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Tensile and Morphological Properties of Microcellular Polymeric Nanocomposite Foams Reinforced with Multi-walled Carbon Nanotubes

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ABSTRACT

Polyamide 6 (PA6) is used in many applications due to its advantages and improving its properties seems essential. For this purpose, in the present study, PA6 was melt compounded with various multi-walled carbon nanotubes (MWCNTs) contents and then was foamed using azodi carbon amide (ACA) as blowing agent under different injection molding conditions. Morphological properties were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) tests. According to the results, no agglomeration of MWCNTs in the matrix was observed and 0.85, 0.94 and 1 Å increase in distance between walls of CNTs was detected. Also, the SEM results illustrated that microcellular structure was achieved in all samples. The results illuminated that mean cell size was improved about 34% in samples containing 1 wt% MWCNT. The tensile properties of samples were investigated and the effect of MWCNTs content was studied on specific tensile and yield strengths. The results indicated that specific tensile strength and yield strength were significantly increased almost 164% and 147% by addition of 1 wt% of MWCNTs, respectively.

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1. INTRODUCTION

Polymeric nanocomposite foams are important materials in a variety of applications due to their inherent advantages such as low density, high specific strength, lightweight, materials savings and low thermal conductivity. These materials have attracted the attentions of industrial and scientific communities due to the aforementioned advantages [1-3].

Multi-walled and single-walled carbon nanotubes have received considerable attention due to their unique and remarkable mechanical, electrical and thermal properties. Therefore, carbon nanotubes (CNTs) have been considered for a wide range of potential applications, especially as fillers in polymer composites [4, 5].

Taguchi approach can reduce the number, time and cost of the experiments several times, with high confidence. This method is a useful approach to optimize systems that different and various factors are effective at them [6, 7].

Polyamide 6 (PA6) is a versatile thermoplastic that finds various applications in a broad range of products due to its good physical and mechanical properties. Different studies were performed on properties of PA6 reinforced with different nanoparticles. Esmaili et al. [8] investigated the mechanical properties of PA6 reinforced with MWCNTs. The results illustrated that addition of 1 wt% of MWCNT caused almost 31% improvements in tensile strength of samples.

Liu et al. [9] studied morphological and mechanical properties of PA6-MWCNT nanocomposites. Mechanical properties showed that the elastic modulus and the yield strength of PA6 containing 2 wt% of MWCNTs were improved about 214% and 162%, respectively compared to pure PA6. The investigation of injection molded microcellular PA6-nanoclay nanocomposite foams was performed by Yuan et al [10]. The results showed that the nanocomposite foam samples had smaller cell size and uniform cell distribution and higher tensile strength compared to

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base pure PA6 microcellular samples. The study of PA6 nanocomposites reinforced with different nanoparticles and PA6 nanocomposite foams reinforced with various nanofillers except MWCNTs have performed previously but the investigation of properties of PA6 nanocomposite foams containing MWCNTs still face with serious challenges.

In the present study, the effect of processing parameters and content of MWCNTs on the properties of PA6 nanocomposite foams were investigated using Taguchi approach. The samples containing various weight percentages of MWCNTs and under different processing conditions were injection molded according to L_{16} orthogonal array of Taguchi method. Morphological and tensile properties of samples were investigated and the influence of different parameters on these properties was studied using ANOVA analysis.

2. EXPERIMENTAL AND STATISTICAL PROCEDURES

In this study, commercially PA-6 (with Trade name of Tecomide NB40 NL E, purchased from Eurotec) with the density of 1.13 g/cm^3, suitable for extrusion and molding process, was used as the polymeric matrix. An industrial grade of MWCNTs with purity of 90% supplied by US Research Nanomaterials, Inc. was used in the experimentations as reinforcement. Inner diameters, outer diameters, and length of nanotubes were 5-10 nm, 10-30 nm, and 10-30 µm, respectively. Azodi carbon amide (ACA) was also used as the blowing agent in chemical foaming process of PA-6/MWCNT nanocomposites.

A ZSK-25 (Coperion Werner & Pfleiderer) twin-screw extruder with 10 kg/h extruding capacity and an NBM HXF-128 injection molding machine with L/D=21.1 and D=37mm of screw were used for melt compounding of the materials and injection molding of specimens, respectively. XRD tests were carried out using a Shimadzu X-ray Diffractometer at room temperature and the scanning rate of 2°/min and using copper target (λ=1.5602 Å). SEM (scanning electron microscopy) tests were performed using MIRA3 FEG-SEM (Tescan) machine. A Gotech-AI-7000M tensile test machine was used to calculate tensile properties of samples.

Before melt compounding, PA-6 was dried using a laboratory oven at 80 °C for 2 hours in order to eliminate the humidity of polymer. Then, PA-6 and MWCNTs were extruded in a twin-screw extruder with different weight percentages of MWCNT at melt temperature of 240 °C and screw speed of 250 rpm to produce the nanocomposite granules. XRD tests were performed on the produced nanocomposites in this step that the results will discuss in the next section. After that, the obtained nanocomposite granules were dried again in the drier unit of injection molding machine at 80 °C for 20 hours. In order to provide foaming conditions, 2 wt% of ACA and 1 wt% of paraffin oil were added to the nanocomposite granules as blowing and softening agents, respectively. Table 1 shows the weight percentages of the materials used in this research. According to the considered processing parameters and their levels (see Table 2), the L_{16} orthogonal array of Taguchi approach is selected as Table 3.

TABLE 1. Weight percentages of materials

Material (wt%)	Level			
	1	2	3	4
MWCNT	0	0.5	1	1.5
ACA	2	2	2	2
Paraffin oil	1	1	1	1
PA6	97	96.5	96	95.5

TABLE 2. Selected processing parameters and their levels

Parameter	Level			
	1	2	3	4
MWCNT (wt%)	0	0.5	1	1.5
Holding pressure time (s)	1	2	3	4
Holding pressure (MPa)	80	100	120	140

TABLE 3. L_{16} orthogonal array of Taguchi approach

Trial	MWCNT (wt%)	Holding pressure time (s)	Holding pressure (MPa)
1	0	1	80
2	0	2	100
3	0	3	120
4	0	4	140
5	0.5	1	100
6	0.5	2	80
7	0.5	3	140
8	0.5	4	120
9	1.0	1	120
10	1.0	2	140
11	1.0	3	80
12	1.0	4	100
13	1.5	1	140
14	1.5	2	120
15	1.5	3	100
16	1.5	4	80

It should be noted that the parameters and their levels were selected according to the previous studies and the experimental procedures. The composite materials were injected to a plate shape mold cavity using the injection molding machine. The injected nanocomposite foams plates were shown in Figure 1. The mold has 17.5, 8 and 0.36 centimeters of length, width and thickness, respectively. For carrying out tensile tests, ASTM-D638 [11] standard samples were cut form produced nanocomposite foam plate shape specimens using NCC laser machine according to Figure 2.

In the present study, morphological properties were investigated using XRD and SEM tests and then tensile properties including specific tensile strength and yield strength were studied.

3. RESULTS AND DISCUSSION

3. 1. XRD Test Thedistance between multi-walled carbon nanotube's walls was calculated using Bragg's law as follow [11]:

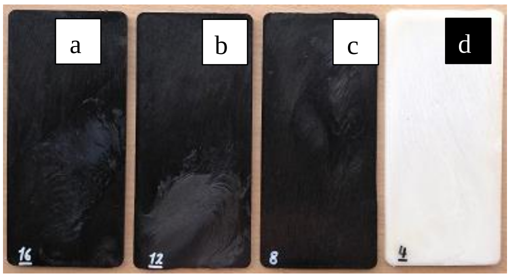

Figure 1. Injected nanocomposite foam samples containing a) 1.5, b) 1, c) 0.5 and d) 0 wt% of MWCNT

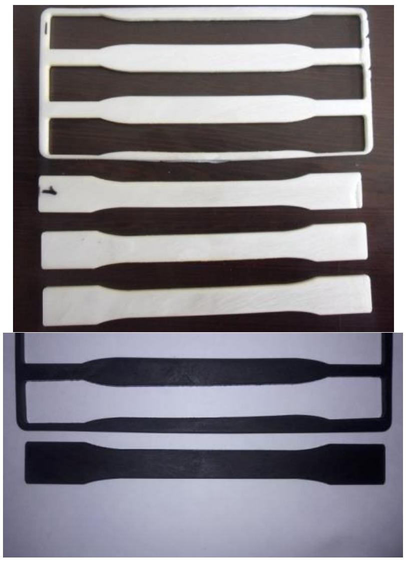
Figure 2. The cut tensile standard samples from plate shapes specimens

$$n\lambda = 2d \sin\theta \qquad (1)$$

where d is the distance between atomic walls of MWCNTs, λ is the wave length of the incident X-ray beam, n is an integer and θ is the angle between the incident X-ray and the scattering planes.

Figure 3 illustrates the X-Ray diffraction pattern of pure PA6 and multi-walled carbon nanotubes. There is a diffraction at $2\theta=26°$ in MWCNT nanopowders that according to the Bragg's law, shows a 0.347 nm in distance between MWCNT's walls. Furthermore Figure 4 shows the X-Ray diffraction pattern for nanocomposite samples.

According to Figure 4, two diffraction peaks were observed that the peak of $2\theta=23°$ belongs to PA6 (see Figure 3-a). The peaks of MWCNTs in the nanocomposites containing 0.5, 1 and 1.5 wt% of MWCNT are $2\theta=20.8°$, $2\theta=20.4°$ and $2\theta=20.1°$, respectively, and consequently the obtained distance of the MWCNT's walls can be calculated as 0.432, 0.441 and 0.447 nm, respectively. The increased distance between MWCNT's walls compared to its pure form indicated that the polymer chains penetrate appropriately in the space between walls. As a result, there is 0.85, 0.94 and 1 Å increase in the distance between MWCNT's walls in nanocomposites containing 0.5, 1 and 1.5 wt% of MWCNTs, respectively.

3. 2. SEM Test Figure 5 shows the SEM picture of nanocomposite foam samples. According to these results, a microcellular structure was achieved in all samples. The mean cell size of different samples was measured and these results were indicated in Table 4. Also, the analysis of variance (ANOVA) results were specified in Table 5. The results illustrated that the mean cell size of samples was decreased by the addition of MWCNTs content (see Figure 6). Smaller cell size leads to better mechanical properties as the literature review indicates [12, 13]. The results demonstrated that mean cell size was improved 34% by adding 1 wt% MWCNTs. This is due to the nucleating role of MWCNTs in the polymer/nano mixture which leads to higher number of bubbles. The ANOVA results indicated that MWCNTs content and holding pressure time are the most effective parameters with almost 45% and 43% contribution, respectively. The P_{value} of these two parameters is less than 0.05 (the error of statistical procedure which takes into account by default) that means these parameters have a significant role in improving mean cell size of samples [14, 15].

3. 3. Tensile Test The tensile properties including specific tensile strength and specific yield strength of samples were indicated in Table 6. A specific tensile property is the tensile property of a sample divided by its density. As an example, Figure 7 shows the force-displacement diagram of sample no. 12 i.e. PA6 nanocomposite foam containing 1 wt% MWCNT. As Figure 8 indicates, specific tensile and yield strengths of samples were improved significantly by addition of MWCNTs content especially in samples containing 1 wt% MWCNTs. This improvement can be due to two different reasons. Firstly, as it was shown previously the cell size decreased by the addition of MWCNTs. This cell size decreasing leads to higher mechanical properties. Secondly, it can be due to the transmitted significant mechanical properties of MWCNTs to the polymeric matrix as shown in [16-18]. The results revealed that the specific tensile strength and specific yield strength were improved almost 147% and 164% in samples PA6-1 wt% of MWCNTs, respectively. Also, the results indicated that the specific tensile properties were decreased in samples containing 1.5 wt% MWCNTs which can be because of agglomeration of nanotubes in high weight fractions. Table 7 illustrated the ANOVA results for specific tensile properties. The ANOVA results demonstrated that MWCNTs content was the most effective parameter on the tensile properties with 90% contribution and the effects of selected processing parameters were negligible.

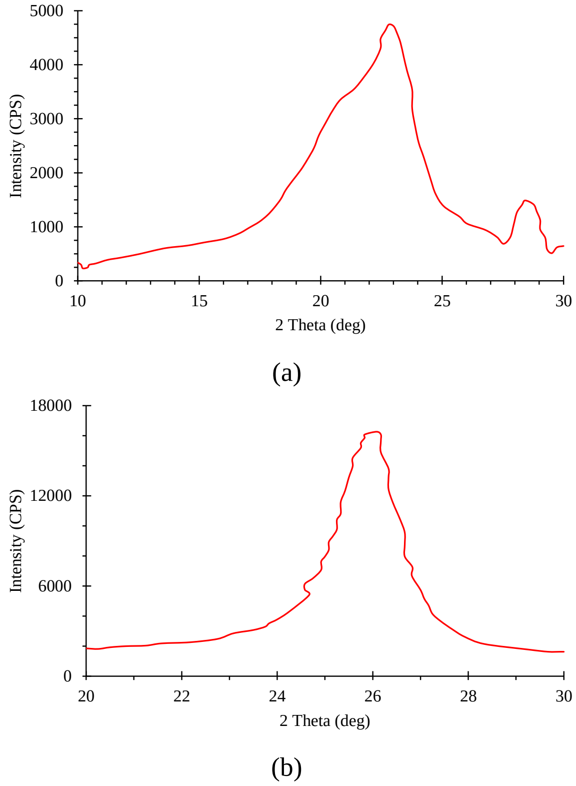

Figure 3. XRD pattern of a) PA6 and b) the multi-walled carbon nanotubes

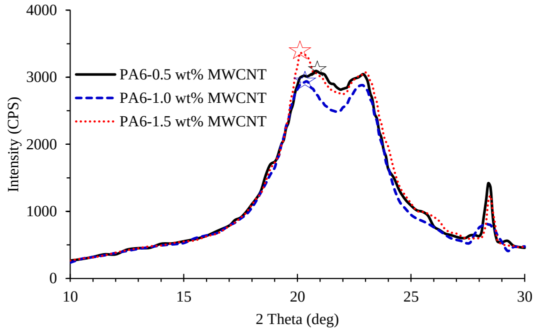

Figure 4. X-Ray diffraction pattern of nanocomposites containing different content of MWCNT

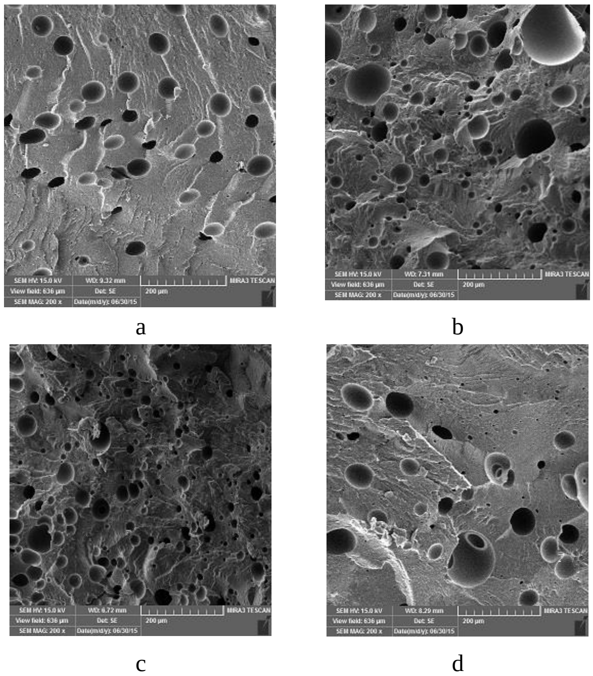

Figure 5. The results of SEM test: a) pure PA-6 foam (T3), and nanocomposite foams containing MWCNT: b) 0.5 wt% (T6), c) 1 wt% (T11) and d) 1.5 wt% (T16)

TABLE 4. Results of mean cell size

Trial	Mean cell size (m)	Trial	Mean cell size (m)
1	31.95 ± 1.546	9	24.12 ± 0.614
2	24.25 ± 1.220	10	16.18 ± 1.247
3	26.09 ± 2.112	11	17.48 ± 1.415
4	25.78 ± 0.854	12	14.02 ± 2.006
5	30.08 ± 1.739	13	28.24 ± 1.382
6	25.16 ± 1.411	14	26.31 ± 2.042
7	16.82 ± 2.086	15	19.10 ± 1.464
8	24.36 ± 1.429	16	23.53 ± 2.571

TABLE 5. ANOVA results for mean cell size

Source	P_{value}	Contribution (%)
MWCNT	0.003	44.81
Holding pressure time	0.004	42.51
Holding pressure	0.094	9.81
Error		2.87
Total		100

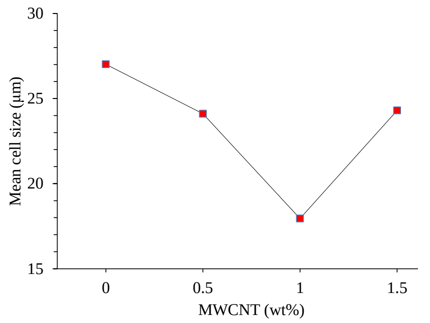

Figure 6. The effect of addition of MWCNTs content on the mean cell size

TABLE 6. Specific tensile properties results

Trial	Specific tensile strength ($MPa.cm^3/g$)	Specific yield strength ($MPa.cm^3/g$)
1	14.42 ± 0.82	8.8 ± 0.47
2	13.93 ± 0.64	9.2 ± 0.32
3	15.72 ± 0.86	8.4 ± 0.62
4	16.78 ± 1.05	9.0 ± 0.40
5	19.74 ± 0.71	11.1 ± 0.41
6	21.57 ± 0.91	11.6 ± 0.33
7	27.64 ± 1.11	15.2 ± 0.32
8	31.03 ± 1.26	17.2 ± 0.50
9	38.09 ± 0.74	25.7 ± 0.39
10	34.18 ± 1.14	19.5 ± 0.71
11	36.98 ± 0.61	22.5 ± 0.53
12	40.94 ± 1.29	25.4 ± 0.38
13	36.35 ± 0.89	20.4 ± 0.61
14	29.72 ± 1.15	17.0 ± 0.52
15	33.79 ± 1.32	20.1 ± 0.50
16	39.29 ± 0.84	23.5 ± 0.83

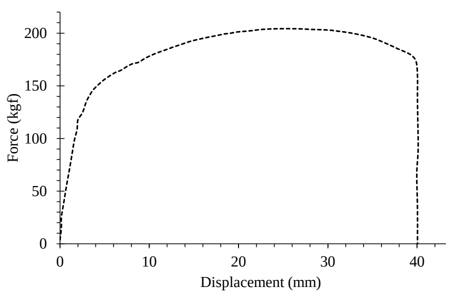

Figure 7. Force-displacement diagram of sample no. 12

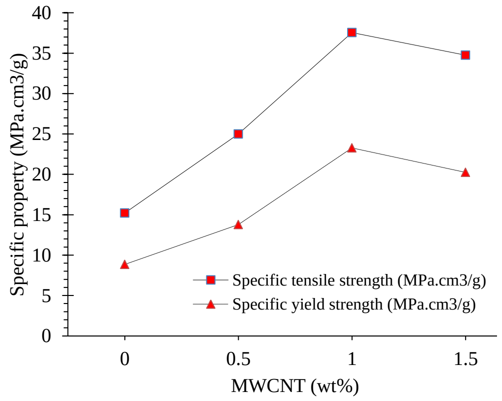

Figure 8. Effect of MWCNTs content on mean cell size

TABLE 7. ANOVA results for tensile and yield strengths

Source	Specific tensile strength		Specific yield strength	
	P_{value}	Contribution (%)	P_{value}	Contribution (%)
MWCNT	0.000	90.01	0.000	89.81
HPT	0.052	7.82	0.148	7.06
HP	0.828	0.50	0.928	0.43
Error		1.67		2.7
Total		100		100

6. CONCLUDING REMARKS

The effect of multi-walled carbon nanotubes content and injection molding processing parameters including holding pressure time and holding pressure were investigated on the properties of polyamide 6 nanocomposite foams. The morphological properties were investigated using XRD and SEM tests. The results showed that appropriate composite materials and microcellular structure were achieved. The results illustrated that the mean cell size of samples was decreased by increasing MWCNTs content. The effect of selected parameters was investigated on the tensile properties including specific tensile and yield strengths. As results showed, the morphological and mechanical properties of PA6 were improved by the addition of MWCNTs to the polymeric matrix. Also, the injection process parameters have affected on the morphological properties but did not have markedly influence on the tensile properties.

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چکیده

پلی آمید 6 به دلیل مزایایی که دارد در کاربردهای مختلفی مورد استفاده قرار می‌گیرد و بنابراین بهبود خواص آن ضروری به نظر می‌رسد. بدین منظور در تحقیق حاضر پلی آمید 6 با درصدهای وزنی مختلف نانولوله کربنی چند دیواره اختلاط ذوبی شد و سپس با استفاده از عامل فوم‌زای آزودی کربن آمید تحت شرایط مختلف فرآیندی تزریق، فوم شد. خواص ساختاری با استفاده از تست‌های پراش اشعه ایکس (XRD) و میکروسکوپ الکترونی روبشی (SEM) بررسی شد. طبق نتایج، کلوخه‌ای شدن نانولوله‌های کربنی داخل ماتریس مشاهده نشد و 0/85، 0/94 و 1 آنگستروم افزایش فاصله در دیواره‌های نانولوله‌های کربنی مشاهده گردید. همچنین نتایج مربوط به تست SEM نشان داد که ساختار میکروسلولی مناسبی حاصل شد و متوسط اندازه سلولی در نمونه‌های فوم نانوکامپوزیتی حاوی 1٪ نانولوله کربنی به میزان 34٪ بهبود یافت. خواص کششی نمونه‌های فوم نانوکامپوزیتی بررسی شد و تاثیر نانولوله‌های کربنی بر روی استحکام کششی و استحکام تسلیم ویژه مورد مطالعه قرار گرفت. نتایج حکایت از افزایش 164٪ و 147٪ در استحکام کششی ویژه و استحکام تسلیم ویژه در نمونه‌های حاوی 1٪ وزنی نانولوله کربنی داشت.

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