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Effect of PVDF-CA Ratio on Electrospun Membrane for Water–Oil Filtration Application

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Abstract

Oil spillage and generation of industrial water–oil wastewater mixture ignite a focus on filtration technology. Electrospinning technique provides a versatile route in producing tunable diameter and pores in nanofiber filtration membrane development. In this work, polyvinylidene difluoride (PVDF) and cellulose acetate (CA) electrospun membrane at different concentration ratios were synthesized for water–oil filtration application. The polymeric solutions were characterized using viscometer and conductivity testing, whereas the membranes were analyzed using contact angle, tensile test, scanning electron microscopy (SEM), and filtration testing of oil (dichloromethane). Conductivity test showed a decreased conductivity along with decrement of CA ratio in the polymeric solution. The viscosity results showed a rising trend along with the increment of CA in the polymeric solution along with the decrement of PVDF ratio. SEM result showed that all membranes had a fiber diameter range of 210–485 nm and pore size range of 235–856 nm. The tensile test showed a decreasing tensile strength as the ratio of PVDF in the electrospun membrane decreased. The membrane with PVDF-to-CA ratio of 90:10 showed optimum performance for water–oil filtration with a flux of 14,111 $Lm^{-2}h^{-1}$ and oil recovery of 94%.

Abstrak

Efek dari Perbandingan PVDF-CA pada Membran Pintal Listrik untuk Penerapan Penyaringan Air-minyak. Kemajuan industri bersama dengan kebutuhan minyak bumi menyebabkan kebocoran limbah industri dan minyak mentah menghasilkan sumber air yang akan tercemar sebagai konsekuensi yang memicu fokus dalam perkembangan terbaru dalam teknologi filtrasi. Teknik elektrospinning telah menyediakan metode serbaguna baru dalam memproduksi nanofibers yang memiliki kisaran konstan diameter dan pori. . Elektrospun membran PVDF dan CA komposit pada rasio yang berbeda telah dibuat untuk aplikasi filtrsi air-minyak. Membran yang ditandai dengan menggunakan Viscometer, pengujian konduktivitas, sudut kontak, pengujian tarik, pengujian filtrasi dan SEM. S2 membran direkam menjadi membran optimal untuk aplikasi filtrasi air-minyak dengan 14111 $Lm^{-2}h^{-1}$ fluks dan pemulihan 94%. Hasil SEM menunjukkan semua membran memiliki diameter serat berkisar dari 210–485 nm dan ukuran pori berkisar dari 856– 235 nm dengan membran S1 memiliki ukuran pori paling sedikit dengan 235 nm diikuti oleh membran S2 dengan 236 nm. Pengujian konduktivitas menunjukkan penurunan konduktivitas bersama dengan penurunant rasio CA dalam larutan polimer. Hasil uji tarik menunjukkan kecenderungan penurunan kekuatan tarik sebagai rasio PVDF pada membran elektrospun menurun. Hasil viskositas menunjukkan tren naik bersama dengan naik CA dalam larutan polimer bersama dengan penurunan rasio PVDF.

Keywords: electrospinning, cellulose acetate, PVDF, filtration technology

1. Introduction

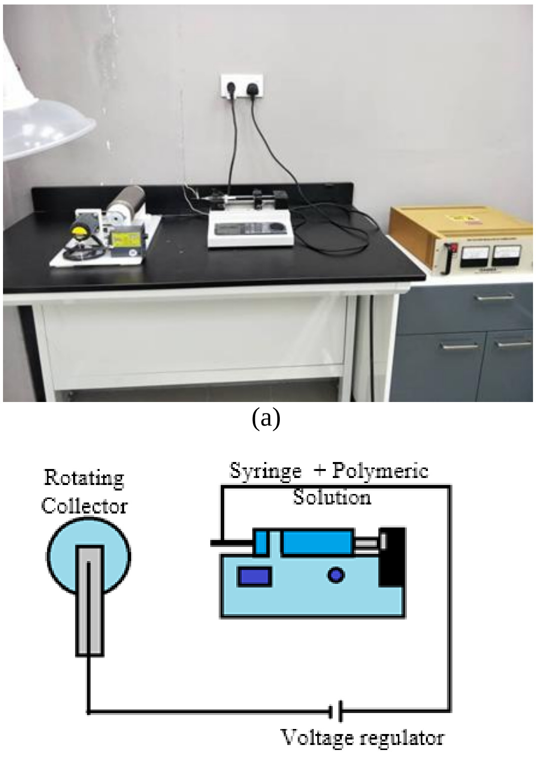
Electrospinning technique has been given enormous attention for an essential and versatile way of producing nanofibers from a polymeric solution [1]. This technique offers spinning flexibility for a wide polymeric fiber; it also enables consistent fiber production in the submicron range, which is challenging to be achieved by other methods [2]. The filtration characteristics of electrospun membrane play an important role in nanofiber applicability, feature high porosity and flux, and allow filtration of certain unnecessary substances. On the other hand, water treatment and filtration are essential in supplying clean water, thus ensuring life sustainability.

Advancement of technology arose with effects on nature and humankind. Industrial waste and raw petroleum leakage had become one of the most significant causes of pollution in the modern era. For example, in 2019, Malaysia had witnessed a solid and concrete proof for the damage caused by humankind to nature as Pasir Gudang was polluted by chemical waste from the local industry, which affected more than 6,000 locals [3]. The incident highlighted the need for resolving pollution; this goal can be achieved by nanofibers. Electrospinning involves the application of high voltage on a contained polymeric solution to produce electrically charged jets of solution that are accelerated through a spinneret toward a grounded target, which acts as a collector. The jets are dried during the spinning process as they approach the collector, forming beads or nanofibers [4]. The acetate ester of cellulose, that is, cellulose acetate (CA), had been widely selected in various studies due to its potential applications as electrospun nanofiber membrane because of its advantageous properties, such as excellent biocompatibility, regenerative properties, high affinity with other substances, high modulus, and adequate flexural and tensile strength [5]. Polyvinylidene difluoride (PVDF) has high mechanical strength, hydrophobicity, and excellent thermal, electrical, and chemical resistance [6]. PVDF-CA membrane has been studied for water filtration. However, the reports on water–oil filtration application especially for high-density oils are limited. The presence of PVDF reduces the efficiency of water filtration, but the addition of hydrophilic CA can enhance the filtration performance. The blending of these polymers can create an excellent and efficient membrane with significant characteristics that can be applied in water–oil filtration. Blending is one of the most practical ways for polymeric membrane modification, and it can be applied to an industrial scale production. The hydrophilic PVDF membrane with desirable properties can be obtained during the membrane preparation process without any pretreatment nor posttreatment procedures [7].

2. Experimental Details

Materials: PVDF (Mw ~275,000, Sigma Aldrich), CA (Mn ~50,000, Sigma Aldrich), acetone (99.9%, J.T Baker), and N,N-dimethylformamide (DMF; 99%, Merck) were used without further purification.

Preparation of electrospun membrane: Polymeric solution (13 wt%) with respect to solvent was prepared by dissolving PVDF and CA at different ratios in the mixture of 30 mL acetone and DMF (1:1). The prepared polymeric solution was electrospun by using a potential range of 10 – 15 kV with a flow rate of 0.1 – 3.5 ml/h at room temperature. Figure 1 shows the electrospinning and schematic setup. The ratios of PVDF and CA were abbreviated as shown in Table 1.



(a)

(b)

Figure 1. (a) Electrospinning and (b) Schematic of Experimental Setup

Table 1. Abbreviations of Polymeric Solution Ratios

Sample	Abbreviation
100% PVDF	S1
90%PVDF:10%CA	S2
75%PVDF:25%CA	S3
50%PVDF:50%CA	S4
25%PVDF:75%CA	S5
10%PVDF:90%CA	S6
100%CA	S7

Characterization of nanofiber: The viscosity and conductivity of the polymeric solution were characterized by using Brookfield DVI viscometer and Thermo Scientific Eutech Handheld Meter Kit, respectively. The morphology of PVDF-CA nanofiber was observed using scanning electron microscopy (SEM; FEI Quanta-450). Contact angle system and optical contact angle with sessile drop technique were used to evaluate the hydrophilicity of the electrospun PVDF/CA membranes. The degree of hydrophilicity of the membrane was decided by finding the angle between the surface of the membrane sample and the meniscus of water drop. The volume of water droplet was 5 µL with medium dispense. Tensile testing was performed by using Shimadzu AGS-X 50 kN Universal Testing Machine. Filtration test of PVDF-CA membranes was performed using a Sartorius Stedim Vacuum Filter Holder system utilizing a mixture of water and dichloromethane (DCM) (1:1). The flux (*F*) was calculated using the following equation:

$$F = \frac{V}{A\Delta t} \tag{1}$$

where V, A, and Δt are the volume of permeate water, membrane area, and filtration time, respectively. Oil recovery (R) was calculated using Equation 2:

$$R = \frac{m_f}{m_i} \times 100 \tag{2}$$

where m_f and m_i are final and initial masses, respectively.

3. Results and Discussions

Viscosity and conductivity of PVDF-CA polymeric solution. Figure 2 shows the viscosity of polymeric solutions with different polymer ratios. S7 showed the highest viscosity (2520 cP) compared with the other solutions. The graph showed an increment trend along with the addition of CA in the polymeric solution. This finding might be due to the increment in molecular weight in relation to the increased CA ratio, resulting in a strong force between interchains of the polymers [8]. Figure 3 demonstrates the polymeric solution conductivity at different ratios. In the electrospinning process, the solution conductivity is crucial in obtaining good nanofibers. Electrospinning process involves an electrical field that is generated between the nozzle and collector when a high voltage is applied (refer to Figure 1). The solution droplet at the nozzle tip formed Taylor's cone through multiple force actions, such as electric field force, Coulomb force, gravity, surface tension, and viscosity force of the solution [9].

S7 possessed the highest conductivity value (614 μScm^{-1}), followed by S6, S5, S4, S3, S2, and S1. The conductivity of the polymeric solution decreased as the ratio of PVDF increased. This finding is due to the electrical resistance properties of PVDF [10]. A previous study suggested that conductivity has a significant relationship with viscosity, that is, conductivity increases linearly with viscosity [11]. Similarly, in this work, the conductivity and viscosity increased linearly as the ratio of CA increased.

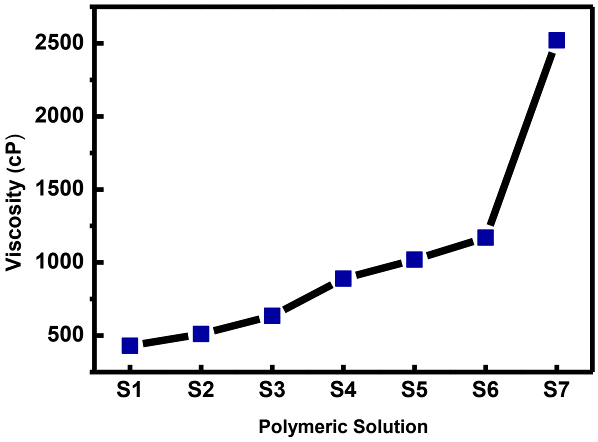


Figure 2. Viscosity of Polymeric Solution at Different Ratios

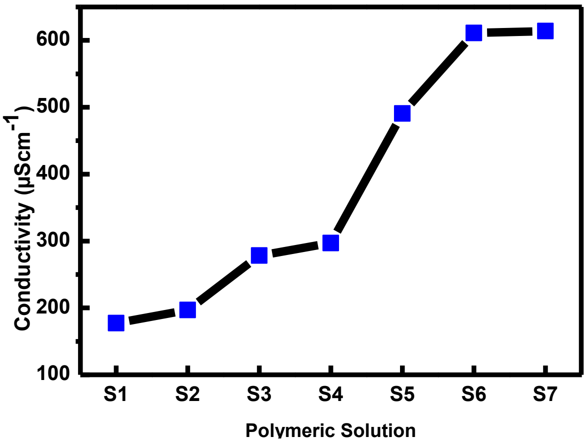


Figure 3. Conductivity of Polymeric Solution

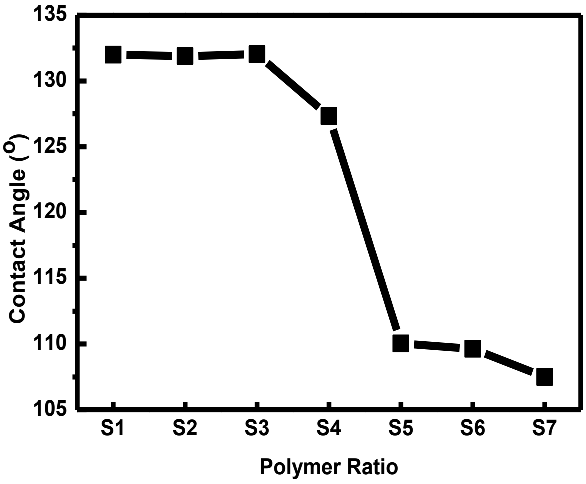


Figure 4. Contact Angles at Different Polymer Ratios of Electrospun Membrane

Contact angle analysis. Figure 4 demonstrates the contact angle for all electrospun membranes. DCM is an organic solvent, and hydrophobicity is a crucial parameter for water–oil filtration. The value of the contact angle decreased as the ratio of PVDF in electrospun membrane decreased. S1, S2, and S3 exhibited almost similar contact angles (133°), which corresponds to hydrophobic properties. The values decreased from S4 (127°) to S7 (107°) due to the hydrophilic properties of CA. PVDF is a polymer with good mechanical strength, high vapor flux, and outstanding anti-wetting and hydrophobic properties [12]. These properties are essential for water–oil filtration, especially in the case of DCM as the target filtered product. The high water contact angle of PVDF-CA fibrous membranes could be attributed to the micro surface roughness of the fibers, which is a principal factor in determining surface wettability [13]. Given the roughness of the surfaces, a substantial quantity of air was present between the uneven fibrous membrane surfaces and liquid droplets.

Tensile strength testing. Figure 5 shows the tensile strength properties for different polymer ratios of the electrospun membrane.

The tensile strength of membrane is an important parameter in determining the membrane performance for any filtration system. Several filtration systems only used gravitational-assisted filtration [14]. However, other filtration systems, such as pressure-driven vacuum system and magnetic-assisted filtration system, use force-assisted filtration to increase the flux value to optimize the filtered product. The graph showed a decrease in tensile strength as the ratio of PVDF in the electrospun membrane decreased. This finding is due to the excellent mechanical properties of PVDF and strong hydrogen bonding in the polymer structure [15].

SEM. Figure 6 shows the morphology of the electrospun nanofiber membrane. All samples showed a smooth surface with no bead formation. Table 2 tabulates the diameters and pore sizes for all membranes. The pore size of the membrane is useful in determining the effectiveness of filtration and filtration type.

Figure 7 shows the electrospun fiber diameter and pore size comparison. No significant trend was observed in the relationship between the fiber diameter and pore size with polymer ratio. However, the graph showed the slightly increasing trend of average pore size as the ratio of CA in the electrospun membrane increased exceptionally for S3. The S5 possessed the smallest average fiber diameter (206 nm), whereas the largest average fiber diameter was possessed by S6 (485 nm). The lowest average pore size recorded was 235 nm (S1), whereas the largest was 855 nm (S7). Viscosity analysis of polymeric solutions is a crucial factor affecting the result of the electrospinning process. At the interface, a molecule is held in liquid phase at the surface by surface tension with a force of $\pi d\sigma$, whereas thermal energy (reflected by the liquid temperature) attempts to move the molecule at a velocity of v. Drag force resists the translational movement of the molecule; thus, the drag

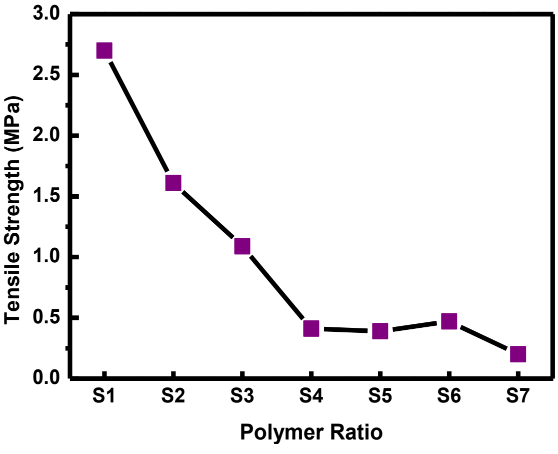


Figure 5. **Tensile Strength Values At Different Polymer Ratios of Electrospun Membrane**

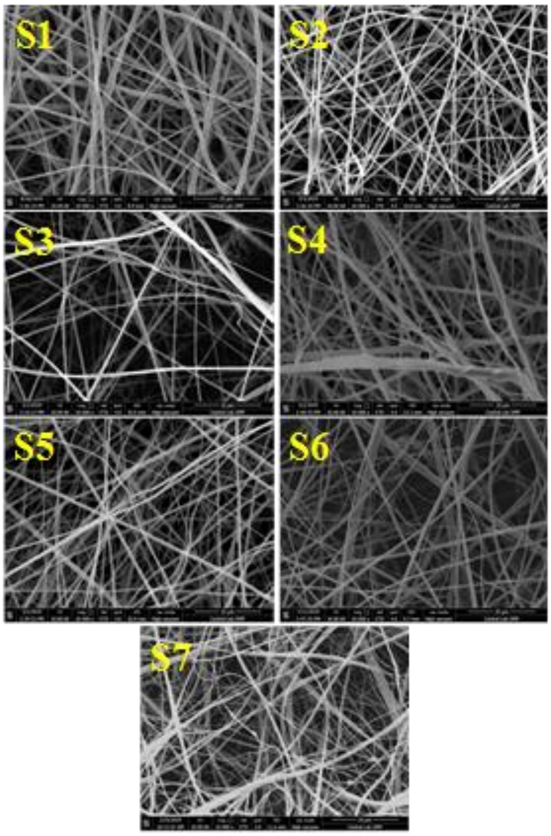


Figure 6. **FESEM of All Membranes at Magnification of 10,000x**

Table 2. **Fiber Diameter and Pore Size of PVDF-CA Membranes at Different Ratios**

Membrane	Fiber Diameter/nm	Average Pore Size/nm
S1	240	235
S2	211	236
S3	350	855
S4	329	271
S5	210	440
S6	485	576
S7	367	639

force experienced by the molecule at equilibrium is equal to the surface force acting on the molecule and can be expressed as below [16]

$$\pi d\sigma = C_D\left(\frac{4d^2}{4}\right)\left(\frac{\rho v^2}{2}\right) \qquad (3)$$

where d is the diameter of the container
C_D is the drag coefficient
v is the velocity
ρ is the density of the fluid
σ is the surface tension

When a small volume of electrically conductive liquid is exposed to an electric field, the shape of the liquid deforms from the original form caused by surface tension. As the voltage increases, the effect of the electric field becomes more prominent. As this effect of the electric field exerts a similar magnitude of force on the droplet as the surface tension, a cone shape with convex sides and a rounded tip forms. The round cone shape will continually form symmetrically as long as the continues flow of polymeric solution is supplied along with constant applied potential [17]. The formation of Taylor cone can be summarized as follows:

$$E_s = \left(\frac{\sigma}{\varepsilon_o L}\right) \qquad (4)$$

where E_S is the tangential electric field
σ is the density of the polymeric solution
L is the length of the Taylor cone
ε_o is the permittivity constant

From Eqs. 3 and 4, viscosity is critical in electrospinning process and determining the electrospun membrane fiber diameter. The viscosity of the polymeric solutions had been recorded to create a benchmark when electrospinning the same type of polymeric solutions, such as PVDF which is more suitable than acetone given its polymer hydrophobic nature, for the optimization process of electrospinning [18]. In this study, the viscosity and conductivity of the polymeric solutions had been recorded. No significant pattern that relates viscosity and conductivity was observed with fiber size.

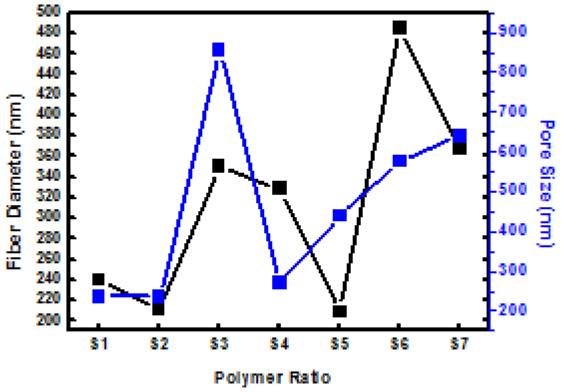


Figure 7. **Comparison Plot of Fiber Diameter and Pore Size at Different Ratios of Electrospun Polymer Membrane**

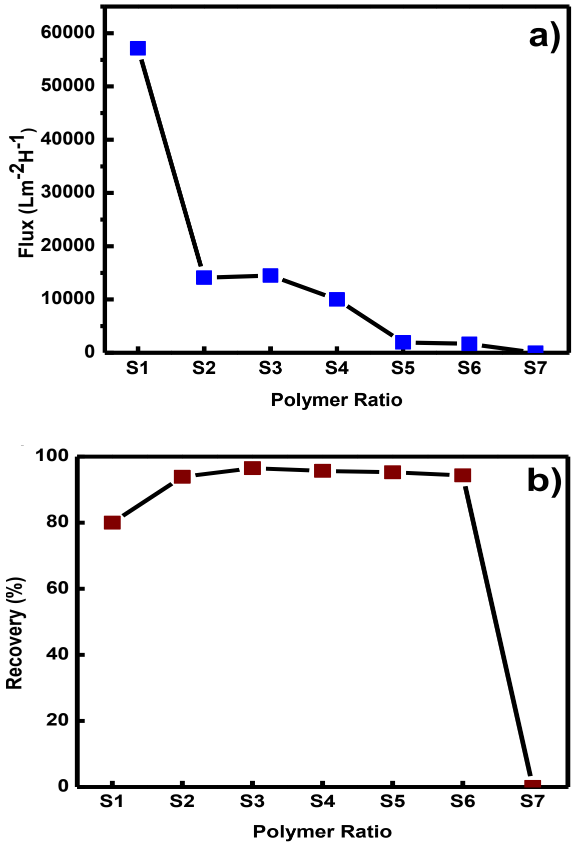


Figure 8. **a) Flux Value and b) Oil Recovery For Water–oil Filtration Testing**

Water–oil filtration testing. Figure 8 shows the flux and oil recovery for water–oil filtration. The flux and recovery for S7 could not be recorded as the membrane dissolved in the mixture of water and DCM during the filtration testing. S1 showed the best flux compared with the other solutions. This finding might be due to the hydrophobic nature of PVDF. No significant trend can be observed in both graphs. However, a slightly decreasing trend can be observed in the flux value of the membrane as the PVDF ratio decreased. The highest flux recorded was 57,143 Lm^{-2}h^{-1} for S1, which also presented the lowest recovery of 81%. S3 possessed the highest recovery of 97% possibly because it possessed the largest pore size compared with the other materials. Overall, in terms of water–oil filtration that requires a high flux optimum filtration, S2 possessed the characteristics of the optimized membrane which can be applied in water–oil filtration application. Although S1 possessed the best flux compared with the other samples, its oil recovery was 81%, which is lower than that of S2 (94%). S2 also possessed the smallest pore size, which is 236 nm higher compared with that of S1. S2 also presented an optimum filtration characteristic. Membrane hydrophobicity and pore size are factors affecting flux. S1 possessed the highest contact angle and hence contributed to the highest flux, but its recovery was lower compared with that of S3.

4. Conclusion

In conclusion, electrospun PVDF-CA membranes were successfully fabricated. The PVDF-CA membranes exhibited different surface morphologies, in which S1 and S2 possessed the least average pore sizes and fiber diameters. The contact angle values of PVDF-CA fibrous membranes could be attributed to the micro surface roughness. S1 had the highest contact angle of 133°. The highest flux recorded was 57,142 $Lm^{-2}h^{-1}$ (S1), which was attributed to the hydrophobicity of the membrane. S2 possessed the best characteristics in water–oil filtration, demonstrating 94% oil recovery and low pore size (236 nm) and fiber diameter (211 nm). The hydrophobicity of S2 membrane, which possessed one of the highest contact angles, can be proven by the contact angle testing and hence contributed to the flux and recovery values. Small nanofiber size can be related to the conductivity of polymeric solutions with one of the lowest conductivity. Although S1 possessed the best flux compared with the other membranes, the recovery of oil was 81%, which is lower than that of S2, indicating the ineffectiveness of S1 in filtrating unwanted substances. PVDF-CA membrane possesses a considerable potential to be applied in water–oil filtration.

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