

OPTIMIZATION OF MICROPOROUS HYDROPHOBIC MEMBRANES BY ELECTROSPRAYING

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Abstract

Polytetrafluoroethylene (PTFE) which is also called as “TEFLON” is a synthetic fluoropolymer of tetrafluoroethylene that has wide applications due to its differentiating properties. In this study, different PTFE dispersions for preparation of polytetrafluoroethylene mesoporous active membranes doped by basalt and carbon particles which were created in high voltage electrostatic field has been studied. The adjusting of process parameters of common electrospinning system (Nanospider) for preparation of membranes with tunable porosity created by nanofibrous assembly (electrospinning) and interconnected particles (electrospraying) has also been investigated. The nanoparticles based on milled basalt and carbon was used for activation and achieving of special effects. Superhydrophobic Polytetrafluoroethylene (PTFE) microporous membranes with different surface structures were obtained by controlling operating parameters in the electrospinning process. The diameters and microstructure of the PTFE microporous membrane were characterized by scanning electron microscopy. The contact angles on the microporous membranes were evaluated by static micro-drop observation, and a modified Yang equation was applied to analyze the contact angles. The superhydrophobic PTFE microporous membranes were also tested for thermal properties. As a result of this study, optimized PTFE blend solutions were identified. The results also revealed that the specific surface area was the key factor affecting the contact angles. The thermal properties revealed that thermal conductivity was higher and thermal resistance was lower for carbon and basalt doped membranes.

Keywords: Teflon, hydrophobic, electrospaying, microporous membrane

1. INTRODUCTION

Polytetrafluoroethylene (PTFE) which is also called Teflon is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The major application of PTFE is due to the fact that PTFE has excellent dielectric property [1]. It can be stretched to contain small pores of varying sizes and is then placed between fabric layers to make a waterproof, breathable fabric in outdoor apparel [2]. It is used widely as a fabric protector to repel stains on formal school-wear, like uniform blazers [3]. It is also used as a film interface patch for sports and medical applications, featuring a pressure-sensitive adhesive backing, which is installed in strategic high friction areas of footwear, insoles, ankle-foot orthosis, and other medical devices to prevent and relieve friction-induced blisters, calluses and foot ulceration [4]. Electrospinning has been established as a simple and effective method to produce polymer fibers with diameters at nanometer or submicron scale. Continuous fibers can be collected in the form of nonwoven fibrous membranes or as aligned yarns [6]. Nanofibers prepared by electrospinning have many superior properties, such as good pore structure and high surface porosity [6, 7]. Recently, several research groups have proved that the surface energy of materials was closely related to the surface properties, especially surface roughness [8], which presented a new way to control material surface wettability. Many theoretical researches on electrospinning process have been done by many teams and groups [9-11]. At the end of the 1500s, Sir William Gilbert explained the behavior of electrostatic and magnetic emanation. He found that by affecting the water droplet by electrostatic field, the water gets cone and hopper shape, and a droplet extrudes from the head of the hopper. This formed the first process of electro-spraying. Electrospinning can be viewed as a kind of electro-spraying. As with

electrospraying, the raw material of electrospinning is linked to a high-voltage power supply to enhance the liquid electrostatic potential [12]. The parameter that has affected morphology, structure, physical and chemical properties of electrospinning fibers is the distance between nozzle and collector. It has the direct effect on final fiber properties based on evaporation rate, deposition time and inconsistency interval. The studies show that by decreasing the distance between nozzle and collector, we have wet electrospinning fiber which has beaded structure. Also in some fibers the morphology of final fibers has changed from circular shape to flat shape [13]. On the other hand, the study shows that for aqueous polymer dispersion, more distance is needed to dry the fiber [14].

In this study, optimization of PTFE blend solution was carried out. The surface energy of microporous PTFE membranes was investigated by static contact angle measurements. The effect of the fibrous structures on the contact angle of microporous membranes was analyzed. The thermal properties of the samples were also evaluated and statistically analyzed.

2. METHODOLOGY

Materials

Polytetrafluoroethylene (PTFE) was used as-received without further purification. The PTFE microporous membranes were prepared based on various compositions of PTFE, organic salt Tetraethylammonium bromide (TEAB), water, surfactant and doping of carbon/basalt nanofibers. The detailed description of the samples is shown in **Table 1**.

Table 1 Description of samples

Sample No.	Sample Description
S002	PTFE +TEAB without water
S003	PTFE +TEAB+Carbon without water
S004	PTFE +TEAB+Basalt without water
S005	PTFE +TEAB+Carbon with water
S006	PTFE +TEAB with water
S007	PTFE +TEAB+Basalt+ with water

Methods

Electrostatic spinning is a method of producing superfine fibers with diameters ranging from 10 μm down to 10 nm by forcing a polymer melt or a solution through a spinneret by electric field and subsequently drawing the resulting filaments as they solidify or coagulate [19, 20]. Electrospinning exerts voltage on polymer solution to get nanofiber which is different from traditional methods. At the beginning, the polymer solution or melt bring thousands of high voltage. The charged droplet in the capillary was accelerated under the force of electrostatic force. When the electric force is large enough, the droplet can overcome surface tension to formation of a thin stream. Due to solvent evaporation in the electric field, nanofibers which are like non-woven mats are collected in the receiver [21].

Polymer concentration plays a major role in the electrospinning process. Under the same electrospinning conditions, an increasing polymer concentration usually increases the diameter of the electrospun fibers. However, Deitzel et al. found that there is often a nonlinear relationship between the solution concentration and fiber diameter [22]. The reason for this nonlinear relationship can be attributed to the nonlinear relationship between the polymer concentration and solution viscosity [23].

Electrospraying (electrohydrodynamic spraying) is a method of liquid atomization by means of electrical forces. In electrospraying, the liquid at the outlet of a nozzle is subjected to an electrical shear stress by maintaining the nozzle at high electric potential [24]. The advantage of electrospraying is that droplets can be extremely small, in special cases down to nanometers, and the charge and size of the droplets can be controlled to some extent by electrical means, i.e., by adjusting the flow rate and voltage applied to the nozzle. Due to its properties, electrospraying is considered as an effective route to nanotechnology. The paper considers the latest achievements in micro and nano thin-film production, including self-assembled nanostructures, in solid nano-particle generation, and in the formation of micro- and nanocapsules.



Figure 1 Rotating roller electrode, Single wire electrode and Rotating wire electrode (from left to right)

“Nanospider” instrument was used to spin the membranes by electrospraying. The Nanospider electrodes which have been developed through last ten years of optimization can give big portfolio for electrospraying as well. Three different electrodes were used to spin the membranes out of which the rotating wire electrode was suitable for preparing the membranes by electrospraying. Since Polytetrafluoroethylene (PTFE) was insoluble in water, it was introduced in “particle” form in the solution. The solution prepared was optimized with the change in concentration of the solution, PTFE composition, organic salt, surfactant, carbon/basalt doping, relative humidity, conditional temperature, distance of the electrodes and substrate speed. The prepared solution was taken in the bath and electrosprayed by using rotating wire electrode. The electrosprayed particles were collected in the polypropylene spun bond nonwoven fabric. The details of spinning parameters are shown in **Table 2**.

Table 2 Spinning parameters

Sample No.	Substrate speed (mm/min)	Voltage (kV)	Speed of electrode (ot/min)	In	Tent	Air
S002	static	-10/30	5	43.1%/22.3°C	43.3%/22.5°C	48.2%/22°C
S003	static	-10/30	5	44%/22.7°C	48%/23.3°C	50.1%/23.1°C
S004	static	-10/30	5	42%/23.4°C	47%/22.7°C	50%/22.1°C
S005	static	-10/30	5	41.4%/22.6°C	47.7%/22.6°C	51.1%/22.4°C
S006	15	-10/30	5	43.3%/22.4°C	48.9%/22.5°C	49.9%/22.5°C
S007	static	-10/30	6	40.8%/22.9°C	45.8%/23°C	50.1%/22.3°C

The microporous membranes with different concentrations were characterized using SEM (VEGA TESCAN Inc. USA) at 30 kV. The contact angle was measured on a See System E is a portable computer-based instrument for contact angle measurement and surface energy determination. Deionized water was dropped onto the sample from a needle on a micro syringe (5 µl) during the test. A picture of the drop was taken a few seconds after the drop set onto the sample. The contact angles could be calculated by analyzing the shape of the drop. For thermal measurements, Alambeta was used. All results were statistically analyzed.

3. RESULTS AND DISCUSSION

Analysis of Microstructures

SEM images of PTFE membranes with different compositions are shown in **Figure 2**. The electrospinning parameters have a strong influence on fiber morphology. The concentration of the polymer solution and the spinning voltage were found to be especially significant. In this study, the effects of concentration and spinning voltage on fiber morphology for PTFE microporous membrane with different blend ratio were observed.

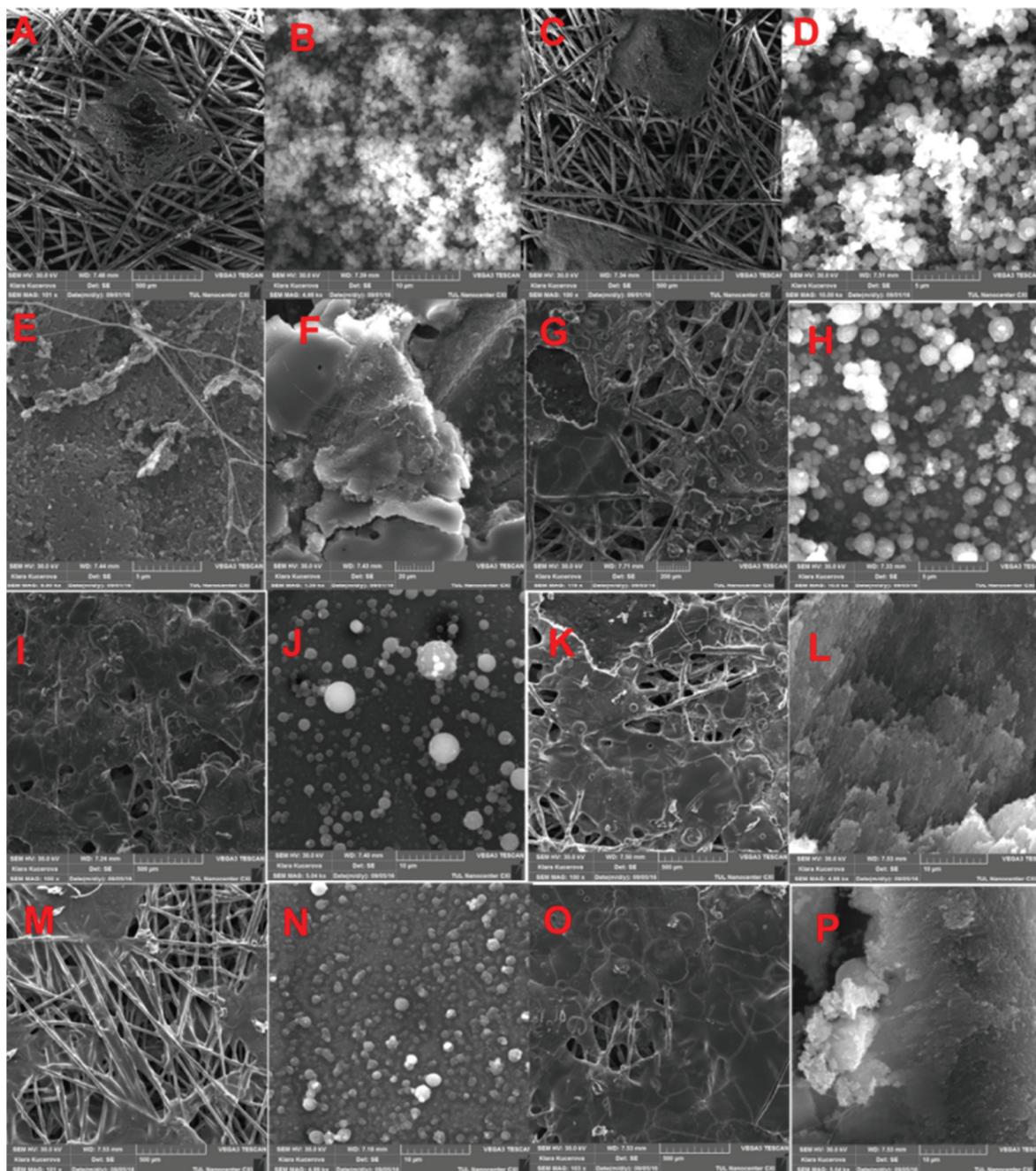


Figure 2 SEM images of PTFE membranes

Electrospinning influences the microstructure of the microporous membrane where the technique utilizes the electrical forces for liquid atomization [25]. Droplets obtained by this method are highly charged. The

advantage of electrospinning is that the droplets can be extremely small (tens nanometers), and the charge and size of the droplets can be controlled to some extent by electrical means. Motion of the charged droplets can be controlled by electric field. The deposition efficiency of the charged spray on an object is usually higher than that for uncharged droplets. The membrane morphologies can be categorized into two main groups: dense and porous. The dense layer can be amorphous, crystalline (of different structures) or amorphous with incorporated particles (intrusions). The porous layer can be reticular, grainy, or fractal like. The membrane morphology depends, on the temperature, the solvent used for spraying, voltage, physical properties of liquid phase (emulsion, dispersion, solution, density and surface tension), distance of collector from source, doping agents and the time of solvent evaporation [26].

It can be seen that the viscosity of the solution and the spinnability increased with the increase of concentration of the solution, which is consistent with other published results [27-30]. When the concentration of the polymer solution is lower, the fibers tend to form beadlike structures. The change in fiber diameter can be attributed to the presence of surfactant in the PTFE emulsion. The existence of surfactant in the solution tends to increase the solution conductivity and decrease the surface tension, thus facilitating the formation of finer fibers [31].

Since surfactant is a part of the PTFE emulsion, the surfactant content changes with solution concentration. At higher concentration, the effect of surfactant tends to be stable, whereas polymer concentration remains as the main influencing factor on fiber diameter, with fiber diameter increasing rapidly as polymer concentration increases. The membranes S002, S003 and S004 had dispersion of 60% concentration (original solution) with the range of different relative humidity. Lowering moisture leads to a slightly larger deposit (higher coverage), but the difference is not substantial.

The membranes S005, S006 and S007 had dispersion of 50% concentration (diluted with water) with the range of different relative humidity. The samples S003, S004, S005 and S007 were spun with carbon and basalt nanofibers. The output range of relative humidity i.e., the decreasing RH leads to a bit higher surface layer, and the difference between 25% and 10% RH is negligible. Diluting the solution does not bring visible change in process or change in surface layer.

Contact Angle Analysis

The results of the static contact angle measurements are shown in **Figure 3**. It clearly reveals that the contact angles of all the microporous membranes are over 90°. The image in **Figure 3** presents a water droplet formed on the PTFE microporous membrane electrospun at 10 to 30 kV. The contact angle increases to 143.2° when the voltage for the electrospinning increases to 30 kV, as illustrated in **Figure 3(c)**. The high contact angle in the image clearly reveals the superhydrophobic behavior of the microporous membrane. The curve in **Figure 3** indicates that the contact angle increases with the specific surface area formed by different voltages. It also, indicates the contact angle for three different wash times (2 mins, 4 mins and 6 mins). 2 mins wash time showed a better contact angle than the 4 and 6 mins wash time. This phenomenon can be interpreted in terms of the Young equation and its modification.

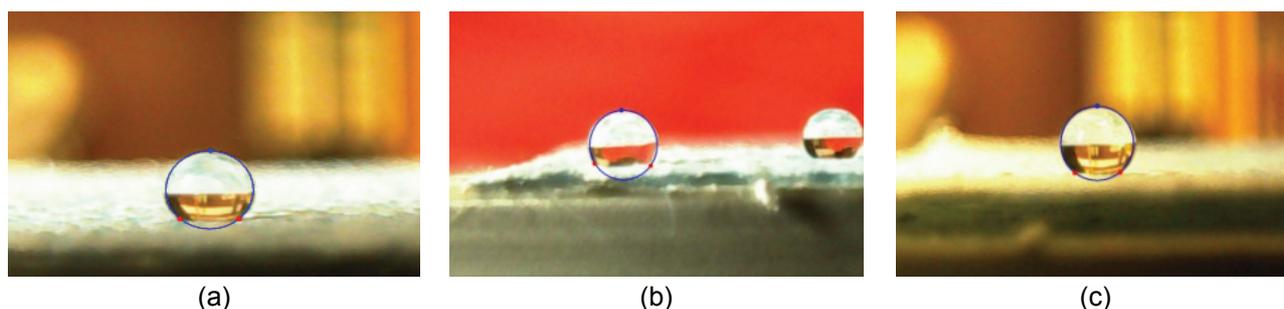


Figure 3 Contact angles of the samples (a) 125.7° (b) 135.3° (c) 143.2°

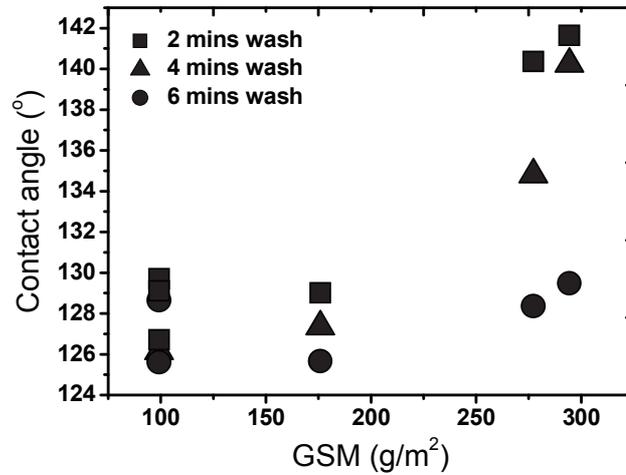


Figure 4 Contact angle of PTFE microporous membranes

The Young equation is the common model to describe the contact angle on a surface:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1)$$

Where θ is the contact angle, and γ_{sv} , γ_{sl} and γ_{lv} are surface energies for liquid-vapor, vapor-solid, and solid-liquid interfaces, respectively. Most practical surfaces, however, are rough and heterogeneous to some extent. Accordingly, different modifications of the Young equation have been proposed to apply to rough surfaces [32, 33]. In this study, it is assumed that all of the nanofibers under the water drop have contact with the water. A roughness factor r is the relation between the real area and the projected area. The model of contact angle for microporous membrane is shown in **Figure 4**. Thus, the contact angle of a microporous membrane can be denoted by:

$$\cos \theta' = \frac{r(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} = r \cos \theta \quad (2)$$

The increase in contact angle with voltage is attributed to the change in roughness factor r , as described by Equation (2). Roughness, however, is so complicated that it is difficult to develop a general method for roughness measurement.

$$B = \frac{S_r}{m} \quad (3)$$

$$r = \frac{S_r}{S_p} = \frac{mB}{S_p} \quad (4)$$

Where S_r is the real surface area of microporous membrane, S_p is the projected area, B is the specific surface area, and m represents the mass of a membrane. For a given microporous membrane, the mass m and projected area S_p are constant and can be easily measured. Consequently, the modified Young Equation (2) can be derived:

$$\cos \theta' = r \cos \theta = \frac{mB}{S_p} \cos \theta \quad (5)$$

It can be seen from Equation (5) that the contact angle, θ_0 , of the membrane depends on the ideal contact

angle, h , and surface roughness, and the specific surface area plays an important role in the material's contact angle. Larger specific surface area leads to higher contact angles.

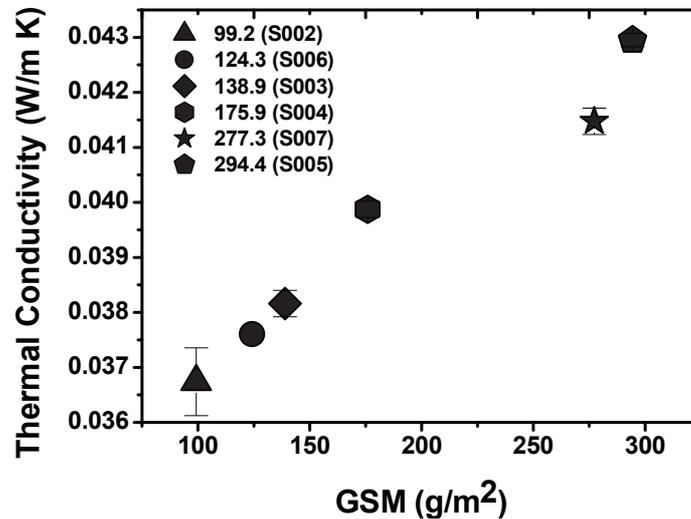


Figure 5 Thermal conductivity of the microporous membranes

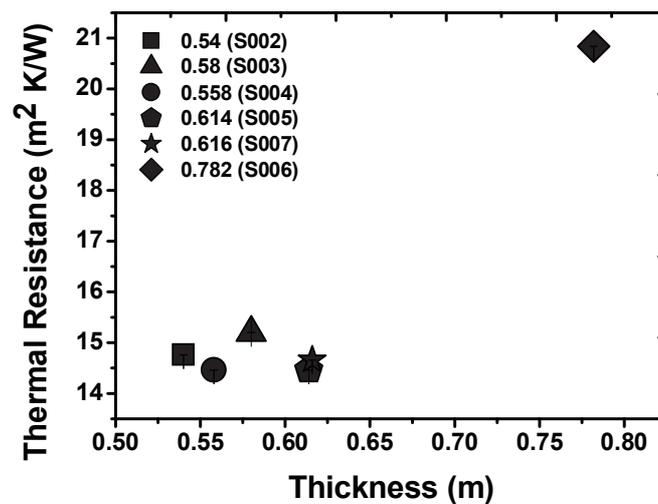


Figure 6 Thermal resistance of the microporous membranes

Figure 5 and 6 contains the thermal properties of the samples. We can see from the Figure 5 that S002 has the lowest thermal conductivity and S005 has the highest thermal conductivity. The thermal conductivity of the carbon doped membrane (S005) is higher than other membranes. From the Figure 6, it can be seen that the membrane S006 has highest thermal resistance than other membranes. The thermal resistance of the membrane S006 is higher due to the higher thickness and also it can be seen from the sample description (Table 1) that the membrane is diluted with water and concentration is reduced to 50%. This can also attribute to the higher thermal resistance of the membrane. Compared to other membranes, carbon and basalt doped membranes have higher thermal conductivity and lower resistance. .

4. CONCLUSION

PTFE microporous membranes were electrospun by optimizing the concentration and processing parameters. By adjusting the process parameters of common electrospinning system, preparation of membranes with

tunable porosity was prepared by nanofibrous assembly and interconnected particles (electrospinning). The surface structures, diameters, and specific surface areas of the electrospun nanofibers were successfully controlled by altering the electrostatic voltage. SEM observations revealed that when the concentration of the polymer solution was lower, the fibers tend to form beadlike structure and also the change in fiber diameter was attributed to the presence of surfactant. The experimental results also proved that the static force applied on the jet might be the key factor affecting the surface structure, as well as the specific surface area. It was concluded by the analysis of the modified the Young equation that specific surface area played the most important role in contact angles of the microporous membrane. The larger specific surface areas resulted in high contact angles. The thermal properties results reveal that thermal conductivity was higher and thermal resistance was lower for carbon and basalt doped membranes as compared to other membranes.

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