

Surface Modification of Polyethersulfone Membrane to Improve Its Hydrophobic Characteristics for Waste Frying Oil Filtration: Radio Frequency Plasma Treatment

Eren Tur,¹ Baran Onal-Ulusoy,² Ebru Akdogan,³ Mehmet Mutlu^{1,3}

¹Plasma Aided Bioengineering and Biotechnology (PABB) Research Group, Department of Food Engineering, Engineering Faculty, Hacettepe University, Beytepe TR 06532, Ankara, Turkey

²Department of Chemistry, Faculty of Arts and Sciences, Aksaray University, Aksaray, Turkey

³Plasma Aided Bioengineering and Biotechnology (PABB) Research Group, Bioengineering Division, Institute for Pure and Applied Sciences, Hacettepe University, Beytepe TR06532, Ankara, Turkey

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ABSTRACT: In this study, polyethersulfone (PES) membrane was subjected to surface modification using hexamethyldisiloxane (HMDSO) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in radio frequency (RF) plasma system to improve its hydrophobic property for recovery of waste frying oil. Structural and morphological changes on the membrane surfaces were characterized by contact angle measurements, Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) and atomic force microscopy (AFM). Permeate fluxes, physical and chemical properties of waste frying oil and waste frying oil-methanol micella (oil/methanol 1/3, 1/1, 1/3, v/v) after filtration through unmodified and modified PES membranes were investigated. The results showed that

PES membranes modified with HMDSO at 75 W for 5 min (discharge power-exposure time) selectively rejected total polar compounds (TPC) and free fatty acids (FFAs) of waste frying oil to the extent of 46.9–48% and 35.3–40%, respectively. Furthermore, the viscosity of waste frying oil was reduced to the extent of 9.4–12.8%. RF-plasma-treated PES membranes appeared to improve the regeneration of waste frying oils and allow these oils to be used for either repeated frying operations or biodiesel production. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3402–3411, 2012

Key words: plasma polymerization; membranes; composites; polyethersulfones; separation techniques

INTRODUCTION

Deep-fat/oil frying is extensively used in food processing. During the frying process, a combination of thermolytic and oxidative reactions take place in oils resulting in formation of polar compounds including diacylglycerols, monoacylglycerols, and free fatty acids (FFAs), monomers, and polymers which have been reported as potentially toxic for human health. The physical changes taking place in oils during frying are color darkening, rise in viscosity and foaming, and decrease in smoke-point.^{1–3} About 40% of edible oils produced in worldwide is used in frying process, and a significant amount of used frying oil is discarded according to physical properties of the oil.^{3,4} However, the degree of degradation in frying oil is often not severe, and discarded oil still has a large proportion of triglycerides.⁴ Therefore, recovery of used/waste frying oils via active filtration^{5,6}

and/or membrane treatment^{4,7–9} for repeated use in frying of foods or using these recovered oils as a feedstock in biodiesel production not only could reduce the waste disposal but also reinforce the effective use of food and agricultural resources.^{10–12}

Active filtration treatment which uses filter aid materials (silica, alumina, etc.) was investigated for regeneration of used frying oil. However, these systems have many disadvantages such as leaching of active filtration materials and metals into the oil, legal issues, and capital costs.¹³ On the other hand, membrane process has many advantages including low energy consumption, no addition of chemicals, low generation of effluents, and retention of nutrients as well as other desirable components. In the last decade, it has been shown that soluble degradation products in used frying oils could be decreased using nonporous hydrophobic membranes having silicone as active layer and polyimide or polysulfone as support layers by separating triglycerides preferentially over polar compounds including oxidation products, polymers, and pigments.^{4,7} However, the nonporous membranes were found ineffective to remove FFA resulting in their enrichment in the processed oils and also have low permeate fluxes.

Correspondence to: B. Onal-Ulusoy (bulusoy@aksaray.edu.tr).

Therefore, membrane separation processes were proposed to be the appropriate approach for the complete regeneration of used frying oils.⁸

Various techniques have been used to modify the surface of polymeric membranes.¹⁴ Recently, plasma treatment has been introduced as an alternative method for modification of polymeric membrane surfaces to change surface character (hydrophilicity or hydrophobicity), permeability, and selectivity of the membrane.¹⁵ Plasma polymerization (PP) has many advantages over conventional polymerization methods; such as short reaction time, one step process, and environmental safety. In addition to the mentioned advantages, commercial low cost membranes can be used for surface treatment, and it only changes the surface properties of the introduced material without affecting its bulk properties. Plasma-deposited polymers possess an extremely different structure. They are capable of forming deposited material containing active groups with high crosslinkages and have good stability, homogeneity, and adhesiveness. The efficiency of PP depends on gas pressure, temperature, type of solid surface and monomer, and discharge power and time of plasma action.¹⁶

To our knowledge, PP technique has not been applied to increase the hydrophobicity of membrane surface that are used in the vegetable oil industry or for recovery of used/waste frying oils recently. Therefore, polyethersulfone (PES) membranes were modified with hexamethyldisiloxane (HMDSO) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) via radiofrequency (RF) type PP to prepare membranes that are more hydrophobic than the unmodified PES membrane. Plasma discharge power and exposure time were optimized by measuring the surface free energy (SFE). Selected membranes from optimization procedure were characterized by Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) and atomic force microscopy (AFM). Attempts were also made to improve the permeate flux by diluting the feed with organic solvent (methanol). The separation performances of unmodified and PP-modified PES membranes were investigated in terms of total polar compounds (TPC), FFA content, total oxidation (TOTOX) value, and viscosity.

EXPERIMENTAL

Materials

PES membranes with MWCO 30,000 Da were purchased from Sartorius (Goettingen, Germany). According to the manufacturer catalogue, these membranes are nonbacked and finger structured. The thickness of its retentive layer is about 0.3–0.5 μm , and membrane total thickness is about 120 μm .

Surface energy of PES membrane is about 40 mJ/m^2 , and there is a small amount of polyvinylpyrrolidone entangled within the PES matrix, which may tend to enhance surface energy of the membrane material. HMDSO (98%) and HFIP (99%) were purchased from Acros Organics (Belgium) and Sigma-Aldrich (Germany), respectively. Argon (Ar) used during filtration of oils and for cleaning of plasma system was high purity. Methanol used for testing the stability of plasma-modified membranes was reagent grade. Waste sunflower frying oil, which was used several times for frying of various foods, was supplied by a local school cafeteria.

Plasma treatment

PES membrane surfaces were modified via PP technique including discharge power and exposure time with HMDSO and HFIP as precursors. RF (13.56 MHz) glow discharge plasma system (Diener Electronics, Germany) was used for modification. The system was consisted of a vacuum chamber with two inlets; one inlet for Ar and one for the monomer, two pressure gauges for both inlets, frequency power components with RF, and electrodes wrapped around the vacuum chamber.

Samples were placed at the plasma chamber, and the reactor was evacuated to 0.1 mbar, and then Ar gas was left to flow at a constant pressure of 0.3 mbar for 10 min to remove the remaining air in the chamber. The flask containing 5 mL of precursor was attached to the monomer inlet. Monomer flask was chilled with liquid nitrogen to degas the monomer in the flask until the systems reached to its initial pressure (0.1 mbar). When the degassing was finished, system was kept under vacuum for 10 min. After defrosting the precursor, monomer valve was opened, and monomer vapors were allowed to flow at a constant pressure and time (0.2 mbar; 5 min) to fill the chamber. Then, power was adjusted, and the solid surfaces were exposed to glow discharge. At the end of the process, monomer valve was closed, and Ar feed valve opened and adjusted to 0.3 mbar pressure. The system was fed with Ar gas for 10 min to remove possible residue monomer gas from the chamber. Modified membrane samples were kept at 0.1 mbar for 10 min under vacuum, and the process was turned off.

Contact angle measurements and surface energy calculations

Contact angle measurements of membranes before and after plasma modification were done by captive bubble technique. The advantage of the captive bubble technique over the other techniques is the complete coverage of the surface with water.^{17–20}

Therefore, surface energy of the interaction between water and solid is supposed to be unchanged during measurement. A special microscope (QX3 computer microscope, 60X, Intel), and a computer system were used to measure contact angles in a three-phase system consisting of water, solid surface, and bubbles of air or liquid *n*-octane.

The glass cell was filled up with ultrapure water, and 2 cm² membranes were placed in it. A special L-shaped syringe needle containing *n*-octane or gas (air) released bubbles beneath the sample. The volume of these bubbles did not exceed 5 μL. A computer screen provided an image of the captive bubble. The supporting computer software (Wettability Pro Classic, version 2.0 from Czech Republic) used these data to calculate the contact angles between *n*-octane and the solid surface, θ_{or} , and between air and solid surface, θ_a . Contact angle experiments were repeated 5 times for each surface to eliminate experimental errors.

The total SFE (γ_{sv}) and the interfacial free energy of water and solid surface (γ_{sw}) of each membrane were determined by contact angle measurements. Contact angle results of air and *n*-octane from captive bubble experiments were used to find the polar (γ_{sv}^p) and dispersive (γ_{sv}^d) interaction components of total SFE. Each parameter was calculated from the equations given by Gulec et al.²¹

FTIR-ATR measurements

FTIR spectra of the samples were recorded using a Perkin-Elmer Spectrum One Fourier Transform Infrared Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. To obtain ATR spectra, Perkin-Elmer Horizontal ATR accessory with ZnSe (45° edges) crystal was used. In this technique, the samples were pressed on ZnSe crystal using a computer-controlled very sensitive pressure arm. The computer had controlled pressing the sample on the sensor to obtain a good contact between the sample and the infrared element (ZnSe crystal) at the interface. All spectra were recorded 100 interferograms at a resolution of 4 cm⁻¹ to yield high signal to noise ratio.

AFM analysis

For screening the topographical changes on the surfaces of unmodified and PP-modified membranes, AFM was used [PSIA (model: XE-100E)]. AFM measurements were performed in contact mode, and an area of 3 μm × 3 μm was scanned at a scan rate of 1 Hz with 256 × 256 pixel resolution. The AFM images were further processed, and the mean square roughness (rms) values were determined with XEI software (PSIA, Park Systems, Korea).

Membrane filtration system

The stirred cell for flat membranes was purchased from Millipore (Billerica, MA) and operated in the batch mode.

Permeate flux measurements

The stirred cell was operated in a batch mode. Experiments were conducted under the Ar atmosphere, and the operating pressure in the stirred cell was maintained by adjusting the pressure regulator of the Ar cylinder. The membrane cell was stirred by a magnetic stirrer, and agitation was provided by the magnetic spin bar fitted into the cell. Oil samples or oil-solvent micella were placed into water bath at 40°C for 15 min before transferring to membrane cell as a feed. Temperature of the magnetic stirrer was also set to 40°C and maintain constant oil temperature during filtration. Unmodified and PP-modified membranes were mounted in the stirred cell, charged with 80 mL of oil or oil-solvent micella, closed, and operated at 2.5 bar Ar pressure. After closing the cell system, the stirring bar was adjusted to 800 rpm, and filtration was started with opening the Ar gas at 2.5 bar pressure. Permeate was collected through a port beneath the membrane support with help of a pump until 50 mL of oil was accumulated. The total and oil permeate fluxes J (kg/m² h) were calculated by eq. (1):

$$J_1 = W_1/(A^*t) \quad (1)$$

$$J_2 = W_2/(A^*t) \quad (2)$$

where W_1 and W_2 are the weights of total permeate and oil content in the permeate (kg), A is the effective membrane area (17.3×10^{-4} m²), and t is the time taken for collecting permeate (h).

Determination of physical and chemical properties of oils before and after filtration

Physical and chemical properties of oil samples in permeates, and initial properties of waste frying oil were determined according to the following methods. The FFA, peroxide value (PV), *p*-anisidine value (*p*-AV), and TPC were determined using AOCS method Ca 5a-40, AOCS method Cd 8-53, AOCS method Cd 18-90, and AOCS method Cd 20-91, respectively.²² TOTOX value, which is an index of oil quality and stability, was calculated according to the following equation:

$$\text{TOTOX Value} = p - \text{AV} + (2 \times \text{PV}) \quad (3)$$

Viscosities of oils were determined using a Brookfield Cone/Plate Model Viscometer at 25°C.

TABLE I
Total SFE and Interfacial Energy Values of PES Membranes Modified with HMDSO Under Different PP Parameters

Monomer	Plasma parameters		Surface free energy values (mJ/m ²)			
	Discharge power (W)	Exposure time (min)	γ_{Sv}^d	γ_{Sv}^p	γ_{Sv}	γ_{Sw}
Plain	–	–	16 ± 3	22 ± 3	38 ± 3	7 ± 1
HMDSO	20	10	84	0	84	71
	40	10	1	10	11	29
	60	5	84	0	84	71
	60	30	84	0	84	71
	75	5	118	0	118	89
	75	30	70	0	70	65
	100	5	7	7	14	24
	100	30	29	2	31	34

Performance parameter

The performance of the membrane process was expressed in terms of percent increment (PI) of permeate flux and percent reduction (PR) of each chemical or physical property of the oil. PI and PR were calculated as follows:

$$PI = 100 * (J_u - J_m) / J_u \quad (4)$$

where J_u and J_m represent the permeate flux obtained from unmodified membrane and each modified membranes for the same feed type, respectively.

$$PR = 100 * (C_w - C_p) / C_w \quad (5)$$

where w and p represent the waste frying oil before filtration and after filtration (processed oil), respectively. C_w and C_p are the concentration of each chemical or physical property in waste frying oil before filtration and processed oils, respectively.

Statistical analysis

Data were analyzed statistically by using the analysis of variance by means of the general linear models procedure of a SPSS 16.0 software package. Statistical significance is expressed at the $P \leq 0.05$ level unless otherwise indicated. Significant differences between means were further determined by Duncan's multiple-range test.

RESULTS AND DISCUSSION

Contact angle measurements and total SFE

Hydrophobic and superhydrophobic surfaces of various substrates are of great interest for fundamental and applied research.^{23–26} The hydrophobicity of a surface depends mainly on its surface energy, chemical functional groups, and physical geometry.^{27,28} HMDSO and HFIP are the most common materials

used for the generation of hydrophobic coatings by PP technique.^{29–32} Surface properties of PES and its modified form with HMDSO and HFIP by PP were assessed in terms of hydrophilicity, hydrophobicity, and total SFE by contact angle measurements. γ_{Sv}^d (dispersive component of SFE), γ_{Sv}^p (polar component of SFE), γ_{Sv} (total SFE or surface energy), and γ_{Sw} (interfacial free energy of water and solid surface) values calculated from contact angles measurements for unmodified and modified PES membranes are presented in Tables I and II.

High γ_{Sv}^p value indicates high hydrophilicity, whereas high γ_{Sv}^d indicates high hydrophobicity. A high γ_{Sw} value indicates a weak interaction of water with the solid substrate (hydrophobic), whereas a low γ_{Sw} value indicates a strong interaction of water with solid surface (hydrophilic).

The γ_{Sv}^d , γ_{Sv}^p , γ_{Sv} , and γ_{Sw} values of the unmodified PES membrane are given in Table I. The γ_{Sv} value calculated for PES membrane was found as 38 ± 3 mJ/m². This result was very close to the value given by the manufacturer (40 mJ/m²) showing that the SFE calculations used in this paper were consistent. In this study, the hydrophobicity of modified and unmodified surfaces was compared according to γ_{Sw} values.

During the modification via PP, deposition and/or etching reactions may occur on the surface of the substrates. The dominant reaction is determined by the PP parameters, which are mainly the discharge power and exposure time. Since the precursors used in our systems are of hydrophobic nature, it is expected that the deposition of these precursors would change the surface to high γ_{Sw} values. On the other hand, etching of the membrane surfaces might yield to surfaces with decreased γ_{Sw} values. This phenomenon was the reason of using different PP parameters in an attempt to optimize PP parameters for having different γ_{Sw} values. The γ_{Sv}^p , γ_{Sv}^d , γ_{Sv} , and γ_{Sw} values of the PES membranes modified with HMDSO at different PP parameters are given in Table I. According to these results, γ_{Sw} values

TABLE II
Total SFE and Interfacial Energy Values of PES Membranes Modified with HFIP
Under Different PP Parameters

Monomer	Plasma parameters		Surface free energy values (mJ/m ²)			
	Discharge power (W)	Exposure time (min)	γ^d_{Sv}	γ^p_{Sv}	γ_{Sv}	γ_{Sw}
Plain	–	–	16 ± 3	22 ± 3	38 ± 3	7 ± 1
HFIP	20	10	23	19	42	8
	40	10	37	24	61	7
	60	5	15	24	39	6
	60	30	32	36	68	2
	75	5	39	31	70	5
	75	30	49	38	87	6

were increased after modification compared with the unmodified PES membrane for all PP parameters used in RF-PP. The increase in γ_{Sw} values indicated that the surfaces had become more hydrophobic than the PES membrane. Indeed, for all the PP parameters applied, the polar component of SFE was decreased compared with the PES membrane. The highest γ_{Sw} value (89 mJ/m²) and the lowest γ^p_{Sv} (0 mJ/m²), i.e., the most hydrophobic surface character was obtained from the PES membrane modified with HMDSO in RF-PP system at 75 W for 5 min (Table I) followed by membranes modified at 20 W for 10 min, 60 W for 5 min, and 60 W for 30 min.

Among the PES membranes modified with HFIP (Table II), the γ_{Sw} values were not significantly changed compared with the γ_{Sw} value of unmodified PES which indicated that the modification with HFIP monomer was not effective for increasing the hydrophobicity of PES membrane.

According to results shown in Tables I and II, membranes with higher γ_{Sw} value and lower γ^p_{Sv} (higher hydrophobicity) were chosen for further investigation. These membranes were; PES modified with HMDSO at 20 W for 10 min, 60 W for 5 min, and 75 W for 5 min in RF-PP system. Even though membranes modified at 60 W for 5 min and 60 W

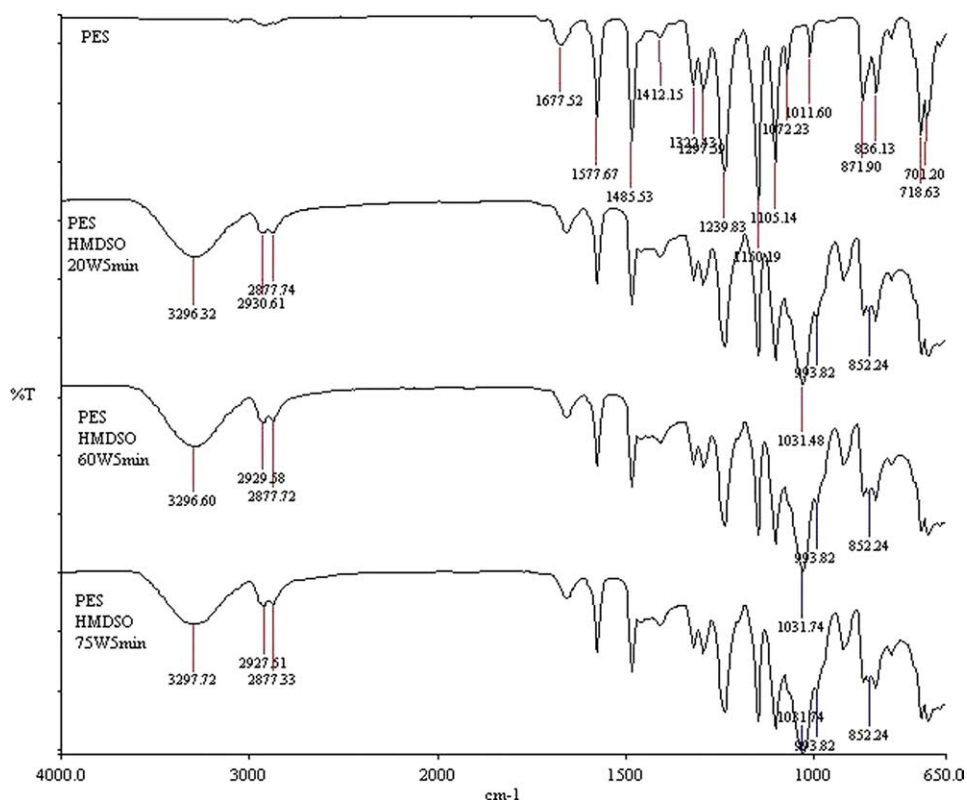


Figure 1 FTIR-ATR spectra of unmodified PES membrane, PES-modified HMDSO at 20 W for 10 min, PES modified at 60 W for 5 min, and PES modified at 75 W for 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

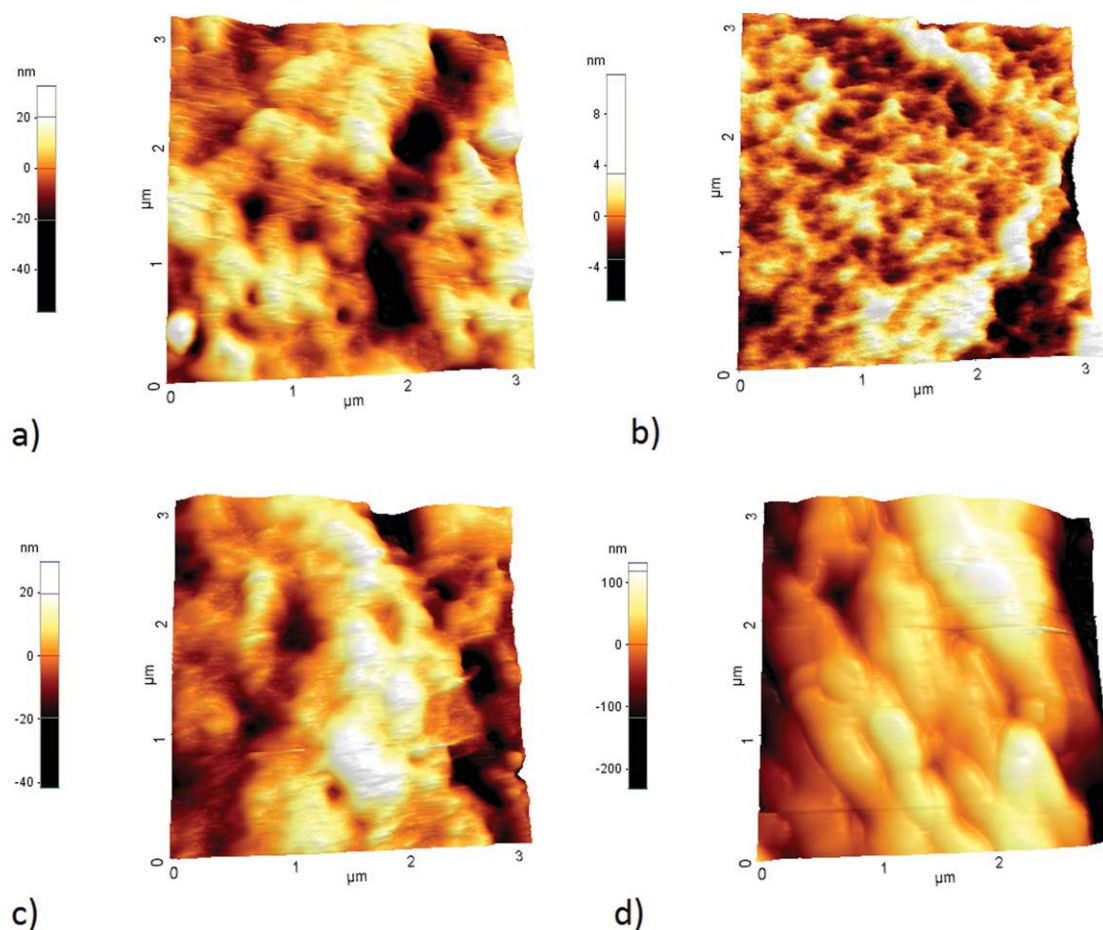


Figure 2 AFM images of (a) unmodified PES membrane (rms value: 10 nm), (b) PES-modified HMDSO at 20 W for 10 min (rms value: 1 nm), (c) PES modified at 60 W for 5 min (rms value: 10 nm), and (d) PES modified at 75 W for 5 min (rms value: 72 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for 30 min had same γ_{Sw} and γ_{Sv}^P values, a membrane modified at 60 W for 5 min was chosen because of the lower exposure time.

Chemical surface analysis of membranes with FTIR-ATR

Chemical surface analysis of three selected membranes was carried out with FTIR-ATR to confirm the plasma modification on the surface.

FTIR-ATR spectra of the unmodified PES membrane and its modified forms with HMDSO are given in Figure 1. On the FTIR-ATR spectra, the broad band at about 3300 cm^{-1} observed for all HMDSO-modified surfaces was attributed to the Si—OH vibration. The Si—OH groups on the surface may be caused by due to the oxidative effect of plasma. The bands at 2928 and 2876 cm^{-1} were assigned to the asymmetric and symmetric CH_3 stretching vibrations of the methyl group, respectively. On the other hand, Si—O—Si bonds have two characteristic IR absorption bands: one was an asymmetrical stretching mode at around 1031 cm^{-1} , and

the other was bending mode at around 851 cm^{-1} . The wagging mode of Si—CH—Si and the stretching mode of Si—O—C were observed in the region of $1100\text{--}1000\text{ cm}^{-1}$. These bands might overlap with the intense band at about 1031 cm^{-1} for Si—O—Si asymmetrical stretching mode. In addition, the shoulder at 995 cm^{-1} was assigned to the rocking mode of Si—CH. FTIR-ATR spectra of modified PES membranes showed that HMDSO was successfully deposited on the membrane surfaces (Fig. 1).

Surface morphology study of plasma-treated membrane surfaces with AFM

AFM images of unmodified and plasma-modified PES membranes are given in Figure 2(a–d). AFM images showed topographic changes of unmodified and three selected modified PES membranes. Surface topography differences between unmodified and modified membranes indicated a modification on membrane surfaces. Unmodified PES membrane showed relatively porous and rougher surface with a rms value of 10 nm, whereas PES membrane

TABLE III
Total Permeate Fluxes (kg/m² h) of Waste Frying Oil (WFO) and WFO–Methanol Micellas Through Unmodified and PP-Modified PES Membranes

Feed type	Oil/methanol ratio (v/v)	Unmodified	PP-modified membranes					
			20 W 10 min	PI (%)	60 W 5 min	PI (%)	75 W 5 min	PI (%)
WFO		1.9 ± 0.1 _a ^a	2.0 ± 0.0 _a ^a	5.3	2.3 ± 0.1 _a ^b	21.0	2.4 ± 0.0 _a ^b	26.3
Micella I	3/1	4.8 ± 0.1 _b ^{a,b}	4.5 ± 0.0 _b ^a	−6.3	4.8 ± 0.3 _b ^{a,b}	0.0	5.0 ± 0.2 _b ^b	4.2
Micella II	1/1	5.1 ± 0.2 _b ^a	6.3 ± 0.1 _c ^c	23.5	5.5 ± 0.2 _c ^{a,b}	7.8	6.1 ± 0.3 _c ^{b,c}	19.6
Micella III	1/3	6.5 ± 0.6 _c ^a	7.4 ± 0.3 _d ^{a,b}	13.8	8.4 ± 0.3 _d ^b	29.2	8.4 ± 0.3 _d ^b	29.2

^{a-c}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

^{a-d}, values in the same column for the same sample with different subscript letters are significantly different ($P \leq 0.05$).

modified at 20 W for 10 min had a lower rms value (1 nm) indicating that the membrane surface had become smoother. PES modified at 60 W for 5 min had a rms value of 10 nm, which was close to the rms value of the unmodified PES. PES modified at 75 W for 5 min had the highest rms value of 72 nm among three modified membranes. From these results, it might be concluded that the plasma modification of PES membrane surface with HMDSO at 20 W for 10 min made the surface smoother, whereas modification of PES surface with same precursor at 75 W for 5 min made the surface rougher. On the other hand, modification with HMDSO at 60 W for 5 min did not change the surface roughness of the PES significantly. The rms values showed no direct correlation with the surface polarities of the membranes, because the rms value of the PES modified with HMDSO at 60 W for 5 min was the same as the rms value of the unmodified PES, however, the polarities of these membranes were significantly different, 17% and 92%, respectively.

Permeate flux measurements of waste frying oil and waste frying oil–methanol micella

Total and oil permeate fluxes of waste frying oil and waste frying oil diluted with methanol through unmodified and PP-modified PES membranes are

given in Tables III and IV. Total permeate fluxes obtained from either unmodified or modified membranes were increased significantly with the dilution of oil with methanol ($P \leq 0.05$). For the same feed type except Micella II (oil–methanol 1/1, v/v), the highest total permeate fluxes were obtained with the filtrations through PES membrane modified at 75 W for 5 min (Table III). Even though PES membrane modified at 60 W for 5 min had higher total permeate flux for Micella II than PES membrane modified at 75 W for 5 min, that difference was not statistically significant ($P > 0.05$).

The oil permeate fluxes through unmodified and PP-modified PES membranes did not change significantly with an increase in methanol dilution up to 1/1 to undiluted oil ($P > 0.05$). At highest methanol dilution (3/1, v/v), however, the oil flux increased during filtration through PES membranes modified at 60 W for 10 min or 75 W for 5 min compared with unmodified PES membranes ($P \leq 0.05$).

Physical and chemical properties of oils after filtration

The initial properties of the waste frying oil are given in Tables V–VIII. TPC is the chemical index used for determination of the degree of cumulative degradation occurred in oil. TPC value of fried oil

TABLE IV
Permeate Fluxes^d (kg/m² h) of Waste Frying Oil (WFO) and WFO–Methanol Micellas Through Unmodified and PP-Modified PES Membranes

Feed type	Oil/methanol ratio (v/v)	Unmodified	PP-modified membranes					
			20 W 10 min	PI (%)	60 W 5 min	PI (%)	75 W 5 min	PI (%)
WFO		1.9 ± 0.08 _a ^a	2.0 ± 0.04 _a ^a	5.3	2.3 ± 0.09 _a ^b	21.0	2.4 ± 0.12 _a ^b	26.3
Micella I	3/1	1.9 ± 0.04 _a ^a	2.0 ± 0.15 _a ^a	5.3	2.4 ± 0.13 _b ^b	26.3	2.3 ± 0.11 _a ^b	21.1
Micella II	1/1	1.7 ± 0.11 _a ^a	2.4 ± 0.01 _b ^b	41.2	2.4 ± 0.12 _a ^{b,c}	41.2	2.6 ± 0.07 _a ^c	52.9
Micella III	1/3	2.1 ± 0.21 _a ^a	2.6 ± 0.19 _b ^b	23.8	3.3 ± 0.18 _b ^b	57.1	3.3 ± 0.16 _b ^b	36.4

^{a-c}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

^a and ^b, values in the same column for the same sample with different subscript letters are significantly different ($P \leq 0.05$).

*Values are calculated oil flux without methanol fraction.

TABLE V
Total Polar Compound (TPC; %) in Permeates of Waste Frying Oil (WFO) and Waste Frying Oil–Methanol Micella

Feed type	Oil/methanol ratio (v/v)	Initial	Unmodified	PR (%)	PP-modified membranes					
					20 W 10 min ^e	PR (%)	60 W 5 min	PR (%)	75 W 5 min	PR (%)
WFO		23.5 ^e	19.7 ^d	16.1	17.9 ^c	24.1	13.9 ^b	41.1	12.5 ^a	47.0
Micella I	3/1	23.5 ^e	19.6 ^d	16.7	16.7 ^c	29.0	14.0 ^b	40.6	12.2 ^a	48.0
Micella II	1/1	23.5 ^e	18.8 ^d	20.0	17.2 ^c	27.1	14.3 ^b	39.3	12.5 ^a	46.9
Micella III	1/3	23.5 ^e	19.6 ^d	16.9	17.2 ^c	27.0	14.4 ^b	38.7	12.4 ^a	47.5

^{a–d}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

**Values in the same column for the same membrane are not significantly different ($P > 0.05$).

TABLE VI
Total Oxidation (TOTOX) Values of Permeates of Waste Frying Oil (WFO) and Waste Frying Oil–Methanol Micella

Feed type	Oil/methanol ratio (v/v)	Initial	Unmodified ^e	PR (%)	PP-modified membranes					
					20 W 10 min ^e	PR (%)	60 W 5 min ^e	PR (%)	75 W 5 min ^e	PR (%)
WFO		62.9 ^d	59.6 ^{b,c}	5.1	55.8 ^b	11.3	51.6 ^a	18.0	51.7 ^a	17.8
Micella I	3/1	62.9 ^e	60.2 ^d	4.2	56.4 ^c	10.3	52.3 ^b	16.8	49.1 ^a	21.9
Micella II	1/1	62.9 ^d	59.9 ^c	4.6	55.0 ^c	12.6	49.9 ^a	20.6	49.6 ^a	21.0
Micella III	1/3	62.9 ^c	60.2 ^c	4.2	55.8 ^c	11.2	51.5 ^a	18.0	49.4 ^a	21.3

^{a–d}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

**Values in the same column for the same membrane are not significantly different ($P > 0.05$).

represents nontriglycerides fraction of the oil, which consists of polymers and decomposition products. TPC value is one measure to determine the fry life of an oil. In many countries, regulations have limited the maximum permissible amount of TPC in frying oil to 25% by mass. The PV is used for the determination of the radicals from various reactions of triglycerides, and *p*-AV gives the amount of unsaturated and nonvolatile α - and β -aldehydes that are secondary products of oxidation. The TOTOX value is the total oxidation value occurring in the primary and secondary oxidation. TPC and TOTOX values of the unmodified and PP-modified membrane-processed oils at different methanol dilutions are presented in Tables V and VI.

Undiluted and diluted oils filtered through PES membrane modified at 75 W for 5 min had lower TPC than did both unmodified and other PP-modified PESs tested. This membrane selectively rejected TPC to the extent of 47–49% for waste frying oil (Table V), and PES membrane modified at 60 W for 10 min and 75 W for 5 min had significantly lower oxidation products (given as TOTOX) than did the other PESs tested ($P \leq 0.05$; Table VI). In case of diluted frying oil, PES membrane modified at 75 W for 5 min selectively rejected oxidation products to the extent of 21–22%. The rejection potentials of unmodified and PP-modified PES membranes for both parameters were not affected from the increase in methanol dilution in the feed.

TABLE VII
Free Fatty Acid (FFA) (% Oleic Acid) Values of Permeates of Waste Frying Oil (WFO) and Waste Frying Oil–Methanol Micella

Feed type	Oil/methanol ratio (v/v)	Initial	Unmodified ^c	PR (%)	PP-modified membranes					
					20 W 10 min ^c	PR (%)	60 W 5 min ^c	PR (%)	75 W 5 min ^c	PR (%)
WFO		1.70 ^d	1.62 ^d	4.7	1.33 ^c	21.8	1.18 ^{a,b}	30.6	1.10 ^a	35.3
Micella I	3/1	1.70 ^c	1.60 ^c	2.4	1.31 ^b	21.8	1.09 ^a	31.8	1.02 ^a	37.1
Micella II	1/1	1.70 ^c	1.66 ^c	2.4	1.26 ^b	25.9	1.12 ^a	34.1	1.06 ^a	37.6
Micella III	1/3	1.70 ^c	1.66 ^c	5.9	1.33 ^b	22.9	1.16 ^{a,b}	35.9	1.07 ^a	40.0

^{a–d}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

**Values in the same column for the same membrane are not significantly different ($P > 0.05$).

TABLE VIII
Viscosity (mPa s) Values of Permeates of Waste Frying Oil (WFO) and Waste Frying Oil–Methanol Micella

Feed type	Oil/methanol ratio (v/v)	Initial	Unmodified	PR (%)	PP-modified membranes					
					20 W 10 min	PR (%)	60 W 5 min	PR (%)	75 W 5 min	PR (%)
WFO		56.9 ^d	53.6 ^c _a	5.7	52.1 ^b _a	8.4	52.4 ^{a,b} _c	7.9	51.5 ^c _a	9.4
Micella I	3/1	56.9 ^d	53.2 ^c _a	6.2	53.4 ^c _b	6.1	52.0 ^b _b	8.5	49.6 ^a _a	12.8
Micella II	1/1	56.9	53.8 ^d _a	5.4	52.7 ^c _b	7.3	51.6 ^b _a	9.3	50.0 ^b _b	12.1
Micella III	1/3	56.9 ^d	54.3 ^c _a	4.5	53.3 ^{b,c} _b	6.3	52.3 ^b _b	8.1	50.7 ^a _b	10.9

^{a–d}, values in the same row for the same sample with different superscript letters are significantly different ($P \leq 0.05$).

^{a–c}, values in the same column for the same sample with different subscript letters are significantly different ($P \leq 0.05$).

The FFA value indicates the hydrolysis of the oils. In many countries, FFA value is still used as the index for regulation of frying oil, but this value tends to increase or decrease during successive fryings.³ Although determination of FFA content of frying oil is not a reliable method for discarding oil used in repeated frying operations, it is important to quantify FFA separately in case of using these oils as a feedstock in biodiesel production. The base catalysts used in transesterification process is reported to be very sensitive to the level of FFA, which should not exceed a certain limit recommended to avoid deactivation of catalyst, formation of soaps, and emulsion.¹⁰ Sharma et al.³³ reviewed the literature and found that when waste cooking oil is used as a feedstock, the limit of FFA is a little bit relaxed, and the value a little beyond 1% (i.e., 2 mg KOH/g) did not have any adverse effect on the methyl ester conversion. The initial FFA content of waste frying was 1.70%, and PES membranes modified at 60 W for 5 min and 75 W for 5 min could reduce FFA content of oil up to 1.1% and 1.0%, respectively (Table VII). Similar to TPC and TOTOX values, methanol dilution works as well for FFA reduction performance of the membranes tested.

Viscosity of oils increases during frying due to the formation of polymers.⁶ The viscosity values of oil in membrane permeates were given in Table VIII. The viscosity of waste frying oil was reduced to the extent of 8% (from 56.9 to 52.4) and 9.4% (from 56.9 to 51.5) using PES modified at 60 W for 5 min and 75 W for 5 min, respectively. In case of membrane processing of methanol-diluted oils, membrane modified at 75 W for 5 min had significantly lower viscosity values compared with the other membranes tested ($P \leq 0.05$), and it provided 9.4–12.8% reduction in viscosity. The decline in viscosity is a direct indication of reduction in polymers, which are the high molecular weight fraction of the degradation products. Dilution of oil with methanol improved the viscosity reduction potential of PES membranes modified at 60 W for 5 min and 75 W for 5 min significantly ($P \leq 0.05$).

CONCLUSIONS

This study has shown a novel way of using PP technique to prepare hydrophobic composite membranes for filtration of waste/used frying oils which have considerably high polar compounds than fresh oils. During membrane filtration, triglycerides permeated preferentially compared with the polar compounds including oxidation and hydrolysis products and polymers. PP-modified membrane filtration approach appeared to improve the life of waste frying oil by recycling and its use in biodiesel production. Thereby, it could reduce fried food or biodiesel production costs and waste disposal. In case of repeated use of same oil for frying, reduction in TPC, TOTOX, FFA, and viscosity values are necessary from a health point of view. Moreover, the reduction in viscosity of used frying oil would also result in reducing oil absorption in the fried foods. Even though the unmodified and modified PES membranes had much better permeate fluxes than other membranes used for filtration of waste frying oil^{4,7} having active layers different from PES or HMDSO, permeate flux would still need to be improved to adopt the membranes in commercial application.

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