Optimizing Mechanical Properties of POM/Graphene Nanocomposites Prepared by Spray Method

H. Asadollahi-Yazdi
Department of Mechanical and Aerospace Engineering,
Science and Research Branch, Islamic Azad University, Tehran, Iran
E-mail: H.Asadollahi82@gmail.com

M. Shariati*
Department of Mechanical Engineering,
Ferdowsi University of Mashhad, Mashhad, Iran
E-mail: mshariati44@um.ac.ir
*Corresponding Author

A. Imam
Department of Mechanical and Aerospace Engineering,
Science and Research Branch, Islamic Azad University, Tehran, Iran
E-mail: al_mimam@yahoo.com

M. Ghatee
Department of Materials Science and Engineering,
Shahrood University of Technology, Shahrood, Iran
E-mail: mghatee@yahoo.com

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Abstract: In this study, a spray approach is applied to produce POM/graphene nanocomposite using a hot press mold and an automatic spray. The layer-by-layer spray method is used to fabricate these composites with different Wt. % of graphene particles, spray pressure, nozzle-to-mold distance at different temperatures. Taguchi approach as a popular method for Designing of Experiments (DOE) was used for statistical control of the parameters influenced by the synthesis process. The main idea in the present study was to determine the optimal characteristics by investigation of interaction effects in the manufacturing of POM/graphene nanocomposite. Thus, the optimal values obtained were 180^{o}C for the mold temperature, 0.55m for the nozzle-to-mold distance and $3*10^5$ Pa for the spray pressure. Finally, the experimental procedure done, showed that in samples fabricated by 1.8 Wt. % of graphene, the fracture strain decreased about 30% and the UTS and elastic modulus improved 40% and 60%, respectively.

Keywords: Graphene, Nanocomposites, POM, Spray method, Taguchi

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Biographical notes: H. Asadollahi-Yazdi is PhD Student of Mechanical Engineering at the Science and Research Branch, Islamic Azad University, Tehran, Iran. His current research focus is nanocomposites. **M. Shariati** is Professor at the Department of Mechanical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran. **A. Imam** is Assistant Professor of Mechanical engineering at the Science and Research Branch, Islamic Azad University, Tehran, Iran. **M. Ghatee** is Assistant Professor at the Department of Materials Science and Engineering, Shahrood University of Technology, Shahrood, Iran.

1 INTRODUCTION

For decades, polymers with properties such as relatively good mechanical properties and low weight have been used for various applications in different industries. However, due to the lower amount of polymer strength compared to metals, strengthening them is necessary. Thus, the use of nanoparticles as amplifier in polymers has opened a new horizon in the name of nanocomposites in various industries [1]. Although research based on empirical tests to determine the mechanical properties of nanocomposites is inevitable; but given that the experimental work takes a lot of time and money, it is necessary to determine the optimum conditions by using test design method and optimization techniques with minimum number of tests.

Prashanta and colleagues [2] produced polypropylene nanocomposite/multi-layer carbon nanotube by injection moulding method; and by the help of Taguchi method that is a method of experimental design, considered the effect and optimum conditions of factors such as injection speed, holding pressure, back pressure and screw rotational speed. Mirmohseni and Zavareh [3] used Taguchi design to find the most ultimate tensile strength and impact strength in the production of epoxy based nanocomposite with three fillers; and by applying the optimal mode, reached to 64% and 168% increase in ultimate and impact tensile strength. Rostamian and colleagues [4] produced a nanocomposite with epoxy, polystyrene and clay combination. They evaluated impact, compression, bending and tensile strength; and as many factors affect the properties of nanocomposites, they used artificial neural network to determine the effect of each polystyrene, clay and epoxy factors on nanocomposites mechanical properties and used a model to predict nanocomposites mechanical properties; then by using genetic algorithm, they found that tensile strength in 6.3 wt. % of polystyrene and 4.1 wt. % of clay is maximum and its value is 66Mpa.

Mohammad Khanlu and colleagues [5] studied the diameter of the fibers of polymethyl methacrylate. They used the method of determining response level that is one of the experimental design methods to determine the optimum conditions, so that the feed rate (1 to 5 ml per hour), tip-to-collector distance (10 to 23 cm) and polymer percentage (13 to 28) were considered as three key factors. They found that the percentage of polymer is the main factor for fiber diameter. They finally used artificial neural network model to predict the diameter of Nano scale polymer fibers. Azadi and colleagues [6] used Taguchi method to evaluate the effect of three factors that include carbon fiber direction, the percentage of nanotubes and clay percentage on buckling strength of epoxy nanocomposites. They considered four bases for each factor and used L16 orthogonal array for testing. In the following, examples were produced based on software designing; and buckling tests were performed on them. The results show that carbon fiber direction has the greatest impact on the resistance to buckling and the percentage of carbon nanotubes and clay are at next levels of prime importance, respectively.

Mashhadzadeh and his colleagues [7] prepared two types of nanocomposites; in the first type, they used epoxy with carbon nanotubes, clay and carbon fiber; and in the second type, they used epoxy and clay, silica and carbon fiber. By using Taguchi method, they found that in first kind of nanocomposite that degrees of carbon fiber direction is 0, weight percentage of a carbon nanotube is 1 and weight percentage of clay is 1.5 and in the second type of Nano composites that degrees of carbon fiber direction is 0, weight percentage of a carbon nanotube is 1 and weight percentage of silica is 1, the greatest impact strength can be achieved. Parvaneh and colleagues [8] used spray method in the production of PVC/CNT nanocomposite. With 5 wt% of carbon nanotubes, they increased ultimate tensile strength and Young's modulus of nanocomposites to 230 and 180 percent, respectively.

The authors of this paper used spray method in the production of POM/graphene nanocomposites for the first time [9]. Given that many factors may affect properties of produced nanocomposites in spray method, in this paper, the aim is to investigate four factors that affect the production of POM/ graphene nanocomposites and to achieve optimal ultimate tensile strength and Young's modulus. In this work by using the Taguchi method, the effectiveness of spray method factors that includes graphene content, mold surface temperature, nozzle-to-mold distance and spray pressure on ultimate tensile strength of nanocomposite, will be discussed.

2 MATERIALS AND METHODS

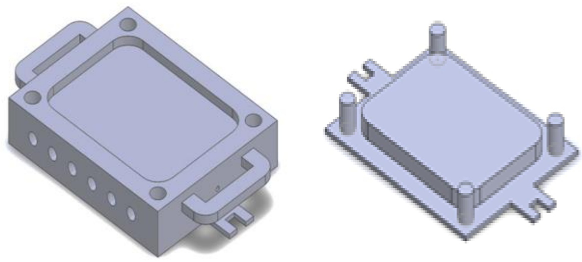
2.1. Material Preparation

Polyoxymethylene (Polyacetal) was used and Polymer belongs to Korea Colon Plastic company and its grade is K300, its density is 1.41 g/cm^3 and its melting temperature is 166 ^{o}c. the grapheme used in this study is purchased from Angstron Materials company. This graphene' length is approximately 7 microns along with the x, y and its thickness is 2 to 3 nm. The solvent used to disperse graphene is THF with 99.8% purity percentage that is purchased from Germany's Merck Company in order to disperse the graphene, THF solution and water were combined at a rate of 6:1 and the resulted solution was inside Ultrasonic bath for an hour with temperature of 70°C. Then functionalized graphene is separated from the solvent by centrifuge and is rinsed with distilled water for several times, until the time that PH has reached to 7, then the product is dried for 24 hours in a heater at a 70°C temperature. Ultimately, graphene solution is provided by adding water for different weights percentages within the POM matrix.

2.2. Production of Nanocomposites

The device consists of three parts of hydraulic press with a capacity of 100 tons; rectangular mold and automatic spray (Fig. 1). In hydraulic press, maxilla is fixed and mandible is variable. The second part of the apparatus is a mold with rectangular cross section which is made of punch and matrix. This mold is designed in the solid work software. Then, this mold is made of steel (50CrMo4) with the yield strength of 780 MPa with dimensions of 60*200*250 mm. the schematic illustration of this mold is presented in Fig. 2. To warm up the mold, six bar elements with power of 750 watts is used; mold temperature is reported to control room via a thermometer. The spraying part of device consists of two stepper motors that its move is provided by microcontroller. Spray device has three entrances for wind flow, materials and solenoid valve. Wind flow is provided by the compressor. Spray output current is controlled by the wind flow and solenoid valve. Solution flow rate and spray cone diameter is adjustable by a knob on the spray.

Fig. 1 A view of press, mold and spray device



(a) (b)

Fig. 2 A Schematic illustration of the mold a) matrix, b) punch

For the manufacture of nanocomposite, at first, solid polymer materials are poured into the mold and then are heated through elements to reach the melting temperature. graphene solution is then sprayed on it by determined weight percentage from graphene by spray tool. Then, the next polymer layer is put on the sprayed surface and is put under 40 ton pressures. This process is repeated for producing subsequent layers so that three layered POM/ graphene nanocomposite is produced.

2.3. Design of Experiment

Taguchi experimental design is a known method that has a simple but effective approach for optimization. In this way, a series of experiments is conducted on this process by the aim of creating known changes in input and observing changes in the output of the process and obtained data leads to performance improvement. Taguchi method can be used to identify variables that influence on the process. Taguchi experimental design process is as follows:

1. Specifying level number of each selected factor.
2. Selecting appropriate orthogonal array and layout of test factors in array.
3. Testing based on orthogonal array order.
4. Test results analysis by using the ratio of signal to noise and analysis of variance.

In Taguchi method, optimum conditions are selected, so that the effects of uncontrolled factors (noise) that affect the response reaches to the least possible amount. In this method, analysis of variance is used to determine the effect of each input factors on response [10]. The purpose of this paper is to reach optimized factors for the production of nanocomposites with high ultimate tensile strength and maximum Young's modulus in spray method. In this method for three factors that include mold temperature, nozzle-to-mold distance and spray pressure, three levels are considered; and for the graphene content factor, six levels are also considered which have been shown in table 1.

Table 1 The selected factors and levels for the Taguchi design

	Factor	Level						Unit
		1	2	3	4	5	6	
G	Grapheme content	0.3	0.6	0.9	1.2	1.5	1.8	wt%
T_m	Mold temperature	160	180	200	-	-	-	^oC
D	Nozzle to mold distance	0.15	0.3	0.55	-	-	-	m
P_s	Spray pressure	$1*10^5$	$3*10^5$	$5*10^5$	-	-	-	N/m^2

According to the factors and their levels, 162 tests must be done without Taguchi method, but with Taguchi method, the number of tests was reduced to 18 and their layout is shown in table 2 for orthogonal array.

2.4. Experiments

A total of 18 samples were produced by using spray method in accordance with Article [9] in Shahrood University. Then produced samples have been cut by laser according to ASTM D638-IV standard and were tested in tensile testing machine in Ferdowsi University of Mashhad as shown in Fig. 3, In order to have more accuracy in calculating the ultimate tensile strength and Young's modulus, in addition to measuring sample strain by using tensile testing machine, bi-directional gauges strain were used on samples that were made in TML Company of Japan.

Table 2 L_{18} orthogonal array used for experimental design

Number	Levels of factors			
	G	T_m	D	P_s
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	1	2
5	2	2	2	3
6	2	3	3	1
7	3	1	2	1
8	3	2	3	2
9	3	3	1	3
10	4	1	3	3
11	4	2	1	1
12	4	3	2	2
13	5	1	2	2
14	5	2	3	3
15	5	3	1	1
16	6	1	3	3
17	6	2	1	1
18	6	3	2	2

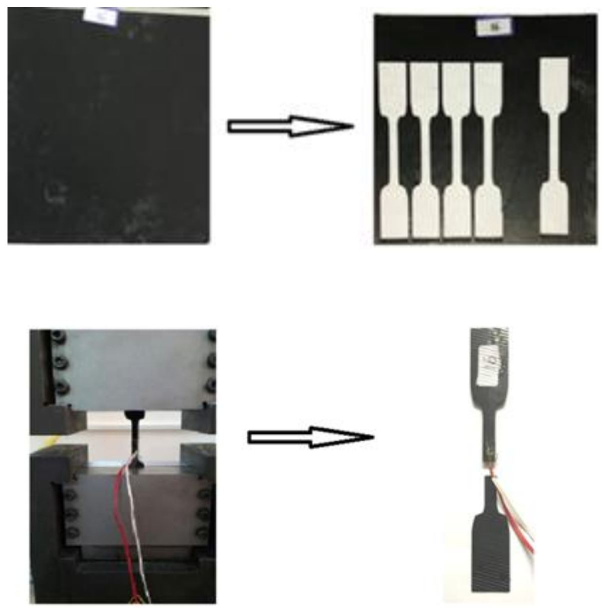


Fig. 3 Tensile Test

3 RESULTS

3.1. Signal to Noise Ratio

Results of ultimate tensile strength and Young's modulus have been extracted for each sample as objective functions in table 3 for all tests. As can be shown, increasing the UTS leads to decreasing the fracture strain which is demonstrated in table 3.

As in analyzing the results, their increases is considered, signal to noise analysis in Eq. (1) with the name of "the greatest the better" [10] in Minitab software in Taguchi part should be used.

$$SN = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (1)$$

Table 3 The mechanical Properties of samples

number	Fracture strain	Young's modulus(GPa) E	Ultimate Tensile Strength(MPa) UTS
1	0.124	1.28	56.9
2	0.118	1.33	58.9
3	0.120	1.31	57.9
4	0.113	1.36	62.3
5	0.114	1.4	63.7
6	0.112	1.38	62.9
7	0.105	1.55	67.1
8	0.103	1.6	69.4
9	0.108	1.53	66.5
10	0.099	1.73	70.9
11	0.098	1.74	71.2
12	0.101	1.72	70.6
13	0.094	1.98	77.5
14	0.089	2.05	79.8
15	0.095	1.97	77.1
16	0.091	2.1	79.1
17	0.088	2.15	80.8
18	0.090	2.12	79.7

That n is number of trials and y_i is the result of i-th test. In Fig. 4 and Fig. 5, signal-to-noise ratio results are achieved for ultimate tensile strength and Young's modulus, respectively. As it can be seen, If the graphene content is placed in the sixth level (1.8 weight percentage), then largest increase belongs to strength and Young's modulus. Also temperature in 180^{o}C has greatest impact on ultimate tensile strength and Young's modulus. With increasing nozzle-to-mold distance till third level (0.55 m) strength and Young's modulus increases, but by changing the spray pressure, a significant impact is not observed on them.

3.2. Analysis of Variance

ANOVA is a parametric test, where the variance is considered for more than two societies. Taguchi method uses analysis of variance to estimate the impact of the input factors on the response, for this purpose P-value is used. So that if P-value is less than 0.05, that factor is effective and if P-value is more than 0.05, that factor is not effective in the final response [11]. As shown in Table 4, in analysis of variance of ultimate tensile strength, P-value for graphene content, mold temperature and nozzle-to-mold distance is less than 0.05 and for spray pressure, it is 0.89 that shows that three factors of graphene content, mold temperature and nozzle-to-mold distance are more effective factors to increase the ultimate tensile strength, but spray pressure is an ineffective factor. In the variance analysis of Young's modulus in Table 4, P-value is 0.97 for spray pressure and is 0.01 for nozzle-to-mold distance, while two other factors are zero, and it shows that except spray pressure, other experiment factors effect on increasing Young's modulus. The results of Taguchi method are very close to the results of paper [12] that has used spray method.

3.3. Interaction of Factors

Interaction effect of factors on each other is performed by analysis of variance. Given that three factors of graphene content, mold temperature and nozzle-to-mold distance have greater impact compared to other factors, so these three factors impact on output is checked. In interaction curve, the amount of each factor effect on the output response is observed as contour.

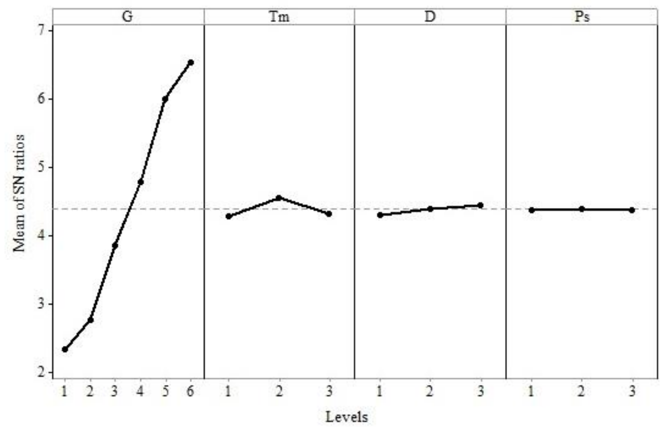


Fig. 4 Mean of SN ratio for selected factors as a function of factors levels for E

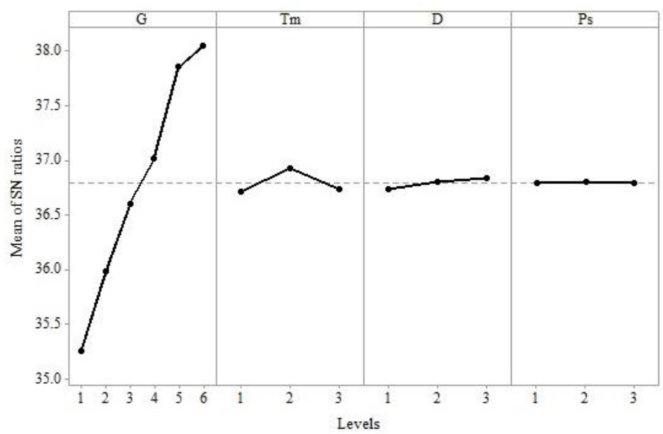


Fig. 5 Mean of SN ratio for selected factors as a function of factors levels UTS

Table 4 The analysis of variance for SN ratio for UTS and E

	Source	Degree of freedom (f)	Sum of square (S)	Variance(S/f)	F-Value	P-Value
UTS	G	5	17.4	3.48	1457	0
	T_m	2	0.158	0.079	33	0.001
	D	2	0.038	0.019	7.9	0.021
	P_s	2	0.0006	0.0003	0.12	0.89
	Error	6	0.0143	0.0024		
	total	17				
E	G	5	43.52	8.7	3116.7	0
	T_m	2	0.238	0.12	42.58	0
	D	2	0.0614	0.03	10.99	0.01
	P_s	2	0.0002	0.00	0.03	0.97
	Error	6	0.0168	0.0028		
	total	17				

In Fig. 6 and Fig. 7, the effect of temperature and graphene content on ultimate tensile strength and Young's modulus are shown, respectively; comparing Fig. 6 and Fig. 7, shows that in high weight percent of graphene, ultimate tensile strength compared to Young's modulus is more sensitive to mold temperature; experimentally, graphene incorporation into the polymer matrix causes defects in polymer; and raising mold temperature repairs some microscopic defects of nanocomposite; these defects are less for lower graphene weight percentages. Because Young's modulus parameter is obtained in less traction mode, compared to ultimate tensile strength parameter, so Young's modulus is achieved before complete conversion of macroscopic defects to microscopic defects.

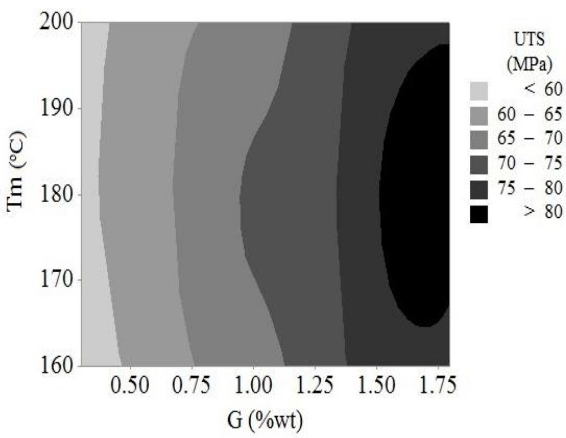


Fig. 6 2D interaction contour plots of graphene content (wt %) and temperature for ultimate tensile strength

In Fig. 8 and Fig. 9, the effect of temperature and nozzle-to-mold distance on ultimate tensile strength and Young's modulus is shown. Results indicate that for achieving high strength and modulus at higher mold temperatures, nozzle-to-mold distance should be in the lowest position and conversely, at lower temperatures, nozzle-to-mold distance should be in the highest position. Empirically, as the proper temperature for the mold is 180°C, when the mold temperature is higher than this value, placing the nozzle in lower position leads to cooling the mold and approaching to 180°C.

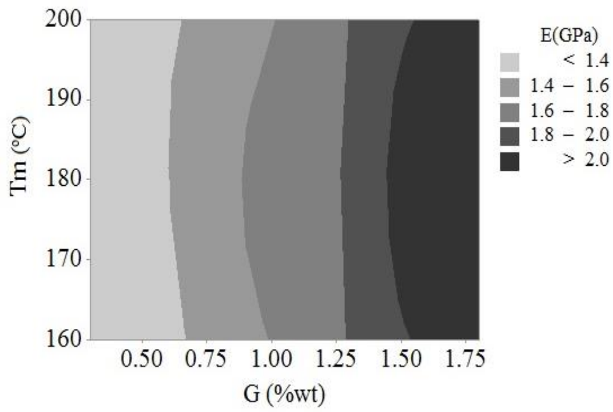


Fig. 7 2D interaction contour plots of graphene content (%wt) and temperature for young modulus

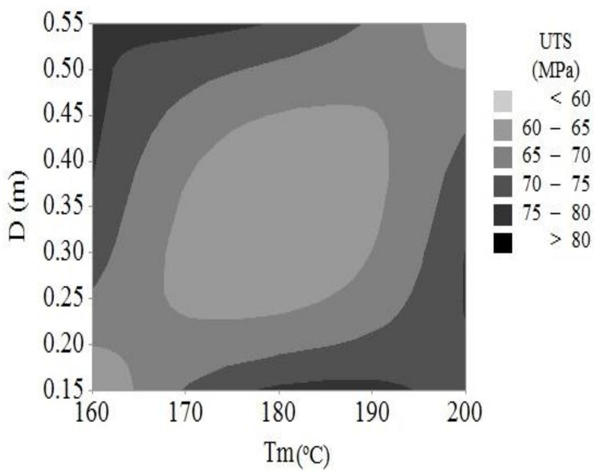


Fig. 8 2D interaction contour plots of temperature and nozzle-to-mold distance for ultimate tensile strength

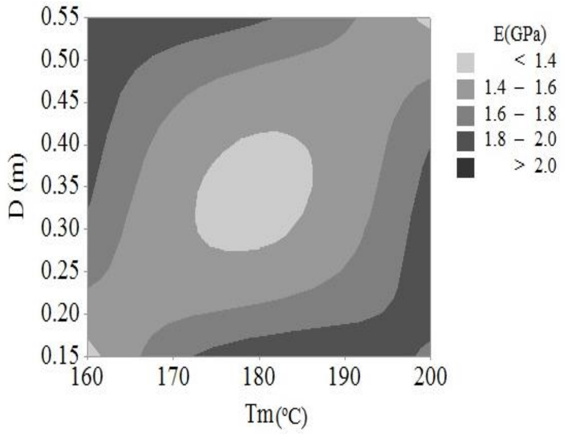


Fig. 9 2D interaction contour plots of temperature and nozzle-to-mold distance for young modulus

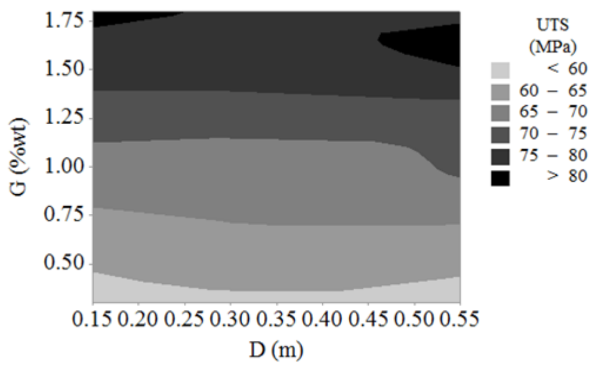


Fig. 10 2D interaction contour plots of nozzle-to-mold distance and graphene content for ultimate tensile strength

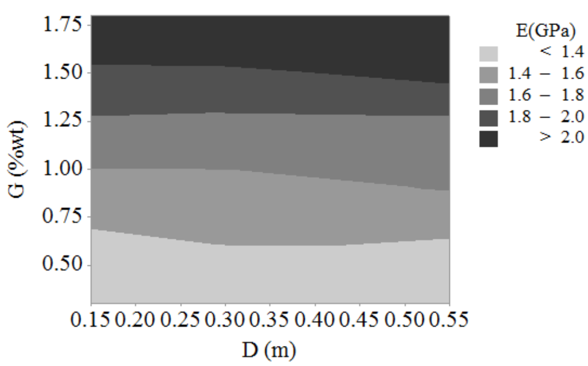


Fig. 11 2D interaction contour plots of nozzle-to-mold distance and graphene content for young modulus

Conversely, when the temperature of the mold is less than 180^{o}C, nozzle-to-mold distance should be more so that spray flow cannot lead to cooling the mold and removing mold temperature from optimum temperature that is 180^{o}C. In Fig. 10 and Fig. 11, effect of graphene content and nozzle-to-mold distance on ultimate tensile strength and Young's modulus is shown. As it can be seen from the contour results, by simultaneously increasing the graphene content and nozzle-to-mold distance, both ultimate tensile strength and Young's modulus increase. But this increase is greater for the ultimate tensile strength compared to Young's modulus. Distribution of graphene is better, when nozzle-to-mold distance is higher. For higher rates of graphene, there is the problem of agglomeration; nozzle-to-mold distance should be in the highest position. In the case of a further increase in ultimate tensile strength than Young's modulus; as Young's modulus is obtained in the elastic mode (low mobility) of material and ultimate tensile strength is obtained in the plastic mode (high mobility) of material, the increase in ultimate tensile strength compared to Young's modulus is justified and is exactly similar to what was noted for Fig. 6 and Fig. 7.

4 CONCLUSIONS

In the present study, POM/graphene nanocomposites are prepared by the spray method and orthogonal array of Taguchi is used for experimental design. Four factors of graphene content, mold temperature, nozzle-to-mold distance and spray pressure were input factors and ultimate tensile strength and Young's modulus of the nanocomposites were considered as output response. The results of signal-to-noise curves as well as analysis of variance for different factors showed that the graphene content has greatest impact on the ultimate tensile strength and Young's modulus and conversely, spray pressure has the least impact. Besides, optimal condition of mold temperature is 180^{o}C for increasing Young's modulus and ultimate tensile strength; but due to the interaction of the nozzle-to-mold distance on the mold temperature, nozzle-to-mold distance should be in minimum distance from the mold in temperature greater than the optimum condition. After graphene content, mold temperature has the greatest impact; and due to the interaction of these two factors, to achieve optimal condition, mold temperature should be increased for higher weight percentages.

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