Afyon Kocatepe Üniversitesi Uluslararası Mühendislik Teknolojileri ve Uygulamalı Bilimler Dergisi

Afyon Kocatepe University International Journal of Engineering Technology and Applied Sciences

AKÜ IJETAS Cilt **6(2)** (2023) Aralık (110-117 s) AKU IJETAS **Vol 6(2)** (2023) December (110-117 pp)

DOI:10.53448/akuumubd.1321014

Araştırma Makalesi / Research Article

e-ISSN 2667-4165 (https://dergipark.org.tr/akuumubd)

Floroetilenpropilen (FEP)/Grafen Hidrofobik Kaplamaların Üretim Parametrelerinin Optimizasyonu

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Recevied :29.06.2023; accepted:20.07.2023

Öz

Akışkan madde taşıyan yüzeylerin hidrofobik malzemelerle kaplanması sürtünme faktörünün azaltılmasında etkili sonuçlar göstermektedir. Bu çalışmada hidrofobik özellik sergileyen floroetilenpropilen (FEP) malzemenin hidrofobik davranışını artırmak için ilave edilen nano grafen katkısının üretim parametrelerinden katkı oranı, kürleme sıcaklığı ve kürleme süresi parametreleri optimize edilmiştir. Optimize edilen üç parametre için üç farklı seviye literatür kaynaklarından belirlenmiştir. Bu seviyeler grafen katkı oranları için ağırlıkça %1, %2, %3, kürleme sıcaklıkları için 200 ˚C, 300 ˚C, 400 ˚C ve kürleme süreleri için ise 30 dak, 40 dak, 50 dak olarak uygulanmıştır. L9 Taguchi dizisine uygun şekilde AISI 304 sac malzeme yüzeylerine floroetilenpropilen/grafen karışımı uygulanmış ve kürleme işlemi fırında tamamlanmıştır. Optimizasyon işlemi yüzeylere bırakılan su damlasının temas açıları yanıtlarına göre gerçekleştirilmiştir. Floroetilenpropilen içerisine ilave edilen grafenin optimum katkı oranı %1, kürleme sıcaklığının optimum değeri 400 ˚C ve kürleme süresinin optimum değerinin ise 40 dak olduğu tespit edilmiştir. Varyans analizinden temas açıları üzerinde en etkili parametrenin %96.78 oranla kürleme sıcaklığı olduğu belirlenmiştir. Floroetilenpropilen kaplama malzemesine ilave edilen katkılara optimum üretim parametrelerin uygulanması pompa, türbin, tesisat vb. uygulamalarda enerji tasarrufuna katkıda bulunabileceği sonucuna varılmıştır.

Anahtar kelimeler
FEP; Kürleme Şartları; Taguchi Metodu; Yüzey Mühendisliği; Temas Açısı

Optimization of Manufacturing Parameters for Fluorinated Ethylene Propylene (FEP)/Graphene Hydrophobic Coatings

Abstract

The coating of surfaces carrying fluid with hydrophobic materials has shown effective results in reducing friction factors. In this study, the optimization of manufacturing parameters, including the additive ratio, curing temperature, and curing time was conducted to enhance the hydrophobic behavior of fluorinated ethylene propylene (FEP) material by incorporating nano graphene additives. Three different levels for the optimized parameters were determined based on the literature sources. These levels were set as 1% wt, 2% wt, and 3% wt for graphene additive ratios, 200 ˚C, 300 ˚C, and 400 ˚C for curing temperatures, and 30 min, 40 min, and 50 min for curing times. Following the L9 Taguchi design, the FEP/graphene mixture was applied to AISI 304 stainless steel surfaces, and the curing process was completed in an oven. The optimization process was performed based on the response of water droplet contact angles on the surfaces. The optimum graphene additive ratio was determined as 1%, the optimum curing temperature was 400 ˚C, and the optimum curing time was found to be 40 min. Variance analysis revealed that the curing temperature had the most significant effect on the contact angles with a contribution rate of 96.78%. Applying the optimal manufacturing parameters to the FEP coating material with added additives can contribute to energy savings in applications such as pumps, turbines, and pipelines.

Keywords
FEP; Curing Conditions; Taguchi Method; Surface Engineering; Contact Angle

1. Introduction

In the majority of engineering applications, fluid substances are transported from one place to another to carry out processes (Yumurtacı and Sarıgül, 2011). One way to achieve energy savings in the transportation of fluid substances is by reducing the friction losses occurring in pipelines. The decrease in the friction factor reduces pressure drop, thus enabling energy conservation. With the recent advancements in surface coating technologies, low surface energy materials can be produced, resulting in the creation of hydrophobic, or water-repellent, surfaces. These surfaces eliminate the no-slip condition at the fluid-solid interface, reducing the shear stress and consequently decreasing the frictional force (Voronov et al. 2007; Choo et al. 2007). It is applied in industrial sectors due to its stated properties. Therefore, surfaces are coated with hydrophobic materials. In line with this objective, the literature studies are as follows. Tanaka and Kawakami (1982) suggested the use of surface engineering technology to prepare hydrophobic and wear-resistant composite coatings by incorporating carbon fibers, graphene, or carbon nanotubes into pure hydrophobic polytetrafluoroethylene (PTFE) coatings. They aimed to enhance the hardness and wear resistance of the coatings (Tanaka and Kawakami, 1982). Takahashi et al. (2011) processed PTFE using reactive ion etching in a plasma reactor with Ar, CF_4, N_2, and O_2 gases, resulting in surfaces with different wetting properties. Particularly, they obtained a surface with a water contact angle higher than 150˚ after CF_4 plasma treatment, demonstrating reduced friction of water droplets (Takahashi et al. 2011). Wang et al. (2015) produced hydrophobic coatings by physically blending SiO_2 and PTFE nanoparticles. They found that the coating surface filled with hydrophobic SiO_2 exhibited better homogeneity compared to untreated SiO_2, and the maximum measured contact angle on the composite coating surface was 163.1° (Wang et al. 2015). Nemati et al. (2016) used a spin coating method to prepare PTFE/graphene oxide composite coatings on stainless steel substrates, showing that a volume fraction of 15% graphene oxide could significantly reduce the friction coefficient and wear rate (Nemati et al. 2016). Wu et al. (2019) created a composite coating using carbon fiber-reinforced PTFE and reported that when the mass fraction of carbon fiber was 20%, the water contact angle reached 122.0 ± 2.0°, indicating excellent hydrophobic properties (Wu et al. 2019). Chen et al. (2022) prepared PTFE/Al_2O_3 composites at 340 ˚C for 30 minutes. They observed that these composites formed a water contact angle of 135˚ (Chen et al. 2022). Furthermore, Wang et al. (2022) prepared carbon fiber-reinforced PTFE composite coatings on 35CrMo steel substrates using a one-step spray method, followed by laser surface modification. They investigated the effects of coatings with 10%, 20%, and 30% carbon fiber content on the contact angle, friction coefficient, and wear rate. They found that the 30% carbon fiber-reinforced coating exhibited the strongest hydrophobic characteristic (Wang et al. 2022).

It is commonly observed in the literature that fluorinated ethylene propylene (FEP) and PTFE materials are frequently used to impart hydrophobicity to surfaces. The addition of graphene, silica, alumina, carbon fiber, carbon nanotubes, and other materials to these mentioned polymers has been found to enhance the hydrophobicity of the resulting composite materials, thereby reducing the friction occurring on the surface. Furthermore, to achieve a hydrophobic surface, coatings are prepared with various manufacturing parameters such as particle size, reinforcement ratio, coating thickness, coating type, curing temperature, curing time, etc. The literature studies investigating the effects of these parameters are as follows. Lin et al. (2016) found that curing PTFE material at 230°C for 50 min resulted in a hierarchical structure characterized by microspheres with numerous nano-pores on the surface, providing excellent water repellency (Lin et al. 2016). Bansal et al. (2020) examined the influence of coating thickness on the hydrophobicity of PTFE coatings and concluded that the PTFE coating with the minimum thickness among the selected thickness parameters exhibited superhydrophobic behavior with a contact angle of 159° (Bansal et al. 2020). Ayyagari et al. (2021) examined the influence of nanoparticle concentration, percentage of PTFE polymer, and rotational coating speed (rpm) on various properties of the coating such as contact angle, roll-off angle, scratch hardness, adhesion, and thickness. They also determined a coating formulation for achieving higher contact angles and mechanical properties (Ayyagari et al. 2021). Sun et al. (2021) demonstrated that the addition of graphene nanoparticle additives to PTFE coatings reduced the amount of wear, which rapidly decreased up to a 2% additive ratio, followed by a slower decrease. The minimum wear rate was achieved in the composite with at least a 10% nanoparticle addition (Sun et al. 2021). Overall, considering the literature, it is observed that hydrophobic coatings applied to material surfaces involve various variable parameters. In this regard, there are numerous studies in the literature. The most influential parameters in enhancing the hydrophobic behavior of FEP and PTFE materials are the type and ratio of additives, coating thickness, curing temperature, curing time, etc. Although there have been studies on the optimization of these parameters, it can be stated that further contributions are still needed in this field.

In this study, the manufacturing parameters of FEP/graphene hydrophobic coatings were optimized using the Taguchi method. The graphene additive ratio, curing temperature, and curing time were considered as the three parameters, each with three levels. The optimum levels for these three parameters were determined based on the contact angles of water droplets deposited on the surface. Additionally, variance analysis was conducted to perform statistical evaluations.

2. Material and Methods

2.1 Material

AISI 304 stainless steel material was used extensively in applications such as pumps, turbines, and pipelines due to its high corrosion resistance performance (Akinlabi et al. 2019). The chemical composition of the AISI 304 sheet material used in this study is given in Table 1 (Özakın and Kurgan, 2022). Sheet material samples were cut into dimensions of 30 × 30 × 1 (mm^3). The surfaces of the substrate material were cleaned with acetone and prepared for the coating process.

Table 1. Chemical composition of AISI 304 substrate (Özakın and Kurgan, 2022)

Chemical composition (%wt)													
Fe	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Ni**	**Cu**	**Al**	**V**	**Co**	**W**	**Mo**
Balance	0.016	0.412	1.466	0.040	0.007	18.273	7.887	0.196	0.007	0.084	0.230	0.011	0.125

2.2 Methods

Within the scope of the study, it was decided to optimize the parameters of graphene content, curing temperature, and curing time for the manufacturing of FEP/graphene hydrophobic coatings. Based on the information in the literature, a L9 Taguchi experimental design was planned with three levels for each parameter (Sun et al., 2021; Pehlivan and Özbey, 2022). The experimental layout conforming to the Taguchi L9 orthogonal array is presented in Table 2.

Table 2. Taguchi experimental design

Experiment No	Control Factor		
	Graphene additive ratio (% wt)	**Curing Temperature (˚C)**	**Curing time (min)**
1	1	200	30
2	1	300	40
3	1	400	50
4	2	200	40
5	2	300	50
6	2	400	30
7	3	200	50
8	3	300	30
9	3	400	40

Figure 1 presents the sequential methods used in the experimental study. In the first stage, nano-sized graphene (5 nm thickness, 30 µm diameter;

Nanografi Inc.) was added to the FEP material obtained from the market at 1% wt, 2% wt, and 3% wt ratios. The mixtures were prepared using a mechanical homogenizer. The obtained mixtures were then sprayed onto the substrate surfaces using a spray gun to achieve a homogeneous distribution, following the experimental design.

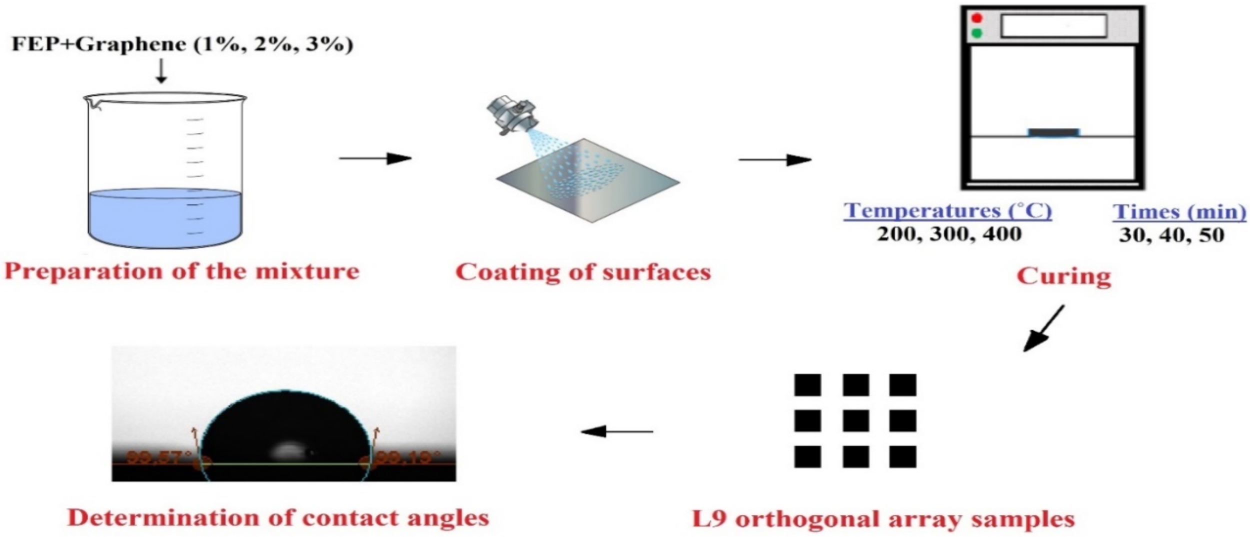

Figure 1. Methods used in the experimental study

The curing process in the study was carried out using a Refsan RS400 furnace. The curing temperature and curing time parameters were linearly increased from room temperature to the curing temperatures to enhance the adhesion of the coating, and they were maintained at those temperatures for 10 min. After the 10 min period, the experimental samples were left to cool inside the furnace. For example, in experiment number 1, the FEP mixture with a 1% graphene additive reached 200°C within a linear temperature increase of 20 min and was kept at this temperature for 10 min. Subsequently, it cooled down in the furnace until it reached room temperature. The samples prepared according to the L9 orthogonal array used in the study are shown in Figure 2.

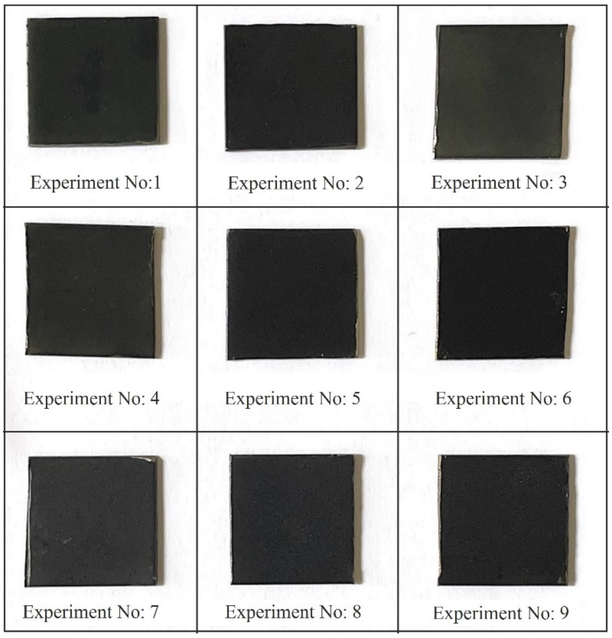

Figure 2. Samples prepared in accordance with the L9 orthogonal array

Contact angles were measured using a contact angle goniometer (Attension Theta Flex, Biolin Scientific, Sweden) at room temperature. A 5 µL water droplet was placed on the sample surfaces, and the image of the droplet was captured in a planar manner using a high-speed camera. The contact angles were measured at two different points, one on the right side and one on the left side of each image obtained from the samples. The contact angle value was calculated as the average of these two measurements. The measured contact angles from the samples prepared according to the L9 orthogonal array are shown in Figure 3. The analyses of the Taguchi method and the analysis of variance (ANOVA) were conducted using Minitab 18 software.

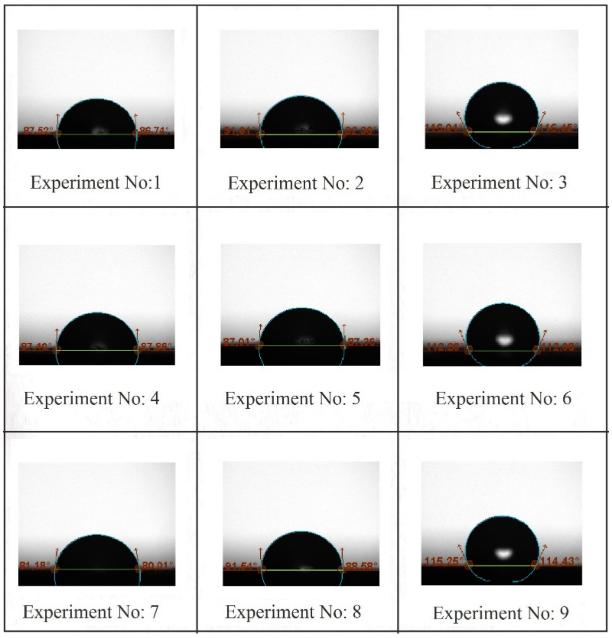

Figure 3. Measured contact angles

3. Results and Discussion

The Taguchi method was employed for the optimization of the manufacturing parameters of FEP/graphene hydrophobic coatings. Signal-to-noise ratios (S/N) were calculated based on the observed contact angles of water droplets placed on the test samples prepared according to the L9 orthogonal array. The contact angle of the water droplet on the material surface, being 90° or above, is an indication of the surface hydrophobicity (Ma et al., 2007). Therefore, the larger the contact angle, the more hydrophobic the surface is. Based on this principle, the S/N ratios were determined using the criterion of "larger is better." The S/N value was calculated according to Equation 1.

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \qquad (1)$$

Table 3 presents the values of contact angles obtained from the experimental studies conducted according to the L9 orthogonal array, along with the signal-to-noise (S/N) ratios determined based on the criterion of "larger is better" for the contact angle responses. The results in Table 3 demonstrate that the FEP coating with 1% graphene addition, cured at 400°C for 50 min, exhibits the maximum contact angle. In contrast, the coating with 3% graphene addition, cured at 200°C for 50 min, shows the minimum contact angle. It was observed that the materials cured at 400°C exhibit significantly higher contact angles on their surfaces.

Table 3. Experimental contact angles and S/N ratios

Experiment No	Parameters			Results	S/N Ratios
	Graphene additive ratio (%)	Curing temperature (˚C)	Curing time (min)	Contact angle (˚)	Contact angle (dB)
1	1	200	30	87.13	38.8034
2	1	300	40	91.69	39.2464
3	1	400	50	116.25	41.3079
4	2	200	40	87.63	38.8531
5	2	300	50	87.19	38.8093
6	2	400	30	112.17	40.9975
7	3	200	50	80.60	38.1267
8	3	300	30	90.06	39.0906
9	3	400	40	114.84	41.2019

The optimal conditions for achieving a high contact angle are shown in Figure 4 through the main effect plots and in Table 4 through the contact angle responses in terms of the S/N ratios. The magnitude of the S/N ratio is the most important indicator for identifying the optimal values. In Figure 4, an increase in graphene addition leads to a decrease in the S/N ratio. Among the three addition levels of graphene (1-3%), the optimal addition ratio is 1%. Similarly, as the curing temperature increases, the S/N ratio also increases. Among the curing temperatures used in the study (200-400°C), the optimal temperature is 400°C. Additionally, the optimal curing time is observed to be 40 min, which corresponds to the higher S/N ratio.

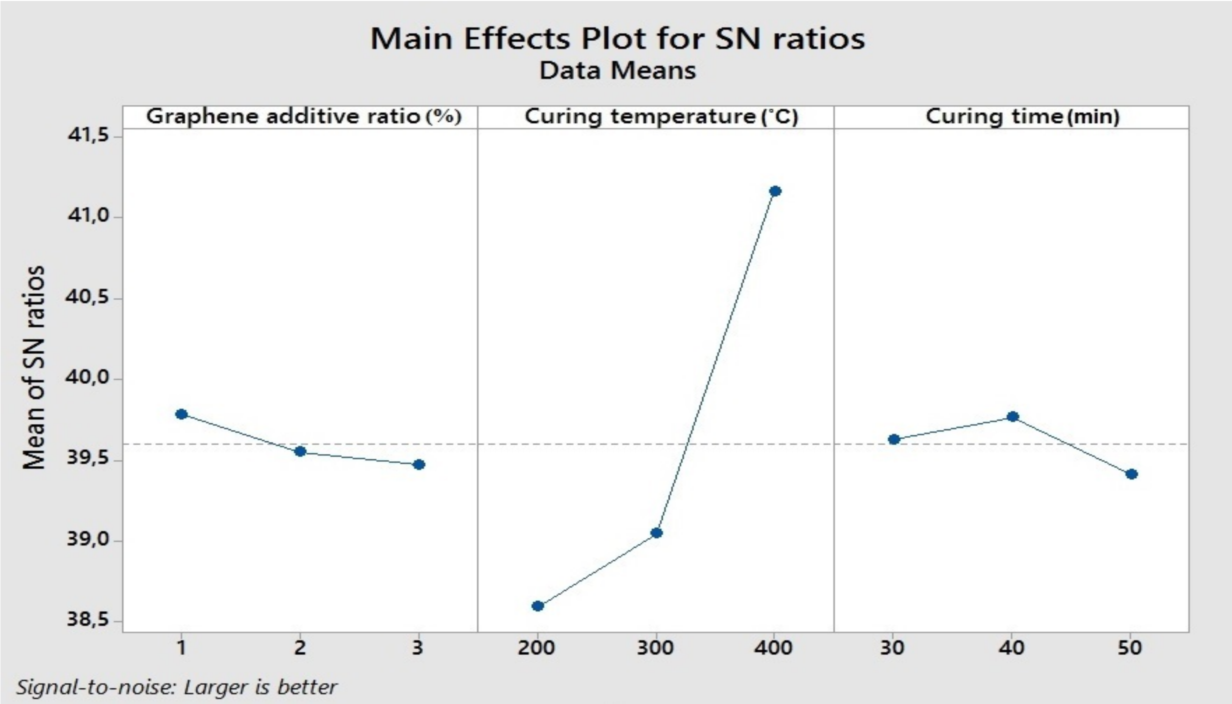

Figure 4. Main effect plots for S/N ratios of contact angles

Table 4 shows the order used to determine the effect of parameters in the analysis of contact angles. From this analysis, it was determined that the curing temperature is the most influential parameter, followed by the curing time, and the least influential parameter is the graphene addition ratio. The optimal parameters were found to be 1% graphene addition ratio, 400°C curing temperature, and 40 min of curing time. As mentioned earlier, it was observed that materials cured at 400°C exhibited significantly higher contact angles on their surfaces. The use of a 1% graphene addition ratio contributed to achieving maximum contact angle on the surfaces. It was also observed that surfaces coated with a curing time of 40 min had the maximum contact angle.

Table 4. Signal-to-Noise (S/N) ratios derived from contact angles responses

Level	Graphene additive ratio (%)	Curing temperature (˚C)	Curing time (min)
1	**39.79**	38.59	39.63
2	39.55	39.05	**39.77**
3	39.47	**41.17**	39.41
Delta	0.31	2.57	0.35
Rank	3	1	2

Analysis of variance (ANOVA) was conducted to determine the effect of coating parameters on the contact angles. ANOVA was applied with a 95% confidence level and a 5% significance level. Table 5 presents the results of variance analysis for the contact angles. According to the ANOVA results, it was found that the curing temperature is the most significant parameter with a contribution rate of 96.78% on the contact angles. This was followed by the graphene addition ratio with a contribution rate of 1.15%. The parameter with the least impact on the contact angles was determined to be the curing time with a contribution rate of 1.11%. One of the striking findings of the study was the significance of the curing temperature as the most important parameter, with an optimal point determined to be 400°C. This is believed to be related to the better spreading of FEP on the substrate material at temperatures above its melting point (Barhoumi et al. 2022). This finding indicates that it contributes to better hydrophobic properties.

Table 5. Analysis of variance for contact angles

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Graphene additive ratio (%)	2	17.68	1.15%	17.68	8.838	1.18	0.459
Curing temperature (˚C)	2	1492.70	96.78%	1492.70	746.349	99.65	0.010
Curing time (min)	2	17.08	1.11%	17.08	8.542	1.14	0.467
Error	2	14.98	0.97%	14.98	7.489		
Total	8	1542.44	100.00%				

4. Conclusion

This study aimed to optimize the manufacturing parameters of nanographene added to FEP, a hydrophobic coating, in order to reduce energy requirements by minimizing the friction factor in fluid transportation. The Taguchi method was employed to optimize the additive ratios, curing temperatures, and curing times. The Taguchi optimization was based on the contact angle measurements of water droplets on the surface. The experimental results yielded the following outcomes.

- It was observed that the optimum graphene addition ratio in FEP was 1%. The optimum curing temperature was determined to be 400˚C. Lastly, the optimum curing time was found to be 40 min.
- According to the variance analysis, the curing temperature was identified as the most influential parameter with a contribution of 96.78% on the contact angles. The graphene addition ratio and curing time had contributions of 1.15% and 1.11% respectively. Considering these ratios, it can be seen that the graphene addition ratio and curing time had similar effects.
- Among the parameters used in the optimization, it was determined that the curing temperature had the most significant impact on the contact angles.
- The FEP/graphene composite materials have shown promising results in reducing the friction factor in the transportation of fluids. Therefore, applying the optimal manufacturing parameters to the FEP coating material with added additives can contribute to energy savings in applications such as pumps, turbines, and pipelines.

Acknowledgements

This study was supported by "TUBITAK 2209-A University Students Research Projects Support Program".

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