the good load transfer effect and the interfacial linking between CNT and HDPE. On the other hand, Xiao et al. [14] stated that when the amount of MWCNT was kept at about 10 wt%, the elastic modulus value increased by 89% and the tensile strength increased by 56% in the MWCNT filled LDPE composites. Ogasawara et al. [15] manufactured polyimide (PI)/MWCNT composites by in-situ polymerization method and found that the glass transition temperature (T_g), elastic modulus and yield strength values of composites increased with the addition of MWCNT. Liu et al. [16] prepared polyetherimide (PEI)/MWCNT nanocomposite films by solution casting and thermal imidization methods. They reported that 1 wt% of MWCNT improved the T_g of PEI about 10 °C and the elastic modulus of PEI about 250%. Phang et al. [17] investigated mechanical properties of MWCNT filled polyamides (PA6) produced by melt-compounding. They found that the elastic modulus and yield strength values of PA6 were improved by about 214% and 162%, respectively with the addition of 2 wt% of MWCNTs.

Polypropylene (PP) is a member of polyolefins and one of the most widely used semi-crystalline thermoplastics existing in various crystalline forms such as the monoclinic α-form and the hexagonal β-form. PP-based parts are commonly used in different industries such as military, marine vehicles, packaging, automobiles and constructions due to their physical and chemical properties as well as their relatively low cost advantage [18]. However, PP exhibits low thermal, electrical, and mechanical properties and also a high coefficient of friction under dry sliding conditions compared to engineering plastics. Bettina et al. [19] investigated the influence of carbon-based additives such as thermally reduced graphite oxide (TRGO), multi-layer graphene, carbon black (CB), MWCNT, and expanded graphite (EG) with different particle sizes and shapes on the flame retardancy and mechanical properties of isotactic polypropylene (iPP). Novais et al. [20] investigated the influence of chemical functionalization and polymer melt blending conditions on carbon nanotube dispersion in polypropylene, as well as its influence on the electrical and mechanical properties. Seo et al. [21] stated that the storage modulus of PP (547 MPa) increased by 52.3% with the addition of 7.5 phr of CNT. Thiebaud et al. [22] determined that the modulus of elasticity of PP composite increased within a range of 26.9–40.2%, and the yield strength improved from 17.3% to 30.3% depending on the increased amount of MWCNT.

Xiao et al. [23] studied the impact and tensile behaviors of PP/MWCNT nanocomposites at low speed. They reported that both tensile strength and impact strength values were increased when the amount of MWCNT was about 0.6 wt%. Dimitrios et al. [24] also studied the mechanical and rheological properties of CNT filled PP nanocomposite. They noted that due to the reinforcement effect of CNTs, the tensile modulus, tensile strength and storage modulus of PP/CNTs nanocomposite increased, however, above a certain CNTs content, the mechanical properties are reduced due to agglomeration of the CNTs.

The rheological properties of composite or nanocomposite can provide quantitative information to access the microstructural features of the system revealing information on the formation of percolated network structure, filler dispersion or agglomeration, orientation, and interfacial interaction between filler and polymer matrix. Furthermore, it is also very important to appraise rheological behaviors of composite samples so as to understand the effect of nanotubes on inner structures and operating properties of polymer/MWCNT nanocomposites [21,25]. Several studies have reported the influence of MWCNTs and polypropylene grafted maleic anhydride (PP-g-MA) on the rheological behavior of PP nanocomposites [25–31]. Po-Hsiang et al. [30] were prepared the functionalized MWCNTs ((f-MWCNT)/PP, pristine MWCNTs (p-MWCNT)/PP and MA-g-PP/f-MWCNT/PP nanocomposites. They investigated the effect of MWCNT and PP-g-MA on the crystallization, rheology, and mechanical behavior properties of nanocomposites. Irena et al. [31] were prepared PP/MWCNT nanocomposites with nanofiller concentrations in the range of 0.05–1 wt% MWCNT and the polypropylene grafted maleic anhydride (PP-g-MA) amount from 0 to 7.5 wt%. The study was conducted to examine the effect of MWCNT and PP-g-MA contents on the thermal, mechanical, and viscoelastic properties of PP/MWCNT nanocomposites. Prashantha et al. [22] investigated the rheological properties of MWCNT-filled PP nanocomposites prepared via melt blending method. According to the results of the rheological tests, the fluid-solid transition was observed in 2% MWCNT filled nanocomposites. When the amount of MWCNT was increased, the MWCNT network formed in the PP matrix and supported the increase of mechanical properties by exhibiting more solid-like (i.e. more elastic) behavior. Prashantha et al. [33] also studied the effect of polypropylene grafted maleic anhydride (PP-g-MA) on the mechanical and thermal properties of MWCNT/PP nanocomposites produced by the extrusion method. They concluded that PP-g-MA increased dynamic moduli and viscosity of the PP/MWCNT nanocomposites. Tensile and flexural moduli and Charpy impact resistance of the PP/MWCNT nanocomposites also increases by the addition of PP-g-MA. Pawan et al. [25] investigated the effect of MWCNTs on the viscoelastic parameters such as complex viscosity (η’), elastic modulus and loss modulus. Incorporation of MWCNTs in the polymer matrix resulted in higher complex viscosity (η’), storage (G’)
and loss modulus (G") as compared to neat polymer, especially in the low-frequency region, suggesting a change from liquid to solid-like behavior in the nanocomposites. Lee et al. [34] also examined the effect of MWCNT and compatibilizer (PP-g-MA) loading on the rheological and electrical properties of MWCNT/PP nanocomposites. Shear viscosity and yield stress values were increased with the MWCNT loading at low shear rate region due to increased interaction between MWCNT particles. However, rheological and electrical properties of highly concentrated MWCNT composites with the PP-g-MA were not improved compared with PP/MWCNT nanocomposites. They are concluded that the PP-g-MA does not play an important role in improvement of the interaction between PP matrix and MWCNT particles. Achmad et al. [27] also examined the rheological and electrical properties of PP composites filled with various amounts of MWCNTs. Zadhoush et al. [35] were prepared the PP/MWCNT nanocomposites using polypropylene and modified carbon nanotubes (CNTs) via melt-extrusion process. Pure PP was compared with maleic anhydride grafted polypropylene (PP-g-MA), reinforced with 0.5, 1, and 1.5 wt% COOH-modified nanotube (PPgCNT) and polypropylene/unmodified CNT nanocomposite (PPCN) in 1 wt% content. They were examined the effect of modified CNT and compatibilizer (PP-g-MA) loading on the rheological and mechanical properties of CNT/PP nanocomposite. As a result of study, nanocomposite with modified nanotube showed higher tensile strength, tensile modulus, and lower elongation at break compare with unmodified CNT/PP nanocomposite. According to the oscillatory rheometry results, storage modulus, loss modulus, complex modulus, and complex viscosity of PPgCNTs were higher than PP and PP/CNT.

As briefly reviewed above, melt-compounded polyolefin composite and nanocomposites are generally prepared by using a considerable amount of compatibilizer, at least two-fold of filler amount for nano fillers. Compatibilizers consist of various functional groups. Compatibilizer usage has been considered as a formulation necessity for polyolefin systems due to (i) non-polar structures of polyolefins, (ii) improve the interfacial interaction between filler and matrix, and (iii) resulting filler dispersion, mechanical, and physical properties of the composite. The present work has aimed to quantify only the effect of MWCNT amount on the physical properties of PP/MWCNT composites without a possible impact of chemical interaction, as a different point of view from the literature. Besides the mechanical and thermal properties, rheological modeling has been performed to understanding the microstructural properties of PP/MWCNT composites. In order to investigate the effect of MWCNT addition on the mechanical, thermal and rheological properties of polypropylene composites a series of PP-MWCNT nanocomposites that have MWCNT loadings within the range of 0.1–2.0 wt% were produced using melt processing method employing extruder and injection molding techniques. Mechanical, thermal and rheological properties of nanocomposite samples were characterized.

2. Materials and methods

Polypropylene was used as matrix material (PP, Exxonmobil Chemical Company, commercial code: PP3374E3) with a specific gravity of 0.9 g/cm³ and a melt flow index (MFI) of 1.3 g/10 min. (at 230 °C and 2.16 kg). Multi walled carbon nanotubes (MWCNTs) were purchased from Detsan A.S. (Turkey). The purity of MWCNT was declared to be higher than 97% by the manufacturer. Average outer-diameter and length of MWCNTs are about 10–20 nm and 10–30 μm, respectively and their surface area is higher than 200 m²/g. Before melt processing, MWCNT powder was dried at 80 °C for 24 h to eliminate moisture. PP/MWCNT nanocomposite specimens were produced with two-step mixing process. In the first step, PP-MWCNT pellets were prepared by using a co-rotating twin-screw extruder operated with a screw speed of 350 rpm and barrel temperature of 160–200°C from main feeder to die. In the second step, nanocomposite pellets were molded into 4 mm thick-plates for mechanical test by using an injection molding machine. The barrel temperature ranged between 215–230°C and the mould temperature was kept at 30°C. The injection pressure and speed were 88 bar and 44 rpm, respectively. MWCNT content in the nanocomposite composition varied within the range of 0.1–2 wt%.

Mechanical properties of injection molded PP/MWCNT specimens were measured with a Zwick-Roell-ZR 100 universal tension/compression test machine at ambient conditions (room temperature and humidity) with a crosshead speed of 10 mm/min according to the ASTM D638 standard. Flexural properties of nanocomposites were determined with the same instrument by employing a three point bending test apparatus with a crosshead displacement rate of 5 mm/min as per the ASTM D790 standard. Charpy notch impact tests were carried out according to the ISO 179-1 standard on a Zwick-Roell-HIT 5-5-P impact pendulum. V type notch specimens sized 4 x 10 x 40 mm were prepared. At least five samples were tested in each nanocomposite composition and average results were reported.

Melting and crystallization behaviors of PP and the nanocomposites were analyzed in a heat flux type DSC (SII Nanotechnology, ExStar 6200). Temperature and heat flow calibration of the instrument were carried out by using high purity calibration standards, indium (In), tin (Sn), and zinc (Zn) metals. In DSC analyses, samples weighing about 9–10 mg in an aluminum crucible were heated from 0 to 220°C with a heating rate of 10°C/min and kept at this temperature for 2 min to remove the thermal history then cooled from 220 to 0°C with a cooling rate of 10°C/min by using an electrical cooling device, Thermo Scientific EK90C/SII intracooler. After completing the melt-crystallization process, samples were kept at 0°C for 2 min. then heated again from 0 to 220°C with a heating rate of 10°C/min. All runs were carried out under nitrogen (N2) atmosphere (flow rate of 50 mL/min) to prevent thermal degradation of samples. Degree of crystallinity (Xc %) values of nanocomposites were calculated by using the following Eq. 1:

\[ X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0(1 - \alpha)} \times 100 \]  

(1)
where $\Delta H_m$ is the experimentally obtained second melting enthalpy value of sample (J/g), $(1-\alpha)$ is the weight percent of PP in sample, $\Delta H'_m$ is the enthalpy value of melting of a 100% crystalline form of PP (209 J/g) [3,20].

Rheological behaviors of PP and PP/MWCNT nanocomposites were characterized by performing several test procedures in melt state in a rotational rheometer, AR-G2 (TA Instruments). Strain sweep tests were carried out from initial strain value of 0.1% to final strain value of 100% with a frequency (f) of 1 Hz ($\omega = 6.283$ rad/s) at 190 $^\circ$C to determine linear viscoelastic (LVE) region of samples. Shear moduli (storage modulus, $G'$ and loss modulus, $G''$) values were recorded as a function of shear strain (%). Then, a time sweep test was performed for PP and PP/MWCNT nanocomposite by applying a shear strain of 10% with a constant frequency of 1 Hz for 10 min at 190 $^\circ$C. In time sweep test, $G'$ and $G''$ values were followed as a function of time. Frequency sweep tests were performed by oscillating sample melt within a frequency range of 0.1–100 rad/s with a particular strain value (5%) in LVE region at 190 $^\circ$C. Viscoelastic moduli ($G'$ and $G''$), dynamic (or complex) viscosity ($\eta$), and loss factor (tangential) were recorded as a function of angular frequency ($\omega$). Then, creep tests were implemented by applying a stress stress value of 100 Pa to sample melted at 190 $^\circ$C for 3 min and resulting shear strain (%) and compliance (J) responses of samples were recorded as a function of time (s). In stress relaxation test, a step strain of 10% was applied to the sample melted in equilibrium state at 190 $^\circ$C and resulting time-dependent decay in shear stress [$\eta$ ($\dot{\gamma}$)] was observed. In each rheology test, new sample was loaded to rheometer and equilibrated in order to avoid possible effects of thermomechanical conditions and deformation history on rheological response of the sample.

Scanning electron microscopic (SEM) images were taken on the fractured surfaces of PP/MWCNT nanocomposite. A thin layer of gold was sputter deposited onto samples. Electron microscopy imaging of the PP/MWCNT nanocomposite was performed under high vacuum with a NANOSEM 650 SEM instrument operating at 5 kV. X-ray diffraction (XRD) method was also used for microstructural characterization of nanocomposites. XRD tests were carried out by using a Panalytical (Empyrean) model wide angle X-ray Diffractometer (XRD) with a Cu Kα, running at 45 kV and 40 mA, scanning from $10^\circ$ to $40^\circ$ with the step of $2^\circ$/min.

3. Results and discussions

The reinforcing effects of nanofillers are mainly governed by their amount and degree of dispersion into the matrix. For this reason, morphological characterization is very important for probing level of nanotube dispersion into polymer matrix [10]. SEM images of MWCNT and fractured structure of PP polymer, 0.3 wt% and 1 wt% MWCNT filled PP nanocomposites were indicated in Fig. 1. It can be seen in Fig. 1(a) that MWCNT's are long and highly entangled tubes having an average diameter of 30–50 nm and length of several micrometers.

Table 1 represents the results of the mechanical properties of PP and PP/MWCNT nanocomposites. The tensile strength is increased from 29.7 MPa for PP polymer to 35.2 MPa for 2% MWCNT filled PP nanocomposite. The rate of increase in tensile strength is 18.4% compared to the unreinforced PP polymer. The better tensile strength obtained might be due to a better dispersion of MWCNT in polymer, the higher surface area of MWCNT and good adhesion between MWCNT and polymer [36,37]. The tensile modulus of PP/MWCNT nanocomposites also increases with the increasing content of MWCNT. This indicates that the addition of MWCNT into PP phase improves stiffness and rigidity of composites. The percentage increase in elastic modulus was determined as 45.0% with respect to the PP. Similar result were obtained by Prashantha et al. [32]. They were observed that the Young’s modulus increased from 26.9% to 40.2% and yield stress increased 17% to 30.3% relative to the unfilled polypropylene with an increase of MWNT concentration. The increase in elastic modulus can be relevant to the stiffness factor of MWCNT. This factor restricts the mobility of PP chains, reduces the flexibility and results in increased stiffness [37]. A similar relationship was also observed by Ansari et al. [38]. They reported that the elastic modulus of PP composites reinforced with MWCNT and feldspar increased with the MWCNT content because of higher aspect ratio of MWCNT and formation of C—C bonding between PP and MWCNT. Dimitrios [24] reported that tensile strength and modulus of PP/MWCNTs were increased with increasing MWCNTs due to nanotubes act as reinforcement agents at lowCNTs (2–2.5 wt%) content while with further increase of MWCNTs, the tensile strength of PP/MWCNTs nanocomposites decreases due to the formed aggregates act as mechanical failure concentrators. Based on the previously reported works and relevant literature on the subject, increase in tensile properties of CNT filled PP composites might be attributed to several factors. Firstly, CNTs generally promote the crystallization of PP and improve the degree of crystallinity values thus nanocomposites may exhibit higher mechanical properties. Increase in degree of crystallinity is also related to the fact that compatibilizers dramatically improve the interfacial adhesion between CNT surfaces to polymer chains therefore induce the nucleation by also reducing the segmental mobility of matrix polymer. Secondly, in the case of well-dispersed CNTs into polymer matrix, fillers allow more uniform load distribution in composite structure. Thirdly, strong interactions between polymer chains and CNTs enable a more efficient load transfer from matrix to nanotubes [18,24,39].

In addition to tensile strength and elastic modulus, impact properties are also important for polymer nanocomposites. Impact strength of PP and PP/MWCNT nanocomposites are listed in Table 1. Impact strength decreases with the increasing content of MWCNT. This decrease is about 18%, depending on the MWCNT content. Reduce in impact strength is more noticeable for the CNT content up to 0.3 wt%. This might be attributed to the existence of nanotube agglomerations in PP that act as stress concentrations and led to crack initiation [32]. Prashantha et al. [32] have obtained similar results in their study of the mechanical properties of MWCNT and clay filled PP composites. Prashantha et al. [33] also stated that the notch impact resistance values of PP nanocomposites are reduced by the addition of MWCNT and PP-g-MA in their another study. Zadkoush et al. [35] stated that unmodified CNT filled PP nanocomposite show weaker properties than PP-g-MA and modified CNT filled PP nanocomposite due
to the lower distribution and crystallization in unmodified CNTs, resulting in less load transmission. Khodabandelou and Agbjeh [40] represented that the impact strength of PP/CNT nanocomposites is slightly higher than that of neat PP. However, the addition of PP-g-MA has a negative effect on the impact resistance of PP, because of its poor mechanical properties relative to the neat PP. Generally, addition of rigid particles into PP reduced the elongation at break. Elongation at break results of PP and PP/MWCNT nanocomposites are also given in Table 1. It is seen that neat PP exhibits ductile behavior specified with the elongation at break of 150%. But, incorporation of MWCNT into PP yielded a significant reduction in the elongation at break. Elongation at break value of PP/2MWCNT sample was found to be 19%. Juan [41] reported that reduction in elongation at break was dependent on the segmental flexibility of the polymer chains. The conformation change of polymer chain is restricted by the MWCNTs, which induces a decline in elongation at break. Mertens and Senthivelan [42] also reported that CNTs restrict the mobility of polymer chains, and thus the percentage elongation of PP reduced with increasing CNTs content from 0.5 to 5 wt%. Dimitrios et al. [18] stated that elongation at break values of nanocomposites are reduced because of the aggregation of MWCNT and high crystallization rates. Prashantha et al. [33] stated that in spite of the better dispersion of MWCNTs to PP matrix with PP-g-MA, elongation at break decreases with increase in MWCNT content. In their study, similar elongation break values were obtained with and without PP-g-MA because of the presence of few masterbatch aggregates.

As shown in Table 1, both flexural strength and modulus significantly increase with the increasing amount of MWCNT. Flexural strength of PP increased from 26.4 MPa to 35.7 MPa by introducing 2% of MWCNT. Flexural modulus of PP/MWCNT nanocomposites were improved significantly as the MWCNT content was increased from 0.1 to 2 wt%. The flexural modulus of PP, 771 MPa, is steadily increased to 815, 886, 924, 1023, and 1148 MPa for the nanocomposites having MWCNT content of 0.1, 0.2, 0.3, 1.0 and 2.0 wt%, respectively. This result suggests that the interfacial interactions allow an effective stress transfer between PP and MWCNT. At the same time, the MWCNT can raise the fracture energy and provide a strong interfacial shear stress, and for this reason crack propagation can be prevented [38]. The flexural modulus increases approximately up to 17.4% and 36.3% in presence of 0.5% by volume of non-functionalized and amino-functionalized carbon nanotubes, respectively. However, further increases of the filler content always induces slight reductions of the same parameter probably due to the formation of clusters or agglomerates, resulting in lower properties at the interface with the hosting matrix and a reduced interface area between CNTs and the matrix [7].

Table 1 – Results of mechanical properties of PP and PP/MWCNT nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Impact strength (kJ/m²)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>29.76</td>
<td>950</td>
<td>150</td>
<td>9.23</td>
<td>26.4</td>
<td>771</td>
</tr>
<tr>
<td>PP/0.1MWCNT</td>
<td>30.27</td>
<td>1020</td>
<td>100</td>
<td>9.05</td>
<td>27.8</td>
<td>815</td>
</tr>
<tr>
<td>PP/0.2MWCNT</td>
<td>32.64</td>
<td>1168</td>
<td>82</td>
<td>8.71</td>
<td>30.2</td>
<td>886</td>
</tr>
<tr>
<td>PP/0.3MWCNT</td>
<td>33.35</td>
<td>1214</td>
<td>39</td>
<td>8.24</td>
<td>32.2</td>
<td>924</td>
</tr>
<tr>
<td>PP/1MWCNT</td>
<td>33.74</td>
<td>1289</td>
<td>28</td>
<td>7.85</td>
<td>33.6</td>
<td>1024</td>
</tr>
<tr>
<td>PP/2MWCNT</td>
<td>35.26</td>
<td>1378</td>
<td>19</td>
<td>7.41</td>
<td>35.7</td>
<td>1148</td>
</tr>
</tbody>
</table>

Fig. 1 – SEM images of a) MWCNT, b) PP polymer, c) 0.3 wt% and d) 1 wt% filled MWCNT/PP nanocomposites.
respectively. The melting temperature \( T_m \), crystallization temperature \( T_c \), and degree of crystallization \( X_c \) of PP and its nanocomposites values are given in Table 2. As represented in Table 2, the crystallization peak onset \( (T_{c,o}) \) and peak maximum \( (T_{c,p}) \) temperatures increase with the addition of MWCNTs. This nucleating effect of CNTs is known and has been described by Beate [43]. For the incorporation of 0.05 wt% MWCNTs caused an increase in the onset crystallization temperature \( T_{c,o} \) of 11 °C and an increase in the maximum crystallization temperature \( T_{c,p} \) of 7 °C in comparison to the comparably processed PA66. Additionally, addition of 2 wt% of MWCNT increased \( T_c \) of PP nanocomposites by 11 °C [39], and addition of 1 wt% long and short length MWCNT increased \( T_c \) value by 13 °C [44]. It was also found that the crystallization enthalpy values of nanocomposites, normalized with respect to the PP amount, were higher than that of PP except the PP/2%MWCNT sample. It is known that the crystallization properties such as degree of crystallinity, spherulite size, and crystallite form (\( \alpha \) or \( \beta \) crystallites) influence the mechanical properties of semi-crystalline polymers. Therefore, understanding the effect of nanoparticles on nucleation and crystallinity development of such materials can be considered as crucial information for quantifying structure–property relationships [24,44]. The effects of CNTs on the crystallization behavior of polymers have been extensively studied by different researchers [24,42,43]. All of them indicated that CNT acted as nucleating agents, which induce easier and faster crystallization under isothermal and non-isothermal conditions. Owing to the very similar crystallinity and numerous nucleating sites, spherulite size in nanotube filled composites is expected to be much smaller than that of unfilled PP. It was obtained that the melting behavior and melting temperature \( T_m \) of PP did not changed much with the addition of MWCNT. The melting temperature range of PP and its nanocomposites was in range of 150–152 °C. This finding is in agreement with the results of other authors [43]. But, the degree of crystallinity \( (X_c) \) values of nanocomposites varied depending on the MWCNT amount. As seen in Table 2, \( X_c \) value of PP increased about 5% with the MWCNT amount increased up to 0.3 wt% then it slightly reduced with the further addition of MWCNT. There are different studies on the effect of MWCNT on the crystallinity of the PP polymer. In these studies, it was determined that the \( X_c \) of PP could remain unchanged, decline or increase slightly as the MWCNT loading increased. Qiu et al. [45] described an increase in the overall crystallinity from 28% to 33–34% with the MWCNT incorporation (1 wt%) depending on the MWCNT functionalization. Grady et al. [46] found about a 2% increase in the \( X_c \) of PP by adding of 1.8 wt% of SWNTs under non-isothermal crystallization run. Mertens and Senthilvelan [42] reported that the \( X_c \) of PP increased from 47.7% to 52.5% when the CNT amount increase from 0 to 1 wt% because of nucleating sites but, the \( X_c \) value reduced to 43.7% in the case of 5% CNT because CNTs restricted the mobility of PP chains and acted as barriers to the crystal growth. Ersoy and Onder [47] also reported the \( X_c \) values of PP/CNT composites (0, 1.8, 4.6, and 8 wt%) determined by the DSC analysis. The \( X_c \) value of PP raised from 39.7% to 44.7% for the CNT amount of 4.6 wt%. But they also found that a further increase in CNT amount up to 8 wt% reduced the \( X_c \) value down to 42%. Irena et al. [31] reported the \( X_c \) value of PP/MWCNT nanocomposites increased from 43.4% to 46.2% by increasing of the MWCNT content from 0% to 5 wt%. They also stated that the addition of PP-g-MA in the range of 2.5–7.5% does not have significant influence on the thermal and crystallization behavior of PP/MWCNT.

### Table 2 – Crystallization and melting parameters of PP and PP/MWCNT nanocomposites determined by DSC analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_{c,o} ) (°C)</th>
<th>( T_{c,p} ) (°C)</th>
<th>( \Delta H_c ) (J/g)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta H_m ) (J/g)</th>
<th>( X_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>112.5</td>
<td>107.6</td>
<td>62.5</td>
<td>152.13</td>
<td>66.1</td>
<td>31.6</td>
</tr>
<tr>
<td>PP/0.1MWCNT</td>
<td>112.7</td>
<td>108.2</td>
<td>71.4</td>
<td>150.81</td>
<td>74.8</td>
<td>35.8</td>
</tr>
<tr>
<td>PP/0.2MWCNT</td>
<td>113.4</td>
<td>108.4</td>
<td>68.6</td>
<td>151.11</td>
<td>75.9</td>
<td>36.4</td>
</tr>
<tr>
<td>PP/0.3MWCNT</td>
<td>113.9</td>
<td>108.6</td>
<td>69.1</td>
<td>151.46</td>
<td>75.6</td>
<td>36.3</td>
</tr>
<tr>
<td>PP/1MWCNT</td>
<td>114.6</td>
<td>109.5</td>
<td>65.8</td>
<td>151.08</td>
<td>69.4</td>
<td>33.5</td>
</tr>
<tr>
<td>PP/2MWCNT</td>
<td>115.5</td>
<td>109.6</td>
<td>61.6</td>
<td>152.25</td>
<td>68.5</td>
<td>33.4</td>
</tr>
</tbody>
</table>

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**Fig. 2 – Crystallization exotherms and melting endotherms of PP/MWCNT nanocomposites.**
PP/MWCNT nanocomposites. The melting and crystallization peaks become broader by increasing the amount of PP-g-MA due to the formation of various sized crystals.

MWCNTs can alter the crystallization process and also crystal structure of nanocomposites [27]. The X-ray diffraction patterns of PP and PP/MWCNTs are given in Fig. 3. The characteristic crystalline reflection of α-form of PP were clearly observed at 2θ of 13.9° (110), 16.7° (040), 18.4° (130), 20.9° (111), 21.0° (041), and 25.3° (060) in these patterns. According to these results, PP did not form β-structure crystals but, MWCNT addition induced the formation of β-crystals (2θ = 15.9°) (300) under identical crystallization conditions. As it can be seen, the samples which contain small concentrations of MWCNTs (up to 2.0 wt%), include the peak which corresponds to the reflections from β-crystals, while for higher concentrations of MWCNTs, the peak disappears due to the strong α-nucleating effect of MWCNTs [18]. Although most studies [27,42,48] point out that MWCNTs could only lead to the formation of α-PP crystals, only a few studies [18,39] declared that MWCNTs may create β-phase PP.

Fig. 4(a) shows G’ values of nanocomposites as a function of shear strain. It is seen that all samples show a Newtonian behavior at low shear strain region up to about 30%. Then, they exhibit a transition region from Newtonian to non-Newtonian behavior. This transition region specifies linear viscoelastic (LVE) range for a sample and the storage modulus (G’) value at this Newtonian plateau is called plateau modulus (G’p). It was found that increasing MWCNT amount improves the G’p, as expected. The G’p values of PP and PP/2MWCNT samples were found to be 4050 and 14,700 Pa, respectively. Fig. 4(b) compares G’ curves of PP and PP/1MWCNT nanocomposite recorded during time sweep test in linear scale. Time sweep test is a fast, practical, and precise indicator for observing effect of thermal issues on rheological behaviors of a polymer melt. If a thermal degradation occurs in a polymer melt, modulus or viscosity values reduce as a result of decrease in molecular weight (Mn) while these values could also show an increase in case of crosslinking and evaporation of solvent or volatile compounds. A variation in G’ (or shear viscosity, η) within ±5% of G’p is generally accepted as the stability limit for a particular test time. It was found that changes in G’p were about 1.0% and 2.5% for PP and PP/1MWCNT samples, respectively. This result indicates that all specimens are stable at 190°C for 10 min and further test procedures can be applied safely.

Viscoelastic properties of PP/MWCNTs nanocomposites as a function of MWCNT contents are presented in Fig. 5(a) and (b). It is seen that both storage and loss modulus of the PP/MWCNT composites increased significantly relative to the PP matrix with addition of MWCNT, especially in the low frequency region. In the low frequency region, this increase is more pronounced for G’ values. This behavior is a characteristic response of thermoplastic composites in LVE regime which generally leads to solid-like or pseudo solid-like behavior. This phenomenon can be explained by the fact that, with increasing MWCNT content, the nanotube-nanotube and polymer-nanotube interactions increased [49] which led to the formation of interconnected or network-like structure of MWCNT, which restricted the segmental mobility of matrix chains [50]. Similar results were reported by Prashantha et al. [33] for the PP/MWCNT nanocomposites prepared with and without PP-g-MA as compatibilizer. At low frequencies, typical homopolymer-like terminal behavior was observed in the case of PP and PP/PP-g-MA/1%MWCNT, while a transition from liquid-like to solid-like behavior was observed for the MWWNT content of 2 wt%. This behavior can be attributed to the formation of a nanotube network in the polymer matrix (as also called percolation threshold). Therefore, the solid-like (or pseudosolid-like) behavior can be attributed to the existence of frictional interactions between the highly anisotropic particles. Lee et al. [34] stated that the G’ and η’ values of PP/MWCNT composites prepared with PP-g-MA (for even more than an amount of 3 wt%) showed similar values to those of PP/MWCNT nanocomposites without PP-g-MA. It could be concluded that the rheological properties of thermoplastic composites are more MWCNT amount than PP-g-MA loading in MWCNT/PP composite system. Improvement in G’ at low frequency region could be used to quantify microstructural features of thermoplastic nanocomposites and determine some important parameters such as aspect ratio, filler dispersion and agglomeration issues, formation of physical network (percolation threshold) and/or polymer-filler interfacial interactions based on several mathematical approaches [25,27,34]. The effect of nanotubes on the rheological behavior is marginal at high frequency region. This behavior suggests that the CNTs act as a reinforcing agent or stiffening agent at lower frequency, whereas at higher frequencies chain slippage may be responsible for the similar rheology [25]. In this study, further quantitative estimations are not attempted because the geometrical features of MWCNT are already well-known.

Fig. 6 demonstrates complex viscosity (η’’) curves of PP and nanocomposites as a function of shear rate which are also known as flow curves. Flow curves of samples were constituted by using dynamic shear viscosity data of frequency sweep test, according to empirical Cox-Merz rule [51]. The Cox-Merz rule simply suggests a connection between the complex viscosity η’’(ω) measured in frequency sweep (at a fixed strain amplitude within LVE regime) and the steady shear viscosity η(γ) measured as a function of shear rate (γ), defined as following Eq. 2;

\[
|\eta(\gamma)| = |\eta’’(\omega)|_{\gamma_{\text{max}}}
\]  

(2)

The Cox-Merz rule has been extensively tested and accepted as a practical way for many polymeric systems since 1958. Flow curves of nanocomposites
were fitted by the Williamson model [52]. Williamson model is defined as Eq. 3:

\[
\eta = \frac{\eta_0}{1 + (K\gamma)^m}
\]

(3)

where \(\eta_0\) is the zero shear rate viscosity (Pa.s), \(\gamma\) is the shear rate (s\(^{-1}\)), \(K\) is the consistency time constant related to the relaxation time (s), and \(m\) is the rate index. Williamson model parameters are given in Table 3.

It was found that the \(\eta_0\) and \(K\) values of nanocomposites readily increased with the increasing amount of MWCNT. This result indicates that introducing of MWCNT improves melt viscosity at low shear rate region and relaxation time of PP due to the reducing chain mobility. But, the flow curves of PP and nanocomposites also imply that the viscosity curves of all samples could possibly merge at high shear rates and become composition-independent. It can be concluded that these PP/MWCNT nanocomposites would not induce a processing difficulty in processing operations conducted at high shear rates such as injection molding, fiber spinning etc. Effect of MWCNT addition on the relaxation times of PP was also determined by employing crossover point. Fig. 7(a) displays representative shear moduli (\(G'\) and \(G''\)) curves of PP and PP/MWCNT sample. Cross-over modulus (\(G_x\)) and frequency (\(f_x\)) where \(G'\) equals to \(G''\), can be simply used to compare melt elasticity and relaxation times of samples. The crossover point is also related to melt strength of a polymer. The relaxation time (\(\lambda\), in s) is expressed as the reciprocal of \(f_x\) (in Hz = s\(^{-1}\)). \(G_x\) and \(\lambda\) values of nanocomposites as a function MWCNT amount is given in Fig. 7(b). It was found that the \(G_x\) values reduced but \(\lambda\) values increased with the MWCNT amount. Improvement in \(\lambda\) values can be quantified with a simple power-law equation given in Fig. 7(b).

Fig. 8(a) represents semi-logarithmic creep compliance (\(J\)) graphs of PP nanocomposites under a stress value of 100 Pa at 190° C. Compliance is known as the inverse modulus (1/G, Pa\(^{-1}\)) mathematically and generally used to calculate long-term deformation of a polymeric system under a particular thermomechanical condition. Lower compliance value refers
to higher modulus and thus lower deformation (strain). Creep compliance curves were fitted with the equation of discrete retardation spectrum (DRS) and $\eta'$ values of nanocomposites were estimated. The equation of DSR can be defined as follows Eq. 4:

$$J(t) = J_0 + \sum \eta_k (1 - \exp(-\frac{t}{\lambda_k})) + \frac{t}{\eta_0}$$  \hspace{1cm} (4)

where $J_0$ is the instantaneous compliance and $\eta_0$ is the zero shear viscosity. The parameters $\eta_k$ and $\lambda_k$ are referred to the compliance and retardation time of the $k$th element, respectively. This equation is a standard rheological model for modeling LVE behavior [53]. Model fit was succeeded with six elements ($k=6$), but $\eta_k$ and $\lambda_k$ values were not reported here. Fig. 8 (b) compares $\lambda_2$ values of nanocomposites as a function of MWCNT amount by two different approaches; Williamson model and DSR. It is clearly seen that different test procedures and mathematical approaches yield almost the same trend in viscosity increase. Introducing 2 wt% of MMWCNT into PP matrix increases the $\lambda_2$ value of PP more than five-fold (from 3000 Pa.s to 16,000 Pa.s).

Stress relaxation curves of PP and its nanocomposites are represented in Fig. 9(a). These curves show the time dependent stress decay of specimens. It was obtained that increasing MWCNT amount increased the initial stress ($\sigma_i$) level. It was found that MWCNT decreased the relaxation rate of PP. This effect can be more precisely seen in Fig. 9(b) which represents the semi-logarithmic stress decay in the initial part of test. Slope of the given lines can be used to compare the initial rate of relaxation. It is obviously seen that the introduction of MWCNT decreases the slope which points out a significant decrease in relaxation rate. As a result, it can be concluded that time-dependent rheological behaviors of PP/MWCNT nanocomposites confirm their strain and frequency-dependent behaviors mentioned before.

4. Conclusion

In this study, a series of PP/MWCNT nanocomposites have been prepared according to melt processing methods using a twin screw extruder and an injection molding. The effects of MWCNTs loading in a range of 0.1–2 wt% on the thermal,
rheological, and mechanical properties of MWCNTs filled PP nanocomposites have been measured depending on the MWCNT amount. It has been found that the tensile and flexural properties of PP/MWCNT nanocomposites increased in line with the increment of MWCNT amount. The impact strength of nanocomposites decreased with the MWCNT addition. Melt rheology tests demonstrated that the storage modulus (G'), loss modulus (G''), and complex viscosity (η*) of samples raised with the increment of the amount of MWCNTs. Based on the thermal and mechanical test results, 0.3 wt% of MWCNT could be considered as the critical filler amount also called as “percolation threshold” for improving the solid-state physical properties of PP/MWCNT nanocomposites. However, rheological measurements did not yield such a distinctive composition. Melt rheology tests showed that PP/MWCNT nanocomposites could be easily processed at high shear rates to produce nanocomposites having improved long-term time dependent physical properties. Consequently, it can be concluded that these composites can be promising candidates for being used in different engineering applications.

Declaration of conflicting interests

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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