The Effect of Acid Addition on Certain Properties of Polyamide 66 Polimeric Membranes

Keila Machado de Medeiros[1*], Damares Oliveira de Jesus Ferreira[1], Joanne Graziela Andrade Mendes[1], Airan Magalhães Moura[1], José Everton Soares de Souza[2], Carlos Antônio Pereira de Lima[2]
[1]Center for Science and Technology in Energy and Sustainability, Federal University of Recôncavo of Bahia, Feira de Santana, Bahia; [2]Department of Sanitary and Environmental Engineering, State University of Paraíba; Campina Grande, Paraíba, Brazil

In this study, four polymeric solutions were prepared to contain 10% of different additives—benzoic, adipic, tartaric, and citric acids—relative to the amount of polyamide 66 (PA66), with the total composition comprising 20% PA66 and 80% hydrochloric acid (HCl). The objective was to analyze these additives' influence on the resulting membranes' microstructure. The polymeric solutions were evaluated for viscosity, and the membranes produced with each additive were characterized in terms of water absorption capacity, porosity, water flux, maximum pore radius, and water vapor permeation. Incorporating acids with varying molecular weights (MW) into the PA66 solutions resulted in a progressive increase in viscosity, corresponding to the increase in molecular weight of the respective additive.

Keywords: Membranes. Polyamide 66. Additives. Microfiltration.

A synthetic membrane is a structure that wholly or partially restricts the transport of one or more chemical species in a mixture [1]. The classification of a membrane as porous or dense is determined by its surface characteristics, which develop upon contact with the solution to be separated. Various materials can be employed in membrane fabrication, directly influencing key properties such as permeability, selectivity, mechanical strength, thermal stability, and chemical resistance. The chemical nature of the membrane material plays a central role in defining the interaction between the polymer and the penetrant species, which is essential in determining separation efficiency and optimal operating conditions [2].

Polyamides, such as PA66, exhibit hygroscopic behavior due to hydrogen bonding between the carbonyl groups of one polymer chain and the amide hydrogen of another. Water molecules can penetrate between the chains, expanding the matrix and integrating into these hydrogen bonds.

The selection of the most appropriate membrane filtration method must consider boundary conditions and the membrane's performance relative to the specific water composition to be treated [3].

Currently, membranes are widely applied in solid-liquid separations and removal of dissolved contaminants. This work aims to investigate the effects of different acidic additives on the structural and functional properties of polyamide 66 (PA66) membranes.

Materials and Methods

Prior to membrane preparation, synthetic PA66 fibers and the selected additives—$C_7H_6O_2$ (benzoic acid), $C_6H_{10}O_4$ (adipic acid), $C_4H_6O_6$ (tartaric acid), and $C_6H_8O_7$ (citric acid)—were dried. These components were then dissolved in hydrochloric acid (HCl) to formulate the solutions. Each of the four solutions contained 10% of the additive relative to the total solids, which comprised 20% of the mixture, with the remaining 80% being solvent (HCl). The additives' molecular weights were accounted for in the formulations: PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$, as summarized in Table 1. These concentrations and ratios were based on previous literature standards for similar membrane systems.

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Address for correspondence: Keila Machado de Medeiros. Universidade Federal do Recôncavo Baiano. Centenário, 697 - Sim. Zipcode: 44042-280. Feira de Santana, Bahia, Brazil. E-mail: keilamedeiros@ufrb.edu.br.

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The prepared polymeric solutions were processed using immersion-precipitation, which involved casting the solution into a non-solvent bath. Each membrane remained immersed until complete precipitation occurred. Following precipitation, the membranes were removed from the bath, rinsed with water, and then submerged in a mixture of 10% hexane and 90% water. Subsequently, the membranes were dried under controlled conditions, with temperature and ambient relative humidity specified. Membranes intended for permeation flux testing were kept submerged in the water-hexane mixture until the test was conducted. Conversely, membranes designated for other characterizations were dried at room temperature (25 ± 2 °C), with relative humidity recorded during drying. This storage protocol aimed to prevent pore collapse due to capillary forces, considering the high surface tension of water.

The polymeric solutions were analyzed for viscosity, and the membranes produced with acidic additives were characterized in terms of viscosity, bubble point, water absorption capacity, porosity, water flux, average pore radius, and water vapor permeation.

Results and Discussion

Viscosity is directly related to the energy required for a fluid to flow and is influenced by the cohesive forces between the liquid's molecules [4]. Figure 1 presents the viscosity measurements of the polymeric solutions containing different acidic additives: PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$. The results revealed that the solution containing benzoic acid exhibited a viscosity of 2841 mPa·s, followed by the adipic acid solution with 2930 mPa·s, tartaric acid with 3000 mPa·s, and citric acid with 3154 mPa·s. These values indicate a gradual increase in viscosity corresponding to the increasing molecular weight of the acids incorporated.

Viscosity during membrane formation increases with the polymer concentration in the polymer-rich phase [1]. As shown in Figure 1, the viscosity of the solutions followed a trend corresponding to the molar mass of the additives. Higher molar mass additives led to higher viscosities—for instance, citric acid ($C_6H_8O_7$), which has the highest molar mass among the four acids studied, resulted in the highest viscosity. Conversely, benzoic acid ($C_7H_6O_2$), the additive with the lowest molar mass, exhibited the lowest viscosity.

Figure 2 presents the porosity results for the membranes: PA66/Benzoic Acid ($C_7H_6O_2$) at 60.8%, PA66/Adipic Acid ($C_6H_{10}O_4$) at 50.5%, PA66/Tartaric Acid ($C_4H_6O_6$) at 45.2%, and PA66/Citric Acid ($C_6H_8O_7$) at 40.4%. These results indicate that porosity varied depending on the additive used due to their distinct chemical structures and interactions with the polymer solution.

During membrane formation, the polymer-poor phase solidifies into pores, while the polymer-rich phase forms the dense matrix of the membrane. An increase in polymer concentration typically reduces the formation of micropores—defined as

Table 1. Composition of PA66 membranes with their additives.

Membranes	HCI (g)	PA66 (g)	Additives (g)	MW (g.mol^{-1})
PA66/ Benzoic Acid ($C_7H_6O_2$)	80.0	20.0	1.0	122.12
PA66/ Adipic Acid ($C_6H_{10}O_4$)	80.0	20.0	1.0	146.14
PA66/Tartaric Acid ($C_4H_6O_6$)	80.0	20.0	1.0	150.10
PA66/Citric Acid ($C_6H_8O_7$)	80.0	20.0	1.0	192.12

Figure 1. Viscosity of the solutions of PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$ membranes.

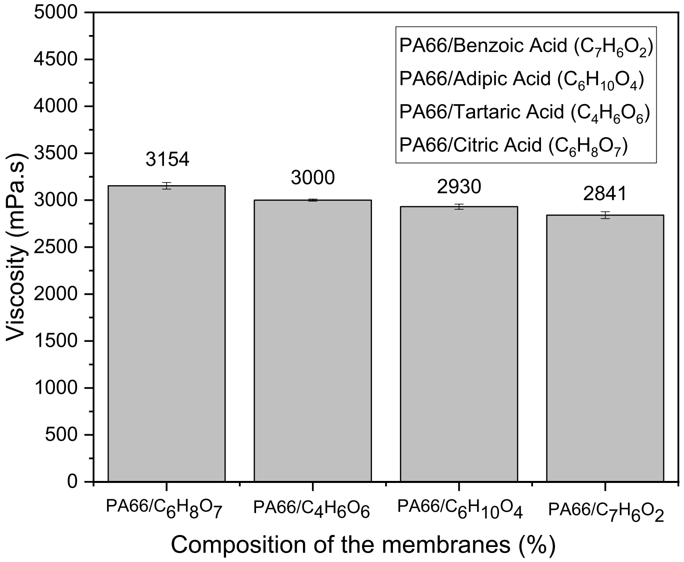
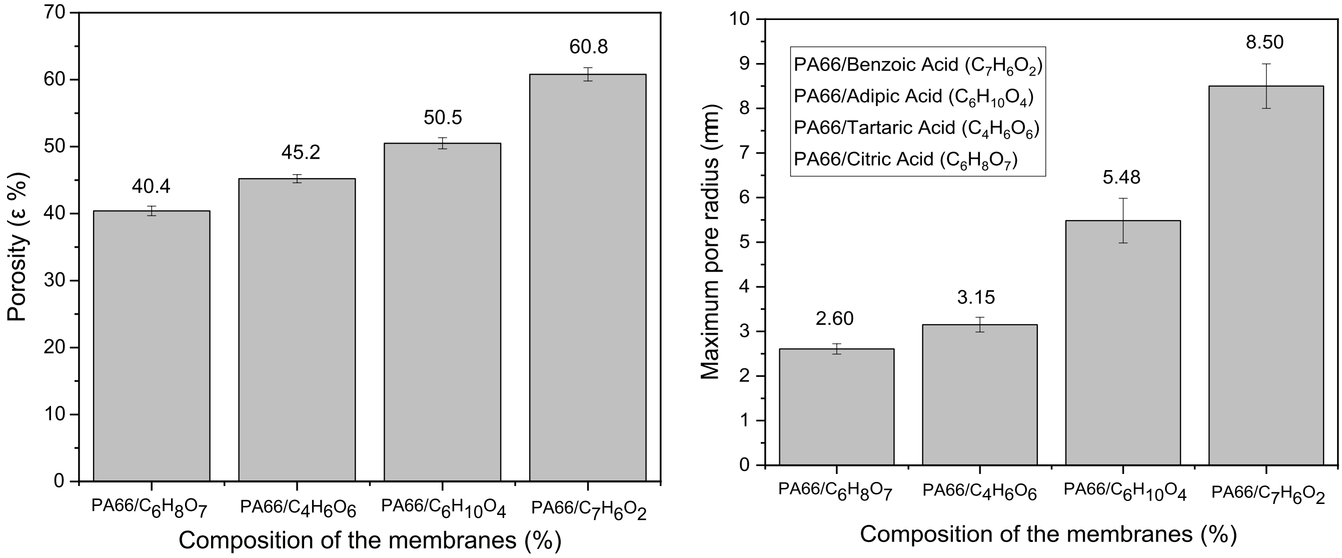


Figure 2. Porosity and Maximum pore radius of the membranes of PA66/C7H_6O_2, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$.



the smallest pore structures—resulting in narrower porous channels. This influences the porosity and the average pore size, often reducing pore diameter while increasing structural integrity [5].

The influence of viscosity on membrane porosity is evident, as higher viscosity solutions tend to form membranes with lower porosity, while lower viscosity solutions promote excellent porosity. Accordingly, the membrane prepared with citric acid—exhibiting the highest viscosity—demonstrated the lowest porosity, whereas the benzoic acid-based membrane, with the lowest viscosity, exhibited the highest porosity.

Porosity directly impacts pore size, as illustrated in Figure 2. The maximum pore radii for the PA66/Benzoic Acid, PA66/Tartaric Acid, PA66/

Adipic Acid, and PA66/Citric Acid membranes were approximately 8.50%, 5.48%, 3.15%, and 2.60%, respectively. The maximum pore radius was determined using the bubble point method, which involves measuring the pressure needed for gas (typically air or nitrogen) to pass through a membrane saturated with liquid [6].

Figure 2 clearly shows that the PA66/Citric Acid ($C_6H_8O_7$) membrane, which had the lowest porosity, also exhibited the smallest maximum pore radius. In contrast, the PA66/Benzoic Acid ($C_7H_6O_2$) membrane presented the largest maximum pore radius, consistent with its lower viscosity and higher porosity. Accurate pore size and distribution knowledge are essential for evaluating and characterizing microfiltration membranes. Smaller pore diameters require higher pressure for water permeation, which enhances filtration performance by increasing selectivity and flow rate [7–8]. Membranes may exhibit microporous, macroporous, or nanoporous structures, with water permeating under applied pressure.

Membrane characterization also includes assessing water absorption capacity, which measures the amount of water absorbed when membranes are immersed in distilled water at room temperature over various time intervals, as well as the total mass loss after immersion. As shown in Figure 3, water absorption capacities for the PA66/Citric Acid, PA66/Tartaric Acid, PA66/Adipic Acid, and PA66/Benzoic Acid membranes were 65.8%, 70.8%, 74.6%, and 81.2%, respectively.

We observed that the PA66/Citric Acid ($C_6H_8O_7$) membrane exhibited the lowest water absorption capacity, approximately 65.8%, compared to the other membranes. In contrast, the PA66/Benzoic Acid ($C_7H_6O_2$) membrane demonstrated the highest absorption rate, at 81.2%. One of the primary factors contributing to increased water absorption is the porous structure of the films, as the presence of pores facilitates the penetration and subsequent retention of water within the polymer matrix [9].

According to the data presented in Figure 4, the water flux under a pressure of 0.5 bar varied over 60 minutes as follows: PA66/Benzoic Acid ($C_7H_6O_2$) ranged from 260 to 85 $L \cdot m^{-2} \cdot h^{-1}$, PA66/Adipic Acid ($C_6H_{10}O_4$) from 90 to 70 $L \cdot m^{-2} \cdot h^{-1}$, PA66/Tartaric Acid ($C_4H_6O_6$) from 75 to 55 $L \cdot m^{-2} \cdot h^{-1}$, and PA66/Citric Acid ($C_6H_8O_7$) from 45 to 40 $L \cdot m^{-2} \cdot h^{-1}$.

The water flux behavior across the four membranes under different pressures revealed notable variations. Due to its porous structure,

Figure 3. Water absorption of the membranes of PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$.

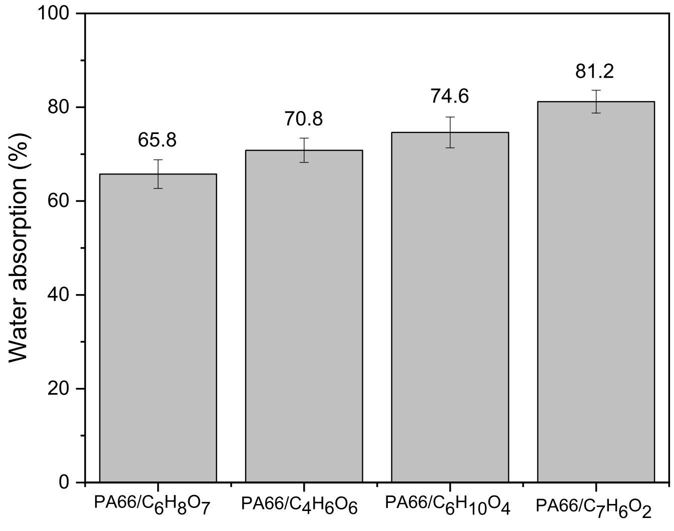
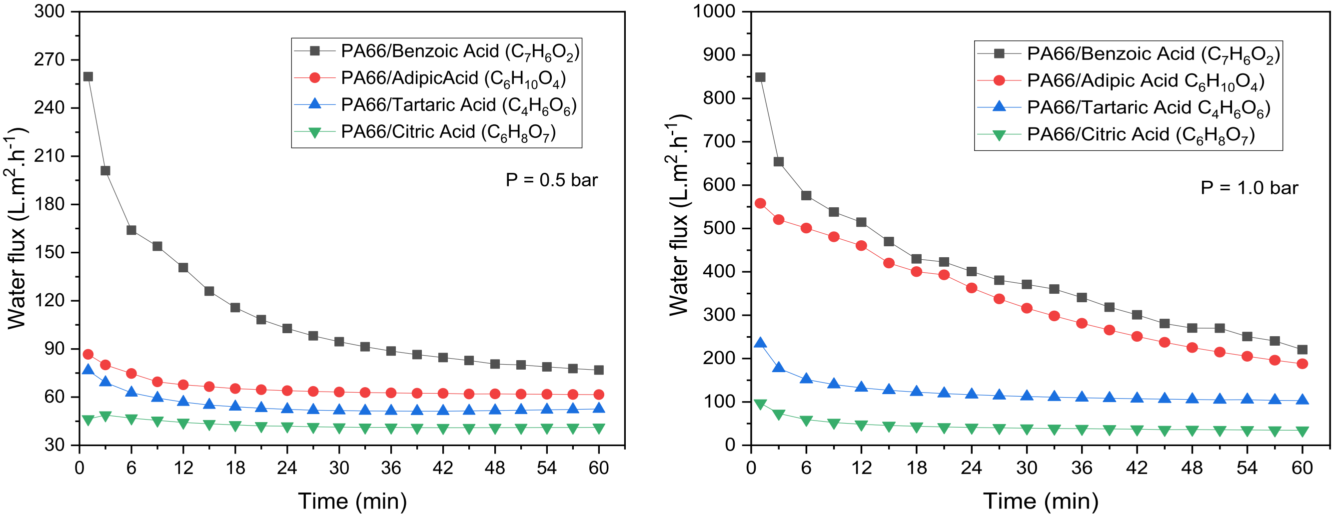


Figure 4. Water flux of the membranes of PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$ at a pressure of 0.5 and 1.0 bar.



PA66 tends to swell upon prolonged immersion in water, which can significantly hinder water passage by narrowing or obstructing pore channels. Consequently, membranes with smaller initial pore sizes exhibit further pore constriction during swelling, drastically reducing permeated flow, although not eliminating it [11].

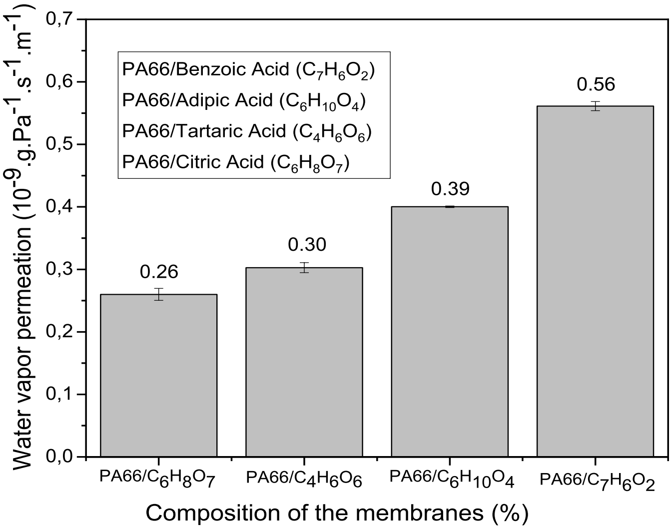
Since additives influence membrane porosity and maximum pore radius, the reduction in flow observed is consistent with structural modifications. The PA66/Benzoic Acid membrane demonstrated higher water flux, though with lower stability at pressures of 0.5 and 1 bar. Conversely, the PA66/Citric Acid membrane exhibited the lowest water flux but showed enhanced flow stability compared to the other membranes. As pressure increases, greater resistance to flow is observed due to the development of a polarization layer and gel layer on the membrane surface, which leads to increased fouling and partial clogging of surface pores [12]. Nonetheless, higher pressures can result in a proportional increase in permeated flow depending on membrane characteristics.

Determining water vapor permeation is necessary to assess the amount of water vapor transferred through the membrane. According to the information in Figure 5, it was observed that the water vapor permeation of the membranes of PA66/Citric Acid, PA66/Tartaric Acid, PA66/Adipic Acid, and PA66/Benzoic Acid were 0.26 x 10^{-9} g.Pa^{-1}.s^{-1}.m^{-1}, 0.30 x 10^{-9} g.Pa^{-1}.s^{-1}.m^{-1}, 0.39 x10^{-9} g.Pa^{-1}.s^{-1}.m^{-1}, and 0.56 x 10^{-9} g.Pa^{-1}.s^{-1}.m^{-1}, respectively.

The PA66/Citric Acid membrane presented fewer but larger pores than the other membranes, increasing water vapor permeation. In contrast, the PA66/Benzoic Acid membrane was primarily composed of smaller pores, which did not allow for effective permeation at a pressure of 1.0 bar. The introduction of acidic additives led to variations in water vapor permeation values. Membranes incorporating lower molecular weight (MW) additives exhibited higher water vapor permeation, whereas those with higher MW additives showed reduced permeability. These variations may be attributed to the incorporation of plasticizing agents, known for their strongly hydrophilic character, which enhance the mobility of water vapor through the membrane matrix [13].

Moreover, increasing the percentage of titanium dioxide (TiO_2) in the polymeric matrix led to a progressive enhancement in water vapor permeability. Membranes containing 1%, 3%, and 5% TiO_2 exhibited permeability values of 0.18 × 10^{-9}, 0.21 × 10^{-9}, and 0.23 × 10^{-9} g·Pa^{-1}·s^{-1}·m^{-1}, respectively. This increase is likely due to the hydrophilic nature of TiO_2 and its physical

Figure 5. Water vapor permeation (WVP) of the membranes of PA66/$C_7H_6O_2$, PA66/$C_6H_{10}O_4$, PA66/$C_4H_6O_6$, and PA66/$C_6H_8O_7$.



interaction with the polymer chains, acting as a porogenic agent and facilitating vapor transport through the membrane [14]. Incorporating hydrophilic additives into the polymeric solution generally enhances water vapor permeation compared to membranes prepared without such additives.

Conclusion

Flat membranes were successfully fabricated from industrial polyamide 66 (PA66) fiber waste with acidic additives using the immersion-precipitation method via the phase inversion technique. The results demonstrated that incorporating additives with different molecular weights into the PA66 solutions led to a progressive increase in viscosity, following the order of benzoic acid < adipic acid < tartaric acid < citric acid. Among the membranes evaluated, the PA66/Benzoic Acid membrane exhibited superior performance, showing the highest values for water absorption capacity, porosity, water flux, maximum pore radius, and water vapor permeation. These findings indicate that this membrane's microstructural properties are particularly favorable for microfiltration applications, especially in treating industrial effluents.

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