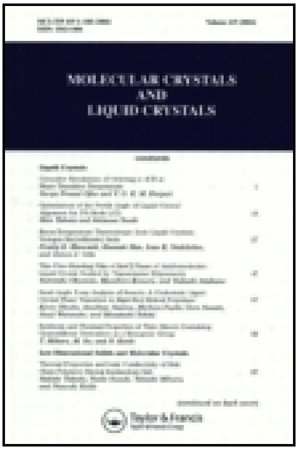

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Cellulose-Based Composites for Membranes by "*In Situ*" Radical Polymerization

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Cellulose-containing composites based on copolymers of acrylic acid with styrene, 4-chloro-methyl-styrene and maleic anhydride were prepared for proton conducting membranes. The influence of the substrate on the copolymer composition as well as the copolymer/cellulose ratio on the basic properties of composite materials is discussed using the FT-IR, optical microscopy, SEM, TGA-DSC and conductivity measurements. Moderate water swelling (2–10%) of the synthesized membranes provided volume resistivities down to $1 \times 10^5\,\Omega \cdot cm$*, adequate for further processing as proton exchange membrane.*

Keywords: acrylic acid; cellulose composite; copolymers; proton exchange membrane

INTRODUCTION

Fuel cell technology and "solid state" electrolysis are promising alternative for future energy needs combined with cleaner environment. Both applications relay on the cell assembly unit that comprises, among others essential parts, the proton exchange membrane (PEM),

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located between the cathode and anode, that transports protons between the electrodes. Proton-conducting polymer electrolyte membranes for high performance PEM have to meet the following requirements [1]: (i) low cost materials; (ii) high proton conductivities; (iii) good water uptakes; (iv) low gas permeability; (v) reliable durability. Up today, the high cost of the cell components impaired their commercialization [1–4].

Recently, intensive research effort is dedicated to developing new materials for this application but so far, only a few types of membranes have been used for proton conduction. Among them are perfluorinated ionomer Nafion, polybenzimidazole/phosphoric acid blend membranes, Nafion membranes modified with inorganic phase (i.e., silicate or zirconium phosphate) and acid-base membranes. The disadvantages of the Nafion membranes are their high price and methanol permeability. Recent literature describes the modification suggested for Nafion membranes in a bind to improve its performance. The approaches described are diverse, ranging from treatment with phosphoric acid, doping with inorganic ions and preparation of organic/inorganic composites by in situ polymerization of embedded polymer precursor witch has proven to be expensive [5–18].

Mixing of negatively and positively charged polyelectrolytes leads to the formation of an electrostatic complex that usually concentrates or precipitates, depending on the dispersion system. In this way, generating the complex precipitation simultaneously with the in situ polymerization lead to a thin continuous film with potential applications in membrane separation process [19,20].

This work investigates systems containing acrylic polyelectrolyte complexes, potential candidates in the synthesis of the membranes with proton conductivity.

The cellulose (C) is a natural material with unique properties due to the presence of the hydroxyl groups. Cellulose-containing composites gain increasing interest due to their (bio)degradability, hence lesser environmental negative impact. The attractiveness of these composites is impaired by the natural low thermal stability of cellulose leading to their reduced recyclability [21–26].

The polyacrylic acid (PAA) is an anionic polyelectrolyte characterized by a high charge density, consequence of the presence of carboxylic groups. Moreover, the acrylic acid (AA) is a monomer with high reactivity in polymerization therefore the obtained complex composite is free of low molecular weight products.

The system PAA-cellulose brings at least two major advantages, first being the low environmental impact of the composite and the second – the possibility of chemical embedment of cellulose domains in PAA matrix by random esterification of the carboxylic groups, during the *in situ* polymerization.

Following these considerations, we chose a copolymerization system based on cellulose and AA, adding as comonomer, styrene (S), chloromethyl styrene (CMS) or maleic anhydride (AM). This insures a broad range of reactivities, possibilities of modulating the polarity of the system and versatility in the following processing steps of the composite as membrane material.

We propose for polyelectrolyte complex synthesis the precipitation polymerization technique. In this particular case, unlike classic heterogeneous systems, the heterogeneity is both initial (due to the presence of cellulose domains) and induced by the insolubility of the polymer in its monomer. This type of polymerization is normally characterized by the presence in the system of the primary particles (oligomers), precursors of the macromolecular compound. It is essential that growth takes place in the cellulose containing phase and no or less as possible new particles without cellulose are formed. For the control of polymerization site in these systems, a narrow selection of stabilization agents are suitable [27].

The utilization of this technique presents the following advantages: fast separation of polymer (simply filtration, without the removal of the surface-active agent), the development of the polymerization processes with high reaction rates, and the synthesis of the products with high molecular weights.

EXPERIMENTAL

Materials

The main monomer was the acrylic acid (AA) from Fluka, distilled under reduced pressure.

The comonomers were: styrene (S), from Fluka, distilled under reduced pressure; maleic anhydride (MA), from Fluka, recrystallized from chloroform and p-vinyl benzyl chloride (p-chloro-methyl-styrene, CMS) from Aldrich, used as received.

The initiator was 2,2′-azo-bis-isobutyronitrile (AIBN), purified by recrystallization from chloroform/methanol mixture.

The cellulose D (C), from Riedel-de Haen, with $DP_n = 400–500$, conditioned overnight at $1 \div 2$ torr and 40°C was used as filler.

Toluene (T), washed with H_2SO_4 $d = 1.84$, K_2SO_4 10% water solution then twice with distilled water and finally rectified, was used as polymerization medium.

The divinyl benzene (DVB) from MERCK was used as crosslinking agent without further purification.

The 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.

Polymerizations

The precipitation polymerization syntheses were carried in micro reactors with mechanical stirring under argon at 75°C for two hours.

Cellulose 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% w/w and the comonomers were used in equimolar ratios.

The obtained composite was separated by filtration, washed with T and dried 24 hours at $1 \div 2$ torr and 60°C.

Film Casting

Each obtained composite was tested in two film compositions, with 3% w/w DVB and without crosslinking agent.

The film composition was prepared in aqueous or dioxane dispersion, evenly cast onto glass plate. The composite membrane was dried at room temperature for at least 24 hours. The final active surface of $3\,\mathrm{cm}^2$ and $55\,\mu\mathrm{m}$ thickness was achieved. The removal of film from the glass plate was realized by swelling in distilled water.

Characterization

All composites were characterized in solid state by FT-IR spectroscopy, using a Bruker 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.

Textural investigation was realized optically using an EUROMEX MIC-2660 microscope and 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.

RESULTS AND DISCUSSIONS

The starting substrate compositions, used for C-containing composites preparation, are presented in Table 1 as four main series of monomer pairs, from which a few compositions fulfilling the criteria for the targeted application were selected.

First evaluation criterion is the influence of the substrate composition on the global yield of composite.

Very good yields are provided by exclusively acrylic substrates (Fig. 1b) and increasing the C content in substrates increases the overall yield up to a ceiling depending on comonomer (Figs. 1a–c).

The comonomer used with AA has an important influence on the yield. The yield threshold for the S (Figs. 1c) is practically the same as for AA homopolymerization, but is diminished by approximately 10% for the CMS and only a narrow maximum at $x_{WAM} = 0.15$ is recorded for the AA – MA substrate. A possible explanation is the competition of complexes monomer-C and monomer-comonomer, some of these with high activation energies and good solubility, leading in turn to soluble oligomer formation, unrecoverable as composite.

The IR spectra show specific peaks (Figs. 2–5) 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 1160 cm^{-1} and $\upsilon_{C=O}$ peak characteristic for AA at 1669–1704 cm^{-1}.

TABLE 1 Compositions and Process Yield

Code	x^*_{wCel}	x^*_{wAA}	x^*_{wCom}	Yield (%)	Remarks
R1	0.8	0.20	–	95.33	AA
R2	0.6	0.40	–	91.76	
R3	0.4	0.60	–	97.15	
R4	0.2	0.80	–	76.31	
L1	0.8	0.08	0.12	82.97	Comonomer: S $n_{AA}/n_S = 1{:}1$
L2	0.6	0.16	0.24	88.12	
L3	0.4	0.24	0.36	92.83	
L4	0.2	0.33	0.47	–	
V1	0.8	0.08	0.12	88.83	Comonomer: AM $n_{AA}/n_{AM} = 1{:}1$
V2	0.6	0.17	0.23	92.33	
V3	0.4	0.26	0.34	79.18	
V4	0.2	0.34	0.46	66.98	
X1	0.8	0.06	0.14	80.24	Comonomer: CMS $n_{AA}/n_{CMS} = 1{:}1$
X2	0.6	0.13	0.27	82.64	
X3	0.4	0.19	0.41	83.10	
X4	0.2	0.26	0.54	80.24	

*Weight fractions.

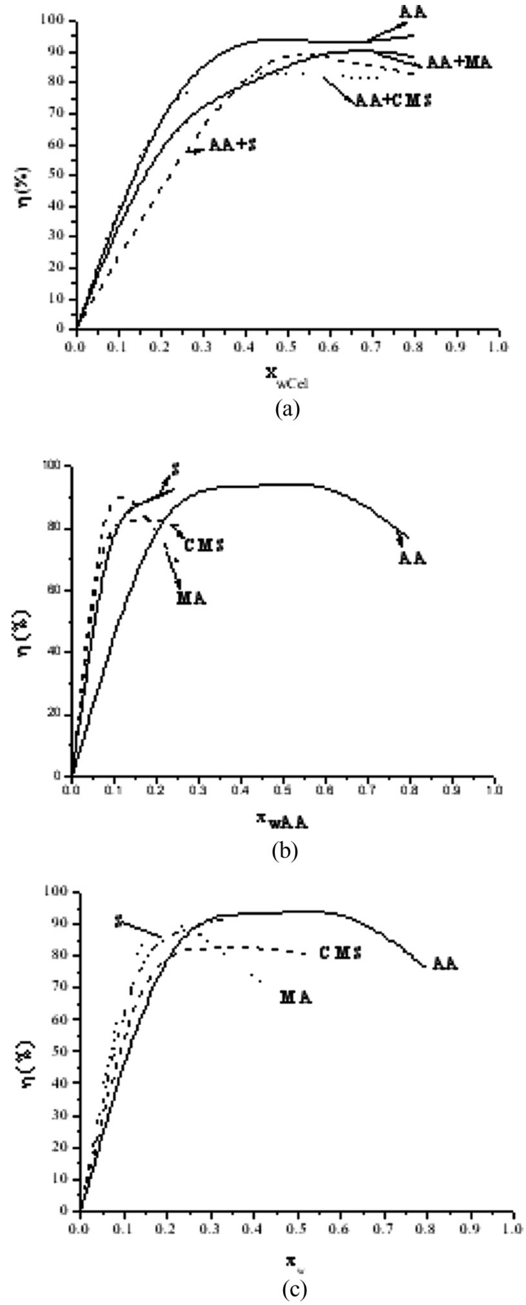


FIGURE 1 The composite yield evolution: a) with C fraction; b) with AA fraction; c) co-monomer fraction.

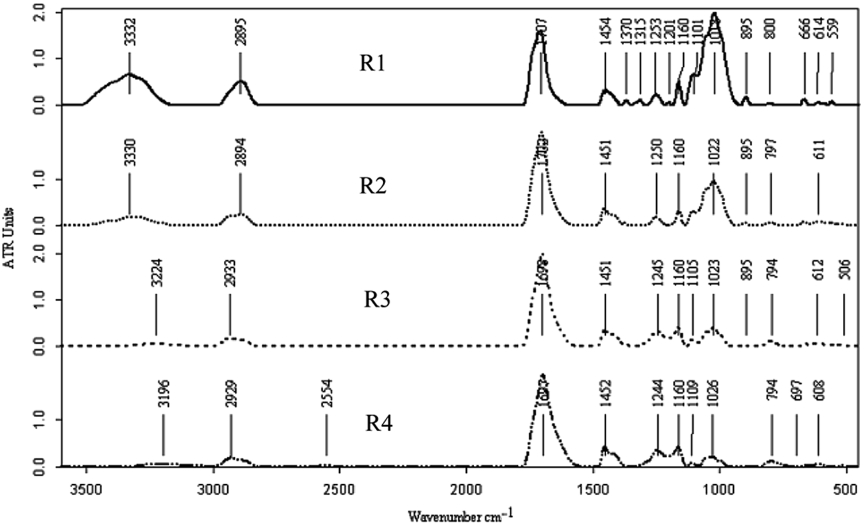


FIGURE 2 The FT-IR spectra for AA-cellulose composites (R series).

All compositions exhibited a new vibration at about 1638 cm^{-1}, that can be assigned to AA-C ester, together with diminishing of the intensity for the peaks at 3196–3450 cm^{-1} specific for the υ_{OH} in hydroxyl and carboxyl group.

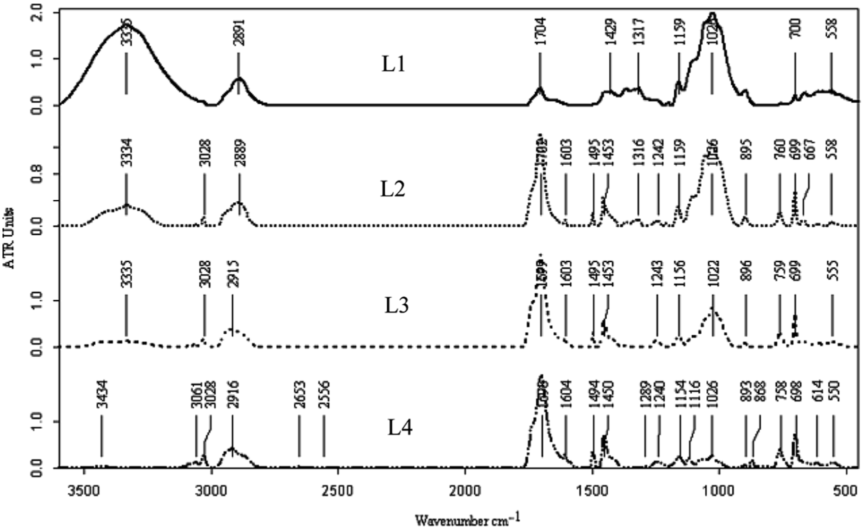


FIGURE 3 The FT-IR spectra for S – AA-cellulose composites (L series).

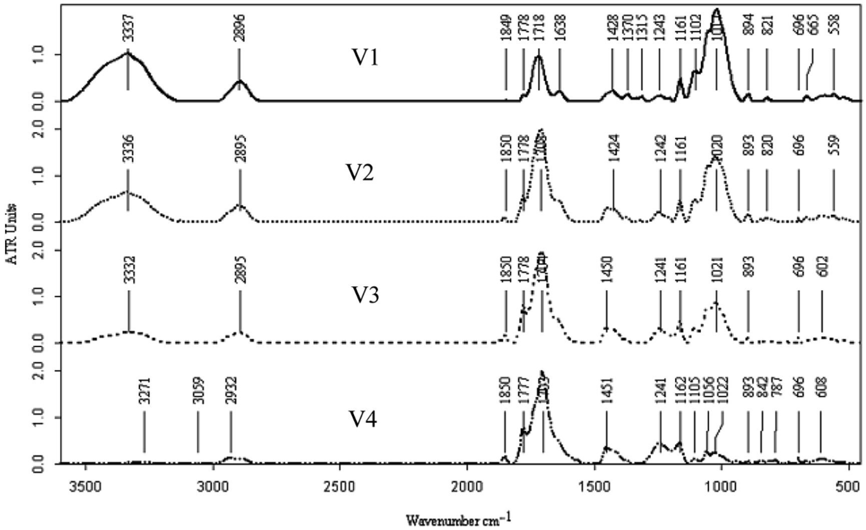


FIGURE 4 The FT-IR spectra for AM – AA-cellulose composites (V series).

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; at 1849–1850 cm^{-1} and 1777–1778 cm^{-1} for MA and at: 819 cm^{-1} and

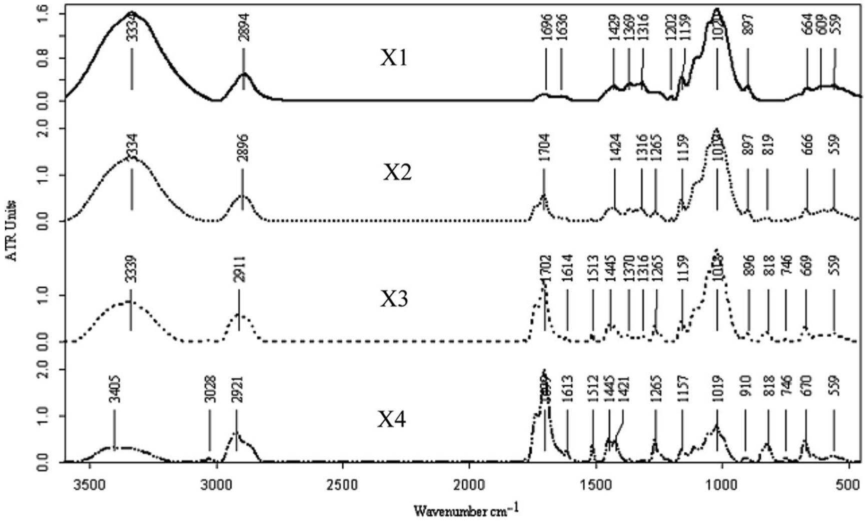


FIGURE 5 The FT-IR spectra for CMS – AA-cellulose composites (X series).

TABLE 2 The Composition of Obtained Samples, Estimated from FT-IR Spectra

x_{cel}^{**}	0.2				0.4				0.6				0.8			
X_{AA}^{*}	0.945	0.74	0.608	0.812	0.83	0.630	0.365	0.652	0.67	0.476	0.214	0.564	0.45	0.158	0.061	0.311
X_{Cel}^{*}	0.055	0.10	0.252	0.115	0.17	0.261	0.55	0.282	0.33	0.450	0.735	0.403	0.55	0.792	0.900	0.636
X_{S}^{*}	–	0.16	–	–	–	0.109	–		–	0.074	–	–	–	0.050	–	–
X_{CMS}^{*}	–	–	0.140	–	–	–	0.085		–	–	0.051	–	–	–	0.039	–
X_{AM}^{*}	–	–	–	0.073	–	–	–	0.066	–	–	–	–	–	–	–	0.053

*Molar fraction in composite.

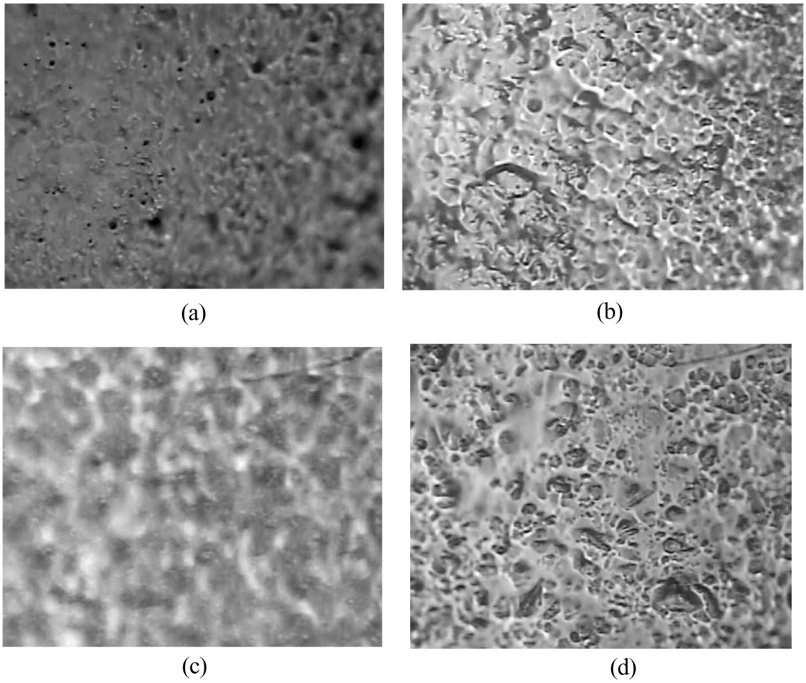
**Molar fraction in substrate.

1202–1265 cm^{-1} for CMS. Using the skeleton stretching vibration at 2890–2940 cm^{-1} as reference, the composition of the resulting material was calculated as previously described [28] and the estimates are summarized in Table 2. Results show that insertion of AA in copolymer is favored for all equimolar comonomer substrates.

Water-swelling of dried membranes showed moderate absorption of $1.8 \div 3.5\%$ w/w. For most of the compositions, the removal of the membrane from the glass support resulted in breaking or complete destruction. Five compositions only could be safely removed from the glass support, two containing AA-S copolymer (samples L2, L3) and three with AA-CMS copolymer (samples X1, X2, X3).

Extreme brittleness of AA-AM compositions can be explained by formation of low molecular weight products that cannot produce continuous film.

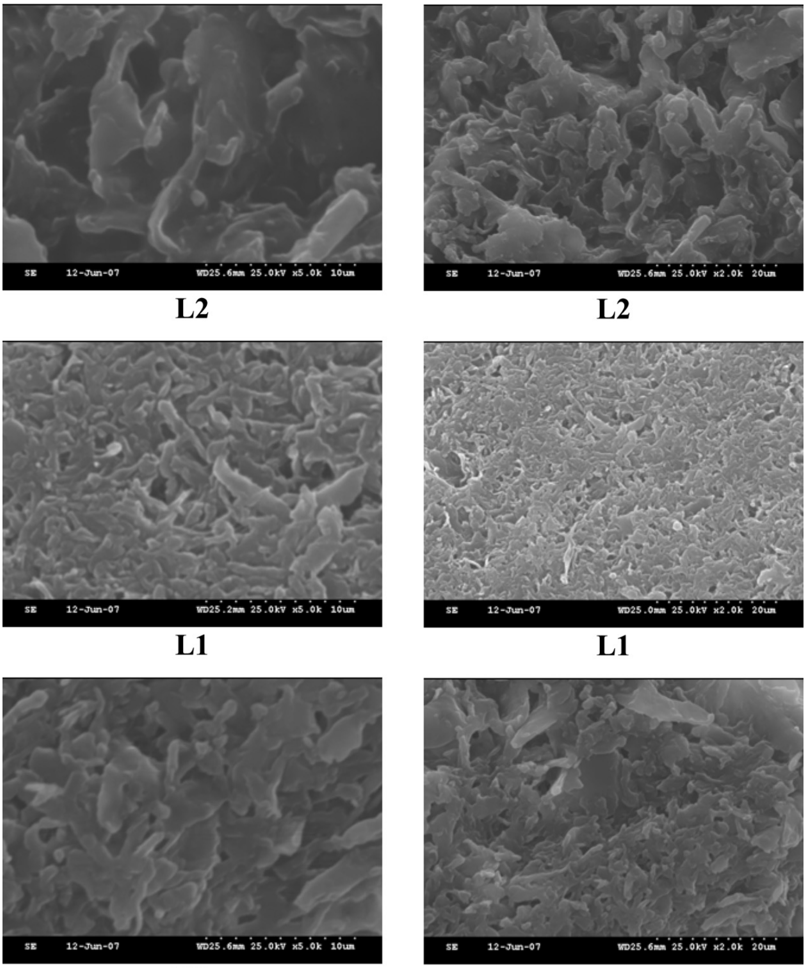
Optical micrographs at 100 magnification in Figure 6 show an increased homogeneity of uncrosslinked samples, parallel to increasing the polymer content in composite but the exclusion of the C at $4/1 = AA/C$ w/w.



(a) (b)

(c) (d)

FIGURE 6 Optical microscopy textures: a) R2; b) R3; c) R4; d) L3.



L2 **L2**

L1 **L1**

X2 **X2**

FIGURE 7 SEM micrographs for the samples with various compositions and good flexibility.

After crosslinking, some of the selected samples – X2 for AA-S copolymer and L2 for AA-CMS copolymer – SEM micrographs presented in Figure 7 – show an uniform texture with regular channels.

Thermal analysis in Figures 8–10 exhibited roughly four stages of degradation. First stage is 1.83– 2.99% water loss in the temperature range of 40–120°C and represents adsorbed water. The second stage, ranging from 130°C to 260°C, is loss of structural water (3.38– 11.16%)

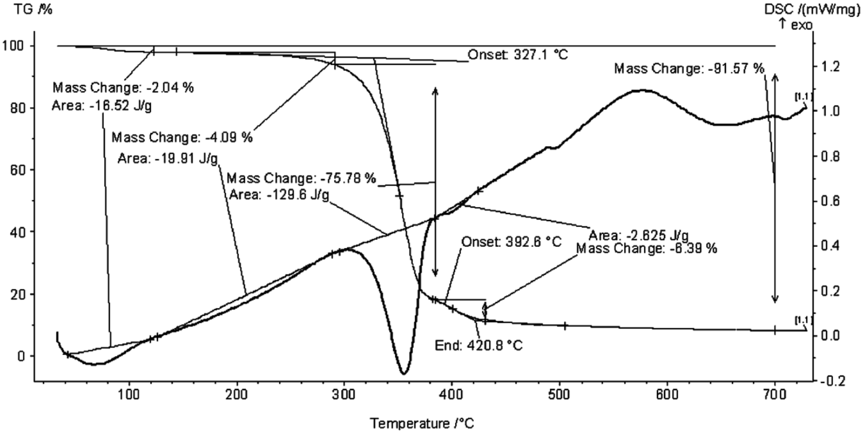


FIGURE 8 TGA-DSC analysis for S – AA-cellulose composite L1.

by mainly intra and intermolecular dehydration. The major weight loss of 37–77% in the range of 300–400°C is the thermal degradation of the polymer backbone. The last degradation stage, above 400°C represents the final destruction of the composite and varies from 18% to 40%. All the samples exhibited coke formation, 8 to 15% residue remaining above 700°C.

Increasing the aromatic comonomer content shifted all the degradation steps to higher temperatures and the higher the aromatic

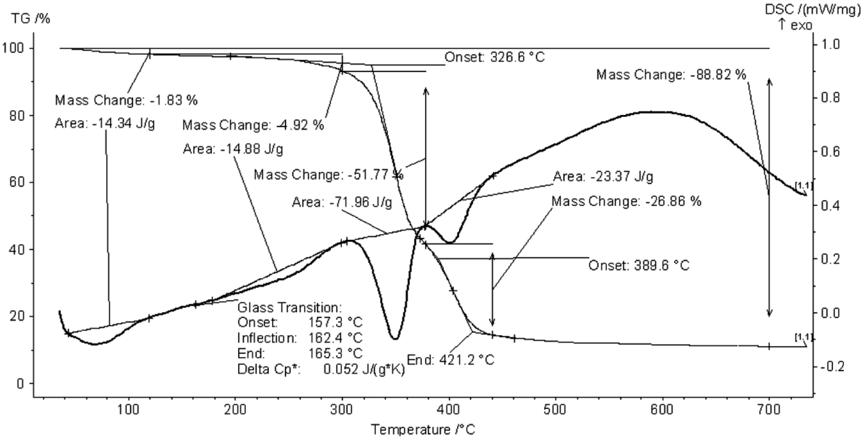


FIGURE 9 TGA-DSC analysis for S – AA-cellulose composite L2.

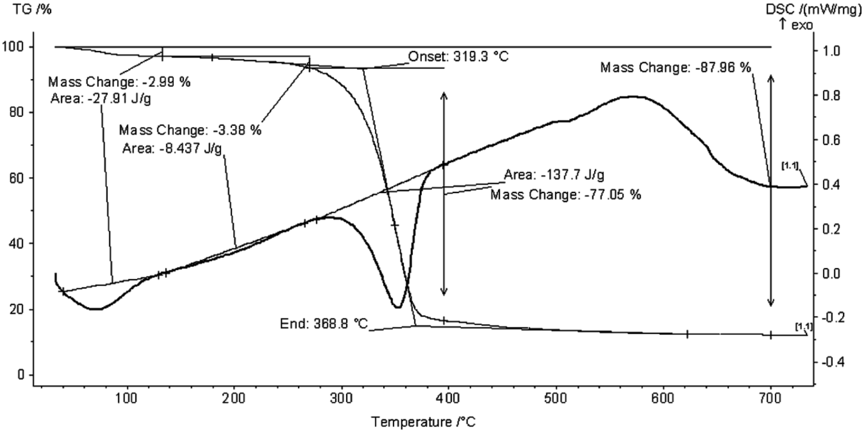


FIGURE 10 TGA-DSC analysis for CMS – AA-cellulose composite X1.

comonomer content was, the higher coke level and lower the degradation in the first three stages were.

Resistivity measurements in dry state showed no differences with composition but water-swelled samples exhibited diminished resistivity (Table 3). The resistivity of hydrated AA-CMS based sample is half of that of AA-S containing sample. This result is in agreement with the higher polarity of CMS and with a possible ionic conduction mechanism in these samples.

The obtained volume resistivities of $9.4 \times 10^6\,\Omega \cdot \text{cm}$ make these materials very promising candidates for further functionalisation (by sulfonation or other) to achieve conduction levels necessary for PEM.

CONCLUSIONS

Polyelectrolyte complex composite membrane films were prepared from cellulose and polymer or copolymer of acrylic acid with different

TABLE 3 Electrical Resistance and Volume Resistivity for the Dry and Water-Swelled Films

Code		Electrical resistance R(Ω)	Volume resistivity $\rho_V(\Omega \cdot \text{cm})$
L2	dry	$3.5 \cdot 10^9\,\Omega$	$3.2 \cdot 10^{11}$
	water swelled	$9 \cdot 10^4\Omega$	$9.4 \cdot 10^6$
X2	dry	$3.4 \cdot 10^9\Omega$	$2.9 \cdot 10^{11}$
	water swelled	$5.3 \cdot 10^4\Omega$	$4.9 \cdot 10^6$

C/polymer ratios. FTIR characterization confirmed the embedment of C in the polymer matrix. Characterization by TGA-DSC revealed the adequate thermal stability of membranes that is essential for PEM applications. Moderate water swelling (2–10%) of the synthesized membrane provided volume resistivities down to approx. $1 \times 10^5\,\Omega \cdot \text{cm}$, adequate for further processing as PEM.

The study reveals the possibility of preparing low cost, environment friendly, polyelectrolyte composite membrane.

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