PROTON EXCHANGE MEMBRANES FROM POLYELECTROLYTES BASED ON CELLULOSE-CONTAINING COMPOSITES

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Studiul nostru relevă obţinerea de filme membranare polielectrolitice ieftine din compozite celulozice şi polimeri sau copolimeri ai acidului metacrilic. Precipitarea complexului simultan cu polimerizarea in situ conduce la obţinerea unui film continuu subţire cu matrice din acelaşi polimer (copolimer) ca cea generată pe particulele de celuloză. Această structură asigură ramforsarea filmului polimeric şi îmbunătăţeşte stabilitatea termică ale celulozei.

Încorporarea celulozei în matricea polimerică şi modificarea sa parţială sunt demonstrate prin FTIR. Caracterizarea prin analiză TGA-DSC relevă stabilitatea termică adecvată a filmelor, esenţială pentru aplicaţiile Membranlore Schimbătoare de Protoni (PEM). Gonflarea moderată în apă (2–10%) asigură rezistivităţi de volum ce scad până la approx. $1x10^{6\div4}$ Ω.cm pentru membranele crude "nereticulate", în timp ce membranele sulfonate au rezistivităţi de approx $1x10^{4\div3}$ Ω.cm, adecvate pentru procesarea ulterioară ca PEM.

Our study reveals the possibility of preparing low cost polyelectrolyte membrane films from cellulose composites and polymers or copolymers of methacrylic acid. The complex precipitation simultaneously with the in situ polymerization leads to a thin continuous film with the matrix of the same polymer (copolymer) as the one generated onto the cellulose particles. This structure provides a reinforced polymer film and improves the thermal stability of the cellulose.

The embedment of cellulose in the polymer matrix and its partial modification are demonstrated by FTIR. The characterization by TGA-DSC revealed the appropriate thermal stability of the films, essential for Proton Exchanging Membranes (PEM) applications. Moderate water swelling (2-10%) provides volume resistivities down to about $1x10^{6\div4}$ Ω.cm for the crude crosslinked membranes, while the sulfonated ones exhibit resistivities of approx. $1x10^{4\div3}$ Ω.cm, appropriate for further processing as PEM.

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1. Introduction

Electrolysis is usually carried out at high temperatures, therefore a major problem when using polymer based proton exchanging membranes (PEM) is to compromise between conductivity (determined by water-swelling and temperature), and stability (inversely influenced by the same factors). As one cannot maximize both of them by synthesis in the same time, complex design using composite membranes, based on organic-inorganic and organic-organic systems, have been recently developed for use at temperatures in excess of 120°C and having an improved conductivity at moderate swelling.

The first attempts have used the well known and expensive Nafion in systems including nanostructured heteropolyacids (like tungsten heteropolyacids) having particles of 30 to 50 nm in a very uniform dispersion that allows reprotonation of the membrane without affecting the stability of the composite, and providing a long lasting membrane/electrode interface [1, 2].

Layer by layer deposition of electrode/membrane assemblies can be an alternative design with the major draw-back that increasing the number of layers reduces the proton conductivity [3]. This effect can be diminished in some extent by a careful alternation of the negatively and positively charged layers. This design requires further basic research for quantifying the interactions between these opposite charged layers, thus allowing the optimization of the deposition process.

Poly(ether-ether-ketone)-based membranes are sometimes uncontrollably swelled at high service temperatures. On the other hand, their very high thermal stability (over 300°C undoped) and their very high proton conductivity in sulfonated state make them good candidates as matrices for PEM [4]. Moderate-to-low sulfonation combined with blending with heteropolyacids can be a solution for their better stability in hydrated state at high service temperature [5÷7].

Another approach is blending of components that can provide high proton conductivity with others that infer mechanical resistance, like sulfonated poly(ether-ether-ketone) (SPEEK) with sulfonated polysulfone (SPSU). The high proton conductivity of SPEEK is supported by the high mechanical, thermal and oxidative stability of SPSU [8÷10]. Other specific drawbacks are compensated by including a third component like polybenzimidazoles.

The use of polypyrazoles and polyimidazoles relies on a different principle. These heterocycles act as a cage for the protic solvent (water, methanol), and the resulting compound exhibits very high proton conductivities [11] at high service temperatures (>100°C).

SPSU compounded with a benzimidazole copolymer [12] gives a membrane with high proton conductivity at low swelling in water or methanol.

Blending poly(vinyl alcohol) with poly(acrylic acid) (PAA) relies on microdomains of compatibilization based on interchain hydrogen bonds [13]. This particular structure allows crosslinking by simple dehydration to interchain ester groups. Until recently, the only major application were alcohols dehydration and superabsorbant structures. The application as PEM was made possible by diminishing or eliminating the transport process. This was done by simultaneous doping (with silica) and controlling the crosslinking degree in order to minimize the diffusion in the cathode space [13, 14].

This type of mixing polyelectrolytes bearing opposite charges usually results in forming strong electrostatic complexes that precipitate or coacervate [15, 16]. Thin films obtained by this precipitating process were used for dialysis, ultrafiltration, reversed osmosis and alcohols dehydration [17]. Lately these polyelectrolyte complexes were considered as candidates for PEM in fuel cells and/or in electrolysis cells [16], using blends of PAA with chitosan (last one used as polyalcohol). These membranes exhibited good mechanical and thermal stabilities at 20-40% swelling in water. Their performances are somehow limited as compared to those of perfluorinated Nafion-based membranes.

Our preliminary study on PAA/Cellulose system – reported in a previous paper [18] – allowed a selection of support-substrate systems.

Hereby we report on the investigation of the polyelectrolyte complex from the copolymethacrylic acid (coPAMA)/Cellulose, obtained by the precipitation polymerization technique. For a better characterization of these composites, the analyses are presented comparatively with those for the same substrates with acrylic acid.

2. Experimental

2.1. Materials

The main monomer was methacrylic acid (MAA) from Fluka, distilled under reduced pressure.

The comonomers were styrene (S), from Fluka, distilled under reduced pressure and p-vinyl benzyl chloride (p-chloro-methyl-styrene, CMS) from Aldrich, which was used as received. The initiator was 2,2'-azo-bis-isobutironitrile (AIBN), purified by recrystallization from chloroform/methanol mixture. The cellulose D (C), from Riedel-de-Haen, with GP_n=400-500, conditioned overnight at 1÷2 torr and 40°C was used as filler. Toluene (T), washed with: H_2SO_4 (d = 1.84), then with K_2SO_4 10% water solution, then twice with distilled water, and finally rectified, was used as the polymerization medium. Divinyl benzene

(DVB) from MERCK was used as crosslinking agent without further purification. 1,4-Dioxane and distilled water were used as dispersion solvent for composite film casting and distilled water was the swelling solvent for film removal.

2.2. Polymerizations

The syntheses were carried in micro reactors with mechanical stirring under argon at 75°C for two hours. We used the precipitation polymerization as the technical procedure. C was dispersed in the reaction medium using mechanical and ultrasonic stirring for preparing a stable dispersion and after that, we added the monomer or monomer mixture and, finally, the initiator. The monomer concentration was 50% by weight and the comonomers were used in equimolar ratios. The obtained composite was separated by filtration, washed with T and dried for 24 hours at 1÷2 torr and 60°C.

2.3. Film casting

Each obtained composite was tested in two film compositions, with 3% by weight DVB and without crosslinking agent. The film composition was prepared in aqueous or dioxane dispersion, evenly cast onto a glass plate. The composite membrane was dried at room temperature for at least 24 hours. The final active surface of 3 cm^2 and 55÷130 μm thickness was achieved. The removal of film from the glass plate was realized by swelling in distilled water.

2.4. Characterization

All composites were characterized in solid state by FT-IR spectroscopy, using a Brucker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device.

Thermal analysis was performed on a NETZSCH STA 449C Jupiter simultaneous TGA-DSC system at 5 K/min, under He atmosphere, hyphenated with an Aeolos II mass spectrometer.

Textural investigation was realized by scanning electron microscopy (SEM) with a HITACHI S-2600N apparatus.

The volume resistivity was calculated according to Romanian Standard 6107 from resistance measurements using as terra-Ohmmeter a Keithley electrometer, model 6517, with a measurement delay of 1 minute from the voltage onset.

Homogeneous substrates, ungrafted on cellulose, were ^{1}H and ^{13}C analyzed using Varian UNITY-INOVA 400, direct detection mode, in deuterated

chloroform, at 25°C. Attached proton test (APT) sequence was used for confirmation of the structure.

3. Results and discussions

The starting substrate compositions, used for C-containing composites preparation, are presented in Table 1.

Table 1

Process characteristics

Code	$x_{w\ Cel}$ *	$x_{w\ comon}$ **	Observations
L2	0.6	0.4	AA-S
X2	0.6	0.4	AA-CMS
L2.1	0.6	0.4	AMA-S
X2.1	0.6	0.4	AMA-CMS

*$x_{w\ Cel}$ – cellulose weight fraction
**$x_{w\ comon}$ – comonomers weight

The copolymer MAA-S exhibits the characteristic signals for aromatic rings at 7.11 ppm in ^{1}H-NMR (Fig. 1) and at 125-127 ppm in ^{13}C-NMR spectra respectively, as well as the acidic proton at 11.93 ppm in ^{1}H-NMR spectrum, and carbonyl signal at 178.17 ppm in ^{13}C-NMR spectrum. Integrals of the corresponding signals in ^{1}H-NMR spectrum allowed the calculation of the average molar composition of the recurring units: MAA/S = 0.96/1.
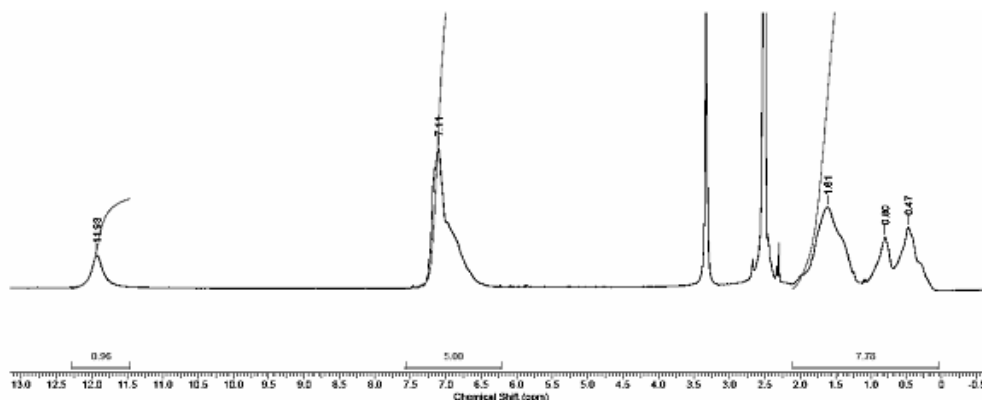

Fig. 1. ^{1}H-NMR spectrum for the MAA-S copolymer

In the NMR spectra for the MAA-CMS substrate, along with the signals for aromatic rings, at 6.91-7.11 ppm, in ^{1}H spectrum and 128-147 ppm in ^{13}C (Fig. 2) spectrum, the signal for methylene unit in chloromethyl group can be

found at 4.67 ppm in ^{1}H and 48.20 ppm in ^{13}C respectively, as well as the acidic proton at 11.98 ppm in ^{1}H spectrum and carbonyl signal at 178.97 ppm in ^{13}C spectrum. Again, the integrals of the corresponding signals allowed the calculation of the average molar composition of the recurring units: MAA/CMS = 0.92/1.
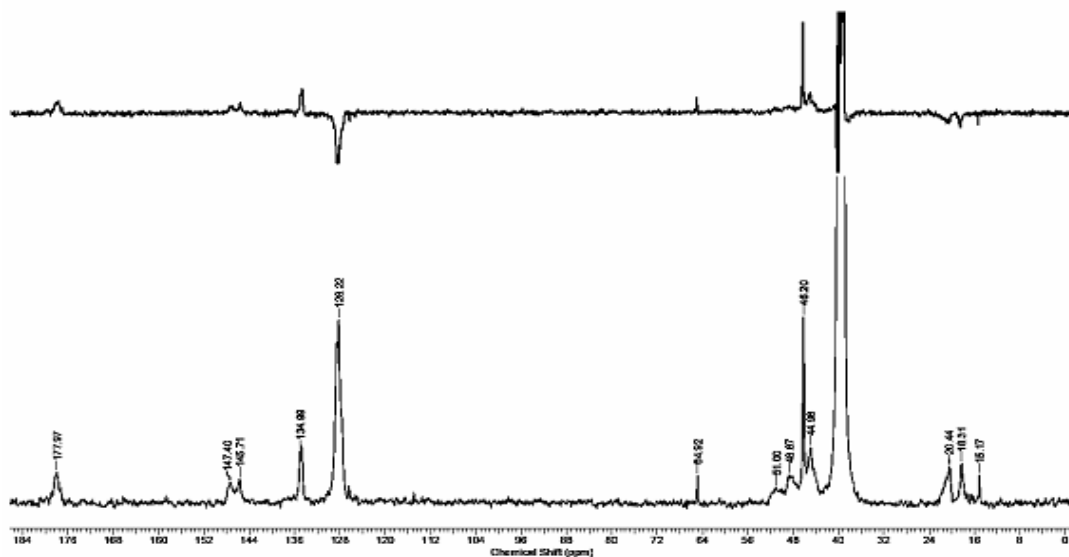

Fig. 2. ^{13}C-NMR spectra for the MAA-CMS copolymer

The actual average composition confirms the higher reactivity of CMS compared to S and, therefore, the formation of a substrate richer in aromatic comonomer.

The starting substrate compositions for composites synthesis (weight fractions) was in all cases: 0.6 for cellulose and 0.4 for mixture monomers (1:1 molar ratio).

The first investigation of the composites was the FT-IR (Fig. 3) analysis which shows the specific peaks that can be used for qualitative and quantitative analysis.

In all spectra we identified the υ_{C-O-C} peak characteristic for cellulose at approximate 1160cm^{-1}, and $\upsilon_{C=O}$ peak characteristic for MAA at 1669-1704 cm^{-1}.

All compositions exhibited a new vibration at about 1638 cm^{-1}, that can be assigned to MAA-C ester, together with diminishing the intensity for the peaks at 3196-3450 cm^{-1} specific for the υ_{OH} in hydroxyl and carboxyl group. In the same time, we identified characteristic vibration of comonomers: at 667-700 cm^{-1}, 758-760 cm^{-1} and 893-895 cm^{-1} for S, and at 1202-1265 cm^{-1} for CMS.
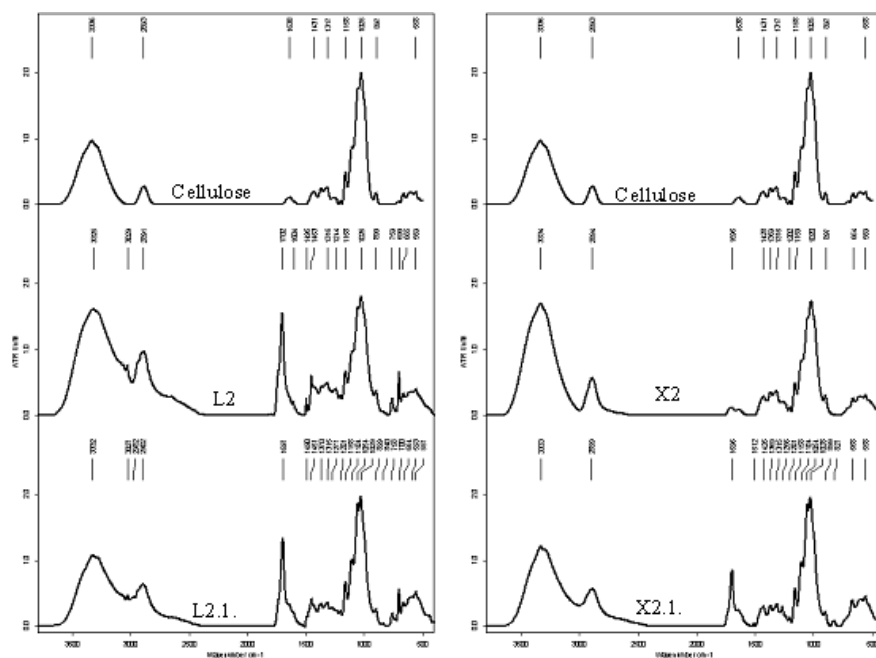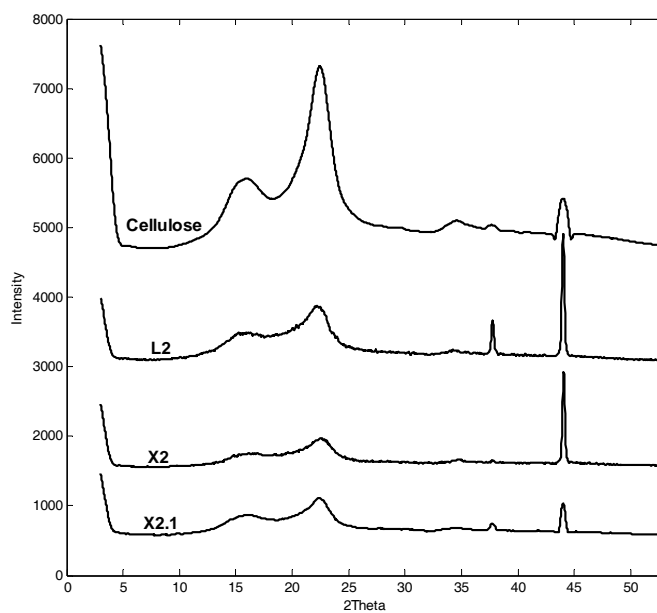
Fig. 3. FT-IR analyses for cellulose and its composites

Fig. 4. XRD analyses

The XRD analysis (Fig. 4) reveals a relative organization in the material structures, by the presence of the peaks at 2θ = 37.77° and at 44°, respectively. These pseudo crystalline organizations can be due to both the aromatic sequences of the polymer matrix, and cellulose microcrystals.

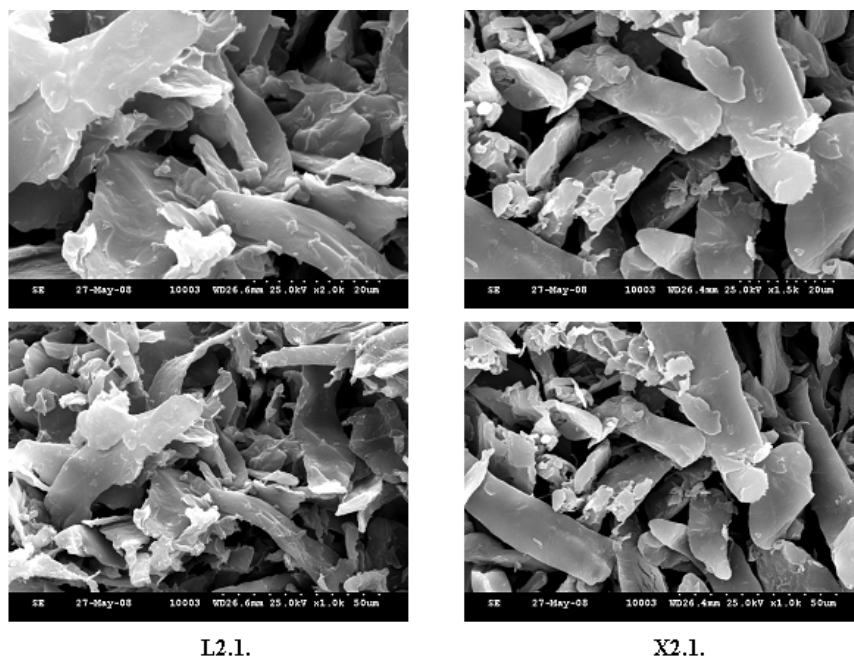The SEM micrographs presented in Fig. 5 show a uniform texture with pores but no regular channels.

L2.1.   X2.1.

Fig. 5. SEM images for the cellulose composites

Thermal degradation of membrane materials follows two broad stages. The first one involves, as expected, the decomposition of cellulose substrate. In the second stage, the synthetic polymer matrix is destroyed. Onset of cellulose substrate decomposition occurs at a remarkably high temperature, 320°C for the MAA-S matrix (Fig. 6), while the cellulose embedded in MAA-CMS matrix (Fig. 7) starts decomposing at 280°C. This feature proves the advanced degree of cellulose modification, since the thermal degradation of virgin cellulose starts at 180°C [18].
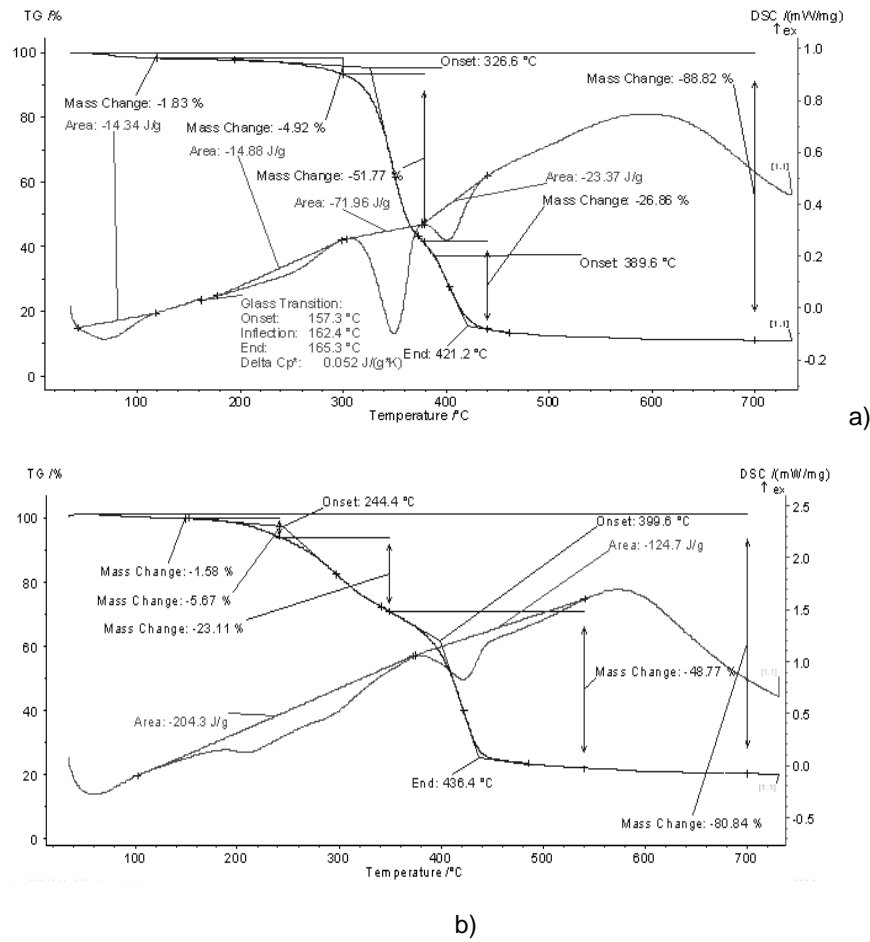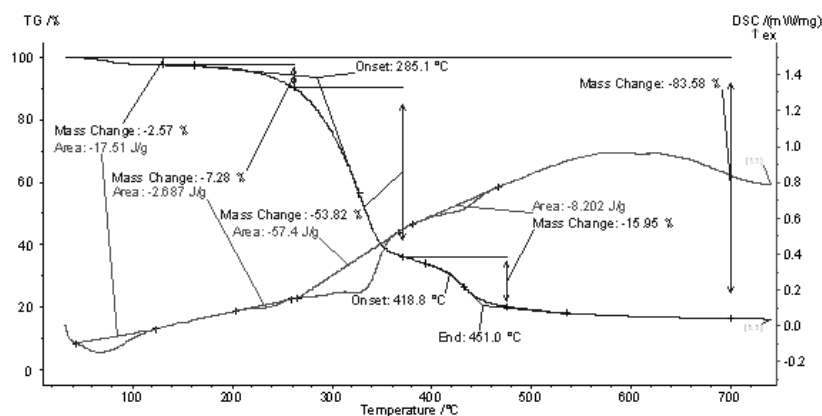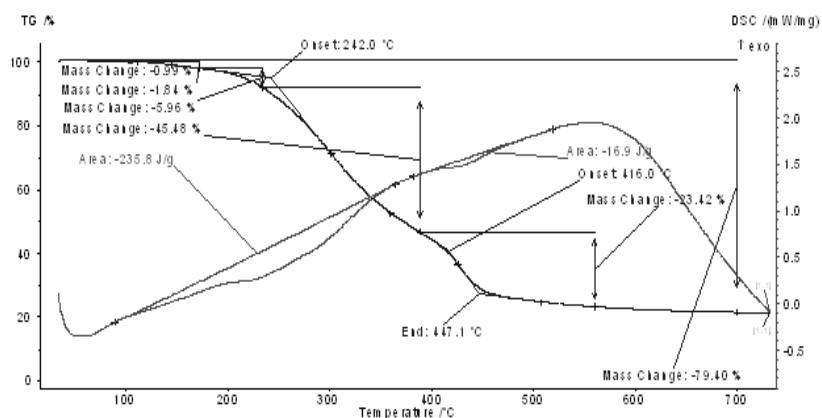
a)

b)

Fig. 6. Thermogravimetric behaviour of the cellulose composites with: AA-S (a), and MAA-S in sulfonated state (b)

a)

b)

Fig. 7. Thermogravimetric behaviour of the cellulose composites with: AA-CMS (a), and MAA-CMS in sulfonated state (b)

Thermal analysis hyphenated with mass-spectrometry shows that sulfonation averages the variations of the C degradation due to different embedment. Indeed, for both matrices (MAA-S and MAA-CMS) the onset of thermal decomposition (Fig. 8 and 9) is at about 240°C. The membrane with MAA-S matrix presents a steeper degradation slope compared to that with MAA-CMS matrix, but the difference is insignificant.

The fragments detected during thermal decomposition reveal the origin of this degradation and the component that degrades first: the $m/z = 64$ (SO_2)

fragment evolves all along the degradation process, suggesting that sulfonation affects both the embedded phase (C) and the matrix. The higher signal of $m/z = 64$ (SO_2) at the beginning of the degradation demonstrates that cellulose is intensely sulfonated, becoming more thermally sensitive. The degradation onset at 240°C keeps our material in favourable perspective for PEM application.
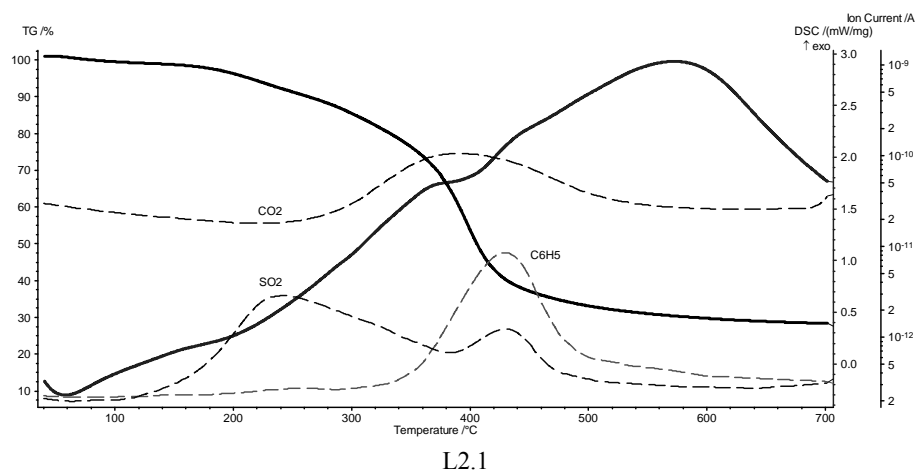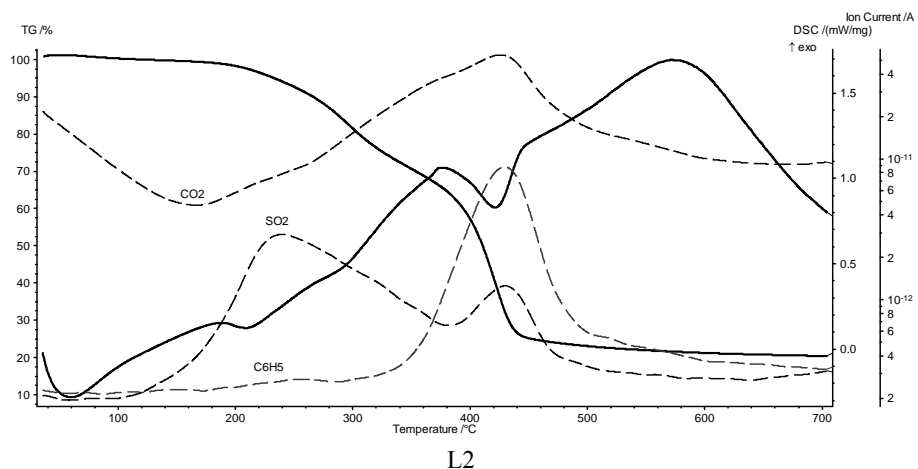

L2

L2.1

Fig. 8. TGA-DSC-MS analyses for the cellulose composites with AA-S and MAA-S in sulfonated state
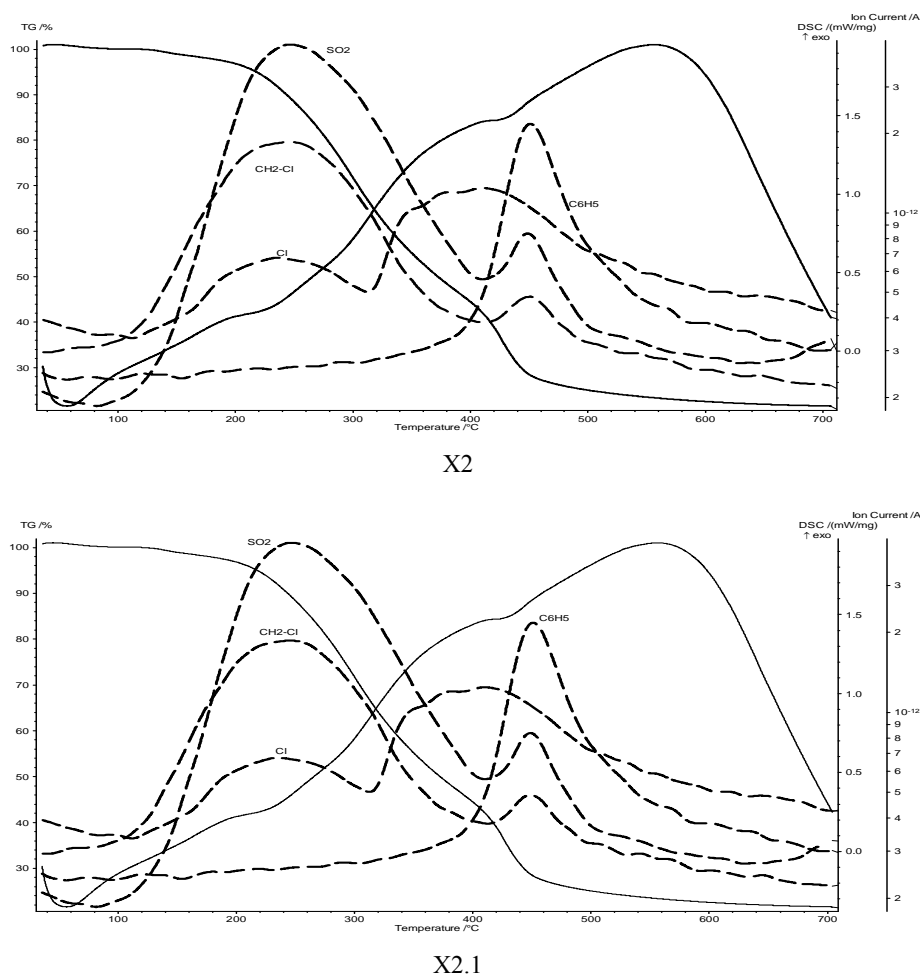
X2

X2.1

Fig. 9. TGA-DSC-MS analyses for the cellulose composites with AA-CMS and MAA-CMS in sulfonated state

Resistivity measurements (Table 2) in dry state showed no variation with composition, but water-swelled samples exhibited diminished resistivity. The resistivity of hydrated MAA-CMS based sample is half of that of MAA-S containing sample. This result is in agreement with the higher polarity of CMS and with a possible ionic conduction mechanism in these samples.

Sulfonated membranes have practically the same volume resistivities as unsulfonated ones, measured in standard conductivity conditions.

Resistivity measurements in dry state and water-swelled samples

Samples State	Code	Electrical resistance $R(\Omega)$	Volume resistivity $\rho_V(\Omega cm)$
Dry	L2.1	$3 \ 10^9$	$1.7 \ 10^9$
	L2.1S	$3 \ 10^9$	$1.7 \ 10^9$
	X2.1	$3 \ 10^9$	$1.7 \ 10^9$
	X2.1S	$3 \ 10^9$	$1.7 \ 10^9$
Water-swelled	L2.1	$1.68 \ 10^3$	$0.97 \ 10^3$
	L2.1S	$2.39 \ 10^4$	$1.31 \ 10^4$
	X2.1	$2.57 \ 10^3$	$1.07 \ 10^3$
	X2.1S	$2.58 \ 10^4$	$1.37 \ 10^4$

4. Conclusions

The obtained volume resistivities, of 9.4×10^6 Ω.cm in dry state and of 2×10^4 Ω.cm in swollen state (both sulfonated or not), make these materials very promising candidates for PEM. Their behaviour in cycling voltammetry will show the type and the level of conduction.

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