Fabrication and filtration of gum arabic doped electrospun PLA membrane for rejection of gray water pollutants

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Water scarcity, which is increasing with global warming and climate change, is one of the environmental problems that require urgent solutions. Gray water treatment is one of the effective methods to address this problem. Gray water from washing machines can contain organic and inorganic pollutants. Electrospun nanofibers show promise in the removal of these pollutants owing to their high surface area and tunable properties. In this study, gum arabic (GA) doped polylactic acid (PLA) nanofiber membrane was produced by an electrospinning method for gray water filtration. GA is a functional and economical additive that complements the deficiencies of PLA and improves the hydrophilicity, mechanical strength, flexibility, and separation performance of the membrane. GA was added to the PLA membranes at 1-5%. The characterization tests revealed that GA doped membranes were successfully produced. In methylene blue filtration, the pure PLA membrane provided over 93% rejection, while this rate increased to 99% with GA additive. Emulsified oil removal was measured as 87% in the membrane with 2% GA additive. Approximately 50% rejection was achieved in linear alkyl benzene sulfonate (LAS) filtration and 100% in microplastic filtration. With GA additive, the surface contact angle decreased from 127° to 118° and hydrophilicity increased. In mechanical tests, the tensile strength of the PLA membrane without additives increased from 7 MPa to 11.8 MPa with 4% AG additive and the mechanical strength and flexibility increased significantly. In conclusion, GA doped PLA membranes are considered as an effective and sustainable option for gray water treatment.

Keywords: Electrospinning; filtration; gray water; multiple impurities; polylactic acid.

INTRODUCTION

The escalation of industrialization and urbanization has led to a significant increase in water consumption. Consequently, water consumption is escalating by 3% annually, rendering water scarcity a significant contemporary issue [1]. In particular, the treatment and reuse of gray water plays an important role in sustainable water management strategies. Gray water contains various organic and inorganic pollutants such as detergent residues, oils, dyes, and microplastics [2]. The effective removal of these pollutants is critical for both environmental and public health. Various wastewater treatment technologies are used to solve this problem [3].

Traditional treatment methods may be insufficient to completely remove such complex pollutants. In recent years, nanofiber membranes produced by the electrospinning method have become one of the most innovative materials in water purification. These membranes effectively retain contaminants thanks to their high surface area, adjustable pore structure, and high permeability. Additionally, the electrospinning method allows for the use of different polymers and additives together, enabling the modification of membrane properties as desired [4, 5]. Electrospinning is a versatile and simple technique used to produce ultra-fine fibers from polymer solutions or melts by applying a high-voltage electric field. In this process, the polymer solution is pumped through a small needle connected to a high-voltage power source. The electric field overcomes surface tension by creating a charge on the liquid surface, causing the solution to form a thin jet. As the jet moves toward a grounded collector, the solvent evaporates and solid nanofibers accumulate, resulting in a nonwoven membrane with a highly porous structure. The diameters of the resulting fibers typically range from ten nanometers to several micrometers, providing an exceptionally high surface area-to-volume ratio that is advantageous for filtration and separation applications [6]. Polylactic acid (PLA) is an aliphatic polyester obtained from renewable sources such as corn starch and exhibits biodegradable properties. Thanks to its high mechanical strength and processability, it is widely used in packaging, textiles, and medical applications. However, PLA's

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hydrophobic structure and low water permeability limit its performance in applications such as water purification. Therefore, modification studies using natural additives are being conducted to improve PLA's properties. For example, studies using biomass-derived fillers such as rice husks have increased PLA's water absorption capacity, making it more effective in water purification applications [7]. In the context of PLA, electrospinning is widely used to produce nanofiber membranes for environmental and biomedical applications. For example, a study by Gao *et al.* [8] demonstrated that nanofiber membranes produced by electrospinning using stereo-complex polylactic acid (SC-PLA) provide high efficiency in effectively trapping particulate pollutants and pathogens. These membranes offer advantages such as high hydrophobicity, small average pore size, and high porosity, supporting their promising potential in water purification applications.

Gum arabic (GA) is a natural, complex, and branched polysaccharide obtained from acacia species (particularly Acacia senegal and Acacia seyal). Due to its biocompatibility, renewability, emulsifying capacity, and low toxicity, it is widely used in the food, pharmaceutical, cosmetic, and biomaterial industries. The arabinose and galactose-based chains in GA's structure contain a high proportion of hydrophilic functional groups. This property makes it an ideal additive in polymeric systems, particularly for imparting hydrophilicity [9]. When used in conjunction with hydrophobic polymers, GA increases surface energy and reduces contact angle, thereby improving water permeability. It also improves filtration performance by increasing porosity [10, 11]. Owing to its ability to enhance mechanical properties, GA-containing polymer membranes become more flexible and durable [12]. Furthermore, its natural origin enables the development of biodegradable and environmentally friendly products. GA's antioxidant and antimicrobial effects also provide advantages in water purification, food, and biomedical applications. For example, in a study conducted by Serio *et al.* [11], nanofiber production was carried out by electrospinning using polyvinyl alcohol and GA. It was observed that GA additive reduced the fiber diameter, increased surface roughness and improved interaction with water by reducing the contact angle. Such composite fibers prepared by electrospinning method have been shown to increase the filtration performance in membrane technology.

In this study, GA doped PLA electrospun nanofiber membranes were produced and their performance in gray water treatment was evaluated. The effectiveness of the produced membranes against contaminants such as methylene blue (MB), oil, microplastics (MP), and linear alkylbenzene sulfonate (LAS) was investigated. Basic characterization tests were performed. Additionally, the surface properties, mechanical strength, water retention, and porosity of the membranes were analyzed.

EXPERIMENTAL

Materials

PLA 2003D was procured from Nature Works, possessing a molecular weight ranging from 120,000 to 160,000 g/mol. Dimethylformamide (DMF) and chloroform (CHCl$_3$) were acquired from Isolab, Turkey. Polyethylene glycol 400 (PEG) was acquired from Merck Chemicals, Turkey. Gum arabic (CAS-No: 9000-01-5) was acquired with a purity of 98%.

Method

A mixture of DMF/chloroform comprising 12.5% PLA (30% DMF by volume) and 20% PEG (by mass of PLA) was prepared at 60 °C until uniform. Prior to spinning, 1-5% GA was incorporated into the solution using the initialization procedure. In this procedure, the GA was initially coated with a thin, diluted polymer before being incorporated into the primary polymer solution. The prepared mixture was homogenized for 30 min using an ultrasonic homogenizer (Bandelin HD4050). The electrospinning procedure was conducted at a voltage of 16 kV, at ambient temperature, with a needle-collector distance of 18 cm and a feed rate of 0.05 mL/min. The fabricated membranes were immersed in distilled water for one day, subsequently dried at ambient temperature, and cured at 60 °C for 30 min.

Membranes produced by the electrospinning method were tested in the filter system shown in Scheme 1. To determine filtration performance, rejection tests were conducted using emulsified oil (soybean oil, 2%), cationic dye (MB, 5 ppm), LAS (100 ppm), and MP (polyester, 200 ppm). The filtration performance was evaluated based on the component rejection (%) as described in Equation (1).

$$R(\%) = \left(1 - \frac{C_f}{C_i}\right) * 100 \qquad (1)$$

where R (%) is the component rejection, C$_i$ is the solute concentration before filtration, and C$_f$ is the solute concentration after filtration.

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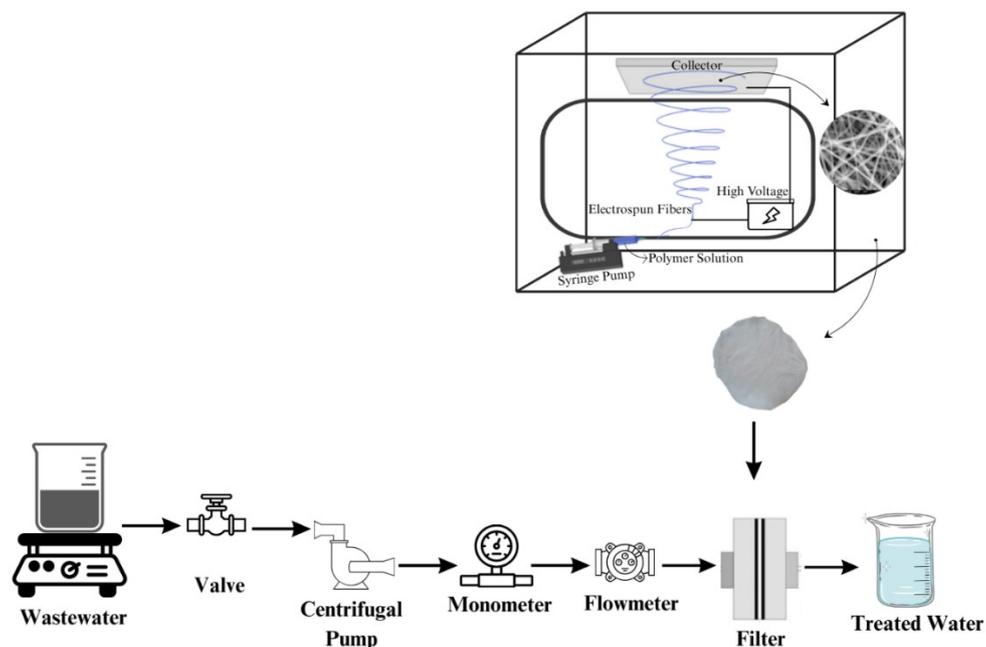
Scheme 1. Schematic diagram of membrane production and filtration test system using electrospinning.
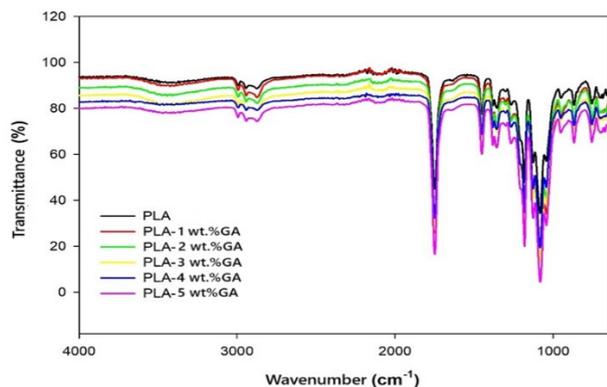
RESULTS AND DISCUSSION

Fig. 1. FTIR spectra of PLA and GA-PLA membranes.

FTIR spectra of PLA and GA doped PLA membranes are presented in Fig. 1. In the spectrum of pure PLA, the strong band around 1750 cm^{-1} represents the characteristic ester carbonyl (C=O) stretching of PLA. The weak bands observed in the spectra in the 2995-2945 cm^{-1} range correspond to asymmetric and symmetric stretching vibrations (-CH$_3$) of methyl groups. In addition, the C-O-C stretching vibrations in the 1180-1080 cm^{-1} range are unique to PLA and indicate that the structural integrity of the polymer backbone is preserved [13]. The fact that GA doping doesn't produced a significant displacement effect on these bands indicates that the dopant is physically dispersed in the PLA structure without forming covalent bonds [14]. It is observed that with the increase in the doping ratio, a broad band in the range of 3300-3400 cm^{1} appeared and this band was especially strong at

4% and 5% GA doping. This band can be interpreted as the contribution of hydroxyl (-OH) groups in the structure of GA to the FTIR spectrum. In the literature, it is reported that -OH groups form broad and overlapping bands in the FTIR spectra of polysaccharide-based natural additives such as GA [15].
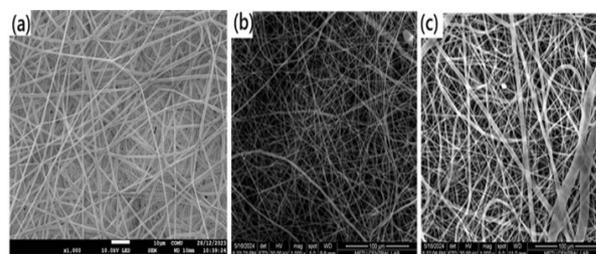

Fig. 2. SEM analysis of PLA(a), PLA-2 wt% GA(b), and PLA-4 wt% GA(c) membranes.

The scanning electron microscopy (SEM) images in Fig. 2 show the fiber morphology of pure PLA (a), 2% GA doped PLA (b) and 4% GA doped PLA (c) samples. Pure PLA fibers show a uniform, bead-free and homogeneous distribution. This structure indicates that the electrospinning conditions were optimized. At 2% GA doping, irregularity in fiber diameters and some thinning were observed. This may be due to the fact that GA increases the conductivity and viscosity of the solution [16]. 4% GA doped fibers showed thicker and more complex structures and the fibers were observed to merge in places. This indicates that the high additive rate creates negative effects such as phase separation and agglomeration.
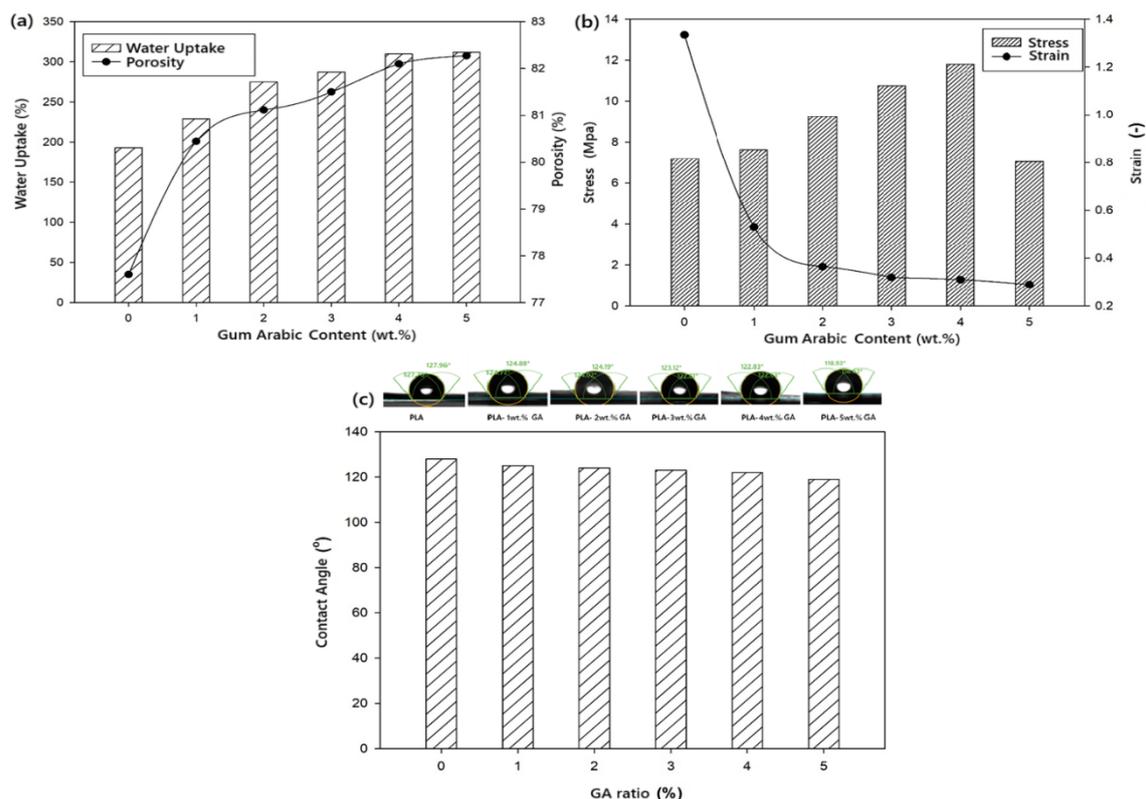
Figure 3. Water uptake and porosity results of the membranes (a), mechanical analysis of PLA and GA doped PLA membranes (b), and the contact angles of PVDF and GA doped PLA membranes (c).

As seen in Fig. 3(a), a gradual increase in both water absorption capacity and porosity was observed with the addition of 1-5% GA to the membranes. While the pure PLA membrane had a water absorption capacity of about 190%, this value reached 310% in membranes containing 5% GA. Similarly, the porosity value increased from 77% to over 82%. This increase is due to the hydrophilic nature and amorphous nature of GA. GA increases water retention by forming hydrogen bonds with water molecules thanks to its hydroxyl and carboxyl groups [17]. It is also reported in the literature that GA is used as an additive to increase porosity and improve water permeability and thus positively affects the filtration performance of membranes [18]. However, after 4%, the increase in water absorption capacity was more limited, indicating that increasing the additive amount above a certain level may indicate saturation or the structure may become too porous and the mechanical stability may decrease. This finding is important in determining the optimum admixture rate.

Figure 3(b) shows the tensile strength and strain values of PLA and GA doped PLA membranes. Significant changes were observed in the mechanical behavior of the membranes as the GA doping rate increased. Tensile strength increases at 1%-4% GA ratios. This increase can be explained by the fact that GA acts as a structural filler in the PLA matrix and increases the interaction between fibers. GA positively affected the strength by forming physical bonds with PLA thanks to its hydrophilic nature and functional groups [19]. However, there is a significant decrease in tensile strength at 5%. This can be attributed to the fact that the additive is not homogeneously distributed in the matrix, causing phase separation and creating weak points in the structure. This situation indicates that the mechanical integrity deteriorates at the point where the optimum additive ratio is exceeded. Elongation values decreased as the GA ratio increased and the structure became more brittle. This is related to the fact that GA reduces the ductility of PLA.

Figure 3(c) shows the contact angle of the membranes. While the contact angle of pure PLA is approximately 127.96°, this value decreases to 118.93° with the addition of 5% GA. This decrease is due to the hydrophilic nature of GA. GA contains many hydroxyl groups in its structure and these groups increase the wettability of the surface by forming hydrogen bonds with water molecules. This has caused the material to gain a more hydrophilic surface character with increasing GA content [17, 20].
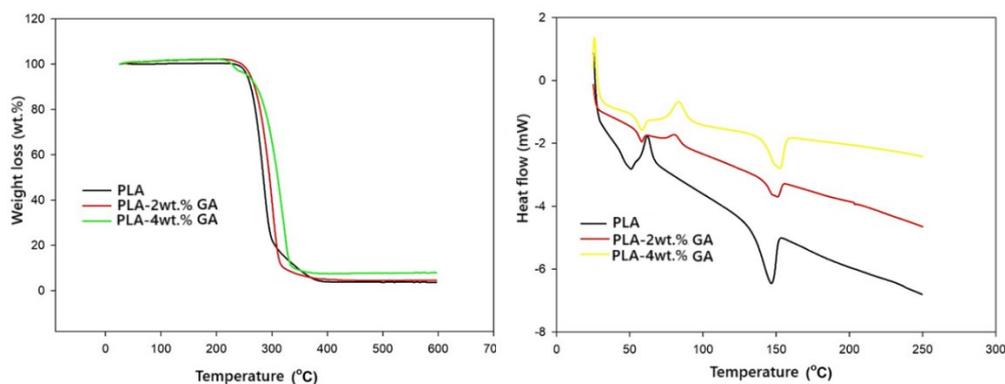
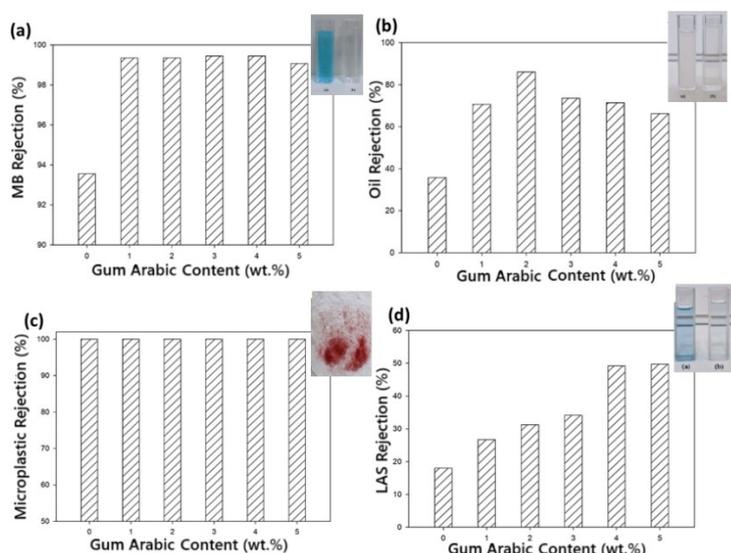**Fig 4**. DSC (a) and TGA (b) analyses of PLA and GA doped PLA membranes.

Fig. 5. Effect of GA-doped PLA membranes on rejection of pollutants: MB rejection (a), soybean oil rejection (b), microplastic rejection (c), and LAS rejection (d).

Fig. 4(a) shows TGA and Fig 4(b) DSC analysis of the membranes. The obtained TGA and DSC results reveal the positive effects of GA on PLA. The increase in thermal stability is evident by the onset of degradation at later temperatures. Moreover, changes in crystallization behavior indicate that the additive has an effect on morphology and structure ordering. The residual mass of the polymer at 2% and 4% loading increases from 3.7% to 5.5% and 8%. This shows an increase in thermal strength. GA added to PLA polymer decreased the initial enthalpy of decomposition as seen first. Because, as stated in the literature, GA does not have a degradation curve at this point and has a Tg point at 55 ºC. These findings support that the use of natural polysaccharides as additives in biodegradable polymer systems can provide not only environmental but also functional benefits [21, 22].

In Figure 5(a), while a separation value of 93% was obtained with pure PLA membrane in methylene blue filtration, dye rejection exceeded 99% in GA-containing membranes. This increase is attributed to the increase in hydrophilicity in the membrane surface properties. The hydroxyl and carboxyl groups present in the structure of GA enhance membrane-molecule interactions, facilitating the adhesion of water and dye molecules to the membrane surface [23].

The oil removal rate shown in Figure 5(b) increased with the GA content up to 2% and reached a maximum of 86%. The primary reason for this is that GA is a natural emulsifier. However, the decreasing performance beyond 3% can be attributed to excessive addition disrupting the pore structure of the membrane, negatively affecting permeability and selectivity. This highlights the need for careful optimization of the additive amount [24].

In Figure 5(c), all PLA membranes exhibit 100% microplastic rejection. Microplastic removal with electrospun nanofiber membranes is primarily governed by membrane porosity, fiber diameter, and surface charges. Reducing membrane porosity and nanofiber diameter results in greater retention of microplastic particles, as larger particles cannot pass through smaller pores. This indicates that microplastics are completely retained by mechanical

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filtration due to their physical size being larger than the membrane pores [25].

Figure 5(d) shows that the LAS removal rate increases gradually with the GA ratio. The removal rate, which was 21.5% in the pure PLA membrane, reached 50% with the addition of 5% GA. Anionic surfactants such as LAS can adhere to the membrane surface due to the surface functional groups and hydrophilic structure provided by GA. Additionally, it is thought that GA enhances the adsorptive properties by increasing the surface roughness [19]. It can be said that the increase in porosity due to GA addition causes an increase in LAS removal. Porosity is suppressed after a 4% loading, and therefore LAS rejection does not increase beyond a 4% addition rate (49.6% at 5%). This indicates that GA addition structurally increases fiber hydrophilicity.

CONCLUSION

In this study, PLA membranes incorporated with GA were successfully fabricated and applied for the treatment of simulated gray water containing various pollutants. The incorporation of GA resulted in a substantial enhancement of the membrane's surface properties, including hydrophilicity, porosity, and water uptake capacity. These properties are critical for efficient pollutant separation. The characterization results demonstrated that the addition of GA not only enhanced the thermal stability and mechanical strength of the PLA membranes—as evidenced by the increase in tensile strength from 7 MPa to 11.8 MPa—but also had a positive effect on their filtration performance. The GA-modified membranes demonstrated remarkable rejection efficiencies, with 100% efficiency for microplastics, 99% for methylene blue, 87% for emulsified oil, and 50% for anionic surfactant (LAS). These results indicate that GA functions as an effective functional additive, compensating for the inherent limitations of PLA in water treatment applications.

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