J. Inst. Eng. India Ser. E (June 2018) 99(1):37–42
https://doi.org/10.1007/s40034-017-0110-3

ORIGINAL CONTRIBUTION

The Study on the Mechanical Properties of Multi-walled Carbon Nanotube/Polypropylene Fibers

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Received: 24 September 2017 / Accepted: 14 December 2017 / Published online: 9 January 2018

Abstract Polypropylene (PP) is an important semicrystalline polymer with various applications. Polypropylene fibers containing 1 wt% of multi-walled carbon nanotube was spun using a conventional melt spinning apparatus. The produced fibers were drawn with varying levels of draw ratio. The mechanical properties of the composites were studied. Tensile strength and modulus of the composite fibers were increased with the increase in draw ratio. Molecular orientation and helical content of the composite fibers were increased after drawing. To conclude, tensile properties and molecular orientation of the composite fibers were higher than those of neat polypropylene fibers with the same draw ratio.

Keywords Carbon nanotubes · Mechanical properties · Melt processing · Nanocomposites · Polypropylene

Introduction

A single-walled carbon nanotube (SWCNT) consists of carbon atoms in only one cylinder, whereas, multi-walled carbon nanotubes (MWCNT) consist of many nested cylinders with different radius [1]. Carbon nanotubes (CNT) have been utilized as a filler in polymer composites because of their high aspect ratio, nano-size, very low density, and excellent physical properties such as their high mechanical strength and high electrical conductivity and thermal stability [2, 3]. Composite materials are used in a variety of applications such as sporting goods, high-performance aircraft and where high stiffness and light weight are required. The correlation between the structure of materials and their properties in composite materials is an important subject from both the academic and industrial points of view [1, 4].

Polypropylene (PP) is an important semicrystalline polymer with various applications [5, 6]. Numerous studies have been focused on the preparation of PP/CNT composites and determination of their physical and chemical properties. PP/CNT nanocomposite fibers have been produced for the purpose of improving the mechanical properties of PP fibers. They indicated an increase in tensile modulus and tensile strength in the nanocomposite fibers [7–12]. Various techniques such as scanning and transmission electron microscopy (SEM and TEM respectively), thermal analysis, Raman spectroscopy and wide angle X-ray scattering (WAXS) have been used to determine the microstructure and morphology of nanocomposite fibers. It has been found that the presence of nanofillers affects significantly the structure and morphology of nanocomposites. Improved dispersion and alignment of CNTs in polymer matrices prominently improve mechanical, electric, thermal, electrochemical, optical and super-hydrophobic properties of polymer/CNT composite fibers [13–16]. Therefore, the challenge is the development and increase the dispersion and alignment of CNTs in the matrix. Thus, the purpose of this study is to investigate the effect of MWCNT on the mechanical properties of PP/MWCNT nanocomposite fibers. Furthermore, the authors intend to study the mechanical properties of the composite fibers as a function of draw ratio.

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Experimental

Materials

Commercial-grade isotactic polypropylene (PP) with a melt flow rate of 16 g/10 min (230 °C/2.16 kg) was obtained from Tabriz Petrochemical Co. (Tabriz, Iran). Multi-wall carbon nanotubes (MWCNT) with the purity of 95%, diameter of approximately 10–30 nm and length of 10 µm were supplied from Petroleum Laboratory of Iran.

Methods

A composite masterbatch was produced by melt blending of PP and MWCNT (1 wt%) by a Brabender model 2000 twin screw extruder. Screw rotation speed was 105 rpm and temperatures of 6 thermal zones were 180, 195, 200, 210, 210, 195 °C. The fiber spinning was performed using a Fourne-Bonn melt spinning machine with the take-up speed of 810 m/min and the temperature range of 210–240 °C. The produced filaments were drawn with varying levels of draw ratio (2, 2.5, 3, 3.5, 4) using a Zinser 520-2 machine at the temperature of 130 °C. Mechanical properties of the fibers were measured by a Zwick-1446 tensile tester. The crosshead speed was 700 mm/min and gauge length was 50 mm. 20 replicates of each sample were tested. A Hitachi field emission scanning electron microscope model S-4160, operating at 30 kV, was utilized to study surface morphology of the fibers. The samples were coated with Au and the images were captured at magnifications of 10,000–30,000. Birefringence of the fibers was measured using a Zeiss polarizing microscope equipped with a 30th order tilting compensator. Five replicates of each sample were measured. A Bomem MB100 FTIR spectrometer was used to record the FTIR spectra between 4000 and 400 cm^{-1} in transmission mode. The resolution of the spectrometer was 4 cm^{-1}, averaging 32 scans.

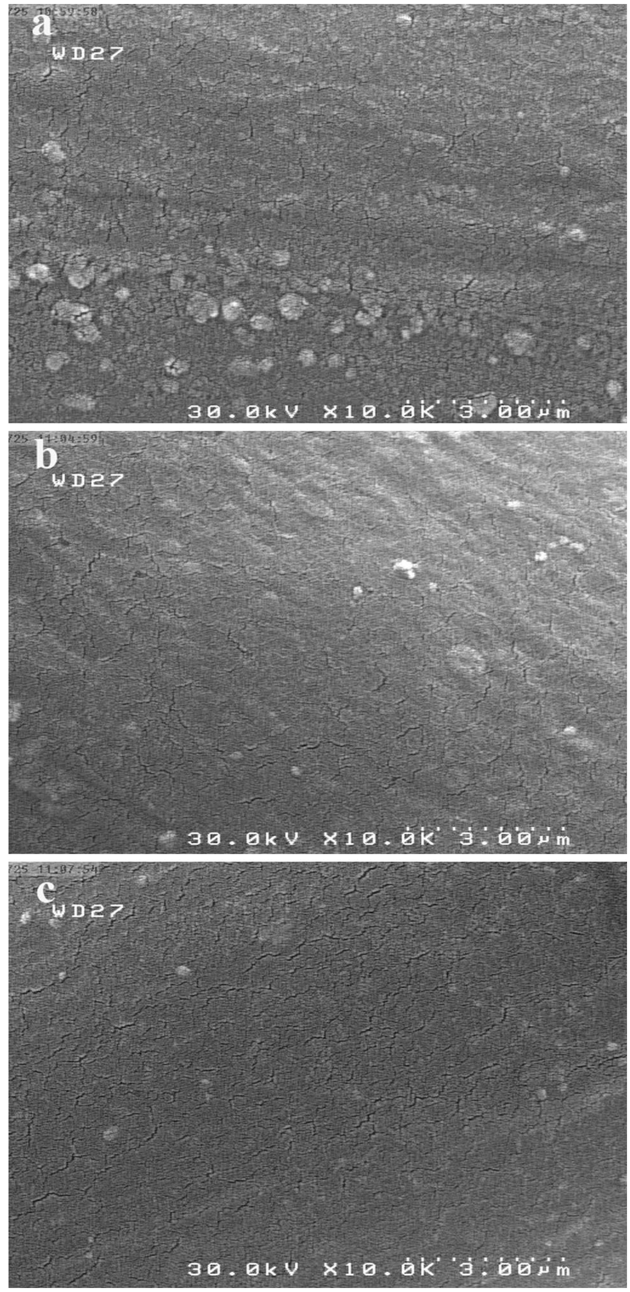

Fig. 1 FESEM images of PP fibers containing 1 wt% nanotubes at **a** 2, **b** 3 and **c** 4 draw ratio

Results and Discussion

Figure 1 shows the FE-SEM images of the surface of samples. As seen in the images, the end of some of the MWCNTs was observed coming out of the surface of the fibers. Besides, no signs of MWCNT aggregation were observed on the surface of the fibers which were drawn with different draw ratios. Image of the drawn sample with the draw ratio of 4 (Fig. 1) shows fewer tips of the nanotubes coming out of the surface of the fibers and it may be due to the more orientation along the drawing axis.

Figure 2 and Table 1 illustrate the breaking stress of the fibers as a function of draw ratio. As expected, breaking stress of the neat PP fibers and the composite PP fibers containing 1 wt% MWCNT were increased with increasing draw ratio (details are shown in Table 2). Analysis of variance (ANOVA) test showed that the difference was significant at 95% confidence level. The results of ANOVA are shown in Table 3. As it is depicted in Fig. 3 and Table 1 the modulus of the fibers (both neat PP and PP/MWCNT) was increased with the increase in draw ratio

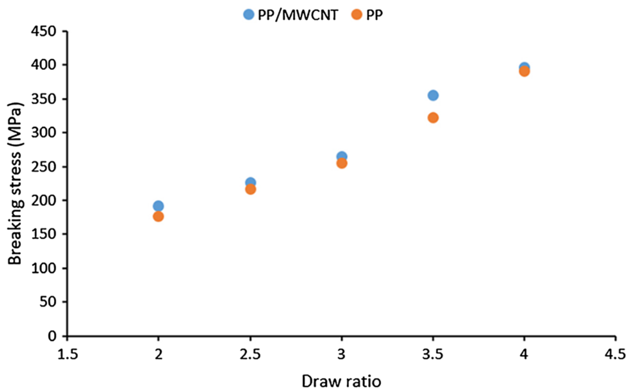

Fig. 2 Breaking stress as a function of draw ratio for neat PP and PP/MWCNT fibers

(details are shown in Table 4). Analysis of variance (ANOVA) tests showed that the difference was significant at 95% confidence level. The results of ANOVA are illustrated in Table 5.

However, the modulus of composite fibers in all draw ratios was higher than that of neat PP fibers. The increase in modulus can be attributed to the load transfer (from the matrix to nanotube) or increase in crystallinity of composite fibers due to the addition of MWCNTs [17, 18]. The reason for this observation may be due to the improvement in mechanical properties which according to references is based on bridging of MWCNTs between crazes and cracks which are formed during the tensile test. The MWCNTs bridge between the gaps which are formed by the cracks; therefore, they decelerate the crack propagation and increase the material toughness [17, 18].

According to the rule of mixture (Eq. 1), for the fibers containing 1 wt% MWCNT with the assumption that both MWCNT and PP were very well-bonded and MWCNTs were uniformly distributed within PP, the composite fibers modulus was given the value of 4.9 GPa [19]. The measured modulus values for the composite fibers drawn by all draw ratios were lower than those of theoretical values. This was likely due to poor adhesion of MWCNTs to the matrix and imperfections and defects in the nanotube structure and slight dispersion of nanotube within the matrix which also resulted in a reduced composite modulus [13].

$$E_c = a_0 a_1 v_{cnt} E_{cnt} + (1 - v_{cnt}) E_{pp} \quad (1)$$

where E_c, E_m, E_{cnt} are the composite, PP and MWCNT moduli, respectively; v_{cnt} is the volume fraction, a_0 and a_1 efficiency factors related to fiber orientation and length [20]. Young's modulus of MWCNT obtained from references was 270 GPa [21] and Young's modulus of PP was 1.47 GPa (a_0 and a_1 were assumed to be 0.75 and 0.95, respectively [20]). Infrared spectroscopy can be used to

Table 1 Summary of mechanical properties for PP and composite samples

Sample name	MWCNT (wt%)	Draw ratio	Average modulus (MPa) [CV %]	Average breaking stress (MPa) [CV %]
PP-2	0	2	1171.30 [16.89]	177.12 [15.41]
PP-2.5	0	2.5	1296.14 [11.73]	215.92 [17.25]
PP-3	0	3	1468.17 [12.72]	255.33 [9.16]
PP-3.5	0	3.5	2103.66 [14.73]	322.30 [17.80]
PP-4	0	4	2383.89 [18.28]	390.65 [9.27]
PP/MWCNT-2	1	2	1305.00 [17.01]	191.88 [6.21]
PP/MWCNT-2.5	1	2.5	1366.92 [14.95]	226.26 [12.39]
PP/MWCNT-3	1	3	1712.70 [17.75]	264.78 [16.2]
PP/MWCNT-3.5	1	3.5	2164.14 [11.53]	354.96 [17.68]
PP/MWCNT-4	1	4	2471.76 [11.22]	395.46 [7.86]

Table 2 Breaking stress of the fibers (MPa)

PP-2	PP-2.5	PP-3	PP-3.5	PP-4	PP/MWCNT-2	PP/MWCNT-2.5	PP/MWCNT-3	PP/MWCNT-3.5	PP/MWCNT-4
163.98	205.83	253.70	303.12	399.51	193.04	247.72	280.27	355.30	405.30
163.89	207.18	242.29	317.88	399.31	180.09	221.35	287.47	368.50	399.00
187.74	221.13	243.71	336.33	387.83	182.12	247.10	280.81	350.00	400.93
185.49	243.63	266.74	325.26	395.91	185.32	217.56	252.96	338.37	398.37
172.98	207.18	245.42	341.91	383.83	193.15	215.94	284.41	351.20	390.99
183.15	233.73	245.90	341.91	368.64	191.35	216.73	280.27	376.07	396.48
183.15	207.18	271.79	343.71	382.53	193.15	216.93	253.43	367.74	397.74
169.56	258.93	260.57	334.53	386.19	196.21	223.78	272.33	328.77	388.77
191.07	209.97	261.49	358.47	401.67	193.24	219.46	280.91	324.84	414.84
185.40	198.81	266.34	290.16	396.49	194.41	240.12	257.82	352.50	381.35
189.99	197.37	261.79	295.65	406.31	192.61	214.41	244.41	352.61	383.91
165.06	203.04	238.87	317.79	386.39	191.44	241.35	232.90	351.25	391.35
197.82	212.85	251.59	325.26	385.38	191.44	219.56	242.89	381.15	391.35
184.32	230.94	261.79	303.03	382.07	193.24	244.40	276.84	376.28	386.48
139.14	232.47	261.27	332.64	400.34	198.10	215.04	247.82	376.08	396.48
158.31	225.36	263.31	319.77	402.01	180.46	226.93	270.18	332.78	399.78
155.97	222.66	255.22	321.57	387.37	191.98	218.19	255.67	375.93	399.93
178.65	225.45	250.97	319.77	389.66	202.24	–	264.75	345.93	399.43
191.07	198.81	253.70	301.23	389.56	202.24	–	264.81	331.35	391.35
195.66	197.37	250.27	316.08	382.16	–	–	–	362.71	–
	194.58								

Table 3 The summary of ANOVA (LSD) of breaking stress of the fibers (MPa)

I	J	Mean difference (I–J)	SE	Sig.	95% confidence interval	
					Lower bound	Upper bound
pp-2	PP/MWCNT-2	− 14.76579	4.38535	0.001	− 23.4175	− 6.1141
pp-2.5	PP/MWCNT-2.5	− 10.34168	4.46603	0.022	− 19.1526	− 1.5308
pp-3	PP/MWCNT-3	− 9.450340	4.38535	0.032	− 18.1021	− 0.7986
pp-3.5	PP/MWCNT-3.5	− 32.66450	4.32876	0.000	− 41.2046	− 24.1244
pp-4	PP/MWCNT-4	− 4.806740	4.38535	0.274	− 13.4585	3.84500

reveal chain conformations. A combination of Fourier transformed infrared (FTIR) spectroscopy and mechanical testing can be effectively used to characterize the orientation behaviour of polypropylene. The ratio of helical content was obtained by dividing the absorbance at 997 cm^{-1} to the absorbance at 973 cm^{-1} which were taken as the References [22, 23]. This ratio has been related to the percentage of crystallinity with some adjustment [6, 24]. The Peak-Fit software was used to calculate the area under the absorbance peaks. Figure 4 shows the helical content versus draw ratio of the fibers. As expected the helical content of the polymer was increased due to the increase in draw ratio. The total molecular orientation of both crystalline and amorphous regions of the samples was measured using a polarized light microscope [25]. Figure 5 illustrates the birefringence values for the samples. Birefringence is the difference between refractive indices for polarized light parallel and perpendicular to the fibers axis. The birefringence for the drawn samples was increased with the increase in draw ratio, which indicated that the total molecular orientation of the fibers was increased with increasing draw ratio. It was also found that the birefringence values or total molecular orientation for composite PP/MWCNT fibers were not higher than that of neat PP fibers for most of the samples. It seems that the nanotubes are less oriented in the direction of the fibers axis. The increase in mechanical properties of composite fibers can be attributed to the MWCNT nucleating effect and probably increase the polymer crystallinity [26, 27]. The same explanation can be regarded as the helical content of the

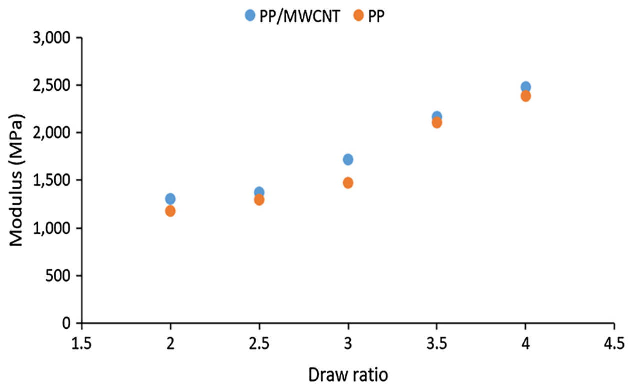

Fig. 3 Modulus as a function of draw ratio for neat PP and PP/MWCNT fibers

samples. The study of the crystallinity of the fibers was carried out in the earlier works [27].

Conclusion

Young's modulus and tensile strength of PP fibers could be enhanced because MWCNTs have higher mechanical properties than PP. However, the polymer/MWCNTs interfacial adhesion is weak, preventing an efficient load transfer from the polymer matrix to MWCNTs. As a result of poor dispersion and inefficient load transfer, the mechanical properties of polymer/MWCNTs composites are often not as good as expected. In this study, the effect

Table 4 Modulus of the fibers (MPa)

PP-2	PP-2.5	PP-3	PP-3.5	PP-4	PP/MWCNT-2	PP/MWCNT-2.5	PP/MWCNT-3	PP/MWCNT-3.5	PP/MWCNT-4
1169.25	1294.14	1466.16	2080.66	2381.88	1303.00	1355.20	1710.69	2162.13	2473.78
1173.31	1291.15	1470.17	2079.97	2385.91	1307.02	1368.95	1714.71	2166.16	2471.75
1159.25	1305.20	1480.01	2124.23	2400.10	1333.20	1395.22	1710.69	2174.00	2475.21
1191.01	1305.23	1470.00	2082.95	2402.00	1322.26	1366.23	1744.18	2163.00	2487.25
1146.05	1301.10	1475.00	2083.69	2351.29	1285.60	1355.05	1690.32	2178.23	2468.35
1149.11	1278.12	1465.23	2108.25	2366.95	1303.25	1364.25	1695.32	2145.63	2459.01
1148.16	1276.21	1477.23	2120.62	2379.89	1298.25	1378.36	1725.36	2153.69	2455.36
1176.51	1287.42	1439.15	2107.93	2391.86	1288.65	1369.40	1729.49	2145.67	2453.89
1181.50	1296.12	1444.25	2085.65	2399.42	1289.69	1396.16	1698.24	2169.24	2467.20
1195.32	1298.32	1468.32	2089.25	2354.69	1299.25	1352.30	1710.69	2177.65	2460.32
1154.62	1297.54	1481.65	2108.23	2365.78	1295.46	1346.25	1706.96	2146.31	2467.32
1145.98	1299.32	1476.32	2105.80	2344.12	1285.36	1368.65	1698.23	2163.02	2476.05
1190.00	1312.12	1477.69	2105.20	2389.36	1332.56	1379.23	1744.73	2160.01	2478.12
1171.30	1305.07	1468.36	2111.32	2393.65	1315.20	1364.17	1720.21	2178.20	2478.31
1173.20	1309.88	1456.71	2112.31	2402.65	1325.64	1352.01	1699.12	2175.03	2469.28
1165.25	1290.23	1449.25	2117.32	2402.52	1285.60	1348.32	1689.91	2163.24	2465.36
1197.54	1280.45	1470.95	2105.32	2379.20	1303.25	1378.01	1691.02	2172.31	2497.36
1185.67	1278.62	1459.98	2109.25	2388.65	1289.36	–	1736.30	2174.09	2488.36
1165.36	1290.65	1482.65	2108.98	2398.54	1332.56	–	1725.23	2145.06	2471.27
1187.65	1303.05	1484.39	2126.39	2399.36	–	–	–	2170.32	–
	1319.15								

Table 5 The summary of ANOVA (LSD) of Modulus of the fibers (MPa)

I	J	Mean difference (I–J)	SE	Sig.	95% confidence interval	
					Lower bound	Upper bound
pp-2	PP/MWCNT-2	− 133.70642	4.76889	0.000	− 143.1148	− 124.2980
pp-2.5	PP/MWCNT-2.5	− 70.779920	4.85662	0.000	− 80.36140	− 61.19840
pp-3	PP/MWCNT-3	− 244.53176	4.76889	0.000	− 253.9402	− 235.1234
pp-3.5	PP/MWCNT-3.5	− 60.483500	4.70735	0.000	− 69.77050	− 51.19650
pp-4	PP/MWCNT-4	− 368.09979	4.76889	0.000	− 377.5082	− 358.6914

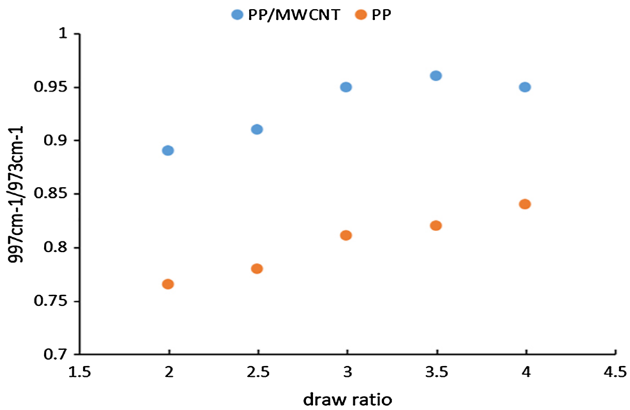

Fig. 4 Changes of helical contents in neat PP and PP/MWCNT fibers

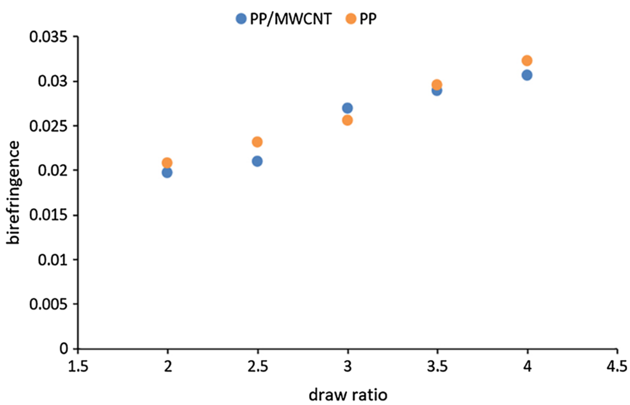

Fig. 5 Changes of birefringence in PP/MWCNT and PP fibers

of drawing ratio on the mechanical properties of PP/MWCNT fibers was investigated. The tensile properties were improved as a function of draw ratio. Modulus in all of the composite samples had a higher value compared to the neat PP fibers. Furthermore, drawing caused an increase in the molecular orientation of the samples as revealed by birefringence measurements. The molecular orientation of composite fibers was not higher than that of neat PP fibers. Even though tensile properties of the composite fibers were higher than those of neat polypropylene fibers with the same draw ratio. It obvious that in order to obtain enhanced tensile properties, surface modification of nanotubes and/or functionalizing of polypropylene is needed for obtaining better interfacial contact between two components.

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