Influence of Alignment and Dispersion Pattern of Carbon Nanotubes in the Polycarbonate and Polystyrene Matrixes on Laser Cutting Workability

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Thermal spread pattern is an effective parameter on laser workability of materials. The thermal behavior pattern of nanocomposites containing carbon nanotubes (CNTs) mostly depends on CNTs alignment and their dispersion within the polymer matrix. This phenomenon makes different their laser workability. The present work is trying to investigate experimentally the influence of alignment and dispersion pattern of CNTs within the polycarbonate (PC) and polystyrene (PS) matrixes on laser cutting workability. In order to reach this purpose, in the first step, the injection and compression molded nanocomposites by different CNT loadings were produced, and then they were cut by laser in different conditions. The transmission electron microscope (TEM) was used to explore the CNTs structure with in the polymer. The results show that the CNTs loading, alignment and dispersion are the effective parameters on outputs. The minimum amounts of kerf width, heat affected zone, burr and kerf taper angle were obtained for compression molded samples. The findings also reveal the CNTs alignment and dispersion pattern are more effective than the CNT loading on kerf width and burr for both of PS and PC polymers matrix. Improving the conditions in lower power and higher cutting velocity is another important finding.

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1. Introduction

The thermal properties of materials are a determinative factor in laser process[1, 2]. The majority of polymers do not have significant thermal conductivity and use as a thermal insulator [3-6]. Recent years researches were tried to improve thermal conductivity of different polymers by adding nanoparticles[7]. Carbon nanotubes (CNTs) are ideal nanoparticles for thermo plastics with special properties that were attended in this field [7-9]. Incorporation of CNTs within the polymer matrixes improves the thermal and electrical conductivity [10-12].

The mixing methods of nanoparticles and polymer matrixes for nanocomposite producing are the most important issues for determination of nanocomposites properties [13-15]. Due to the higher production speed and good mixing power, the mechanical mixing by extrusion is used in a wide range between methods[16, 17]. The produced nanocomposite pellets are mainly shaped as a sample via injection and compression molding that each of these methods has a different effect on alignment and dispersion pattern[16, 18].

The injection molding partially aligns the CNTs in the in-flow direction and generates the minimum contact between them. This method will be useful when the mechanical properties are considered[15, 19]. The compression molded sample also can utilize to reduce the electrical resistivity because this method does not align the CNTs in specific direction but increases the contact between CNTs[20, 21].

The CNTs transfer the majority of heat along their main axis[22, 23]. The most thermal conductivity of CNT-based nanocomposite in aligned direction is a considerable phenomenon [24-26]. As regards, the alignment of CNTs within the nanocomposites are different and depend on production method, it can be concluded that the thermal spread pattern is also a function of nanocomposite production method. Therefore, the injection and compression molded nanocomposites will show different behaviors in laser cutting process.

PC and PS are amorphous polymers with excellent mechanical and thermal stabilities and are known for their high stiffness and hardness[27]. These polymers have a wide utilization in different industries. On the other hand, the CNT-based nanocomposites with polycarbonate (PC) and polystyrene (PS) matrixes also have the special mechanical and electrical properties. The circuit boards, filtration, tissue template, heat sinks in electric or electronic systems, biomedical uses and electromagnetic interference (EMI) shielding are the some applications of these nanocomposites[7, 28]. Improving electrical and thermal conductivity and tensile strength are as remarkable properties that the numerous researches have attended to them [17, 29, 30]. In the matter of these nanocomposites, investigation of the factors effects such CNTs alignment and their dispersion pattern on laser cutting is an interesting challenge that has not been studied. But several researches investigated the laser cutting of polymeric composite materials. The researches which have been conducted in machining and laser cutting process of carbon fiber-reinforced plastics (CFRP) filed [31-35] confirm the thermal properties and fiber orientation are the determinative factor. Laser cutting of carbon fibre-reinforced polyesters were explored by Tagliaferri et al. The thermal properties of the fibers and matrix were founded as the principal factors which affect cutting[1]. Al-sulaiman et al. studied laser cutting of carbon multi-lamelled composites. They found the kerf width depends on laser power and particles orientation. The generated heat is also transmitted along with the direction of fibers[36].

Riveiro studied the effect of continuous wave and pulse mode CO2 laser on epoxy CFRP. The best surface quality in continuous wave (CW) mode was their important achievement[37]. Recently, Herzog et al. were able to cut carbon fiber reinforced plastic by ultra-high power fiber laser system. They have disclosed that using of high power and high cutting speed is an effective method for HAZ reduction [38].

As is evident from prior works, the comprehensive research has not been done about the effect of alignment and dispersion pattern of nano-fiber within polymer matrixes on laser workability. In addition, the prior researchers studied the microfiber effects and the nanoparticles effects rarely were attended. The present work is trying to investigate experimentally the influence of alignment and dispersion pattern of CNTs within the PC and PS matrixes on laser cutting workability.

2. Experimental and set up

The masterbatches of 20 wt% multi walled carbon nanotubes (MWCNT)/PC and MWCNT/PS (Hyperion Catalysis International, Cambridge, MA), were used. In order to produce the MWCN/PC nanocomposites into different CNT loadings, the masterbatch of MWCN /PC was diluted to 3 and 5 wt% by adding neat polycarbonate (Calibre 1080_Dow Chemical). The masterbatch of MWCNT/PS was also diluted to 3, 5 and 10 wt% . The characteristics of polymers matrix are shown in Table 1 (According to the supplier). In this table, the transparency and absorbance properties were measured by UV-visible test (Instrument Ltd-T70PG) in the range of 190-1100nm that the current reported amount is for wavelength of 1024nm. The MWCNTs were also grown by the chemical vapor deposition (CVD) method. The characteristics of used MWCNTs in the masterbatch are also tabulated in Table 2.

Table 1 Characteristics of polymer matrixes

Characteristic	PS	PC
Density (g/m^3)	1.05	1.2
Melt flow rate (g/10min)	11 (200ºC/5k)	11 (250ºC/5 kg)
Thermal conductivity (W/mK)	0.14	0.12
Elastic Module(Gpa)	3	2.2
Elongation (%)	7	80
Transparency (%)	98	88
Absorbance at 1024nm(Au)	0.01	0.05

Table 2 Characteristics of used MWCNTs

Characteristic	Amounts
Purity	> 90%
Outside diameter	10-15 nm
Inside diameter	<5 nm
Length	1-10 µm
SSA	90-120 m^2/g
True density	~1.75 g/cm^3
Aspect ratio	660-1000

A twin extruder machine was utilized to dilute. For this purpose, first the MWCNT/PC and MWCNT/PS pellets were dried for 5h at 120°C and at 90°C in the oven, respectively. Then, a Coperion ZSK25 co-rotating twin-screw extruder was used to produce blends. The water was used as coolant. Then the drenched blends of MWCNT/PC and PS were cut into pellets and also dried for 24 hours at 120 °C and 90°C, respectively. Table 3 shows the extruder parameters that were set to produce of nanocomposites.

The samples were produced by two different compression molding and injection molding method. A manually operated four-post compression molding machine (Carver, Model 4122) was used to fabricate the compression molded nanocomposites. The machine's maximum clamping force was 12 tons, and it was equipped with cartridge heaters in both the top and bottom platens. The compression molding process of MWCT/PS samples was carried out for 6 minutes under 380 bar and at 200 °C. The production of MWCNT/PC samples were also performed for 6 minutes under 380 bar and at 250 °C [23, 30, 39, 40]. The samples were 50×50×0.8 mm in size. In order to produce nanocomposite samples by injection molding, a mold containing four cavities with dimension of 25 × 10 × 0.8 mm were used. Nanocomposite specimens were produced using a Poolad-110-380 plastic injection molding. Table 4 indicates the injection molding parameters[17].

After producing nanocomposite samples, transmission electron microscopy (TEM) images were taken to evaluate the dispersion of nanotubes in the polymer matrix. The TEM analysis of the nanocomposites was carried out on ultramicrotomed sample sections using a Tecnai TF20 G2 FEG-TEM at 200 kV acceleration voltage. The PS and PC samples were ultramicrotomed to sections of ~ 70 and 75 nm at room temperature using a Leica EM UC6, respectively.

Melt flow index of produced nanocomposites were measured by Zwick-Roell melt flow index testers(C-Method). Two kinds of polymers were tested by different conditions according to ASTM D1238. The used weight for tow polymers were 5 Kg and the temperature was 200 °C for PS and 250 °C for PC. Thermal conductivity of different produced nanocomposites was also measured by using PAS-machine at 50°C according to ASTM D5470.

Laser cutting of the nanocomposite samples is performed using a laser system consisting of 150 watts CO_2 laser (Persian Laser Aria PLA-1318F), two axes CNC controlled table with work volume of 1850×1300 mm. The type of laser was continues wave (cw) by wavelength of 1024nm and power laser density of 4.77×10^5 W/cm^2. The compressed air was used as covering gas with 0.28 bar pressure. Focal point is fixed on middle of the work piece [41]. Type of used lens was stable and its ideal cutting (spot diameter) width was 0.2 mm. Fig.1 displays the shape of samples before and after laser cutting.

Heat affected zone (HAZ) and kerf characteristics were measured using an Olympus optic microscope with magnification of 100x. In order to investigate the edges and xerography, the same condition was used. The disk micrometer (Mitutoyo, Japan) was also utilized for measuring of burr.

The method of samples production (two methods), MWCNT concentration (in three levels), laser power (in three levels) and cutting velocity (in three levels) are considered as the variable parameters. For PS nanocomposites, the CNT loading 10% and 20 % also were studied. Table 5 depicts the variable parameters and their levels. Designs of experiment (DOE) are carried out by full factorial method and every experiment run is replicated three times.

Table 3 Extruder parameter

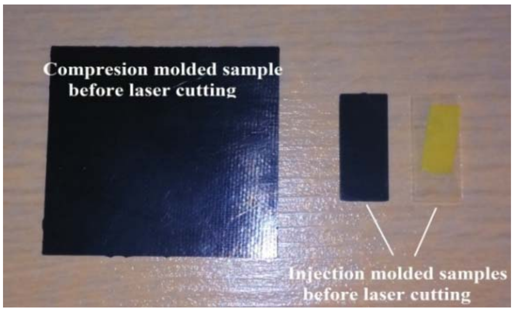
Parameters	Unit	PC	PS
Barrel zones temperatures	ºC	220 - 230 – 240-250 - 260 - 255	180 - 185- 190-195 - 200 - 205
Screws rotational speed	rpm	130	150

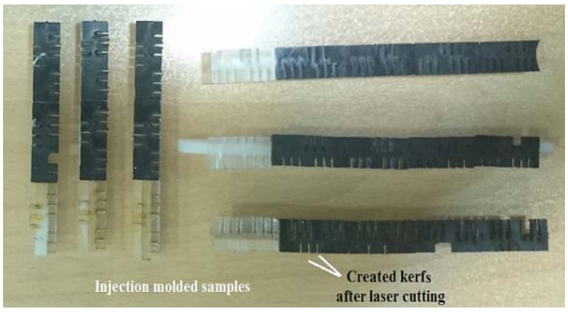
Table 4 Injection parameters

Parameter	Unit	MWCNT/PC	MWCNT/PS
Injection pressure	Bar	150	140
Holding pressure	Bar	100	90
Barrels temperature	ºC	240 – 250 – 260 – 270	170-180-190-200
Injection speed	mm/sec	200	200
Cooling time	Sec	15	10
Holding time	Sec	4	3

Table 5 Levels of the parameters

parameters	Levels of the processing parameters of this research Levels			Symbol
Method of samples production	Injection molding (Composite-A)		Compression molding for5% CNT loading (Composite-B)	**C**
MWCNT concentration (wt%)	0	3	5	**M**
Laser Power (watt)	48	64	80	**P**
Cutting velocity (m/min)	0.7	1	1.3	**V**





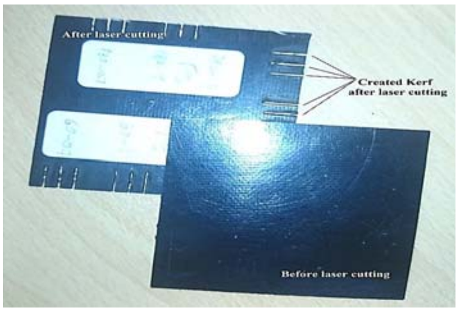
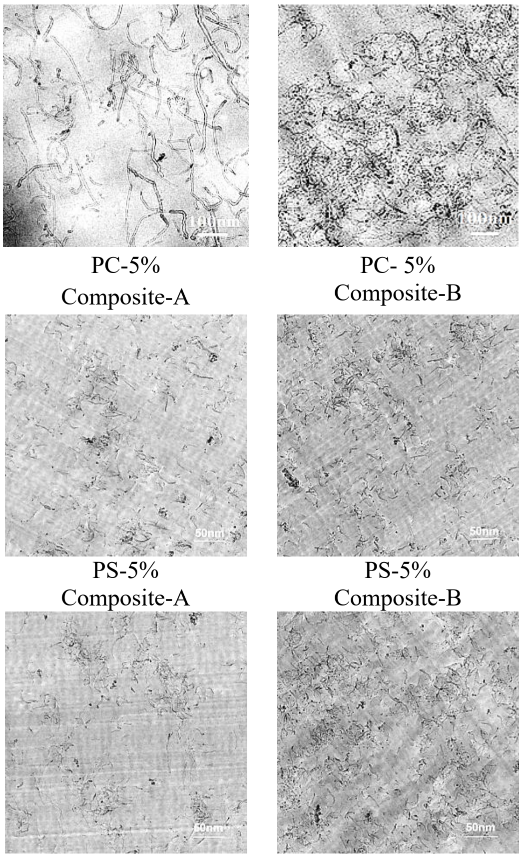


Fig.1 the samples shape before and after laser cutting

3. Results and discussion

3.1 Morphology

The TEM micrographs of some produced nanocomposites samples are shown Fig.2. Investigation of micrographs proves that the CNTs alignment of injection molded and compression molded nanocomposites is different. The partial alignment of CNTs within the in-flow direction is a prominent point that produced by injection molding process but for composite-B the specified alignment is not observed. The contact between CNTs that can out shine the electrical conductivity is occurred in low level for composite-A while is in high degree for composite-B.



PC-5% Composite-A | PC- 5% Composite-B

PS-5% Composite-A | PS-5% Composite-B

PS-3% Composite-A | PS-10% Composite-A

Fig. 2 TEM micrographs of nanocomposites

3.2 Kerf

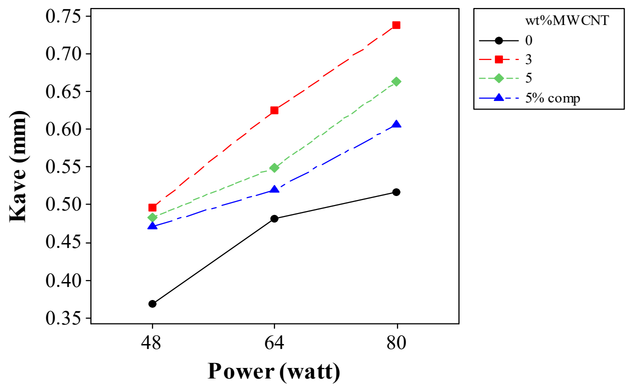
Fig.3 shows the effect of various parameters on the kerf width (K_{ave}) of PC-based nanocomposites. K_{ave} is the average amount of K_u (upper kerf) and K_l (lower kerf). Fig.3 (a) depicts the effect of power for various MWCNT/PC nanocomposites. As can be seen in this figure, the minimum value of Kave was obtained for neat PC. Adding of CNTs from 0% to 3% causes to increase Kave and increasing the MWCNTs from 3% to 5% decreases the Kave. The condition of thermal transmission is the most important factor to analyze the kerf forming. Neat PC is transparent and can transmit the part of laser beam at 1024nm wavelength. This property is eliminated by CNT presences. The CNTs increase the thermal conductivity of PC and cause to transmit easily generated heat in laser cutting[39, 42]. This phenomenon can extend the Kave amounts. In the case of nanocomposite contain 5 wt% MWCNT, the thermal percolation of MWCNTs in the PC matrix occurs with loading below 3 wt%. When the thermal conductivity is enhanced excessively (after thermal percolation) by adding MWCNTs (from 3% to 5%), the thermal focus perishes[16]. This alternation transmits rapidly the produced heat by laser beam and hinders to develop the kerf.

It can be also seen the amounts of Kave are smaller for compression molded nanocomposite with loading 5%. This can be attributed to the higher alignment of CNTs in injection molded nanocomposite which effectively contributes to the transfer of heat along the main axis of the MWCNTs. According to the TEM micrographs (Fig.2) for compression molded nanocomposites, the CNTs do not have a specific alignment within the PC matrix, thereby the heat transfer direction anticipating is not possible in laser cutting process. Therefore, the generated heat is transmitted in random directions and causes to decrease the kerf width (Fig.4). On the other hand, the thermal conductivity of composite B is trifle lower than composite A[40]. When the generated heat cannot be transferred easily, the Kave would not be developed. This is also observed evidently that the kerf width depends on the power. The power is a deciding parameter on the produced heat. Increasing the power enhances the heat and consequently the kerf width is developed.

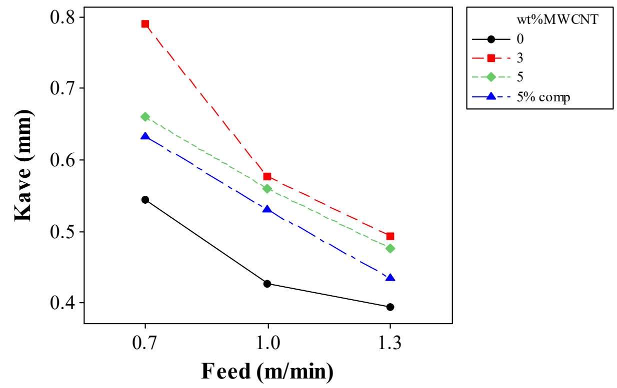
Fig.3 (b) also depicts the effect of feed rate for various MWCNT/PC nanocomposites. According to this figure, increasing the feed decreases the Kave. The changes of feed rate impresses the contact time between laser beam and work piece. When the contact time decreased the generated heat dwindles and holds back to develop the kerf width.

Fig.3 (c) and (d) shows the effect of various parameters on the kerf width of PS-based nanocomposites. Fig.3 (c) depicts the effect of power for various MWCNT/PS nanocomposites. The maximum amount of Kave was obtained for neat PS. The neat PS does not behave like neat PC because their cutting mechanisms are different. The laser beam contact with PC evaporates easily it while for PS first the melted layers are shaped that do not allow to pass the laser beam through the work piece. As can be also seen, increasing the MWCNTs concentration decreases the Kave. It seems that the thermal focus reducing is occurred in low CNT loadings for PS that cause to smaller kerf. There is not the chief change for concentration between 5 and 20%. The results of thermal conductivity measurement for different nanocomposites are shown Fig.5. As can be seen in this figure, the thermal percolation of PS occurs in low concentration and increasing the CNT loading up to it, has not main effect on thermal conductivity[40]. For compression molded nanocomposite, like PC the amounts are slightly smaller than injection molded samples. As regard the mentioned analysis, it is related to the CNTs alignment.

Fig.3 (d) also depicts the effect of feed for various MWCNT/PS nanocomposites. For MWCNT/PS nanocomposites can be seen the Kave amounts decreased by increasing the feed.



(a)



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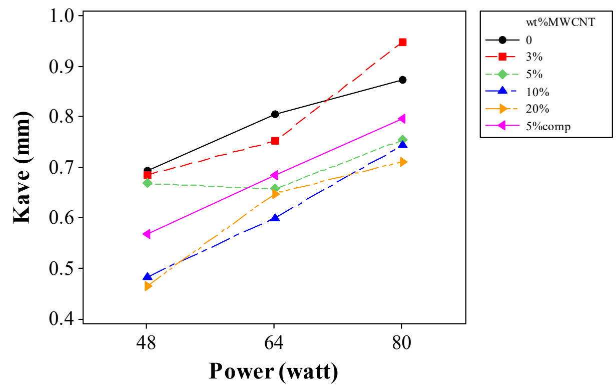

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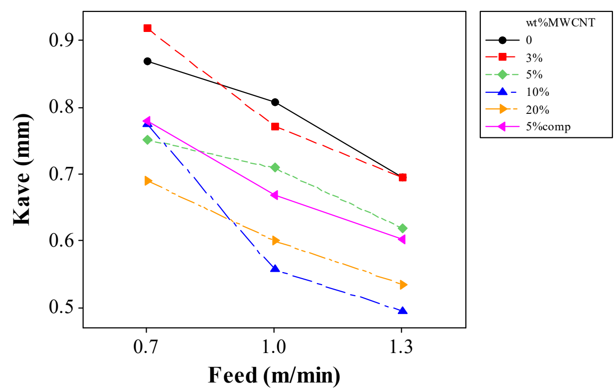
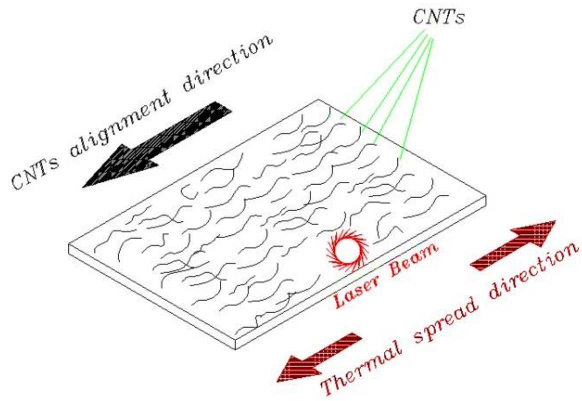
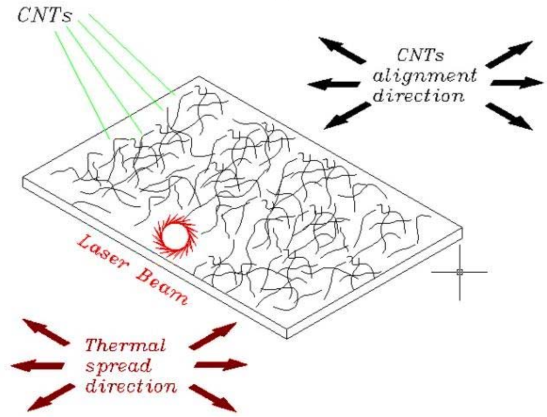


(d)

Fig.3 Effect of various parameters on the kerf width (Kave) (a) and (b) for MWCNT/PC - (c) and (d) for MWCNT/PS



(a)



(b)

Fig.4 Thermal spread pattern for different nanocomposites(a)injection molded samples - (b)compression molded samples

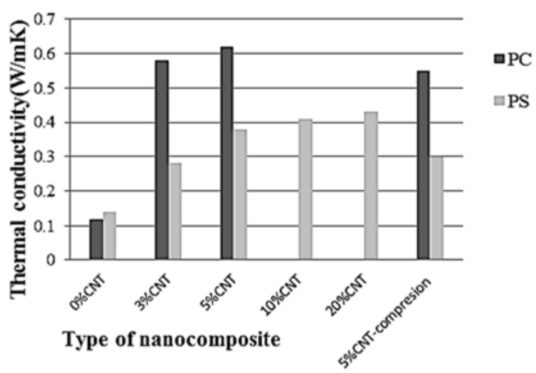


Fig.5 The results of thermal conductivity measurement for different nanocomposites.

3.3 Taper angle of kerf

Two type of kerfs that are observed normally in single pass laser cutting process are shown Fig. 6. Majority of references reported that the upper kerf (K_l) is bigger than the lower kerf(K_u)[43, 44] but some researchers found the inverse result[35, 45]. In this work, both kinds of kerfs were observed during the experiments. The comparison between prior works reveals the type of nonmaterial is the most important factor on kerf type forming[44, 45]. Fig.6 shows the effect of various parameters on the kerf tapper angle (α). The kerf tapper angle is a factor for evaluating of laser workability that is impressed by method of heat transfer. When α amount approaches to zero, it means that the conditions are set at in appropriate values. Fig. 7 (a) and (c) depict the effect of power for various MWCNT/PC and PS, respectively. As can be seen in these figures the presence of CNTs up to 5% in PC and PS could decrease the angle of cut edge. In the matter of PS matrix, it is evidently observed that the higher CNTs loadings (10 and 20%) make bigger α. It seems that according to Fig.5, thermal conductivity improving could assist to decrease α.

Due to the better CNTs alignment in injection molding process the amounts of α for these samples are higher in comparison with compression molded samples. According to TEM micrographs, the CNTs are not aligned within the polymer matrix by compression molding process. The amounts of generated heat in laser cutting transfers dominantly in the axil direction of CNTs[22, 23], so it can be concluded that the thermal conductivity does not have a specific direction for compression molded samples. This property probably can decrease α value. The negative α amounts for injection molded PS by 5wt% CNT loading is a remarkable finding. It seems this result is due to the thermal percolation because the maximum thermal conductivity for PS is reached for 5wt% CNT loading. When the thermal conductivity is increased excessively, the generated heat is transmitted rapidly and causes to deviate the edge[40].

Developing of α for PS and PC nanocomposites by power can also be seen in these figures. The laser power is a key parameter for determining the generated heat. So, by power increasing, the temperature of cut zone will be enhanced and subsequently the cut edge will find more slanted.

Influence of feed rate on α for MWCNT/PC and PS can be seen in Fig.7 (b) and (d), individually. According to these figures, the angle of cut edge reduced when the feed rate increased. This finding is a common result which has been reported [46].

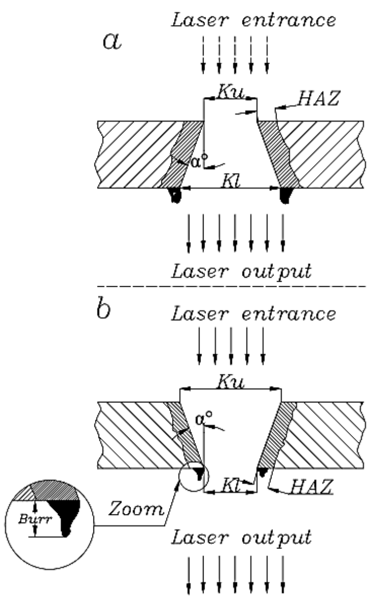


Fig.6 Generated kerfs in laser cutting process

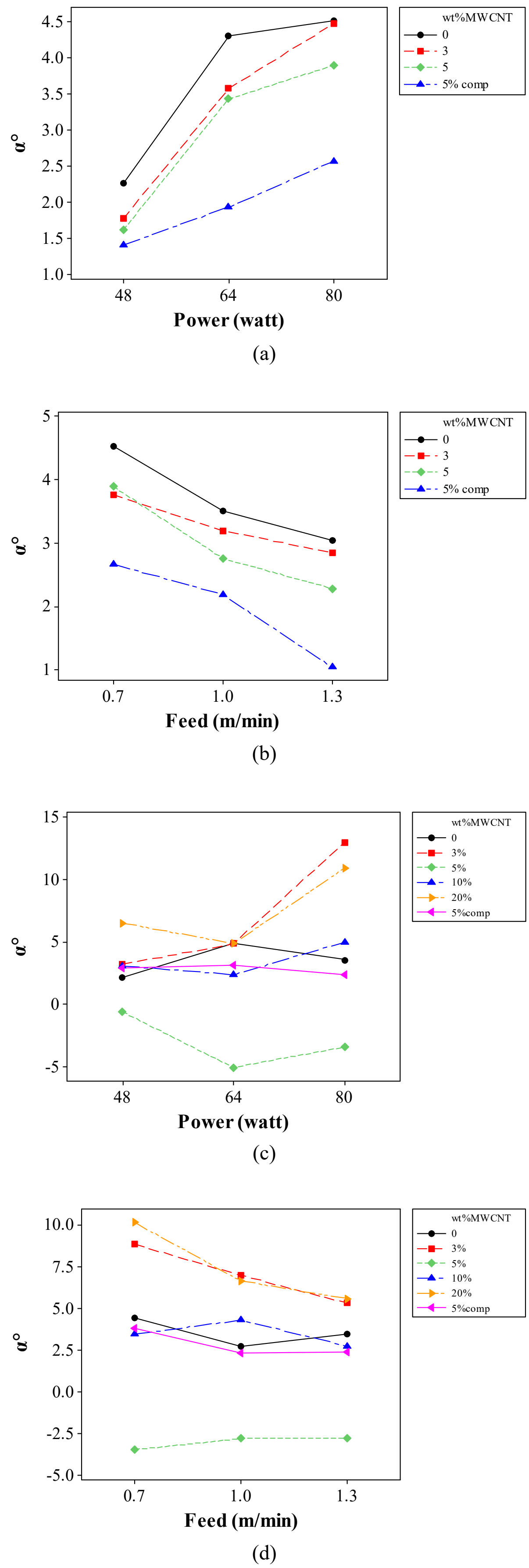


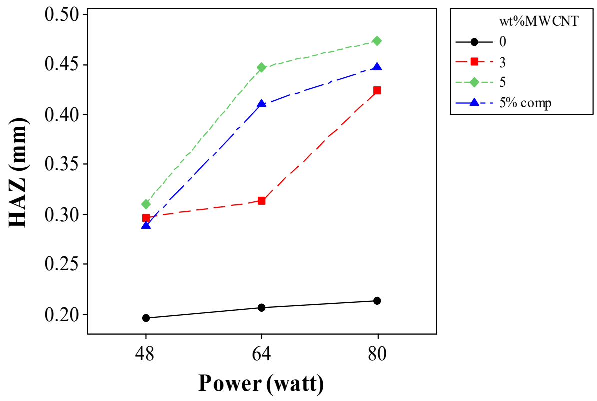
Fig.7 Effect of various parameters on the taper angle of kerf (α) (a) and (b) for MWCNT/PC - (c) and (d) for MWCNT/PS

3.4 HAZ

The heat-affected zone (HAZ) is produced during laser cutting near the cutting zone. This area is appeared on work piece when the temperature rises above the critical transformation point. The study of this area is important because the structural change happens in it and the microcraks are also shaped in HAZ and out shines the properties of produced parts. HAZ can be observed easily by using optical microscope which its color is darker. The HAZ amounts for various conditions are shown Fig.8. Fig.8 (a) also shows the effect of power on HAZ amounts of PC for various CNT loadings. The increasing of HAZ by power is the manifest point in this figure. As it has been described in the taper angle kerf part, increasing of power enhances the temperature in laser cutting process and consequently the HAZ will be developed. The effect of MWCNT loading on the HAZ increasing is another visible point. As can be seen, the thermal conductivity increasing by existing of CNT within the PC matrix developed the HAZ amounts. The HAZ values for compression molded samples of PC are lower than injection molded samples. In compression molded samples the CNTs have not a specific direction with in the polymer matrix but for injection molded samples the CNTs are aligned partially in the in-flow direction[16]. On the other hand, the MWCNTs transfer the majority of heat along the main axes[22, 23]. In the present study for injection molded samples can be said, the developing direction of HAZ is parallel with CNTs axes (Fig.4). Therefore, generated heat transmits rapidly along the CNTs axes in laser cutting process and the HAZ would be produced bigger. But for compression molded specimens, the heat transfer has not recognizable direction. Therefore, the generated heat transfers in many different directions and thus created HAZ values are smaller (Fig.4).

Fig.8 (b) also shows effect of feed rate on HAZ amounts of PC for various percent of MWCNTs. As can be predictable, acceleration of feed could do considerable help for HAZ reduction. When the samples would be cut with higher cutting velocity (feed rate), the contact time between laser irradiation and under cutting part is reduced and consequently the HAZ is diminished[46].

Fig.8 (c) also shows effect of power on HAZ amounts of PS for various present of MWCNTs. As can be seen, the results for PS nanocomposites are not like the PC. First by adding of CNT up to 3%, the HAZ developed, after that it decreased. In order to present logical reason for this finding, the thermal behavior of PS by adding of CNTs should be studied. According to thermal conductivity results, incorporation of CNTs with in the PS matrix up to 3% leads to increase in thermal conductivity. This change continued up to 5% CNTs loading, but after that the sensible alternation is not occurred[40]. It seems that thermal conductivity increasing up to 3 % CNT loading cause to increase in HAZ amount then the higher CNT loading has destroyed the thermal focus. In this condition the input temperature to the work piece is transferred so rapidly and the time would not be provided to broaden the HAZ. It can be also concluded the compression molded samples of PS and PC nanocomposites have the same behavior. It is feasible, this ambiguity would be considered that PS nanocomposites shows twofold behavior on HAZ and Kave. It should be mentioned, there is a difference between shaping temperature of HAZ and kerf. The CNT-based nanocomposites show different thermal conductivity in diverse temperatures[16]. Fig.8 (d) also shows effect of feed rate on HAZ amounts of PS for various percent of MWCNTs. The decreasing in HAZ value by feed increasing is another presumable point that is in agreement with PC's results.



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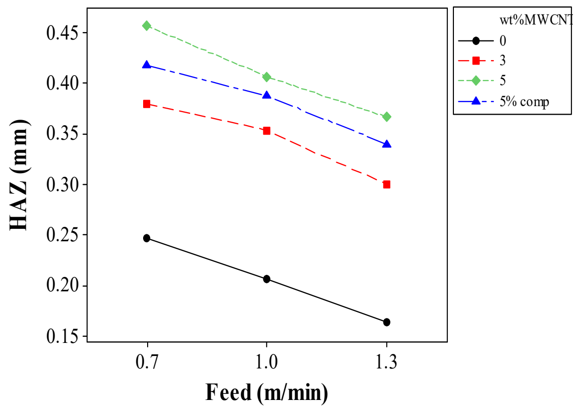

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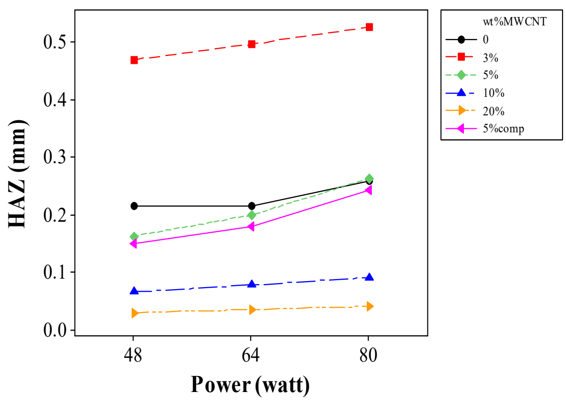

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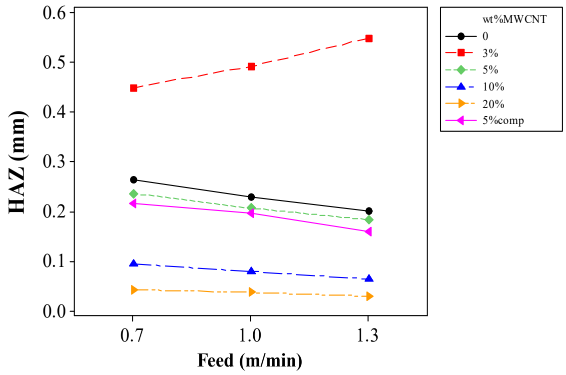


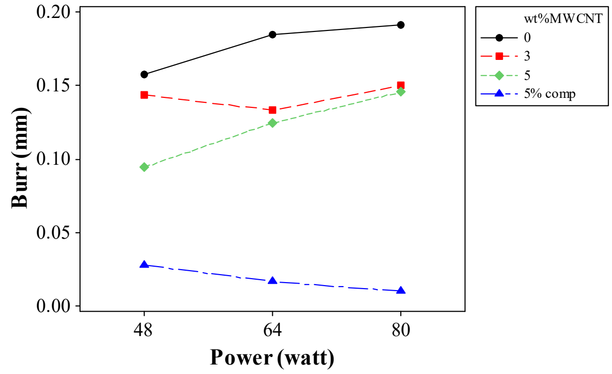
(d)

Fig.8 Effect of various parameters on HAZ
(a) and (b) for MWCNT/PC - (c) and (d) for MWCNT/PS

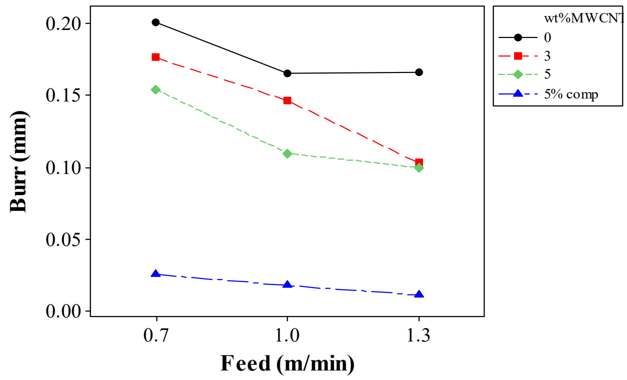
3.5 Burr

After transmission of laser beam and creating the kerf, part of melted material adheres to edge of lower kerf and remains an excrescent shape which is called burr (fig.6). The effect of MWCNT and power on burr amounts of PC is demonstrated in Fig. 9 (a). According to Fig.9 (a), when the MWCNTs concentration is increased the burr decreased. This result clearly confirms that CNTs can be useful for decreasing burr. The change of thermal properties of PC by adding of MWCNTs can explain this finding. Other reason for this phenomenon is the rheological properties alternation. Fig.10 shows the melt flow index (MFI) of different blends after extrusion process. MFI enlightens the viscosity condition and rheological alternation. It is observed the MFI reduced by incorporation of CNTs. Therefore, it can be concluded that the present of CNTs makes less the viscosity of polymers matrix. The reduction of viscosity by CNT loading can be as a good reason for burr decreasing. It can also be seen in Fig.9 (a), the minimum amount of burr was obtained for compression molded nanocomposites. The pattern of thermal spread is an important category that plays a major role on outputs in laser cutting. As it has been explained, in the case of nanocomposites, the pattern of thermal spread is depends on the CNTs alignment. According to morphology results the alignment of CNTs for composite A and B is different. This property causes to make different result for burr. It seems, the pattern of randomly CNTs alignment is more effective for burr reduction. The effect of MWCNT and cutting velocity is shown in Fig. 8 (b). As seen in this figure, the inverse relationship is present between burr and cutting velocity. Increasing the cutting velocity accelerates to remove materials and creates lower burr. Finally, it can be inferred, the power increasing and cutting velocity provide the optimum conditions of cutting and can reduce the burr.

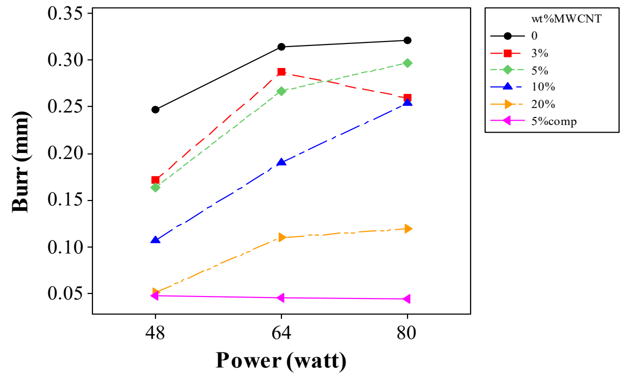
Fig.9 (c) and (d) show the effect of various input parameters on burr for different MWCNT/ PS nanocomposites. The comparison between PS and PC results show both of them have the same behavior about burr.



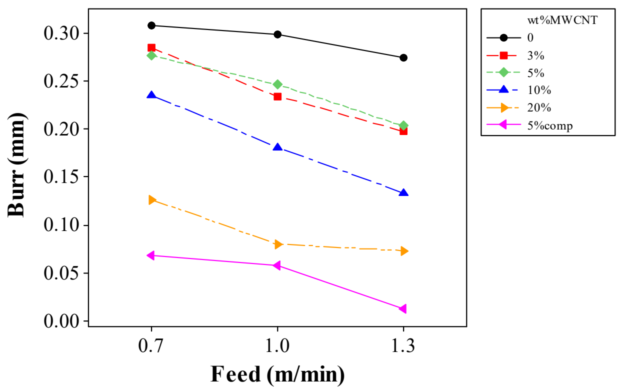
(a)



(b)



(c)



(d)

Fig.9 Effect of various parameters on burr
(a) and (b) for MWCNT/PC - (c) and (d) for MWCNT/PS

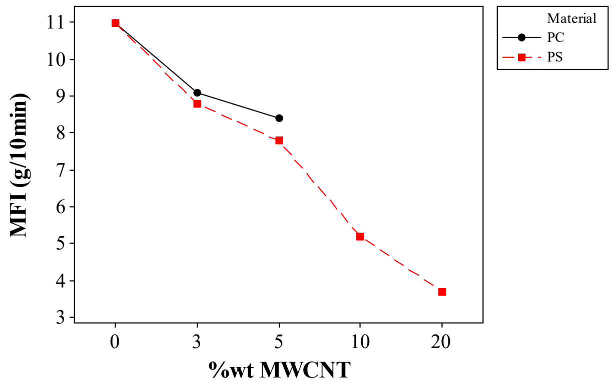


Fig.10 Melt flow impact (MFI) for different nanocomposites

4. Conclusion

The effect of carbon nanotubes alignment and dispersion pattern on laser workability of MWCNT/PC and PS were experimentally investigated. In order to reach this aim, first the nanocomposites were prepared by injection and compression molding methods. In the next stage the samples were cut by laser in different conditions. The prominent results can be summarized as follows:

- The alignment and dispersion pattern of carbon nanotubes within the nanocomposites that shapes by production method are as determinative factor on laser cutting of CNT-based nanocomposites.
- In the case of MWCNT/PS, more aligned CNTs and increasing in CNT loading provide the better conditions to achieve more favorable outputs in laser cutting, excluding taper angle of kerf which for MWCNT/PC, the CNT increasing is an useful factor on kerf width, taper angle of kerf and burr.
- The minimum amounts of kerf width, heat affected zone, burr and kerf taper angle was obtained for samples without specific CNT alignment (compression molded) samples. So, in general, the randomly alignment is preferable for laser cutting.
- For both of PS and PC polymers matrix, the CNT alignment and dispersion pattern are more effective than the CNT loading.
- In general vision, lower power and higher cutting velocity make appropriate conditions in laser cutting of MWCNT/PS and PC.

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