Natalia Arbelaez¹, Tulio A. Lerma^{1*}, Alexander Córdoba¹

¹ *Research Group in Science with Technological Applications (GI-CAT), Department of Chemistry, Universidad del Valle, Cali-Colombia.*

Corresponding author: tulio.lerma@correounivalle.edu.co

Graphical abstract

Modification of membranes by insertion of short-chain alcohols on reactive porous substrates: Effect of chain length on the surface free energy

Abstract

Molecules of low molecular weight have a different effect on the interface compared with polymers. Surface is less sensitive to changes in the solution when liquid-solid interface is analyzed. However, properties associated with nature of chain could be strongly affected by its length. The objective of this work was study the effect of chain length on surface free energy when molecules with low molecular weight are grafted to porous membrane. This procedure produces a surface change in order to make a more hydrophobic surface without to change the functional properties of the membranes (permeability, porosity, thickness, etc.). The development of this type of modified membranes could permit the making of anti-biofouling surface by decrease of interaction between the surface and extracellular polymeric substances. Results evidence that interpenetrating polymer network (IPN) can be made using polypropylene membranes as support and poly(allyl alcohol) as secondary network. In addition, alcohols can be inserted by urethanization

Keywords

Polymer network
Surface modification
Urethanization
Grafting

reactions previous to the activation of surface with a diisocyanate. It is concluded that surface energy of membrane is increased with the number of Carbone on linear alcohol. Besides, the main contribution was the dispersive component in all cases.

Modificación de membranas por inserción de alcoholes de cadena corta sobre sustratos porosos reactivos: Efecto de la longitud de la cadena sobre la energía libre superficial

Resumen

Moléculas de peso molecular bajo tienen un efecto diferente sobre la interface en comparación con los polímeros. La superficie es menos sensible a cambios en la solución cuando la interface líquido-sólido se analiza. Sin embargo, las propiedades asociadas con la naturaleza de la cadena podrían ser fuertemente afectada por la longitud de esta. El objetivo de este trabajo fue estudiar el efecto de la longitud de la cadena sobre la energía libre superficial cuando moléculas con bajo peso molecular son insertadas a membranas porosas. Este procedimiento produce un cambio superficial con el fin de fabricar una superficie más hidrofóbica sin cambiar las propiedades funcionales de la membrana (permeabilidad, porosidad, espesor, etc.). El desarrollo de este tipo de membranas modificadas permitiría la construcción de superficies antibiofouling por disminución de la interacción entre la superficie y sustancias poliméricas extracelulares. Los resultados evidencias que redes poliméricas interpenetrantes (IPN) puede ser fabricadas usando membranas de polipropileno como soporte y poli(alcohol alílico) como red secundaria. Además, los alcoholes pueden ser insertadas por reacciones de uretanización previo a la activación de la superficie con una molécula de diisocianato. Se concluye que la energía superficial de la membrana se incrementa con el número de carbonos de alcoholes lineales. Además, la principal construcción fue la componente dispersiva en todos los casos.

Palabras claves

Redes poliméricas
Modificación superficial
Uretanización
Injerto

Recived: 05-03-2017

Accepted: 20-04-2017

Publishing date: 15 - May - 2017

Revision Code: 20170305-AAAA [Pag. 75-83]

Corresponding author:

tulio.lerma@correounivalle.edu.co

Modification of membranes by insertion of short-chain alcohols on reactive porous substrates: Effect of chain length on the surface free energy

Natalia Arbelaez¹, Tulio A. Lerma¹, Alexander Córdoba¹

¹ *Research Group in Science with Technological Applications (GI-CAT), Department of Chemistry, Universidad del Valle, Cali-Colombia.*

Corresponding author: tulio.lerma@correounivalle.edu.co

Abstract

Molecules of low molecular weight have a different effect on the interface compared with polymers. Surface is less sensitive to changes in the solution when liquid-solid interface is analyzed. However, properties associated with nature of chain could be strongly affected by its length. The objective of this work was study the effect of chain length on surface free energy when molecules with low molecular weight are grafted to porous membrane. This procedure produces a surface change in order to make a more hydrophobic surface without to change the functional properties of the membranes (permeability, porosity, thickness, etc.). The development of this type of modified membranes could permit the making of anti-biofouling surface by decrease of interaction between the surface and extracellular polymeric substances. Results evidence that interpenetrating polymer network (IPN) can be made using polypropylene membranes as support and poly(allyl alcohol) as secondary network. In addition, alcohols can be inserted by urethanization reactions previous to the activation of surface with a diisocyanate. It is concluded that surface energy of membrane is increased with the number of Carbone on linear alcohol. Besides, the main contribution was the dispersive component in all cases.

Keywords

Polymer network
Surface modification
Urethanization
Grafting

1. Introduction

Fouling is the main problem in membrane separation processes, and it is a major factor in the determination of practical applications. Membrane fouling includes inorganic fouling/scaling, organic fouling, particulate/colloidal fouling and biofouling (or microbial/biological fouling). Biofouling is the grown of microorganisms in the pore and on the surface of membrane. In addition, fouling due to organic and inorganic components and microorganisms can occur simultaneously, and these com-

ponents may interact in terms of mechanism [1-4]. Different mechanisms of fouling formation have been described: pore blocking and cake formation, however, these are useful for fouling produced by non-biotic systems because their features are associated directly to the process factors [4-5]. In the case of microorganisms or biotic systems, in addition of process factors must be considered aspects directly related with the microorganisms (feed nutritional composition, type of microorganisms, presence and absence of oxygen, etc). Biofouling can have several negative effects on

membrane systems, including: membrane flux decrease, additional resistance being needed to consider the biofilm resistance, membrane biodegradation, reduced quality of the product due to the accumulation of dissolved ions in the biofilm and on the membrane surface, increasing the degree of concentration polarization, increased energy consumption due to higher pressure being required to overcome the biofilm resistance and the flux decline, and biological contamination of product [1].

An alternative to reduce biofilm formation consists to carry out a specifically control of the secretion of extracellular polymeric substances, which is a key stage involved in biofilm formation mechanism. Extracellular polymeric substances allow bacteria to anchor, adhere to surfaces, and begin the biofilm formation [6]. The hydrophobicity of microfiltration membranes is thought to play a crucial role in the adhesion of extracellular polymeric substances because hydrophobic interactions facilitate that this type of substance attaching on the surface, usually causing irreversible biofouling [1,6]. Other surface properties such as: charge density, pore size, and roughness may also influence extracellular polymeric substances and microbial cell attachment [6].

Since membrane surface characteristics such as hydrophobicity and charge can affect the extracellular polymeric substances secretion and, in consequence, microbial cell attachment; the modification of these properties can be used to prevent biofouling. Examples of this strategy have been previously published for different researches [6-10].

By the above, the surface modification of membranes is an alternative for the incorporation of surface hydrophobicity, and thus, to minimize the interaction of extracellular polymeric substances. To carry out the modification, an alternative is the formation of polymer brushes. A polymer brush corresponds to an array of macromolecular chains attached to a surface and in sufficient proximity so that the unperturbed solution dimensions (in a good solvent) of the chains are altered. As a result of this close proximity is produced the overlap of adjacent chains and thus significantly alters the conformational dimensions of individual polymer chains such that they extend or alter their normal radius of gyration to avoid unfavorable interactions [11,12].

The grafting can be performed from polymer solutions or melt and, in general, higher concentrations of polymer lead to higher grafting densities by the *grafting-to* method, permitting grafting density can be regulated by grafting time. Often it has been argued that the *grafting-to* technique will not produce dense polymer brushes because the attachment of chains may be impeded by the existence of previously attached chains. When grafting process is finished, usually by separation of the support with grafted polymer from the polymer solution/melt or by rapid cooling, the residual ungrafted polymer can be removed by solvent extraction. On the other hand, *grafting-from* involves an *in situ* polymerization of an initiator functionalized surface with monomer. In general, the *grafting-from* technique can produce polymer brushes of high grafting density because the grafted layer is swollen by the monomer solution that feeds the growing chains. In this case, the growth of chains is not limited by the diffusion of monomer unless a very high grafting density is approached [12]. However, the *grafting-from* technique may suffer complications because of the limitation of initiator surface coverage, initiator efficiency, and the rate of diffusion of monomer to active polymerization sites; in addition, this method can lead to a broader molecular mass distribution [12-15].

What would happen if the graft chains were not macromolecules but chains of low molecular weight molecules?

The above question can be analyzed from different point of view. Thus, molecules of short molecular weight have a different effect on the interface compared with polymers. Surface is less sensitive to changes in the solution when liquid-solid interface is analyzed. However, properties associated with nature of chain could be strongly affected by its length. Here, we study the effect of chain length on surface free energy when molecules with low molecular weight are grafted to porous membrane. This procedure produces a surface change in order to make a more hydrophobic surface without to change the functional properties of the membranes (permeability, porosity, thickness, etc.). The development of this type of modified membranes could permit the making of anti-biofouling surface by decrease of interaction between the surface and extracellular polymeric substances.

2. Experimental section

2.1. Reagents and materials

N,N'-Methylene-bis-acrylamide (Merck), benzoyl peroxide (Merck) and allyl alcohol (Aldrich) were used in the modification of polypropylene micro-filtration membranes (Millipore) by the formation of interpenetrating polymer networks (IPNs). 4,4'-Methylene-bis-phenyl isocyanate (MDI, Aldrich) was used in the formation of chemically active surfaces by direct reaction with hydroxyl groups of IPN.

Ethanol (Merck), 1-butanol (Merck), 1-hexanol (Merck), 1-octanol (Merck) and 2-phenylethanol (Merck) were used in the formation of short chain grafts. Bi-distilled Water, ethylene glycol (Merck) and 1,3-propanediol (Aldrich) were used in the contact angle measures. 1,4-Dioxane (Aldrich), dimethyl sulfoxide (DMSO, Merck) and bi-distilled water were used as solvents.

2.2. Modification of polypropylene membranes by IPNs

Modification of polypropylene membranes was carried out by the method of IPNs. For that, different amounts of allyl alcohol (2.94, 5.88, 8.82, 11.76 and 14.70 mmol) were separately dissolved in 5.0 mL of dioxane. After, N,N'-methylene-bis-acrylamide (20.0 % mol with respect to allyl alcohol) and benzoyl peroxide (3.0 % mol with respect to the monomers) were added to each solution. Subsequently, membranes were immersed in the reaction solution and system was brought to 70 °C for 2 h under nitrogen atmosphere. Finally, filters were removed from the reaction mixture and washed with bidistilled water in order to remove the unreacted substance.

2.3. Chemical activation of modified membranes

Formation of the chemically active surfaces was carried out by the reaction of the hydroxyl groups on allyl alcohol with the isocyanate groups on the MDI. For that, 1.07 mmol of MDI was dissolved in 5.0 mL of DMSO. After, each previously modified membrane was immersed in the MDI solution for 2 hours. Finally, excess MDI was removed by washing with acetone.

2.4. Inserting of short chain grafts

Formation of brush-like surface by inserting of short chain grafts was carried out by the reaction of alcohols of different chain length with the isocyanate groups of the chemically active surfaces previously developed. For that, 5.0 mL of alcohol (*i.e.*, ethanol, 1-butanol, 1-hexanol, 1-octanol and 2-phenylethanol) was added to the reactor. After, each chemically-activated membrane was immersed in the alcohol solution for 3 h at room temperature. Finally, the filter was removed from the reaction solution and washed with water. The identification used to describe the surfaces modified according to the alcohol used is shown in Table 1 (see section "Results and discussion").

2.5. Characterization experiments

2.5.1. Percentage of modification: Modified membranes were washed with double distilled water using an ultrafiltration cell (Amicon) and dried at room temperature to constant mass. Mass of the membrane was determined before and after each modification. Details of this procedure have been previously published [16].

2.5.2. Surface analysis by infrared spectroscopy: Unmodified and modified membrane surfaces were analyzed by infrared spectroscopy with Fourier transform - attenuated total reflectance (ATR-FTIR, IR-Affinity-1) for the identification of functional groups. For that, the incidence angle was 45° and a reflection crystal of ZnSe was used.

2.5.3. Permeability analysis: Permeabilities of unmodified and modified membranes were evaluated by measuring the permeate water mass as a function of time at different pressures (50, 100, 150, and 200 kPa). Thus, by Darcy's law, the flux (J) of water is related with applied pressure (P) by

$$J = LP \quad (1)$$

Being the hydraulic permeability the proportionality constant (L) [17].

2.5.4. Contact angle measurements and calculation of surface energies: Contact angle measurements were performed by sessile drop method. For that, three drops of different solvents (water, ethylene glycol and 1,3-propanediol) were deposited on 1

cm² of membrane and procedure was capture in video using a semiprofessional camera Cannon. Later, image of exact time when drop is deposited were digitally analyzed in order to determine the observed contact angle, θ (*i.e.*, the angle between the solid-liquid interface and liquid-air interface) [18, 19]. Changes in surface energies were calculated using van Oss-Chaudhury-Good theory [20-21]. In this approach the work of adhesion of a liquid phase (W_{ad}) onto a solid substrate can be expressed as:

$$\frac{\gamma_l}{2} = \frac{(\gamma_l^{nd} \gamma_s^{nd})^{0.5} + (\gamma_l^+ \gamma_s^-)^{0.5} + (\gamma_l^- \gamma_s^+)^{0.5}}{(1 + \cos \theta)} \quad (2)$$

where γ_l^{nd} , γ_l^+ , γ_l^- , γ_s^{nd} , γ_s^- , γ_s^+ are dispersive, basic, and acidic components of the liquid and of the solid respectively. From the measurement of contact angle, a set of three non-linear equations with three unknowns is derived from equation.

3. Results and discussion

3.1. Making and characterization of membrane

Figure 1 shows the results of ATR-FTIR analysis of unmodified polypropylene surfaces, modified propylene via IPNs and the chemically activated surfaces. In the unmodified polypropylene surface spectrum, two characteristic bands of the polypropylene polymer matrix can be observed, at 2920 cm⁻¹ and 1375 cm⁻¹ corresponding to tension and deformation vibration of the C-H bond, respectively. For the modified surfaces by IPNs, a band at 3290 cm⁻¹ corresponding to the tension vibration band of the O-H bond was observed, this band is characteristic of the allyl alcohol used in the modification. In addition, the characteristic bands of the polymer polypropylene matrix can be identified. These results suggest the satisfactory formation of a secondary network from allyl alcohol in the polypropylene membrane. Polypropylene surface is a surface without functional groups, therefore, its infrared spectrum is relatively simple compared with membranes with surface functional groups. The making of a IPNs using polypropylene porous as primary network and a functional polymer as secondary network requires avoid the phase segregation. If polymer constituting the secondary network is hydrophilic then the network is not compatible with polypropylene support. In our case, the allyl alcohol is a monomer compatible with

polypropylene surface, however, hydroxyl groups gives hydrophilicity to poly(allyl alcohol). In order to avoid the phase segregation we use N,N'-methylene-bis-acrylamide to produce a fast crosslinking.

On the other hand, in the ATR-FTIR spectrum of the chemically activated surfaces, it can be observed the appearance of a band at 2345 cm⁻¹ which is characteristic of the isocyanate group. This is evidence that on the surface of membrane there are unreacted isocyanate groups, suggesting that MDI molecules were anchored to the surface. The characteristic bands of the polypropylene matrix and unreacted hydroxyl groups were also observed. Therefore, the results indicate a satisfactory insertion of MDI molecules and the presence of isocyanate groups that act as anchor points for molecules with hydroxyl groups. MDI is a small molecule, with two isocyanate groups at the ends of the molecule. Thus, one isocyanate group reacts with the hydroxyl group of poly(allyl alcohol) producing a urethane group, but at the same time, the second isocyanate group stays unreacted "activating" the surface for a second reaction.

Figure 2 shows the results of the ATR-FTIR analyzes of the brush-like surface developed. Thus, it can be identified, in all the spectra, two bands in the regions of 3300 to 3600 cm⁻¹ and 1650 to 1680 cm⁻¹ characteristics of the tension vibrations of the bonds N-H and C=O, respectively, associated with the formation of the urethane groups.

Figure 1. ATR-FTIR spectra of unmodified and modified porous surfaces of polypropylene.

Figure 2. ATR-FTIR spectra of modified membranes.

In addition, the total disappearance of the vibration band corresponding to the isocyanate group at 2345 cm^{-1} was evidenced. These results suggest the effective insertion of the different alcohols used in the chemically active surfaces. Thus, surface with unreacted isocyanate groups when are immerse in an alcohol solution, hydroxyl group on alcohol molecule reacts with isocyanate group and produce an urethane group with a short chain depending of alcohol used.

In the Table 1 values of percentage of modification, permeability and relative permeability for all systems under study are shown. In general, percentage of modification by IPN was relatively low (*i.e.*, among 5.9 and 15.4 %). However, this result can be explained by the relatively low amount of monomer used for the making of secondary network (for the longer amount of allyl isocyanate). However, the insertion of alcohols was low for 1-hexanol and 2-phenylethanol; but also, in general, the density of chains R-urethane was low in all the case. On the other hand, the strong decrease of permeability in the stage 1, making of IPN, suggests two situations: (1) a decrease of surface porosity and effective pore size (the secondary network increase the hydrophilicity surface, in consequence, permeability should increase if changes in the surface porosity and pore size no occur), and (2) this decrease can be only explained by the formation of IPN. When alcohols were inserted, a second decrease of permeability suggest that the hydrophilicity surface was decrease.

3.2. Analysis of surface energies

For analysis of surface energies is needed to measure contact angles for different liquids. These results are shown in the Table 2. In general terms, the contact angle of membranes decreased when water was used as test liquid, this is congruent with the formation of IPN. On the other hand, when alcohols were inserted, only it was observed a significant change for M3 and M4 (*i.e.*, 1-hexanol and 1-octanol, respectively).

By van Oss-Chaudhury-Good theory can be determined the adhesion work and surface energies (see Table 3).

Table 1. Sample identification, alcohol used, percent of modification, permeability (L) and relative permeability (L_{rel}) in different modification stage: making of IPN (stage 1) and insertion of alcohol molecules (stage 3).

Sample	Alcohol	Modification (%)		$L \times 10^{-8}$ ($\text{m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	
		Stage 1	Stage 3	Stage 1	Stage 3
Polypropylene	---	---	---	206	---
M1	Ethanol	5.9	4.1	1.81	0.34
M2	1-Butanol	14.2	4.4	1.33	0.23
M3	1-Hexanol	11.3	0.7	0.88	0.53
M4	1-Octanol	9.9	4.8	0.56	0.39
M5	2-Phenylethanol	15.4	1.5	0.50	0.76

Table 2. Contact angle measurements determined for each modified surface with three solvents, water (S1), ethylene glycol (S2) and 1,3-propanediol (S3).

Sample	Contact angle measurements (°)					
	Stage 1			Stage 3		
	S1	S2	S3	S1	S2	S3
Polypropylene	95.9 ± 3.4	72.4 ± 8.9	75.4 ± 4.4	95.9 ± 3.4	72.4 ± 8.9	75.4 ± 4.4
M1	72.5 ± 9.7	80.4 ± 4.8	69.9 ± 2.6	53.1 ± 1.7	60.5 ± 5.7	55.9 ± 7.6
M2	74.6 ± 7.9	61.4 ± 1.2	78.7 ± 7.8	73.4 ± 3.3	48.5 ± 9.3	61.8 ± 1.8
M3	62.7 ± 3.4	59.5 ± 1.5	54.8 ± 6.8	81.2 ± 9.3	85.1 ± 8.3	77.2 ± 9.9
M4	65.0 ± 4.7	64.7 ± 7.9	73.8 ± 3.3	122.0 ± 9.0	62.1 ± 2.3	60.1 ± 9.0
M5	72.4 ± 2.3	70.8 ± 9.9	57.1 ± 1.3	60.6 ± 3.6	55.0 ± 9.0	74.9 ± 5.1

Table 3. Adhesion work and surface energies calculated for each modified membrane.

Sample	W_{sa}	γ_s	γ_s^d	$\gamma_s^{(-)}$	$\gamma_s^{(+)}$
	(mN/m)				
Polypropylene	248 ± 71	362 ± 124	318 ± 119	6 ± 2	84 ± 35
M1	127 ± 1	79 ± 16	54 ± 33	15 ± 5	15 ± 10
M2	234 ± 40	104 ± 20	58 ± 17	1.8 ± 0.1	29.4 ± 36
M3	192 ± 93	434 ± 140	412 ± 126	1.1 ± 0.3	131 ± 55
M4	424 ± 112	860 ± 347	446 ± 280	159 ± 89	294 ± 135
M5	552 ± 110	1000 ± 405	636 ± 245	34 ± 0.8	973 ± 306

Adhesion work (W_{sa}), surface energy (γ_s), dispersive contribution (γ_s^d) and polar contributions (basic $\gamma_s^{(-)}$, acid $\gamma_s^{(+)}$)

Results show an increasing in the surface energy of membrane as alcohol chain length was increased (from 79 to 1000 for M1 to M5). Clearly, this result groups the combination of all modifications performed (making of IPN, functionalization with MDI and insertion of alcohols), in consequence, the superposition of polymer structures in the IPN produces a greater cohesion of all structure and therefore the forming of a new surface requires a greater energy. In general, dispersive contribution was larger in all cases, being the order $M5 > M4 > M3 > M2 > M1$. This can be understood considering that the main contributions are produced by polypropylene chains and chains of alcohols.

4. Conclusions

Results evidence that interpenetrating polymer network (IPN) can be made using polypropylene membranes as support and poly(allyl alcohol) as secondary network. In addition, alcohols can be inserted by urethanization reaction previous to the activation of surface with a diisocyanate. It is concluded that surface energy of membrane is increased with the number of Carbone on linear alcohol. Besides, the main contribution is the dispersive component in all cases.

Acknowledgments

Authors thanks to Universidad del Valle and to the Program for Scientific Knowledge Diffusion of Mindtech s.a.s. (PSKD 2016-2020) for funds associated to the publication costs.

Conflict of interests

The authors declare no conflict of interest.

References

- [1] T. Nguyen, F. A. Roddick, L. Fan. Biofouling of Water Treatment Membranes: A Review of the Underlying Causes, Monitoring Techniques and Control Measures. *Membr. (Basel)* 2 (2012) 804–840.
- [2] H.C. Flemming, T. Griebe, G. Schaule, J. Schmitt, A. Tamachkiorow. Biofouling-The Achille's heel of membrane processes. *Desalination*. 113 (1997) 215–225.
- [3] K.C. Marshall, B.L. Blainey. Role of bacterial adhesion in biofilm formation and biocorrosion. In: Flemming H.-C., Geesey G.G., editors. *Biofouling and Biocorrosion in Industrial Water System*. Springer-Verlag; Heidelberg, Germany: 1991. pp. 29–46.
- [4] M. Palencia, B.L. Rivas, E. Pereira. Metal ion recovery by polymer-enhanced ultrafiltration using poly(vinyl sulfonic acid): Fouling description and membrane-metal ion interaction. *J. Membr. Sci.* 345 (2009) 191-200.

- [5] M. Palencia, B. Rivas, H. Valle. Size separation of silver nanoparticles by dead-end ultrafiltration: description of fouling mechanism by pore blocking models. *J. Membr. Sci.* 455 (2014) 7–14.
- [6] R. Malaisamy, D. Berry, D. Holder, L. Raskin, L. Lepak, K. L. Jones. Development of reactive thin film polymer brush membranes to prevent biofouling. *J. Membr. Sci.* 350 (2010) 361–370.
- [7] N. Hilal, V. Kochkodan, L. Al-Khatib, T. Levadna, Surface modified polymeric membranes to reduce (bio)fouling: amicrobiological study using *E. coli*, *Desalination* 167 (2004) 293–300.
- [8] V. Kochkodan, N. Hilal, V. Goncharuk, L. Al-Khatib, T. Levadna, Effect of the surface modification of polymer membranes on their microbiological fouling, *Colloid J.* 68 (2006) 267–273.
- [9] J. Lin, J.C. Tiller, S.B. Lee, K. Lewis, A.M. Klibanov, Insights into bactericidal action of surface-attached poly(vinyl-n-hexylpyridinium) chains, *Biotechnol. Let.* 24 (2002) 801–805.
- [10] T. Carroll, N.A. Booker, J. Meier-Haack, Polyelectrolyte-grafted microfiltration membranes to control fouling by natural organic matter in drinking water, *J. Membr. Sci.* 203 (2002) 3–13.
- [11] W. J. Brittain, S. Minko. A Structural Definition of Polymer Brushes. *J. Polym. Sci.: Part A: Polym. Chem.*, 45 (2007) 3505–3512.
- [12] S. Minko. Responsive Polymer Brushes. *J. Macromol. Sci. C: Polym. Rev.*, 46 (2006) 397–420.
- [13] J. D. Willott, T. J. Murdoch, G. B. Webber, E. J. Wanless. Physicochemical behaviour of cationic polyelectrolyte brushes. *Prog. Polym. Sci.*, 64 (2017) 52–75.
- [14] I. Lilge, H. Schönherr. Synthesis and characterization of well-defined ligand-terminated block copolymer brushes for multifunctional biointerfaces. *Polym.* 19 (2016) 409–420.
- [15] J. J. Keating, J. Imbrogno, G. Belfort. Polymer Brushes for Membrane Separations: A Review. *Appl. Mat. Interfaces* 8 (2016) 28383–28399.
- [16] M. Palencia, M. Vera, B. Rivas. Modification of ultrafiltration membranes via interpenetrating polymer networks for removal of boron from aqueous solution. *J. Membr. Sci.* 466 (2014) 192–199.
- [17] M. Palencia, A. Córdoba, M. Vera. Membrane Technology and Chemistry. In: Visakh P.M. and Olga Nazarenko (eds.) *Nanostructured Polymer Membranes*. Scrivener Publishing LLC. 1 (2016) pp. 27–54.
- [18] M. Palencia, M. Vera, E. Combatt. Polymer Networks Based in (4-Vinylbenzyl)-N-methyl-D-glucamine Supported on Microporous Polypropylene Layers with Retention Boron Capacity. *J. Appl. Polym. Sci.* 131 (2014) 40653–40663.
- [19] M. Palencia, T. Lerma, A. Arrieta. Desarrollo de compositos hidrofóbicos híbridos basados en bentonita y poli(vinilestearato). *Rev. Latinoamer. Metalur. Mater.* 37 (2017) 11–18.
- [20] J. Salazar, J. Pacheco, M.J. Jiménez. Determinación de la resistencia a la tracción de ligantes asfálticos (abs) y el trabajo de adhesión ($w_{a,s}$) de los ligantes asfálticos, mediante determinaciones de ángulo de contacto. *Métodos y Materiales*. 4(2014) 17–23.
- [21] M. Farahat, T. Hirajima, K. Sasaki. Adhesion of Ferroplasma acidiphilum onto pyrite calculated from the extended DLVO theory using the van Oss–Good–Chaudhury approach. *J. colloid Interf. Sci.* 349 (2010) 594–601.