Surface Modification of Electrospun ABS/ENR Blend Membranes using Polyvinyl Alcohol-Citric Acid Coating

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ARTICLE INFO	ABSTRACT
               	Polymeric membranes, designed for selective permeability to efficiently separate oil from water, present an innovative solution for oil-water separation and offer a rapid and environmentally friendly response to spill incidents. In this study, micro-nanofiber membranes are fabricated using acrylonitrile-butadiene-styrene (ABS) and its blend with epoxidized natural rubber (ENR) using electrospinning method. The electrospun fiber membranes are then coated with polyvinyl alcohol (PVA) containing various concentrations of citric acid (CA), to investigate the impact of PVA coating variations on the physical and mechanical properties of the ABS/ENR membranes. It was found that mechanical properties of the ABS/ENR membrane are superior to that ABS membrane, as demonstrated by higher values of tensile strength and modulus. ENR rubber introduces elasticity and flexibility to the rigid ABS, which leads to enhanced mechanical properties. Addition of ENR was also found to improve hydrophobicity of the membrane as demonstrated by the increase in contact angle. The inclusion of CA was observed to have a beneficial impact on the strength and toughness of the ABS/ENR membrane. The presence of CA promotes the hydrophilic property in both the ABS and ABS/ENR membranes. A finer and more uniform strands were observed for ABS/ENR membranes than ABS membranes, which reflects their higher tensile strength values. From this study, it can be concluded combination of electrospinning and coating method is efficient in producing porous membranes with tailored hydrophobic/hydrophilic property crucial for efficient oil-water separation.

1. Introduction

The oil-water separation is considered as one of the crucial subjects nowadays as contamination has been happening quite frequently nowadays resulting in water pollution. The increasing demand for efficient and cost-effective methods for oil-water separation has led to the need for the development of new materials and techniques [1,2]. Phase inversion, and sol-gel technology have

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been widely used in recent years to produce membrane, but they are difficult to produce in large quantities due to their labor-intensive preparation procedures [3]. These days, making nanofibers using electrospinning is fairly simple and inexpensive. Electrospinning produces membranes by creating fine polymer fibers through a high-voltage electrostatic field, resulting in highly porous structures with uniform fiber diameters, which make it ideal for filtration, biomedical, and energy applications. Consequently, it has become a widely used approach for producing nanomaterials. As a result of their highly active surface area, increased functionality with the flexibility to modify the properties, and nano-scale dispersion, nanofibers have recently attracted the attention of researchers seeking to create effective oil/solvent-water separation systems [4-6]. The phenomenon of superwetting is frequently used to separate oil, solvent, and water.

Electrospun ABS membranes have been shown to have potential for oil-water separation [7-9]. However, pure ABS membranes are relatively brittle, limiting their impact resistance and flexibility, which can restrict their use in dynamic environments. Blending is recognized as a highly effective technique for the formulation and fabrication of membranes, significantly enhancing their properties [10]. Mixing with rubber can improve thermal stability, allowing the membrane to perform effectively over a wider temperature range. The addition of rubber, such as epoxidized natural rubber (ENR), imparts improved toughness and elasticity, reducing the brittleness and enhancing flexibility [11,12]. Combining ABS with ENR resulted in membranes that exhibit enhanced flexibility, strength, and chemical resistance. The electrospinning process ensures a fine fibrous structure, optimizing the unique properties of rubber blend for various applications. The surface properties of ABS membranes may also not be optimal for applications such as hydrophobicity for water-oil separation. Rubber can enhance these surface properties, providing better hydrophobic and oleophobic characteristics [13].

Oil-water separation processes often involve the accumulation of solids, sludge, or particulate matter. Hence, ABS membranes can be prone to fouling and clogging, leading to reduced flow rates and increased maintenance requirements. Moreover, ABS membranes may degrade due to prolonged exposure to UV radiation, oxidation, or chemical attack. This degradation can lead to reduced separation performance and shorter membrane lifespan. As a result, they need to be modified before application or any additional processing, such as coating with functional materials.

Surface modification of electrospun membranes by coating methods has been documented in previous studies. Shaulsky *et al.,* [14] reported on the polymer coating of electrospun PVDF-HFP fiber mat substrates. Yoon *et al.,* [15] demonstrated an ultrafiltration polyacrylonitrile membrane by applying a water-resistant chitosan coating. Park *et al.,* [16] performed surface modification of hydrophobic PVDF nanofibers by dip coating them into hydrophilic PVA. Additionally, Chin *et al.,* [17] reported the surface coating of PP on electrospun PP membranes via solvent-exchange to produce superhydrophobic membranes. However, there is no reported study on the effect of citric acid in PVA coating solutions on ABS or ABS/ENR membranes.

In this study, the surfaces of electrospun ABS and ABS/ENR membranes will be modified by coating with PVA containing various concentrations of citric acid. Tensile, wettability and morphological properties will be evaluated to assess the effects of CA on these two membrane systems. Thus, the aim of this research is to develop a deeper understanding of PVA coating formulations in order to synthesize surface-modified electrospun ABS membranes with customizable hydrophilicity and hydrophobicity, suitable for various applications such as oil-water separation.

2. Methodology

2.1 Materials

Acrylonitrile butadiene styrene (ABS) and epoxidized natural rubber (ENR) were utilized for fabricating the polymer blend membranes. ABS, a thermoplastic polymer known for its toughness and impact resistance, was sourced from Toray Plastics. Meanwhile, ENR was selected for its flexibility and chemical resistance and obtained from Guthrie Malaysia. The rubber was exposed to ultraviolet irradiation to obtain low molecular weight liquid epoxidized natural rubber (LENR). Acetone as solvent and citric acid were obtained from Sigma Aldrich. All chemicals were used as received without further purification.

2.2 Sample Preparation

The ABS polymer was dissolved in acetone at a concentration of 25 wt% and stirred for 24 hrs before mixed with LENR and further stirred for 5 hours to prepare the ABS/ENR electrospinning solution. Two compositions were used in this study: 100% ABS and ABS/ENR (70/30) blend. The electrospinning process was performed using a custom-built apparatus consisting of a high-voltage power source, syringe pumps and a flat aluminum collector. Two syringe pumps with a 10-ml syringe were used to release the solution in the electrospinning process. The injection rate and the applied voltage were 4 ml/h and 20 kV, respectively. The distance between the tip and the collector was fixed at 15 cm.

The electrospun membranes were subsequently coated with PVA using dip coating method. The 5 wt% PVA dipping solution was prepared by dissolving PVA in water at 95 °C with constant stirring for 6 h. Various concentrations of citric acid (CA) were prepared separately before mixed with the PVA solution to obtain PVA-CA dipping solution. The nanofibers were then soaked in dipping solution at 60 °C for 1 h. A roller was used to remove the excess PVA solution. Then, the samples were dried in the oven at 100 °C for 10 min. Table 1 shows the various compositions of the coating solution prepared in this study.

Table 1
Coating formulations of PVA-CA coated ABS/ENR membranes

Polymer	PVA conc. (%)	Citric acid conc. (%)
ABS	5	0
ABS	5	20
ABS	5	30
ABS	5	40
ABS/ENR (70/30)	5	0
ABS/ENR (70/30)	5	20
ABS/ENR (70/30)	5	30
ABS/ENR (70/30)	5	40

2.3 Characterization

A tensile test was performed to determine the tensile characteristics of thin fiber membranes. Samples with a dimension of 15 mm x 5 mm and a thickness ranging from 0.20 to 0.30 mm were tested. The samples were clamped using a tensile testing apparatus and subjected to a tensile loading at a speed of 2 mm/min until failure. During the test, the machine monitors the load and displacement and computes the material's tensile strength, elongation at break, and tensile modulus. The measurements of three specimens were used to calculate the average values of these properties.

The contact angle measurement system was set up in a controlled environment and calibrate it using reference liquids. The membrane is placed on a flat surface and a small water droplet was deployed using a microsyringe. A high-resolution image of the water droplet on the ABS/ENR membrane was captured, and then analyzed using image analysis software to determine the contact angle. Multiple measurements were repeated at various locations of the membrane, and the data was interpreted to assess its wettability properties.

The scanning electron microscope was utilized to investigate the fracture surfaces of differently coated neat ABS and ABS/ENR fiber membranes. To ensure accurate results, the scanning process took place in a vacuum to eliminate any potential interference from air or moisture. Each sample was thoroughly examined by capturing multiple frames at various magnification.

3. Results
3.1 Tensile Properties

Figure 1 shows the citric acid amount dependence of tensile strength and elongation at break, for both neat ABS and ABS/ENR blend membranes. As shown in the Figure 1, across all coating formulations, ABS/ENR blend membranes exhibit higher tensile strength than neat ABS membranes. ABS/ENR membranes show tensile strength in the range of 5-7 MPa, while neat ABS shows a range of 2-4 MPa. These findings align closely with the tensile strength values reported by Sithornkul *et al.,* [18] for ABS/NR membranes.
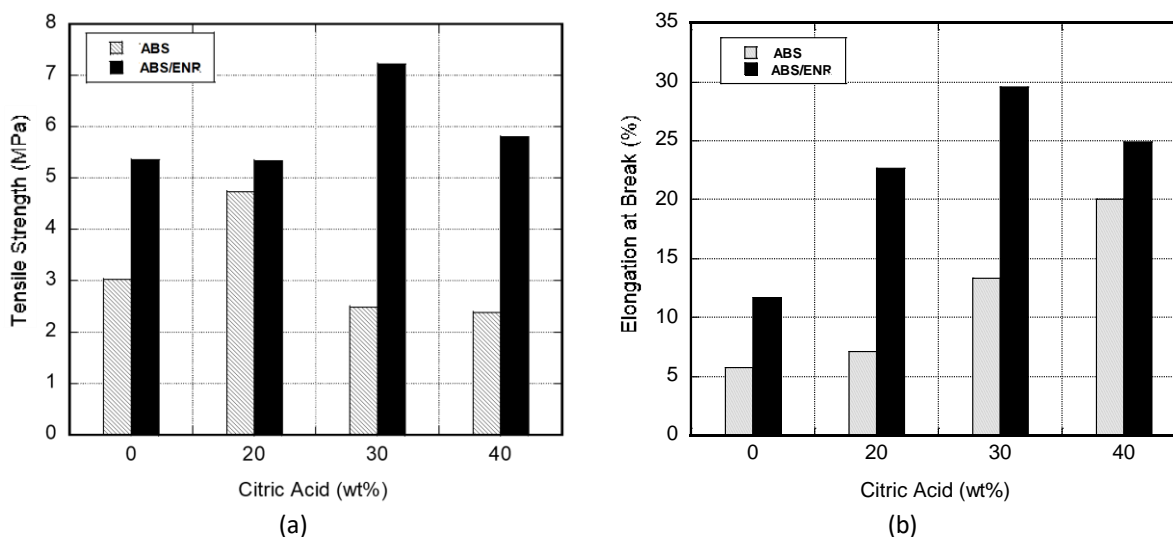

Fig. 1. The effects of citric acid amount of ABS and ABS/ENR (70/30) membranes (a) Tensile strength (b) Elongation at break

For ABS/ENR membranes, the samples coated with PVA in combination with citric acid showed improved tensile strength compared to the sample coated with PVA only, with 30 wt% CA shows the highest at 7.25 MPa. On the other hand, the neat ABS membrane only shows an increase (+56.1%) of tensile strength for PVA containing 20 wt% CA. However, when CA content is further increased to 30 and 40 wt%, tensile strength slightly decreases. Comparing the elongation at break values between the two compositions, it is evident that in general, the ABS/ENR (70/30) membranes exhibit higher elongation values compared to the neat ABS membranes. This suggests that the presence of ENR in the ABS matrix contributes to increased flexibility and elongation capabilities of the fibers. It makes ABS/ENR blend membranes more versatile and suitable for applications where durability and resistance to dynamic stress are important.

Inclusion of CA into the coating formulation is found to be effective in improving elongation at break of the membranes. Significant increases of elongation at break (+250.8% and +154.1%) were recorded at 40 wt% CA, for neat ABS and ABS/ENR membranes, respectively. The improved elongation values associated with the presence of a CA in PVA coating, can be probably attributed to the improved adhesion of the PVA coating with the polymeric membrane [19]. Furthermore, CA also can act as plasticizer, hence contributes to the increase in plasticity of the PVA coating, allowing for greater deformation before failure [20,21].

The findings from this study highlight the significance of coating composition in influencing the tensile strength of electrospun fibers. The addition of PVA and citric acid in the coatings demonstrated a positive effect on the tensile strength and elongation at break of both ABS/ENR and ABS samples, indicating improvement in toughness and impact resistance. These results can be attributed to the improved intermolecular interactions and enhanced bonding within the fiber structure.

3.2 Wettability

The water contact angle measurements provide valuable insights into the wetting behaviour and surface characteristics of the different samples. By analyzing the data, we can observe how the amount of citric acid in the PVA solution influences the contact angles, allowing us to infer the hydrophobic or hydrophilic nature of the samples. The water contact angles for ABS and ABS/ENR (70/30) coated with various PVA-CA compositions are listed in Table 2.

Table 2
Water contact angle of ABS and ABS/ENR membranes with various coating formulations

Polymer	Contact angle (°)
ABS (CA0)	67.66
ABS (CA20)	74.24
ABS (CA30)	32.06
ABS (CA40)	27.98
ABS/ENR (CA0)	116.89
ABS/ENR (CA20)	113.64
ABS/ENR (CA30)	104.99
ABS/ENR (CA40)	102.63

The contact angles images of water droplet on the ABS and ABS/ENR membranes are shown in Figures 2 and 3, respectively. By comparing the contact angles between the neat ABS and ABS/ENR (70/30) samples, it is evident that the neat ABS samples generally exhibit lower contact angles, indicating a relatively more hydrophilic behaviour. The contact angles for the neat ABS samples range from 27.98 to 74.24 degrees. As the concentration of citric acid in the coating increases (CA30 and CA40), the contact angles decrease to 32.06 and 27.98 degrees, respectively, indicating enhanced hydrophilicity with the addition of CA. The addition of citric acid introduces more polar sites within the PVA matrix [22,23]. These polar sites interact favourably with water molecules, thus increasing the wettability and hydrophilicity of the PVA coating.

On the other hand, the ABS/ENR (70/30) samples generally show higher contact angles, indicating their more hydrophobic nature compared to the neat ABS membranes. The contact angles for the ABS/ENR (70/30) samples range from 102.63 to 116.89 degrees. Rubber materials often have inherently hydrophobic properties. When blended with ABS, these hydrophobic characteristics can transfer to the membrane surface, reducing its affinity for water. Similar to what was observed in

neat ABS, the contact angle decreases with increasing citric acid concentration, indicating an increase in hydrophilicity.
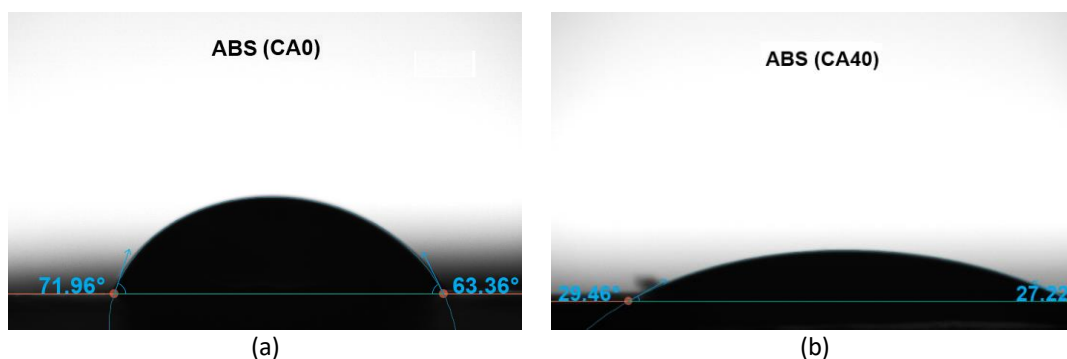

Fig. 2. Contact angle images of water droplet on ABS membrane coated with (a) PVA coating (b) PVA coating containing 40% CA
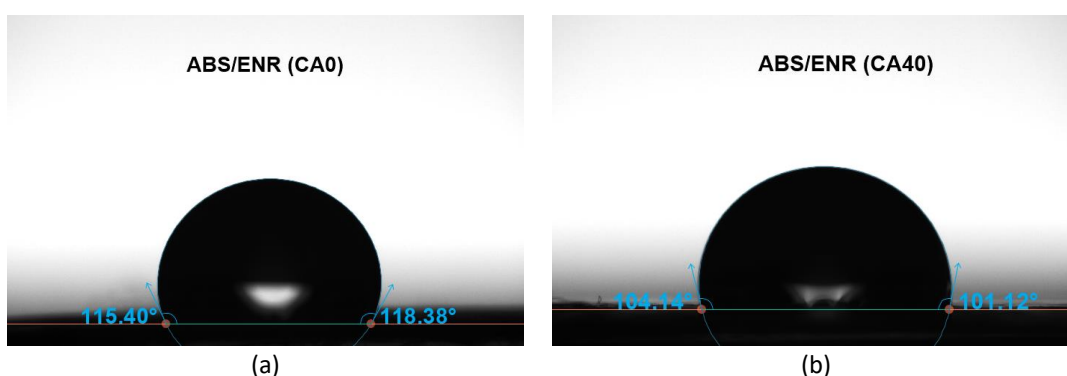

Fig. 3. Contact angle images of water droplet on ABS/ENR (70/30) membrane coated with (a) PVA coating (b) PVA coating containing 40% CA

Overall, the contact angle measurements indicate that the presence of citric acid in the PVA coatings leads to a decrease in contact angles for both the neat ABS and ABS/ENR blend samples. This implies an increase in hydrophilicity, indicating a stronger affinity for water. The specific composition and concentration of the coating components play a significant role in determining the wetting properties of the fiber surfaces.

It is worth noting that the surface modification of the electrospun ABS and ABS/ENR membranes can provide controlled surface properties, allowing for the manipulation of hydrophobicity or hydrophilicity. The ability to tailor the wetting behaviour of fiber membranes is of great interest in various applications such as filtration, separation processes and biomedical engineering. Understanding the relationship between surface composition and contact angle can contribute to the development of advanced materials with specific wetting characteristics tailored for diverse applications.

3.3 Microscopic Analysis

Figure 4 shows the SEM images of fractured surface of ABS membrane and ABS/ENR (70/30) membranes. It is evident that membrane made of electrospun ABS/ENR blend is better in terms of homogeneity in shape and size. The size of fibers in the ABS membrane are non-homogeneous and varies from 10 to 50 μm. In contrast, the ABS/ENR membrane displays homogeneous fibers consistently around 10 μm in size. Smaller fibers generally lead to higher mechanical strength and

toughness due to a more uniform distribution of stress and the ability to absorb and dissipate energy more effectively. Homogeneous fibers result in a more uniform distribution of stress across the membrane, leading to improved mechanical strength and durability. Smaller fibers also tend to align more readily during the electrospinning process, especially in the direction of the electric field or collector. This alignment creates anisotropic properties where the material exhibits different characteristics along different axes.

The homogeneity of electrospun fibers in ABS membranes is crucial for ensuring consistent mechanical properties, wettability and filtration efficiency [24]. Homogeneous fibers lead to more reliable and predictable membrane performance, while inhomogeneous fibers can introduce weak points, variability, and inefficiency. Therefore, achieving fiber homogeneity is essential for optimizing the properties and functionality of ABS membranes for specific applications.
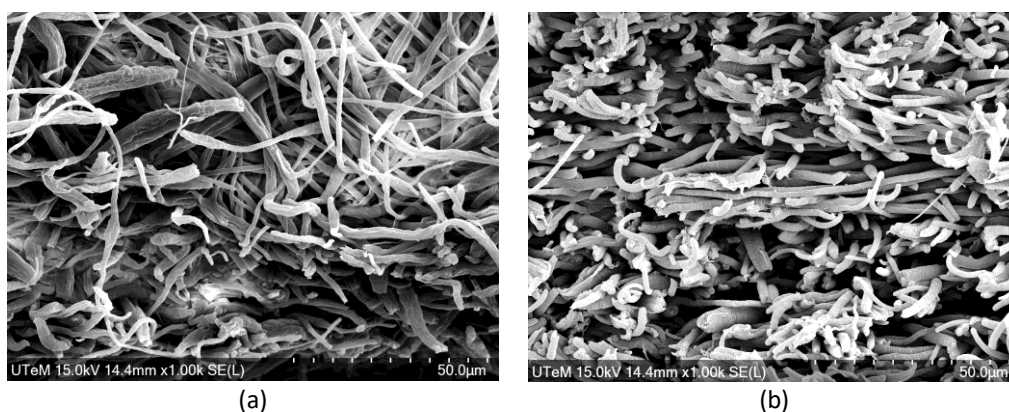

(a)   (b)

Fig. 4. SEM images of fractured surface (a) ABS membrane (b) ABS/ENR (70/30) membrane at 1000X magnification

Figure 5 shows the SEM images of ABS membrane coated at two different coating formulations. It is observed that addition of CA in the coating solution changes the morphology of the ABS fibers. The PVA coating containing CA demonstrates overall rougher surface than the coating consists of PVA only. The rougher surfaces often allow water spreads more easily across the surface rather than forming droplets, thus improve wetting properties [25]. This behaviour is associated with lower contact angles and increased hydrophilicity as demonstrated by the results of wettability in section 3.2 above. Rough surfaces also tend to have higher surface energy due to the presence of more active sites and irregularities. This higher surface energy promotes stronger interactions with polar molecules like water, enhancing hydrophilic behaviour.
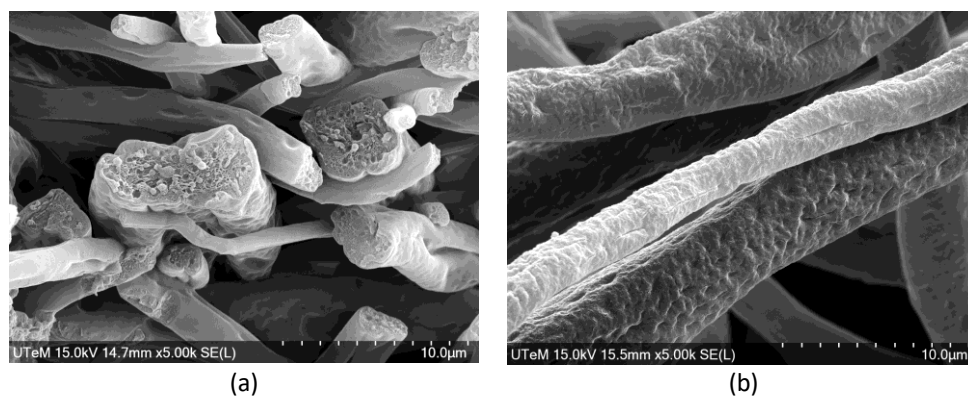

(a)   (b)

Fig. 5. SEM images of electrospun fibers of ABS membrane coated with (a) PVA coating (b) PVA containing 30% CA at 5000X magnification

4. Conclusions

Neat ABS membranes and ABS/ENR blend membranes have been prepared by eletrospinning method. The resulted membranes were dip coated in PVA coating solution containing various concentration of citric acid. The incorporation of ENR into the ABS polymer was found effective in promoting finer and homogenous fibers, and significantly enhances the tensile strength and elongation at break of the resulting fiber membranes, indicating the positive impact of ENR as a reinforcing agent. Addition of citric acid in PVA coating of the electrospun fibers, further contributes to improving the mechanical characteristics of the membranes. Regarding wettability, while ENR addition enhances the hydrophobicity of the membrane, CA addition in PVA coating, oppositely enhance the hydrophilic property of the membranes. The synergistic effect between ENR addition in the polymer solution and citric acid in coating solution, imparts additional strength and resilience to the fibers, enhancing their overall performance. In conclusion, the composition and coating strategies employed in the fabrication of electrospun fiber membranes play a crucial role in determining their mechanical properties and wetting behaviour.

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