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Effect of single-walled carbon nanotube on the physical, rheological and mechanical properties of thermoplastic elastomer based on PP/EPDM

Abstract: The effect of the incorporation of single-walled carbon nanotubes (SWNT) on the morphological, physical, rheological and mechanical properties of thermoplastic elastomer based polypropylene (PP)/ethylene propylene diene (EPDM) (80/20) is reported. The morphological study showed that the size of the dispersed phase decreased by the addition of SWNT, this effect being more appreciable with 0.5 wt.% of SWNT. The results of differential scanning calorimetry showed that the addition of SWNT increased the crystallinity of PP/EPDM/SWNT nanocomposites. This effect was not linearly dependent on SWNT content, particularly at high SWNT concentrations. The rheological results revealed that addition of SWNT increased the storage modulus and complex viscosity at low frequencies. The Izod impact strength and tensile strength improved when 0.5 wt.% of SWNT was used. Furthermore, the tensile modulus increased remarkably by increasing the SWNT content, but the elongation at break of the material decreased.

Keywords: mechanical; morphological studies; physical properties; rheological; SWNT.

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1 Introduction

Polypropylene (PP) as a thermoplastic has a number of advantages such as good mechanical properties, low density and low cost. However, its application as an engineering thermoplastic is somewhat limited because of its relatively poor impact resistance. Therefore, in order to improve toughness and impact resistance, blending of ethylene propylene diene (EPDM) with PP is a well-known technique [1, 2]. The addition of the elastomeric phase gives rise to the toughness of PP, while some PP properties such as rigidity and hardness decrease. Thus, nanoparticles as fillers can be used to compensate for the reduction of stiffness [3–5]. The addition of carbon nanotubes (CNTs) as nanofillers is a significant way to further toughen the PP/EPDM blends [6]. The CNTs are used to generate special distribution structures in the blends which improve the mechanical properties [7, 8]. Thus, a major issue for some application is to achieve an optimum balance of stiffness and toughness. Development of the polymer/CNT composites has been widely studied because of its remarkable mechanical, thermal, stiffness and rheological properties [9]. These unique properties make CNTs a preferred candidate to be used as fillers into various polymer matrices to enhance the performance of the polymer [10]. Effective utilization of CNTs in composite applications depends strongly on the ability to homogeneously disperse them throughout the matrix without destroying their integrity. In order to disperse CNTs in the polymer, the entanglement of CNTs produced by synthesis and agglomerates of CNTs caused by the intermolecular van der Waals force must be broken for homogenization to make more filler surface area available. Furthermore, good interfacial bonding is required to achieve load transfer between the CNT and matrix at the interface, which is a necessary condition for improving the mechanical properties of composites [11].

In non-polar PP, highly dispersed CNTs are difficult to achieve; thus, PP has been grafted with maleic acid anhydride to achieve better dispersion of the CNT in the PP matrix and to improve the stiffness of PP nanocomposites [12]. As a result of it, in order to improve the dispersion of carbon nanotube in the matrix, maleic anhydride polypropylene (PP-g-MA) as a compatibilizer was used [6, 13–15]. In this study, the effect of the incorporation of SWNT on the morphological, thermal, rheological and mechanical properties of PP reinforced and toughened with EPDM-based elastomer made by melt mixing was investigated. The ratio of PP-g-MA/SWNT was constant at 2.

2 Experimental

2.1 Material

PP was used as a matrix, EPDM was used as a minor phase, and SWNT and PP-g-MA were used as fillers and compatibilizers in this study, respectively. All products and their main characteristics are shown in Table 1.

Table 1 Characteristics of the materials.

Materials	Brand	Supplier	Characteristics
PP	AP230	Arak Petrochemical Co., Iran	MFI=0.51 g/min at 210°C under 2.16 kg
PP-g-MA	PB 3150	Uniroyal Chemical Co., USA	MFI 50 g/10 min, MAH index of 1.5%
EPDM	KEP-270	From Kumho Polychemical Co., Korea	Mooney viscosity 71, PE content 56.5
SWNT	AP-grade	Iljin Nanotech Co., Korea	Diameter 1–1.2 nm and length 2–20 μm

MAH, Maleic acid anhydride.

2.2 Nanocomposites preparation

To produce nanocomposites, an internal mixer (type HBI SYS 90) was operated at a temperature of 190°C and a rotor speed of 60 rpm. The compositions of the PP/EPDM/SWNT nanocomposites were prepared with various SWNT contents as listed in Table 2. Compounding was carried out by first feeding PP into the mixer and after 3 min of mixing, EPDM was put into the mixer and mixed for 3 min. Then, PP-g-MA and SWNT were added into the mixer and mixing was continued for 3 and 6 min, respectively; finally, the mixture was discharged after 15 min. Sheets were prepared by compression molding with a hydraulic pressure of 10 MPa at 200°C for 5 min. The molded sheets were then cooled down to room temperature.

Table 2 Compositions of the PP/EPDM/SWNT nanocomposites.

Sample code	PP (wt.%)	EPDM (wt.%)	PP-g-MA (wt.%)	SWNT (wt.%)
PP-EPDM	80	20	–	–
PP-EPDM-S 0.5%	78.75	19.75	1	0.5
PP-EPDM-S 1%	77.50	19.50	2	1
PP-EPDM-S 3%	72.50	18.50	6	3
PP-EPDM-S 5%	67.50	17.50	10	5

2.3 Characterization

Scanning electron microscopy (SEM) was performed on a Cambridge S360 SEM to examine the fracture surface morphology of PP/EPDM/SWNT nanocomposites. SEM micrographs of cryogenically fractured surfaces of specimens were collected. The samples were fractured in the direction perpendicular to the flow direction of liquid nitrogen. The fracture surface of PP/EPDM/SWNT nanocomposites was etched with n-heptane for 24 h at room temperature, to remove the EPDM phase.

Crystallization studies were carried out using a differential scanning calorimetry (DSC) scanning calorimeter under a nitrogen atmosphere. Samples of about 5 mg were taken from the molded sheets. Tests were carried out under non-isothermal conditions by heating the samples to 265°C at a heating rate of 10°C/min and maintained at this temperature for 5 min in order to eliminate any pervious thermal history and then cooled to -30°C for the crystallization temperature. The crystallization temperature (T_c), enthalpy of crystallization (ΔH_c) and melting temperature (T_m) were calculated by determining the area under the exothermic and endothermic peaks, respectively. The degree of crystallization (X_c) was determined from the second heating curve by using the following relation:

$$X_c=(\Delta H/\Delta H_0)\times 100$$

where (ΔH) is the enthalpy of fusion of PP as calculated from DSC results and ΔH_0 is the enthalpy of fusion of the 100% crystalline polypropylene. For PP, the value was 209 J/g [16].

Rheological characterizations of the PP/EPDM and its nanocomposites were performed using a parallel plate rheometric mechanical spectrometer (UDS 200, Paar-Physica Co.). The experiment was performed in a 25-mm parallel-plate geometry with a 1-mm gap under a nitrogen atmosphere at 200°C with an angular frequency range of 0.1–625 rad/s and a strain amplitude of 1%.

Tensile testing was preformed according to ISO 527-1, and a TCS 2000 COTECH tensile tester was employed. The tensile modulus, tensile strength and elongation at break were measured at a constant crosshead speed of 50 mm/min. Five specimens were tested and the average was recorded. The notched Izod impact strength was determined with a COTECH pendulum impact tester according to the procedure described in ASTM D256. The specimen dimensions were according to this standard. Notches of 2.54 mm depth were created on the impact test specimens

before this test. The final property data were the average of the measured results of at least five samples.

3 Results and discussion

Figure 1 shows the SEM experiment of the PP/EPDM and both the 0.5 and 5 wt.% SWNT of PP/EPDM/SWNT nanocomposites. As shown in this figure, when 0.5 wt.% of SWNT was added, the EPDM particle size became smaller and more uniformly dispersed in the PP matrix, compared to PP/EPDM. This effect can be related to the increase in viscosity of the matrix phase in the presence of SWNT which led to the decrease in the viscosity ratio of PP/EPDM [17, 18]. However, the addition of 5 wt.% SWNT does not further help to promote the dispersion of EPDM particle size, compared to PP/EPDM. This was because of the increase in the viscosity ratio of EPDM to PP by increasing the SWNT content; as a result of it, the break-up process of EPDM particle became more difficult [6, 17–19]. Thus, the viscosity ratio of the dispersed phase to the matrix plays an important role in controlling the particle size of the dispersed phase, as reported by Liu et al. [19]. As a result, the addition of SWNT resulted in the change in the viscosity ratio of PP/EPDM which played an important role in determining the morphology of samples.

The effect of the incorporation of SWNT on crystallization temperature (T_c), melting temperature (T_m), enthalpy

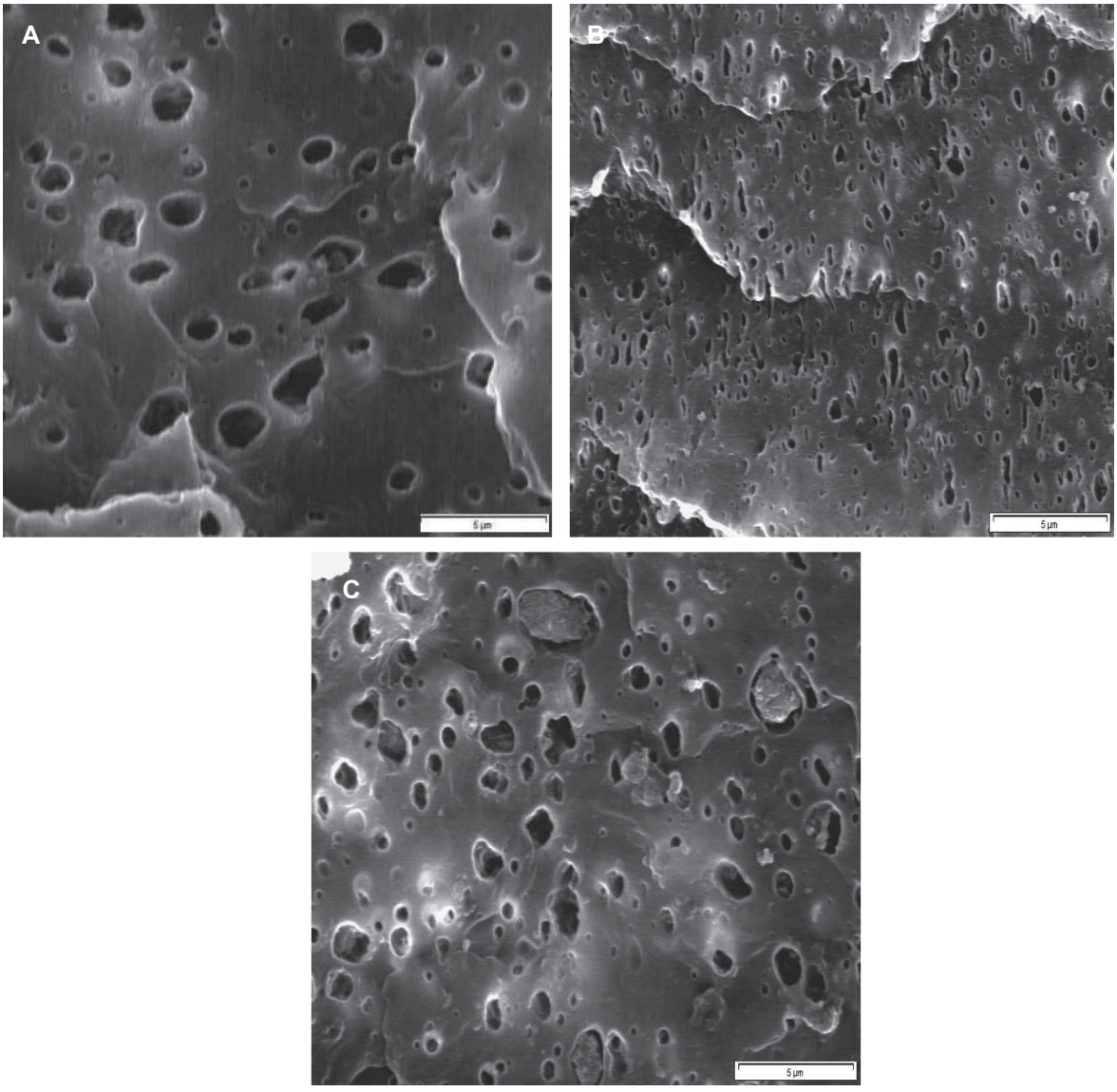

Figure 1 SEM micrographs of PP/EPDM/SWNT nanocomposites: (A) 0, (B) 0.5, (C) 5 wt.% of SWNT.

of crystallization (ΔH_c) and crystallinity (X_c) using DSC of the PP/EPDM and its nanocomposites is reported in Table 3. The crystallization temperature (T_c) of PP/EPDM/SWNT nanocomposites significantly increased from 108.1°C to 115.6°C as the SWNT content was increased to 5 wt.%, compared to PP/EPDM, as can be seen in Figure 2A. This behavior can be attributed to the fact that SWNT acted as an effective nucleating agent, allowing the crystallization of polymer molecules to occur at a higher crystallization temperature [14, 20–22]. The enthalpy of crystallization (ΔH_c) of PP/EPDM/SWNT nanocomposites decreased with an increase in SWNT content, due to a decline in the PP concentration of the composites [8, 12, 22]. The melting temperature (T_m) of PP/EPDM/SWNT nanocomposites increased slightly from 156.5°C to 158.6°C as the SWNT content was increased to 0.5 wt.%, compared to PP/EPDM, whereas it decreased gradually to 157.1°C with an increase in SWNT content to 5 wt.%. As clearly seen in Figure 2B, the crystallinity (X_c) of PP/EPDM increased when SWNT was added to the composite; in other words, SWNTs behave as an effective nucleant agent for PP matrix. It is interesting to note that this effect increases when increasing the SWNT content up to the maximum for the composite with 0.5 wt.% of SWNTs. Further increase in SWNT produces a negative effect, showing a decrease in the PP crystallization rate. This behavior can be attributed to the increase in nucleation at the SWNT-matrix interface with the SWNT content. In contrast, the same SWNT could be responsible for the impingement effect on spherulitic growth [6, 22]. Therefore, it can be concluded from these results that the incorporation of SWNT affected the crystalline behavior and structure of the polymer matrix and also confirmed the function of the SWNT as a reinforcement in composite materials. In particular, SWNTs accelerated the nucleation and crystal growth mechanisms of PP, this effect being more appreciable with 0.5 wt.% of SWNT.

Figures 3 and 4 show the storage modulus and complex viscosity of PP/EPDM and its nanocomposites reinforced with SWNTs, respectively. As shown in the figures, the storage modulus and complex viscosity of PP/EPDM were

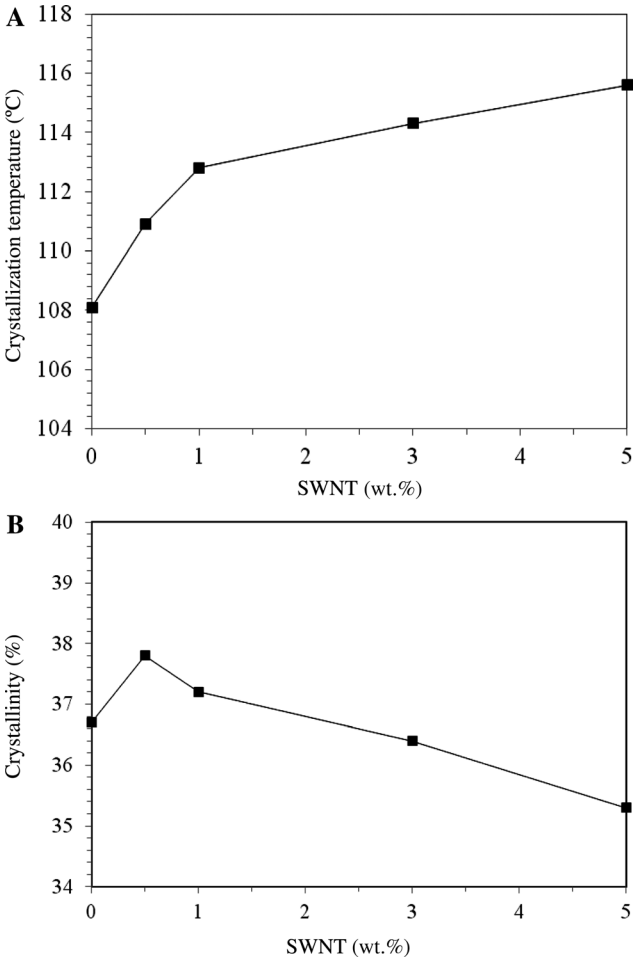

Figure 2 (A) Crystallization temperature (T_c) and (B) crystallinity (X_c) of PP/EPDM/SWNT nanocomposites.

Table 3 Thermal characteristics of PP/EPDM/SWNT nanocomposites.

Sample code	T_m (°C)	T_c (°C)	ΔH_c (J/g)	X_c (%)
PP-EPDM	156.5	108.1	76.8	36.7
PP-EPDM-S 0.5%	158.6	110.9	79.1	37.8
PP-EPDM-S 1%	158.2	112.8	77.7	37.2
PP-EPDM-S 3%	157.9	114.3	76.2	36.4
PP-EPDM-S 5%	157.1	115.6	73.8	35.3

increased by the stiffening effect of the SWNT, which was particularly significant at a concentration of SWNTs equal to 0.5% at low frequencies. Sung et al. [23] reported that the rheological properties of polymer composites at low frequency region (terminal region) reflect the formation of filler-filler network. So, because of the homogenous dispersion of SWNT in the matrix, when SWNT concentration in the nanocomposite was increased to 0.5 wt.%, there was an available polymer for the formation of SWNT network structure. As a consequence of it, at low frequency, the time was long enough to unravel the entanglements so a large amount of relaxation occurred, so the physical interaction between the SWNT and the matrix was enhanced, representing the rheological behavior of the material to transition from liquid-like to solid-like, which was responsible for the improvement in mechanical properties [4, 24–26]. It was also observed from these figures that the terminal slopes of the storage modulus vs. angular frequency decreased; moreover, a non-Newtonian

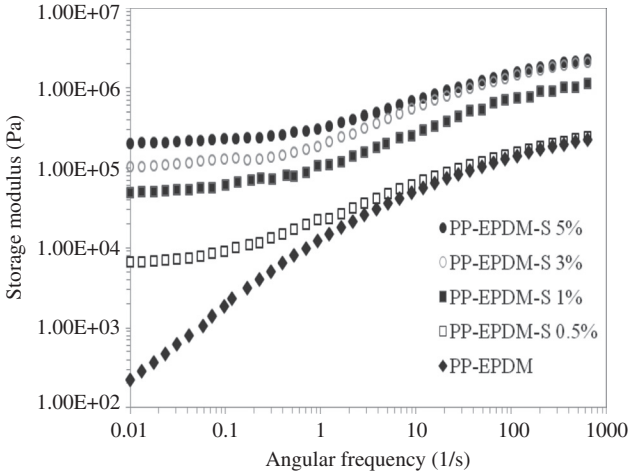

Figure 3 Storage modulus vs. angular frequency of PP/EPDM and its nanocomposites reinforced with SWNT.

behavior was found at low frequencies for complex viscosity with the addition of SWNT content, indicating a transition from liquid to solid-like viscoelastic behavior [24, 27]. Moreover, PP/EPDM/SWNT nanocomposites exhibited a shear thinning behavior. It was also found from Figure 4 that the increased complex viscosity of PP/EPDM/SWNT at low frequency was more significant than at high frequency. This behavior was attributed to the formation of SWNT network structure which resulted in the restriction of the long range motion of polymer chains. As a result, the viscosity of samples increased [18, 24, 27]. In contrast, at high frequency, PP/EPDM and its nanocomposites showed better processability and melt viscosity was less sensitive to the addition of SWNT content [24, 26]. Therefore, from

Table 4 Mechanical properties of the PP/EPDM/SWNT nanocomposites.

Sample code	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Izod strength (J/m)
PP-EPDM	1514	11	1602	189.90
PP-EPDM-S 0.5%	1952	13.14	1571	219
PP-EPDM-S 1%	2103	12.68	1498	193
PP-EPDM-S 3%	2300	12.10	1405	175.50
PP-EPDM-S 5%	2420	11.76	1300	155.02

the obtained results of morphological and rheological properties of PP/EPDM/SWNT nanocomposites, it was suggested that the morphology and rheological properties of PP/EPDM/SWNT were found to be sensitive to the viscosity ratio of PP/EPDM and SWNT content.

The effect of the incorporation of SWNT on the tensile properties of PP/EPDM and its nanocomposites is presented in Table 4. In Figure 5A and B, the impact strength and tensile strength are plotted vs. SWNT content. As clearly seen, there is a peak in these two figures; this peak has a maximum at the 0.5 wt.% SWNT. In Figure 5A, the Izod impact strength increased from 189.9 to 219 J/m as the SWNT content increased to 0.5 wt.%, compared to PP/EPDM. This behavior was due to the reinforcing effect of SWNT in reducing the size of dispersed particle, leading to a decrease in the viscosity ratio of PP/EPDM as evidenced by morphological study [27]. However, this effect declined by increasing the SWNT content. This was because of the impact-induced damage in the

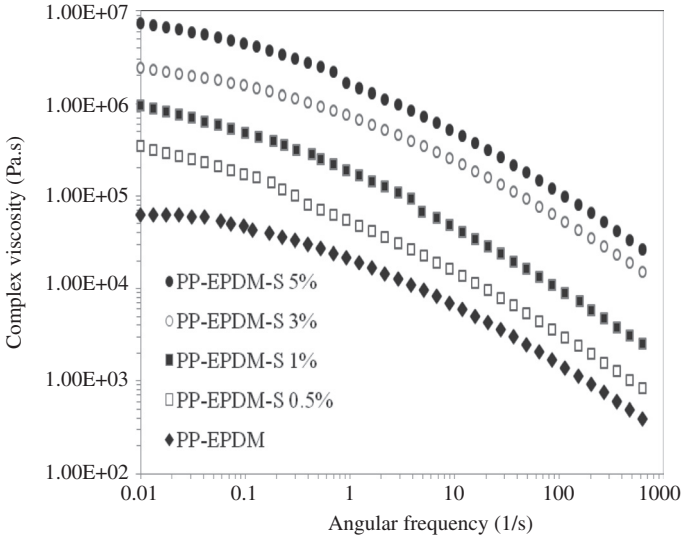

Figure 4 Complex viscosity vs. angular frequency of PP/EPDM and its nanocomposites reinforced with SWNT.

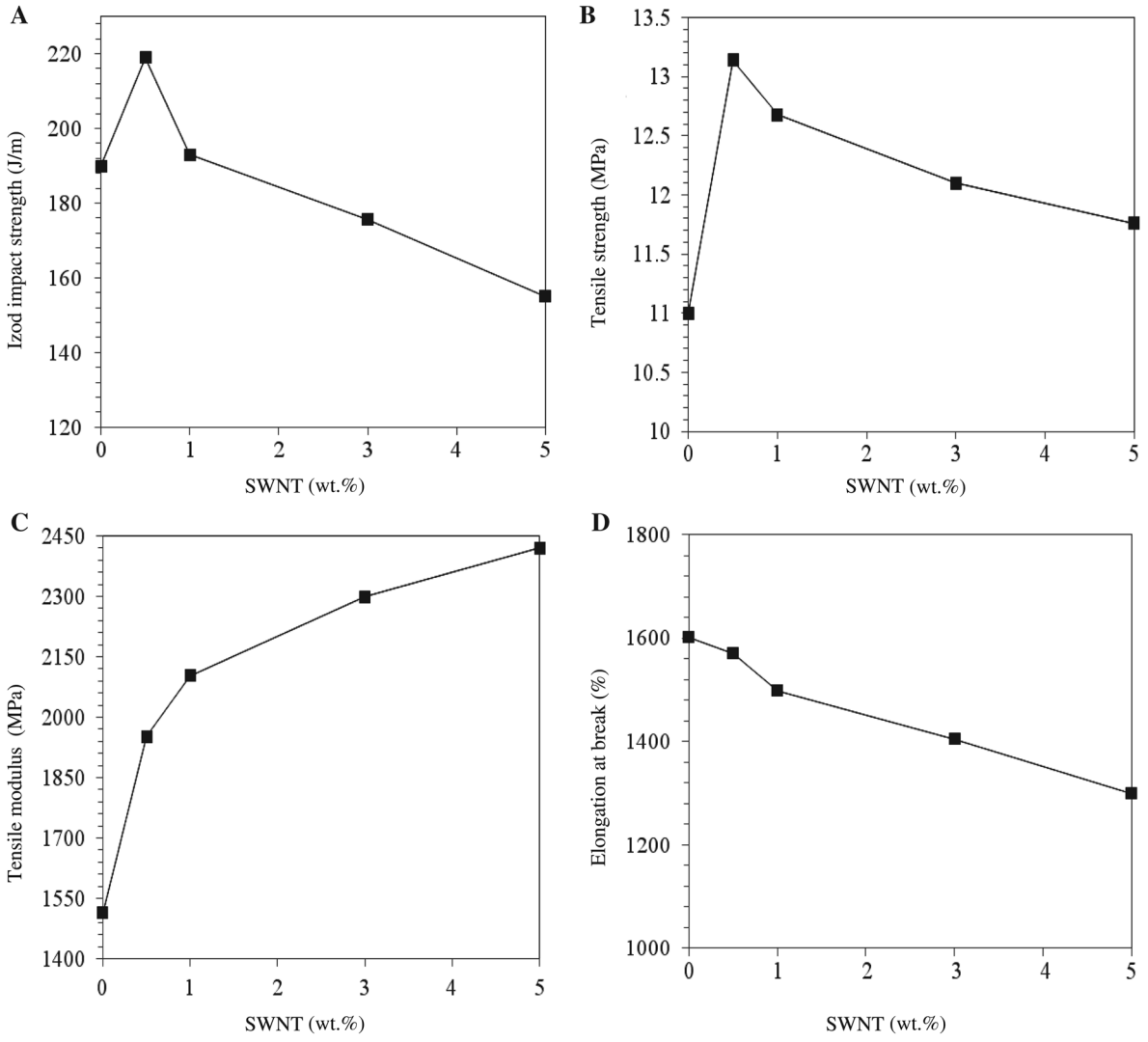

Figure 5 Mechanical properties of PP/EPDM/SWNT nanocomposites: (A) Izod impact strength, (B) tensile strength, (C) tensile modulus, (D) elongation at break.

composites; the damage zone acted to magnify the stress locally because of matrix cracking [28, 29]. In Figure 5B, the tensile strength was increased from 11 to 13.14 MPa as the SWNT concentration increased to 0.5 wt.%, compared to PP/EPDM. This increased effect was due to better dispersion of SWNT in the matrix, leading to the promotion of interaction between the SWNT and the matrix, which was responsible for the increase in storage modulus and complex viscosity [27, 28]. However, tensile strength continued to decrease to 11.76 MPa with increasing SWNT to 5 wt.%. It can be explained by the fact that entanglement of SWNTs was higher, which was caused by the inability of SWNT to support stresses transferred from the matrix, due to the non-uniform dispersion of SWNT in the matrix [6, 18, 24, 30]. It was also found that the decrease in tensile strength of nanocomposites correlated well with the reduction in crystallinity [26]. In Figure 5C and D, the tensile modulus and elongation at break vs. SWNT content are plotted. It can be observed that the tensile modulus increased remarkably from 1514 to 2420 MPa, as the SWNT content increased by 60% to 5 wt.%, compared to PP/EPDM. This was because rigid SWNT particles restricted the mobility and deformability of the matrix; as a result, the complex viscosity increased. This behavior was also observed by rheological results. However, the elongation at break decreased by 19% with increasing SWNT content to 5 wt.%. This rapid decrease in elongation at break was due to the decreased deformability of a rigid interface between the SWNT and the matrix [29, 30]. Therefore, it was observed from mechanical results that

the incorporation of SWNT resulted in the improvement of the mechanical properties of PP/EPDM/SWNT nanocomposites, but the reinforcing effect of SWNT was not noticeable by increasing the SWNT content.

4 Conclusion

The effect of the incorporation of single-walled carbon nanotube (SWNT) reinforced thermoplastic elastomer based on PP/EPDM was analyzed in the present work. From morphological study, it was shown that the addition of SWNT as reinforcement reduced the size of EPDM dispersed phase in PP matrix by 0.5 wt.%, due to a decrease in the viscosity ratio of PP/EPDM. But this effect was not considerable by increasing SWNT content. From the physical properties, it was demonstrated that the incorporation of SWNT affected the crystalline behavior of the matrix. Moreover, this change was very important to confirm the function of SWNT as a reinforcement in composite materials. SWNTs accelerated the nucleation and crystal growth mechanisms of PP, this effect being more appreciable at 0.5 wt.%. This effect was attributed to the interaction between SWNTs and the matrix, leading to a higher dispersion and offering a higher surface for crystal nucleation. The rheological results confirmed the reinforcing effect of SWNT. In fact, the incorporation of 0.5 wt.% SWNT was caused by the formation of SWNT network structure because of the physical interaction between the SWNT and the matrix, which was responsible for the increase in storage modulus and complex viscosity; this effect was not noticeable at higher SWNT content. Mechanical results confirmed the reinforcing effect of SWNT for these systems based on PP/EPDM blends. The incorporation of SWNT gives rise to a more rigid material, which is reflected by the marked increase in complex viscosity. Therefore, it can be concluded from these results that the properties of PP/EPDM/SWNT nanocomposites were found to be sensitive to the viscosity ratio of PP/EPDM and SWNT content, which was particularly significant at a concentration of SWNT equal to 0.5 wt.%.

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