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An optimization of superhydrophobic polyvinylidene fluoride/zinc oxide materials using Taguchi method

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ABSTRACT

This article is focused on the preparation and characterization of PVDF/ZnO composite materials. The superhydrophobic surface was prepared through spray coating of a mixture of PVDF polymer and ZnO nanoparticles on aluminum substrate. Stearic acid was added to improve the dispersion of ZnO. Taguchi's design of experiment method using MINITAB15 was used to rank several factors that may affect the superhydrophobic properties in order to formulate the optimum conditions. The Taguchi orthogonal array L9 was applied with three level of consideration for each factor. ANOVA were carried out to identify the significant factors that affect the water contact angle. Confirmation tests were performed on the predicted optimum process parameters. The crystallinity and morphology of PVDF–ZnO membranes were determined by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The results of Taguchi method indicate that the ZnO and stearic acid contents were the parameters making significant contribution toward improvement in hydrophobicity of PVDF materials. As the content of ZnO nanoparticles increased, the values of water contact angle increased, ranging from 122° to 159°, while the contact angle hysteresis and sliding angle decreased to 3.5° and 2.5°, respectively. The SEM results show that hierarchical micro-nanostructure of ZnO plays an important role in the formation of the superhydrophobic surface. FTIR results showed that, in the absence or present ZnO nanoparticles, the crystallization of the PVDF occurred predominantly in the β-phase.

1. Introduction

Recent developments in nanotechnology and the demonstration of various quantum size effects in nanoscale particles imply that most of the novel devices of the future will be based on properties of nanomaterials. Surfaces of materials strongly affect functional properties such as mechanical, biological, optical, acoustic and electronic properties of materials, particularly at the micro/nano scale. Surface effects stem from the interplay of surface morphology and surface chemical properties. Superhydrophobic surfaces have attracted a lot of attention because of their unique properties such as self-cleaning, antisticking, and anticontamination [1–3]. In nature, there are many superhydrophobic species such as lotus and tro leaves [1,4,5]. The surfaces of these leaves have micrometer-scale roughness, resulting in water contact angles up to 170°, because air that is trapped between the droplets and the wax crystals at the plant surface minimizes the contact area. In the preparation of artificial superhydrophobic surfaces, the simple and low-cost fabrication approach is very crucial; however, its durability is also very important, in practice, but is rarely considered [6,7]. Several methods have been employed to generate engineering surfaces that can mimic the structure and chemistry of natural superhydrophobic surfaces [8].

As imitations, the artifacts adopt the secret of keeping high water repellence with low surface energy and rough microstructure. Superhydrophobic surface can be created through two-stage process, which used by many researchers. In this two-stage process, they usually create a rough surface and then modify the surface with materials of low surface free energy, such as fluorinated or silicon compounds. This process has been widely used for the fabrication of superhydrophobic surfaces on special solid substrates such as Al alloys and glass. Polymer coatings or layer-by-layer deposited particles with both low surface energy and microstructures can be attached to the bulk to achieve superhydrophobic properties [9,10].

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Poly(vinylidene fluoride) (PVDF), which has the molecular unit (CH_2=CF_2), is one of the most popular polymeric materials because of their high mechanical strength, excellent thermal and chemical stabilities, and ease of fabrication into asymmetric hollow fiber membranes. It exhibits interesting electric properties, such as piezoelectricity and ferroelectricity when it exists in special crystalline forms. In addition, the history of PVDF being used as a long-term architectural coating can be traced for more than thirty years, and it has exhibited excellent durability [11,12]. These advantageous properties, coupled with its hydrophobicity, make it an outstanding membrane material particularly for industrial applications, from simple protective coating for pipes and buildings to transducer devices and detectors [13–15]. PVDF exists in at least four main crystalline structures: α-, β-, γ-, and δ-phases [14,16]. The crystalline structure of PVDF influences the polarity of this polymer, where, α- and β- phases denote nonpolar and polar properties, respectively. PVDF has a good solubility in many common organic solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and N,N′-dimethylacetamide (NMBA) [17–20].

Recently, inorganic nanoparticles such as silica (SiO_2) [21,22], titanium dioxide (TiO_2) [23,24], alumina (Al_2O_3) [25,26], zinc oxide (ZnO) [27], and zirconium dioxide (ZrO_2) [28] are widely used in polymer materials in order to improve the characteristics of polymer to suit a particular commercial application. The common feature of these modifications is the addition of a higher proportion of inorganic materials. Among these inorganic materials, ZnO particles have received much attention due to their stability; availability; suitable mechanical strength; unique combination of electrical, optical, and piezoelectric properties; as well as good compatibility with organic solvents used to prepare the PVDF solution [27]. Nanoscale particles are different from bulk materials due to their small size as a result of that their increased surface area.

Various techniques have been employed to produce superhydrophobic materials with a water contact angles above 150°, including chemical vapour transport and condensation (CVTC), pulsed laser deposition (PLD), chemical vapour deposition (CVD), and hydrothermal growth [29–33]. However, most of these techniques have strict conditions (such as poisonous chemicals), expensive materials, and complex processing methods. Therefore, a simple and easy method without high cost problem and the limitation in large-scale superhydrophobic surfaces production should be widely used. The spray coating is a fairly facile and commercially available method for the widest array of applications, which is not specific to a particular substrate and can be easily applied to large surface area; moreover, it does not typically require other complicated and costly application processes [34].

Statistic tools, such as the design of experiments (DOEs), have been taken from the exclusive world of the statistician and brought into the world of manufacturing, aiming at determining how different parameters influence the final properties of the coated materials. For example, Naidu and Gowda [35] employed Taguchi method of obtaining process parameters for optimum coating thickness of teflon in spray-painting application.

However, only few reports are available in the literature regarding superhydrophobic PVDF–ZnO nanocomposites prepared by spray coating. Therefore, this study is part of a larger research project which was conducted to provide a better understanding of the effects that the addition of ZnO nanoparticles would have on the hydrophobic properties of PVDF polymer materials using one-step facile spray-coating process. Taguchi method was used to minimize the number of considered experiments, in order to investigate all levels of independent parameters and to filter out some effects due to statistical variations. Confirmation tests with the optimal levels of selected parameters are carried out. The stability and icephobic properties of the prepared PVDF/ZnO composites will be publish elsewhere.

2. Design of experimental matrix

The design of experiments (DOEs) is a statistical approach to the experimental investigation that allows the analysis of the effects of several independent factors and their interaction on a dependent variable. An experimental matrix is implemented and it is composed of control factors at different levels for each run, which is the intensity assumed by each independent variable in a particular experiment [36,37]. Conventional statistical experiment design can determine the optimum condition on the basis of the measured values of the characteristic properties; while Taguchi's experimental design does this on the basis of the variability of characteristic properties [38].

Taguchi methods have been developed by Genichi Taguchi to supply a systematic approach for conducting experimentation to determine optimum settings of design parameters [39]. The advantages of this method are reduction of effort in conducting experiments, considerable savings in experimental time with decreasing cost, and discovering significant factors in a faster way. Also, the Taguchi method allows for the analysis of many different parameters without a prohibitively high amount of experimentation. In this way, it allows for the identification of key parameters that have the most effect on the performance characteristic value so that further experimentation on these parameters can be performed and the parameters that have little effect can be ignored. Taguchi suggested the use of orthogonal arrays, which are the shortest possible matrix of permutations and combinations. The evaluation of results has been standardized by this method, which can easily be applied by researchers [39–41]. In order to analyze the results, single-to-noise ratio (S/N), where *S* is the standard deviation of the performance parameters for each array experiment and *N* is the total number of experiment in the orthogonal array, was used. The S/N ratio characteristics can be divided into three categories: nominal the better, smaller the better, and larger the better. In addition to the S/N ratio, a statistical analysis of variance (ANOVA) can be employed to indicate the impact of selected parameters and estimate the optimal levels of process parameters.

In this work, the L9 orthogonal array of the Taguchi method was implemented in order to investigate the effects of the PVDF; ZnO; and stearic acid contents, and spraying distance (independent variables) on the superhydrophobic properties, represented in the water contact angle (dependent variable). Applying the simple factorial design for optimization of the assigned three levels of each parameter, the numbers of permutations would be 3^4 (degree of freedom = 9 − 1 = 8). However, the fractional factorial design reduced the number of experiments to 9. Each independent variable was analyzed at three levels. The independent variables, along with their values at selected levels, are given in Table 1. With the aim of taking into account the highest degree of interaction, a full balanced factorial plan was implemented, as shown in Table 2.

Table 1
Process parameters with their different levels of observation.

Parameter designation	Variable	Variable level		
		Low	Central	High
A	ZnO (g)	0.5	1	1.5
B	PVDF (g)	2.5	3.75	5
C	Spraying distance (cm)	25	30	35
D	Stearic acid (g)	0.15	0.25	0.35

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