

Surface Modification of Polypropylene Membrane by Acrylate Epoxidized Soybean Oil to be Used in Water Treatment

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Received 21 January 2011; accepted 16 July 2011

DOI 10.1002/app.35269

Published online 28 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Surface modification of a microporous polypropylene (PP) membrane was performed by graft polymerization of acrylated epoxidized soybean oil (AESO) using UV radiation. This is a simple, environmentally friendly, and low cost method. The factors affecting the grafting degree such as monomer concentration and reaction time were studied. The morphological and microstructure changes of the membrane were characterized by scanning electron microscopy (SEM) and information regarding elemental composition was obtained by energy dispersive X-ray spectroscopy (EDS). Surface functionalization was studied by X-ray photoelectron spectroscopy (XPS). Thermal properties were analyzed by differential scanning calorime-

try (DSC). The hydrophilicity increment was confirmed by pure water contact angle and swelling measurements. The filtration capability of the modified membrane was analyzed by determining color, turbidity, and chemical oxygen demand (COD) removal from a residual raw water. The results indicated that the contact angle of pure water on the grafted membrane decreased from 90° to 57°. The modified membrane shows filtration capability by removing color in 52% and reducing 95% of turbidity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E147–E153, 2012

Key words: surface modification; acrylated epoxidized soybean oil; polypropylene (PP); graft polymerization

INTRODUCTION

Over decades, polymer surface modification has been an important issue in many fields.^{1,2} In several applications, polymeric surfaces must be chemically modified to add desirable features such as change in hydrophobic character, keeping other original polymer properties unchanged. Since most polymer surfaces are hydrophobic and nonpolar, they have problems in adhesion, coating, painting, lamination, packaging, and colloidal stabilization.³ To overcome such drawbacks, a significant amount of research has been devoted to surface modification of polymeric materials. As result of these attempts, different chemical and physical techniques have been developed. Within this context, several synthetic routes can be employed to introduce graft chains into the

system of interest. UV,^{4–6} plasma,^{7–10} γ -ray,^{11–15} and O₃¹⁶ initiated graft polymerization have been used to graft monomers. Polypropylene (PP) is widely used in a variety of industrial applications such as waste water treatment and separation process, because of its low cost and its good mechanical, thermal, and chemical stability. However, the hydrophobicity of PP membrane limits its use within the membrane industry. Many monomers have been reported in the literature to be used for modified PP surface membrane.^{17–19}

Vegetable oils represent a promising route to renewable chemicals and polymers due to their ready availability, inherent biodegradability, and low toxicity.²⁰ Chemically, vegetable oils consist of mainly triglycerides formed between glycerol and various fatty acids. The carbon–carbon double bonds in the fatty acid chains of the vegetable oils can undergo various reactions to append different polymerizable functionalities, such as acrylates, to increase the reactivity of the vegetable oils.²¹ During the last decade, a variety of vegetable oil based polymeric systems have been developed.²² Acrylated epoxidized soybean oil (AESO Fig. 1), synthesized from the reaction of acrylic acid with epoxidized

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Contract grant sponsor: SIyEA of UAEMex; contract grant numbers: 2618/2008, 2796/2009.

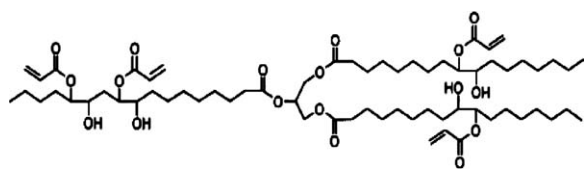


Figure 1 Acrylate epoxidized soybean oil (AESO).

soybean oil, has been extensively studied in polymers and composites.²³ AESO contains both residual unreacted epoxy groups and newly formed hydroxyl groups, both of which can be used to further modify AESO.^{21,23}

We are interested in modifying PP membrane using vegetable oil as monomer to produce a sustainable membrane, which has filtration capability and after reuse, could have the possibility of biodegradation. In this study we report the use of acrylated epoxidized soybean oil as a monomer for a graft polymerization over a PP membrane by an easy, low cost and environmentally friendly method for microporous polypropylene membrane surface modification. This process consists of a graft polymerization of acrylated epoxidized soybean oil by using UV radiation method. This method does not involve temperature or photoinitiator. The irradiation technique is a clean and effective method for polypropylene modification. The effects of polymerization conditions on the grafting degree were analyzed. ATR-FT-IR, SEM-EDS, XPS, and water contact angle characterized the grafted membranes. Finally, the modified membrane was applied to residual raw water filtration.

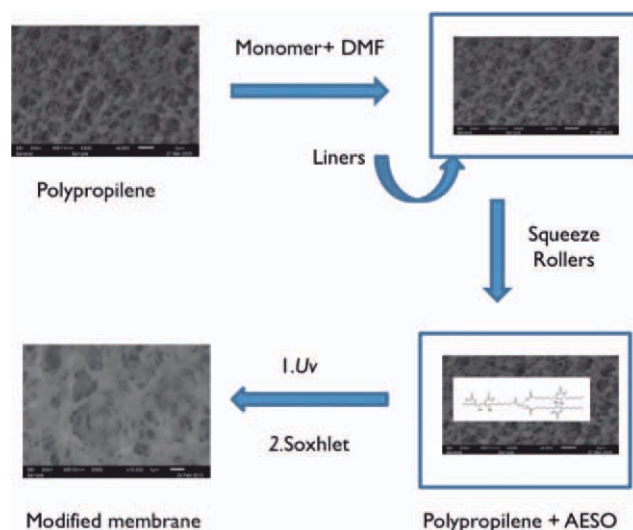
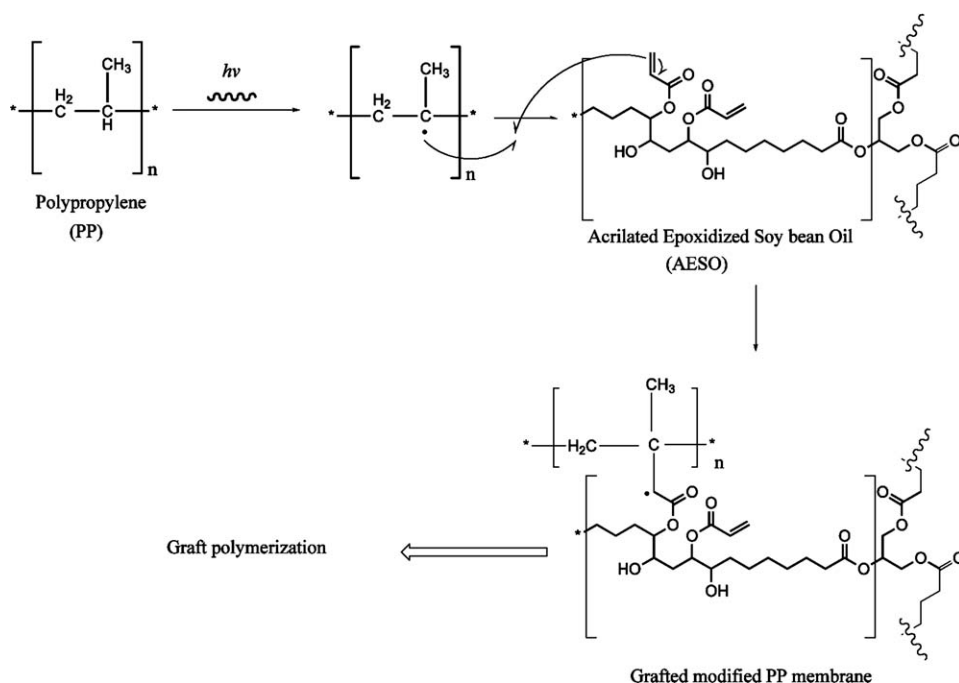


Figure 2 Schematic process of grafting acrylate epoxidized soybean oil on the surface of PP membrane using radiation UV [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Flat sheets of polypropylene microporous membrane from 3M company were used as the grafting substrate. Its pore size was 0.45 μm with a thickness of 114 μm and a porosity of 84.6%. Commercial acrylated epoxidized soybean oil and dimethylformamide were provided by σ -Aldrich and were used without prior treatment.



Scheme 1 Possible mechanism for grafting AESO onto PP membrane.

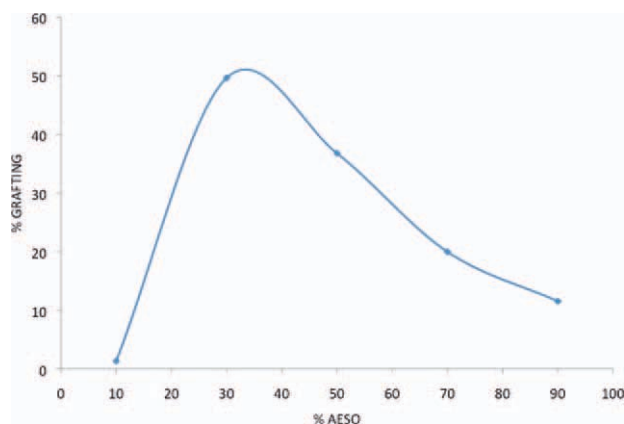


Figure 3 Effect of acrylated epoxidized soybean oil concentration on grafting degree. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Wastewater samples were collected from a treatment plant located in an industrial park. This facility receives the industrial discharge of 144 different factories. All of the industrial effluents enter the waste treatment plant together. The samples were collected at the biological activated sludge reactor in plastic containers and cooled down to 4°C.

Graft polymerization

The polypropylene membranes were cut into square shape pieces (5 × 5 cm) that were immersed into a solution of AESO-DMF between two liners, placed in squeeze rollers and transferred to a glass plate. Membranes were then irradiated with UV for 4 h. After this time the sample was removed from the glass plate and immersed into ethanol and were extracted (Soxhlet) with hot methanol for 24 h to remove the residual monomer. The grafted membrane was dried under vacuum for 1 h. The degree of AESO grafting was calculated from the equation

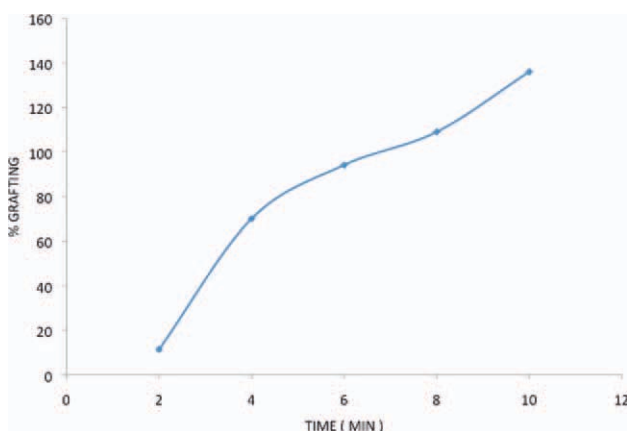


Figure 4 Grafting yield of AESO onto PP membrane as function of reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

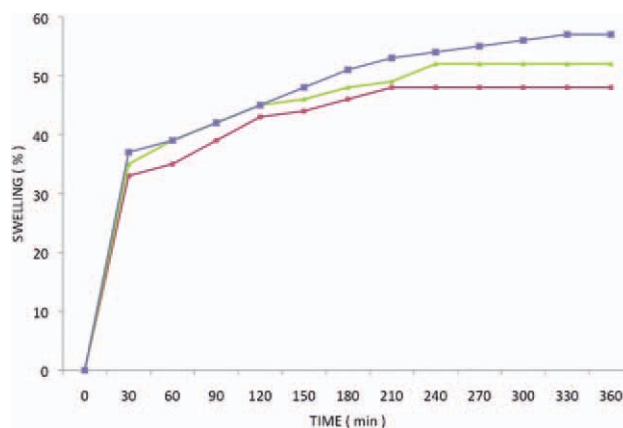


Figure 5 Swelling as function for grafting yields of PP modified as different graft percentages: (χ) 10%, (ρ) 30%, and (\subseteq) 50%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\%D_g = (W_1 - W_0)/(W_0) \times 100$, where W_0 and W_1 are the mass of the unmodified membrane and grafted PP membrane, respectively. The schematic process of grafting on the surface of polypropylene membrane using UV radiation method is illustrated in Figure 2.

Characterization

ATR/FTIR (attenuated total reflectance technique) spectra of membranes before and after modification were obtained using a Perkin-Elmer ATR-FTIR. Thermal stability (DSC) was measured by using a thermogravimetric analyzer TA Instrument. X Ray diffraction patterns were collected by using a Bruker D8 Advance, Cu- $k\alpha$ at 1.5404 Å at 2θ 5–60° at 30 kV and 20 mA. Scanning electron microscopy (SEM-EDS) was carried out in a JEOL JSM-6510LV microscope to establish the differences in surface morphology between unmodified and modified membranes. The water contact angle on the PP

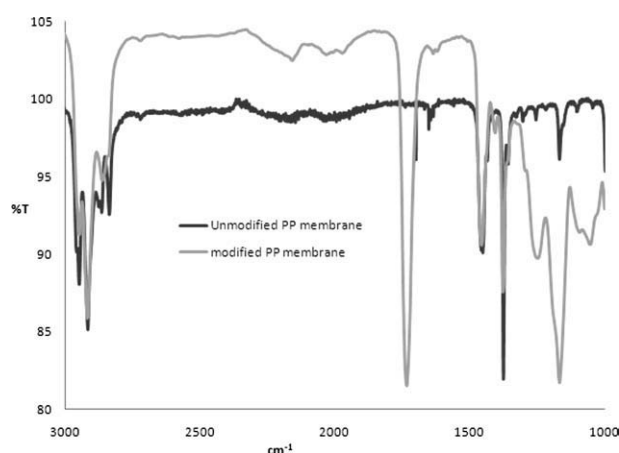


Figure 6 ATR-FTIR of unmodified PP and grafted PP membrane.

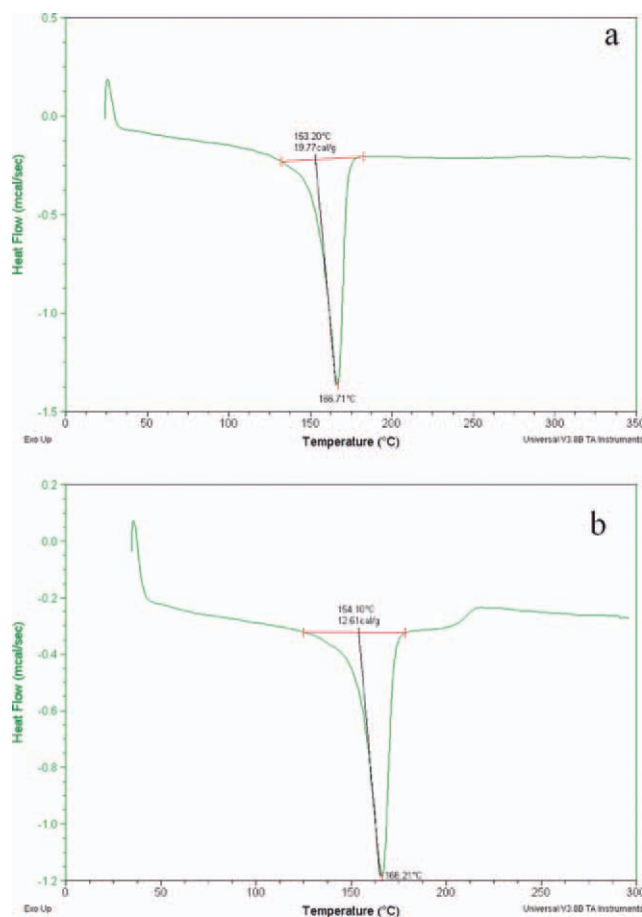


Figure 7 DSC curves of (a) unmodified PP (b) grafted PP membrane with 30% of monomer [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

membranes was measured by using a Kruss model G-1. XPS spectra of grafted membrane were obtained using a JEOL JPS-9200 and a HACH DR/4000 U Spectrophotometer was employed to evaluate the water quality parameters.

For determination of equilibrium water absorbency, samples were immersed into distilled water for different periods of time. The water excess on the surface of unmodified and grafted PP membranes were wiped off with filter paper and the swollen samples were weighted. The swelling % was determined by the following equation:

swelling (%) = $[(W_s - W_i)/W_i] \times 100$, where W_s and W_i are weights of the swollen and initial membrane, respectively.

RESULTS AND DISCUSSION

Graft polymerization reaction

The possible mechanism for grafting AESO onto PP membrane is shown in Scheme 1. UV irradiation generates free radicals on the trisubstituted carbon atoms of the PP membrane, which react with the acrylate group of AESO, producing a link between the membranes and grafting monomer. Similar mechanisms have been proposed for other grafting reactions.^{24,25}

Figure 3 evidences the dependence of grafting degree (D_g) on monomer concentration. The grafting yield of the reaction system could change with the different reactant concentrations. It can be seen that an increase of the monomer concentration

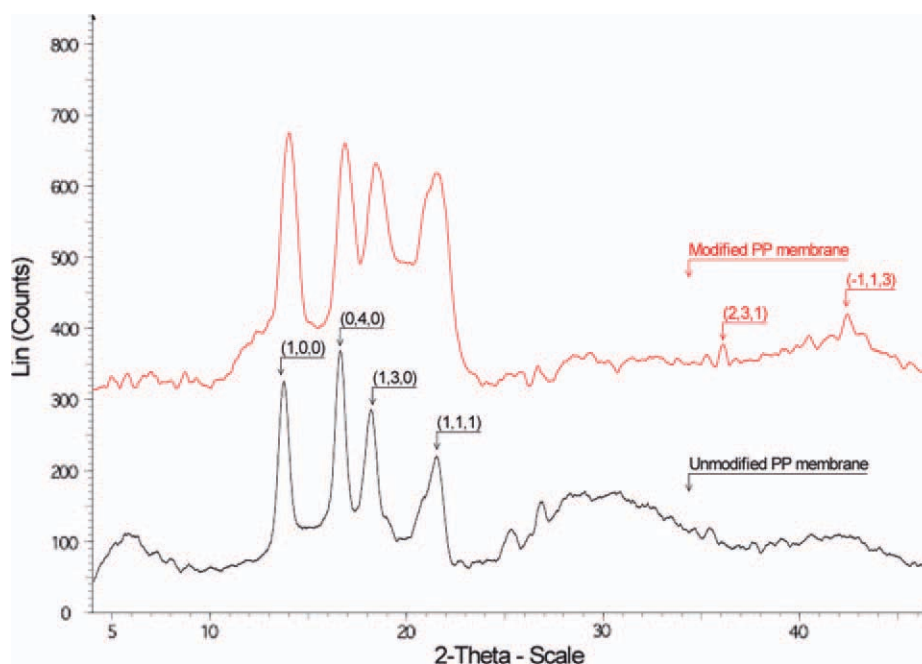


Figure 8 X-ray diffraction analysis of unmodified PP and grafted PP membrane [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

leads to a D_g enhancement. This is due to the increase of AESO concentration allowing more AESO monomer to reach the PP membrane surface, reacting with the active sites, thus more monomer can be grafted onto PP backbone. As AESO concentration increased, so did the degree of grafting, until a maximum of 30% and then decreased. The initial positive slope of the plot is explained by increment of the grafting reaction due to greater concentration of the reactant. When the reactant concentration further increased, the homopolymerization was also appreciably enhanced and also an increase in the viscosity of the grafting mixture was observed, producing a difficult diffusion of AESO into the PP membrane. These results indicate that the grafting degree can be easily controlled by the monomer concentration. This behavior has been observed before with other monomers in graft reactions.²⁶

The increase in grafting yield as a function of reaction time for irradiated PP samples is shown in Figure 4. Graft polymerization is proportional to the reaction time, where the films presented the highest yields of grafting at 10 h at 136%.

The kinetics of swelling, in water at room temperature, of modified membrane at three different graft percentages (10, 30, and 50%) was followed by gravimetry and it is presented in Figure 5. The equilibrium is observed at 180, 210, and 240 min for each graft sample. At the equilibrium, it is possible to observe that an increment of 20% of grafting gives 5% more of swelling. The percentage of swelling increases with grafting yield because of hydrophilicity augmentation. The results clearly indicate that higher grafting of AESO into the PP membrane yields an increased capability of the material to absorb larger amount of water.

Characterization and properties of unmodified PP and grafted PP membranes

ATR-FTIR analysis

The ATR-FTIR analysis can confirm that the AESO was grafted onto the PP membrane surface. Figure 6 depicts the ATR-FTIR spectra for unmodified PP and grafted PP membranes. The absorbency peaks at 1380, 1450, and 2900 cm^{-1} correspond to the basic PP structure and can be ascribed to CH_3 and CH_2 groups. The spectrum of the grafted PP membrane shows peaks around 1733 and 3500 cm^{-1} , which are not observed in the spectrum of the unmodified PP membrane. These peaks can be attributed to the stretching of the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups, which indicates that the monomer was successfully grafted onto the PP membrane surface.

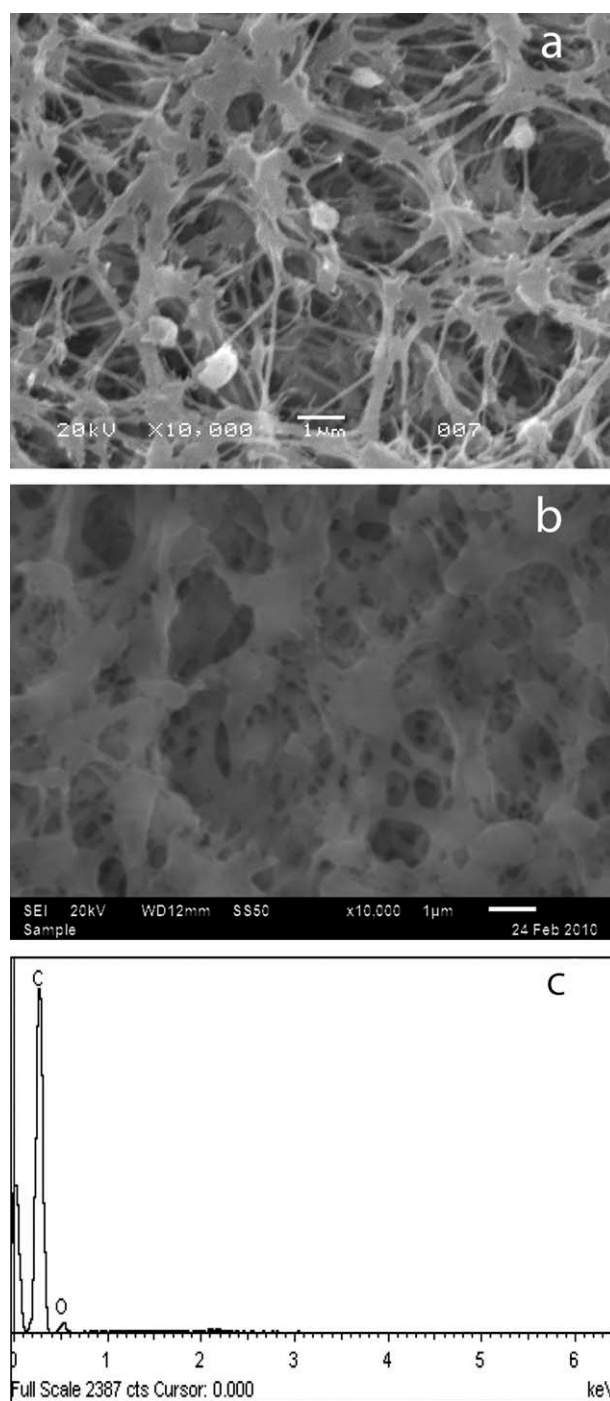


Figure 9 SEM photographs of (a) unmodified PP, (b) grafted PP with 30% of monomer concentration, and (c) EDS analysis of grafted PP membrane.

Thermal properties and X-ray analysis

The thermal properties of unmodified PP and grafted PP membranes are presented in Figure 7. It can be observed that they have same melting temperature (166°C), but different energy requirement. The unmodified PP membrane needs further 7.16 cal/g to reach the melting point than grafted membrane due to their different crystal arrangement. It is

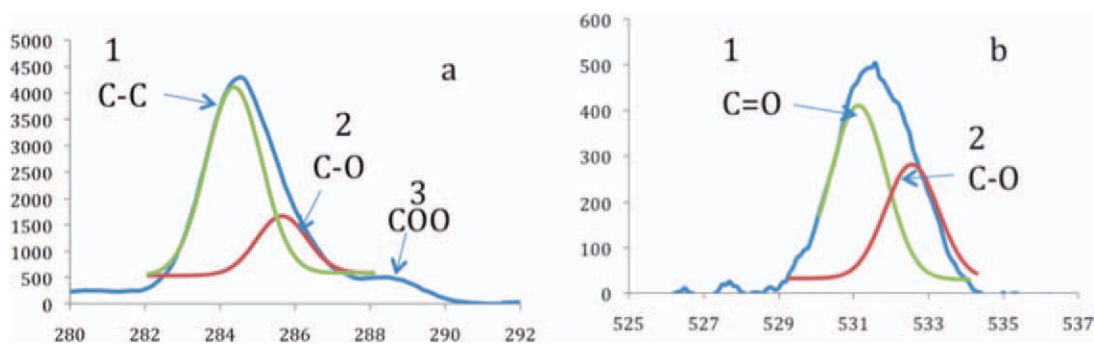


Figure 10 Deconvolution (a) of C 1s and (b) of O 1s atoms on grafted PP membrane [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

possible to observe the loss of crystallinity by X-ray diffraction analysis. XRD patterns were collected over $5\text{--}65^\circ$, though the most significant differences in the diffraction pattern of the respective phases appear in the range of $36^\circ < 2\theta < 43^\circ$. For example (2, 3, 1) and $(-1, 1, 3)$ reflections of modified PP membrane are observed at 2θ angle as shown in Figure 8.

SEM and EDS analysis

To study the changes on surface morphology of the grafted PP membrane, an SEM analysis was carried out. Figure 9 illustrates SEM images of both membranes. In Figure 9(a) it can be observed that the unmodified PP membrane is constituted by a large number of well-defined pores, whereas pores appear swollen up in the grafted PP membrane, as shown in Figure 9(b). With the increase of D_g the porosity and pore size of the grafted PP membrane were evidently decreased. This occurs because the grafted AESO chains locked the surface pores and covered the PP membrane surface. The EDS analysis provided information regarding elemental composition. The elements of soybean oil in the grafted membrane, such as oxygen atoms of carbonyl or hydroxyl groups, can be observed in Figure 9(c).

XPS analysis

The XPS analysis also shows that the monomer was grafted onto the membrane (Fig. 10). The deconvolution of the signals of C and O atoms reveals the presence of C=O, C–O, C–C, COO bonds which correspond to the monomer. The orbital 1s of carbon atom in Figure 10(a) presents a deconvolution in three peaks, the first one, at 284 eV, corresponds to aliphatic carbon bonds. Peak two, at 286 eV, represents the C–O bonds and the last peak, at 289 eV, could be associated to COO group. The orbital 1s of the oxygen atom [Fig. 10(b)], deconvoluted in two peaks, one for C=O moiety at 531 eV and other at 533 eV for C–O bonds.

Water contact angle analysis

The water contact angle measurement is an easy and effective way to characterize the hydrophilicity of a membrane surface. The water contact angle of the unmodified membrane was 90° . While grafted PP membranes decrease the angle with the increase of the monomer concentration. At 10% of monomer concentration the angle was an 89° , at 30% was 69° and with 50% the contact angle was 57° . These results show that the AESO monomer modified the hydrophobicity of the polypropylene membrane.

Application in water filtration

Wastewater samples were collected from a treatment plant located in an industrial park. The complexity of these wastewaters makes difficult the development of an effective technology for removing color and organic content, as melanoidins and humic acid.^{27,28} The efficiency of the grafted PP membrane in residual raw water filtration was studied using some water quality parameters such as color, turbidity, and COD. Table I summarizes the results of the filtration experiments.

The unmodified membrane does not change the quality parameters but the modified membrane significantly reduces these quality values. When using the modified membrane, the color of the filtrated water was reduced by 52% with respect to the residual raw water; turbidity was reduced in 95%, and

TABLE I
Quality Water Parameters of Residual Raw Water with Unmodified and Modified PP Membrane

Sample	Color	Turbidity	COD
	(Pt-Co)	(FAU)	(mg/L)
Residual raw water	442	52	98
Water filtrated with unmodified PP membrane	400	50	96
Water filtrated with modified PP membrane	216	3	72

the COD changed by 26.5%. It is possible that the melanoidins were removed due to the formation of hydrogen bonds and other weak interactions between these organic molecules and the grafting monomers.

CONCLUSIONS

Acrylated epoxidized soybean oil was grafted onto the surface of microporous polypropylene membrane by using UV radiation method. This is a simple low cost and environmentally friendly method. By varying the monomer concentration one can control the grafting degree. Water contact angle changed 33° after surface modification, indicating the excellent hydrophilic character of the grafted membrane. The hydrophilicity increment, due to the increment of polar groups on the membrane surface, was confirmed by pure water contact angle and swelling measurements. The modified membrane possesses filtration capability and removed 52% of color and reduced 95% of turbidity from industrial residual water.

We thank the Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Professor Ronald F. Childs from Chemistry Department at McMaster University for invaluable comments, Dr. Reyna Natividad Rangel and Dr. Gabriela Roa Morales for the analysis of water parameters, Dr. Susana Hernandez López for the IR-ATR spectra, and Gustavo López Tellez, M.Sc., for the SEM and XPS analysis. 3M company provided the propylene membrane.

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