Degradation profiles of poly(methylene oxide) and poly(glycolic acid) for inflow control devices in oil wells

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ABSTRACT: The viability of the application of hydrolysable polymers, such as poly(methylene oxide) (PMO) and poly(glycolic acid) (PGA), in formation treatments in oil wells, was studied; we examined their addition to inflow control devices (ICDs), which are instruments used to control the oil-flow profile along production intervals. Thereby, the structural and morphological changes of PMO and PGA samples exposed to common chemicals, such as hydrochloric acid (HCl) and sodium chloride (NaCl) solutions and xylene, used in the procedure were evaluated under conditions similar to those observed in southeastern Brazilian offshore oil fields (temperature range = 50–130 °C, 41.4 MPa). The aim of this study was to verify whether the polymers hydrolyzed and could be further removed from the ICDs. Techniques including high-pressure liquid chromatography, ion chromatography, ^{13}C-NMR, differential scanning calorimetry, scanning electron microscopy, and optical microscopy were applied in this study. Xylene did not produce expressive effects in the samples. PMO was significantly affected by 15% HCl at 75 °C but was not completely dissolved after 24 h of exposure; this counter indicates its use. The PGA hydrolysis profile in NaCl brine was suitable for application around 75 °C. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43786.
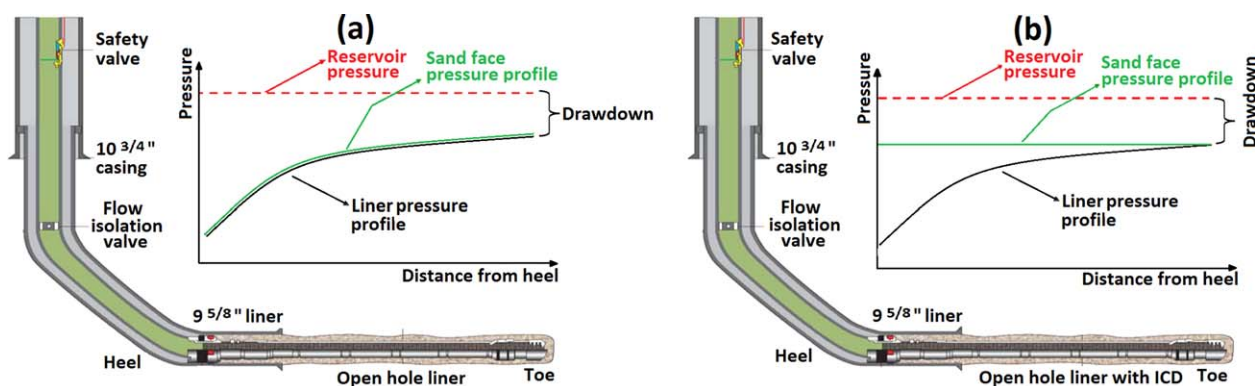
INTRODUCTION

Hydrolysable polymers have found many applications in recent years.[1] From degradable materials to the simple reduction of plastic's environmental impact to outstanding drug-delivery studies, several uses can be found for these materials.[2,3] Among them, there are some potential new applications in formation stimulation, one very important branch of the oil industry.[4]

The process of building an oil well almost always introduces a reduction in the rock permeability near the well bore, an effect known as *formation damage*.[4] To remove this flow restriction and increase hydrocarbon production, oil companies have been spent billions of dollars every year; this indicates the importance of improvements in treatment techniques such as formation acidizing stimulation. One way of enhancing those treatments is to develop better ways to distribute chemical treatments along the formation interval, a process called *fluid divergence*, in which hydrolysable polymers may play a very important role.[4] To pro-

mote divergence, some mechanical devices can be associated to perform complementary functions. One example of this equipment is inflow control devices (ICDs), which can be represented by tubes with a designed perforation gradient (diverting liner and Controlled Acid Jet (CAJ) liner) and tubular accessories for flow restriction provided by specialized companies.[5–7] They provide friction loss by channeling fluids (such as in acid treatments) through a designed set of holes. The imposed friction loss alters the natural formation flow profile during oil production [Figure 1(a)] or during the injection of any kind of fluid in long formation intervals. For the purpose of this study and to simplify the discussion, all of the equipment used are considered ICDs because they all had similar work principles.[6,7]

Normally, IDC cannot be designed to simultaneously control production flow and treatment divergence because these two conditions need different friction loss profiles.[7–9] In high-rate oil wells, the application of ICDs designed for divergence can introduce undesirable friction loss to the oil flow [Figure 1(b)]

Figure 1. Flow profile behavior (a) without an ICD and (b) with an ICD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and can, therefore, cause production impairment. In this study, we proposed that the concomitant use of some suitable polymers and ICDs could provide dual functions: they could control production flow and distribute the treatment along the formation interval without causing a production impairment. This effect was achieved in ICDs through the blocking of an extra set of holes with polymers that could be removed during the completion phase; this changed the pressure behavior and, consequently, the flow profile [from Figure 1(b) back to Figure 1(a)], to achieve the conventional production behavior or any desired combination between these two conditions.

The well completion phase encompasses all operations performed after the drilling of the well to prepare it for production; this includes formation stimulation. Therefore, the selected polymers must have enough sensitivity to be attacked by some of the fluids applied in this phase but still resist until the end of completion.[10] In the same way, the running of a piece of equipment in a well is not a delicate operation, so thermoplastics have to withstand mechanical efforts such as pressure and impact. During completion, the drilling fluid used to drill the well is changed by the completion fluid.[11] The most common of these fluids is a saline solution of sodium chloride (NaCl), whose concentration can vary from 10 to 24% w/w. All equipment used in this phase is exposed to this brine during its installation process; thus, polymers selected to be used in ICDs have to resist the installation period, which can vary between 5 and 20 days. Therefore, sensitive polymers such as poly(glycolic acid) (PGA) have to withstand this period of exposure to temperatures and pressures commonly observed in Brazilian offshore fields: 50, 75, 100, and 130 °C and 41.4 MPa.[12,13] In addition to brine, these polymers will be exposed to stimulation fluids.[4] Stimulation operations are normally performed after the installation of completion equipment, whereupon the polymers are exposed to hydrochloric acid (HCl) and xylene. It is important to note that the selected polymers are rapidly attacked by HCl (15%) because this acid corrosivity limits the equipment exposure time to 24 h, especially at higher temperatures. Xylene, on the other hand, does not affect metal equipment but may affect some equipment elastomers if the exposure time is prolonged beyond 24 h. In addition, it is important to completely remove the polymers from the ICDs before the begin-

ning of well production to avoid the production platform; in this way, the impact of undesirable friction loss in well productivity.

Because of economic and time constrains, two engineering polymers, both commodities, were selected according to treatment products and also the well environmental conditions observed in southeastern Brazilian offshore oil wells. The polymers were poly(methylene oxide) (PMO) and PGA.

PMO is known for its mechanical resistance and sensitivity to strong acids such as HCl.[14–16] It has enough resistance to brine and could probably be removed by acid hydrolysis during stimulation operations. Nevertheless, to be suitable for the proposed application, the PMO hydrolysis must be fast enough to prevent the undesirable acid corrosion of the completion equipment.

PGA has good mechanical behavior and hydrolyzes in contact with aqueous fluids, despite the fact that it is also sensitive to HCl.[17,18] Nonetheless, PGA must endure a long exposure to completion fluid that results from the completion equipment installation process and still promote isolation of the extra holes in the ICDs. In this scenario, these polymers can have different uses for the proposed application in ICDs, the completion process, and the realization or not of stimulation operations.

The purpose of this study was to evaluate the effects on the PMO and PGA samples of HCl solution and xylene (both of which are normally used to remove formation damage) and NaCl solution (which is commonly used in oil wells for completion fluids). The test parameters (temperature, pressure, and exposure time) were defined to simulate the oil well environments observed in Brazilian offshore oil fields (temperature range = 50–130 °C, pressure = 41.4 MPa, and exposure time = 24 h to 20 days) to determine the applicability of these polymers in ICDs for divergence and oil production improvement.

EXPERIMENTAL

Materials

PMO samples were received from Plastecno Representações e Comércio, Ltd., and PGA was obtained from Kureha Corp. Both polymers were used as received to prevent the introduction of new variables in the experiments. The products used in the tests
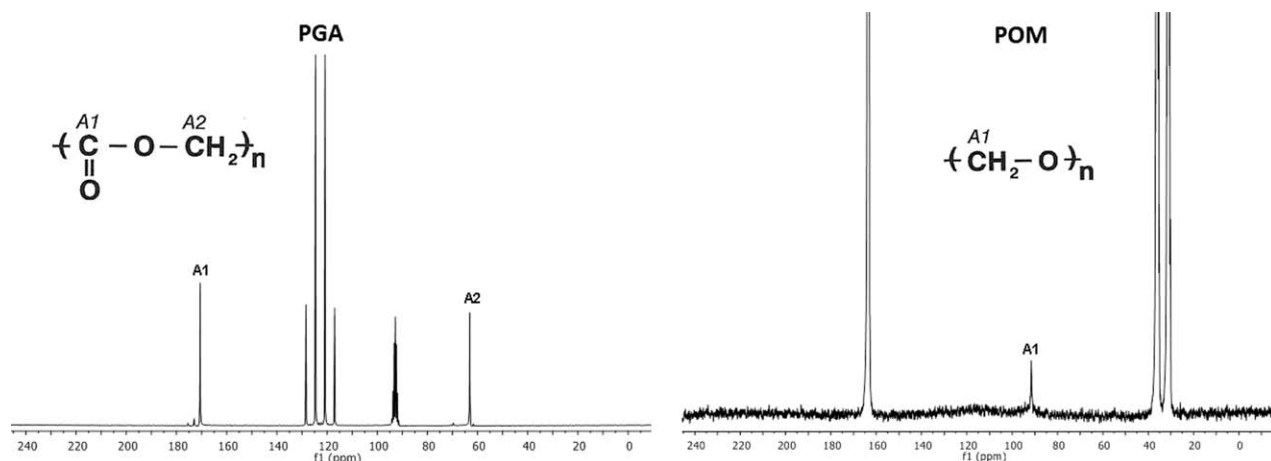
Figure 2. ^{13}C-NMR spectra for PGA in D$_2$O hexafluoracetone (signals from 90 to 130 ppm) at 50 °C and for PMO in dimethylformamide (signals at 30 and 40 ppm and at 160 and 170 ppm) at 80 °C.

were HCl and xylene (analytical grade, Vetec Química Fina, Ltd.) and NaCl (analytical grade, Isofar, Ltd.).

Methods

^{13}C-NMR. Before chemical exposure, all of the polymer samples were characterized by ^{13}C-NMR in an Agilent INOVA300 model instrument (7.05-T magnetic field) with an NMR tube of 10 mm. PGA was analyzed in hexafluoracetone with D$_2$O at 50 °C, and PMO was analyzed in dimethylformamide at 80 °C. The applied frequency was 75,439 MHz, and the spectral window was 20 KHz with an acquisition time of 1.3 s and a 9.4-μs pulse with intervals of 5 s (PMO) and 10 s (PGA) between pulses. The uncoupled nucleus was ^{1}H, and the numbers of transients were 15,000 (PMO) and 1024 (PGA) with nny decoupling mode and a processing line broadening of 5 s.

Scanning Electron Microscopy (SEM). Polymer samples were subjected to SEM to obtain a reference for evaluation of the exposed polymers in a Zeiss EVO LS-15 microscope in a magnification range that was varied from 50 to 5000×. Samples were assembled on a conductive brass support and coated with a thin carbon film in an Emitech K950X vacuum metallizer and then set on a conductive aluminum support. All of the micrographs were taken in a high vacuum at 12.50 mm through secondary electron imaging under an accelerating voltage of 20 keV. Exposed samples micrographs were taken under an accelerating voltage of 5 keV because of its sensitivity to the electron beam.

Optical Microscopy. Sample pictures were taken in a Celestron model 44302-A handheld digital microscope with a magnification range of 50–100 × at 10 mm to observe the samples' general aspects after chemical exposure.

Differential Scanning Calorimetry (DSC). Before chemical exposure, DSC experiments were carried out in a Texas Instruments DSC Q2000 V24.11 calorimeter under a He atmosphere. First-order transitions, the melting temperature (T_m) and the crystallization temperature (T_c), and the second-order transition glass-transition temperature (T_g) were determined. Sample masses varied from 9.4 mg (T_m and T_c scans) to 9.7 mg (T_g scans). The procedure for determining the first-order transitions

were described as follows with a rate of 30 °C/min. We heated the samples from 25 to 200 (PMO) or 250 °C (PGA), and a 1-min isotherm was held at each one of these temperatures. They were then cooled from 200 (PMO) and 250 °C (PGA) to −120 °C. There was a 1-min isotherm at −120 °C, and then, the samples were heated at 20 °C/min to 200 or 250 °C.

Chemical Exposure. The polymer samples were exposed to chemical products in a cylindrical cell made of steel N316 and Hastelloy C276, with capacity for 443 mL, with prototypes developed by Petrobras.[14,15] Cells, polymer samples and chemical solutions were preheated to the test temperature to reduce temperature variation during the experiments. Each cell was filled with approximately 100 g of polymeric samples and the respective liquid media. After that, the cells were closed and pressurized to 41.4 MPa with 20 mL of mineral oil with manual pumps.[14,15] Upon retrieval, samples exposed to 15% w/w HCl and a saturated 26% w/w NaCl neutral solution (NaCl brine) were washed with water over slow filtration with Vetec filter paper. Samples exposed to xylene were washed with water and neutral detergent and water before filtration. All of the exposed samples were dried at 50 °C for 12 h before the analyses.

Characterization of the Acid Hydrolysis Products. The hydrolysis products of PMO were analyzed by high-pressure liquid chromatography (HPLC) in an Argilent Technologies 1200 Infinity chromatographer with ultraviolet irradiation with a Argilent Zorbax Eclipse XDB-C18 250/4.6 column. PGA hydrolysis products were analyzed by ion chromatography (IC) in a Metrohm Metrosep Organic Acids 250/7.8 with a conductometric detector with a Metrohm 862 IC column.

HPLC. PMO exposed to HCl was filtered, and the solution was rested for 24 h at 80 °C for complete hydrolysis. The remaining solution was diluted to 50% v/v with deionized water. From this solution, 600 μL was diluted to 100 mL with HPLC-grade acetonitrile (ACN). A sample of 1 mL was than diluted to 50 mL with ACN with HCl and 7.5 mg of 2.4-dinitrophenilhydrazine and was then analyzed under the following conditions: column temperature = 22 °C; mobile phase: solvent A with 30% v/v ACN, and 70% v/v deionized water and solvent B with 98% v/v

Table I. Mass Loss (Δm) after Chemical Exposure at 50 and 75 °C and 41.4 MPa for 24 h

Polymer	Chemical	Temperature (°C)	Initial mass (g)	Final mass (g)	Δm (g)
PMO	HCl (15% w/w)	50	101.20	88.30	12.90
		75	103.70	57.20	46.50
PGA		50	100.40	99.70	0.70
		75	100.00	48.60	51.40
PMO	Xylene	50	106.80	106.80	0.00
		75	100.90	100.90	0.00
PGA		50	100.03	99.90	0.13
		75	100.00	99.80	0.20
PMO	NaCl (23% w/w)	50	103.00	103.00	0.00
		75	102.60	102.60	0.00
PGA		50	100.90	100.90	0.00
		75	102.80	102.00	0.80

ACN and 2% v/v deionized water; injected solutions concentration = 0.1%; injected volume = 10 µL; and mobile phase flow rate = 1.0 mL/min.

IC. PGA exposed to HCl was filtered, and the solution rested for 24 h at 80 °C for complete hydrolysis. The remaining solution was diluted at 0.01% with deionized water and then analyzed under the following conditions: column temperature = 22 °C; mobile phase: perchloric acid (0.8 mmol/L) plus 2% ACN; injected solutions concentration = 0.1%; injected volume = 20 µL; and mobile phase flow rate = 0.7 mL/min.

RESULTS AND DISCUSSION

^{13}C-NMR

Figure 2 presents the obtained ^{13}C-NMR spectra with the characteristic signs for both polymers. PMO presented a characteristic bond signal at 92 ppm (ether group), whereas PGA presented two characteristic signals at 170 ppm (carboxyl group) and at 62 ppm (carboxyl–methyl group). Secondary signs were produced by the solvents used in the analysis. The spectra provided a good characterization of both polymers and did not present indications of significant amounts of contaminants in the samples.[19,20]

DSC

The DSC results obtained for PMO and PGA were compatible with the analyzed polymers and were within the limits provided by the manufacturers. PMO presented a T_m value of 162 °C and a T_g value of −67 °C. PGA, on other hand, exhibited a T_m of 218 °C and a T_g of 37 °C.[21,22]

Mass Loss

Table I presents the effects on PMO and PGA of chemical exposure to 15% w/w HCl, xylene, and 26% w/w NaCl for 24 h at 50 and 75 °C. The effects of HCl on PMO were very evident from 50 °C and increased significantly at 75 °C, with an expressive loss of polymer mass at higher temperatures. PGA was not significantly attacked at 50 °C but presented a similar mass loss to that of PMO at 75 °C.

That higher degradation at 75 °C suggested a more significant influence of the temperature on the hydrolysis of PGA than on the degradation of PMO under the test conditions. Some authors have indicated that the degradation speed of amorphous regions tends to be greater than that in crystalline regions, especially above T_g, and increases the hydrolysis velocity.[23] However, the DSC results indicate that the glass-transition temperature of PGA (37 °C) was below the tests conditions, so the acceleration of

Table II. PGA Mass Loss (Δm) after Exposure to NaCl (23%) at 41.4 MP for Different Exposure Intervals and at Different Temperatures

Polymer	Chemical	Exposure time (days)	Temperature (°C)	Initial mass (g)	Final mass (g)	Δm (g)
PGA	NaCl (23% w/w)	5	50	100.47	96.13	4.34
		15	50	100.06	93.74	6.32
		20	50	100.11	79.23	20.88
		5	75	100.14	77.6	22.54
		15	75	100.31	28.57	71.74
		20	75	100.96	15.56	85.4
		1	100	100.04	51.43	48.61
		1	130	100.04	0.00	100.04

PGA presented a narrow range of hydrolytic products that could be related to glycolic acid and, therefore, to a homopolymeric structure, as indicated by the manufacturer.
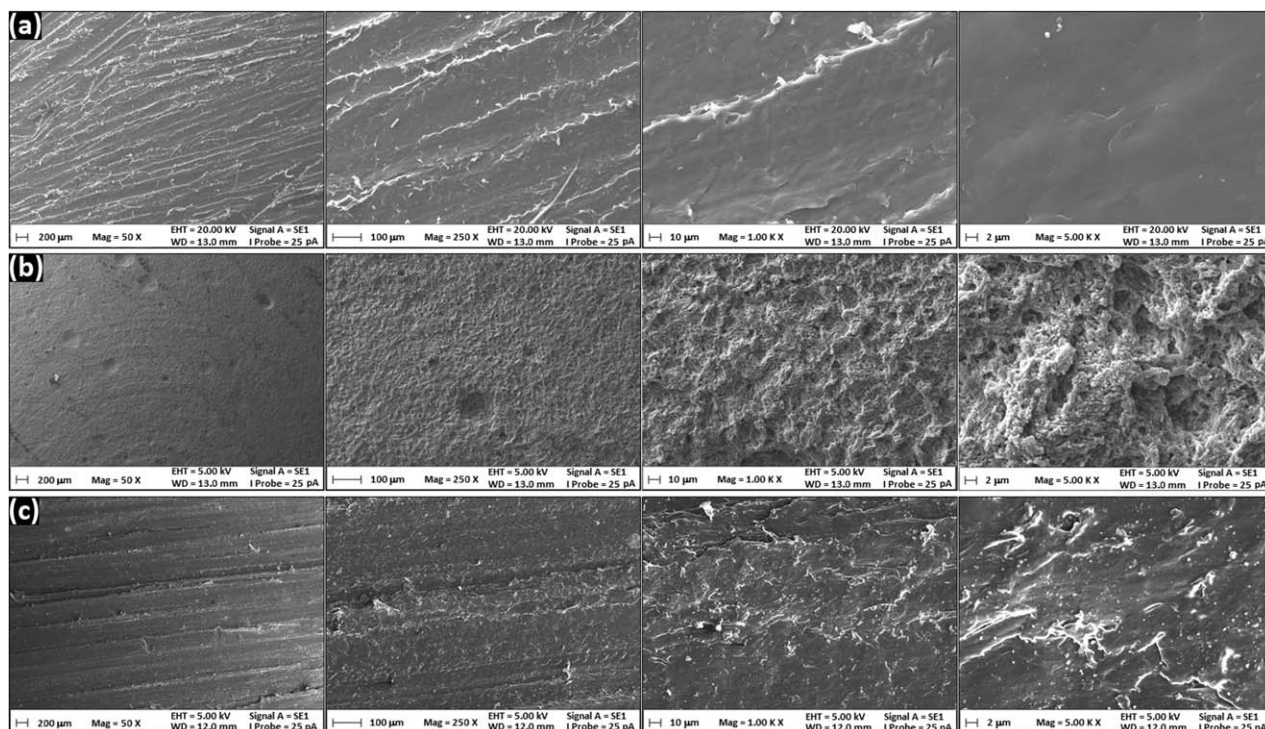
Figure 3. SEM micrographs of (a) PMO without chemical exposure, (b) PMO exposed to HCl (15%) at 50 °C and 41.4 MPa for 24 h, and (c) PMO exposed to xylene at 75 °C and 41.4 MPa for 24 h.

PGA hydrolysis with temperature was not likely to have been especially related to the T_g parameter in the performed tests.[16,18,24] Similar effects were observed in previous studies that compared the behavior of PMO and PET exposed to HCl at lower temperatures and pressures with the same exposure time; this resulted intense degradation of the polyacetal and just mild hydrolysis of the polyester at relatively low temperatures.[14,15,25,26]

The corrosivity of HCl prevents its use for more than 24 h because conventional corrosion inhibitors are not capable of ensuring the integrity of well equipment beyond this period of time. Therefore, further effects of a longer HCl exposure over PMO and PGA were not investigated.[27]

None of the polymers was significantly affected by xylene exposure; therefore, this solvent could not be used to remove them from the ICDs after well completion.

PGA is sensitive to hydrolysis in more friendly media, such as NaCl solutions; this is very common in most completion operations.[28] Therefore, instead of rapid hydrolysis, PGA needs to last long enough to allow ICD installation in the well. With taken in to account, tests involving NaCl solutions were extended for some weeks. Table II shows the results obtained for PGA exposed to NaCl brine.

PGA was highly affected by NaCl brine at exposure times greater than 5 days. We was observed that under the test conditions, the temperature seemed to be more important to PGA hydrolysis than the exposure time; the effect at 75 °C was much greater than that at 50 °C for the same test period.

In addition to hydrolysis, an important alteration in mechanical integrity was observed in exposed PGA samples. Despite the preservation of their general shape after testing, PGA samples were reduced to powder by the washing process and had to be

Figure 4. Optical micrographs of PMO exposed to HCl (15%) at 50 °C and 41.4 MPa for 24 h in normal light: (a) 50 × magnification, (b) 50 × magnification, and (c) 150 × magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
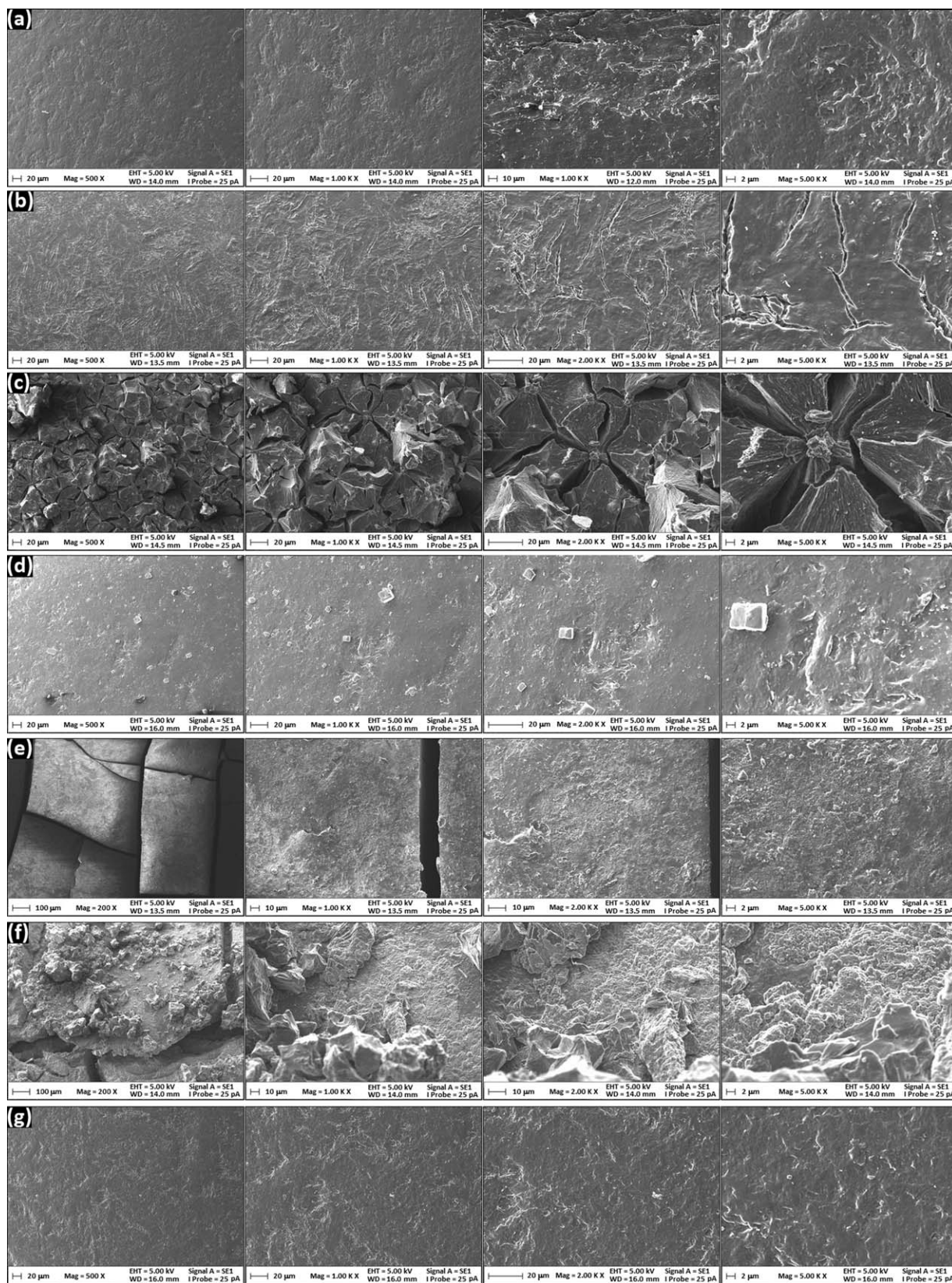
Figure 5. (a) PGA without chemical exposure, (b) PGA exposed to HCl (15%) at 50 °C and 41.4 MPa for 24 h, (c) PGA exposed to HCl (15%) at 75 °C and 41.4 MPa for 24 h, (d) PGA exposed to NaCl at 50 °C and 41.4 MPa for 24 h, (e) PGA exposed to NaCl at 75 °C and 41.4 MPa for 24 h, (f) PGA exposed to NaCl at 75 °C and 41.4 MPa for 5 days, and (g) PGA exposed to xylene at 75 °C and 41.4 MPa for 24 h.

filtered on a paper filter to measure the residual mass. The resulting powder was not subjected to SEM once it could not be compared to PGA pellets tested under further conditions.

In general, PGA suffered significant hydrolysis even at 50 °C, and this degradation could probably have been extended by an increase in the exposure time.[29] Provided that it could easily last more than 5 days to start well production after completion process, this period could be understood as the minimum exposure time expected in the field. In this way, PGA could probably be removed from ICDs at all tested temperatures, and this would produce the required reduction in ICD friction loss and its undesirable impacts on oil production.[30]

Morphological Analysis
SEM micrographs obtained before and after the polymers were subjected to chemical exposure are presented in Figures 3–5. There were remarkable differences in the PMO behavior compared to those of PGA. The PMO samples appeared to have suffered a relatively uniform attack when exposed to HCl; this produced a regular porous structure at the sample surface, as shown in the SEM micrographs in Figure 3(b). When that fragile porous structure was removed from the sample, we observed a practically intact PMO core forming an inner layer (Figure 4).

This structure suggested a relatively uniform and progressive degradation process at the polymer surface; this created a porous media made of partially attacked and probably more crystalline PMO.[14,16,24,26] The hydrolysis process seemed to be dominated by the mass transport of HCl through the porous layer to the sample core; this favored the continuous degradation of the core surface and the growth of the porous layer thickness, despite its own hydrolysis.[24,26]

PGA samples, on the other hand, presented a different behavior, showing surface cracking. In acid media, the intensity of that effect seemed to increase with temperature, as suggested when in the comparison of Figures 5(b) and 5(c). The number and size of the cracks were significantly higher at 75 °C than at 50 °C. The hydrolysis probably started and was more intense in the amorphous regions between crystalline zones. There, tie-chain segments, free-chain ends, and chain folds degraded into fragments until the fragments reached the stage at which they could be dissolved into the media; this formed voids through selective dissolution that became cracks after dehydration.[18] Despite the dehydration effect, the increase in the cracking intensity with test media aggressiveness reinforced the preferential attack to amorphous areas; this produced weakened and voided regions that deformed and opened around crystalline and mechanical resistant structures.[31,32]

A similar effect was observed in PGA exposure to NaCl brine, with surface cracking occurring within 24 h of exposure at 75 °C but not at 50 °C; this provoked a less intense and relatively uniform hydrolysis of the polymer surface. Those observed effects emphasized the importance of the temperature in the PGA hydrolytic process regardless the test media. Figure 5(f) presents the effects of 5 days of NaCl brine exposure at 75 °C in PGA. The number of cracks did not seem to have grown at 200×; this was similar to what we observed when PGA was exposed to HCl [Figure 5(c)]. However, the cracks became larger, and the

Table III. Chromatographic Analysis of the Hydrolytic Products

Polymer	Analyte	Concentration (mg/L)
PMO[a]	Formaldehyde	63,900
	Acetone plus acrolein	14,000
	Butanone	3,300
	Valeraldehyde	6,200
PGA[b]	Glycolate	32,000
	Formate	900

[a] HPLC.
[b] IC.

areas among the cracks were much more affected than in the sample exposed for 24 h at the same temperature. PGA samples exposed to NaCl brine at 100 and 130 °C were severely attacked in a short period of time (1 day); they completely lost their mechanical integrity, although they had not been entirely hydrolyzed. This degree of attack reinforced the importance of the temperature in the PGA hydrolysis process. The powder SEM analysis did not produce representative results that could be used in this study.

Chromatographic Analysis
Table III presents the resulting products of PMO and PGA hydrolysis from chromatography. PMO hydrolysis resulted in a relatively complex solution composed of five different products. The simple structure of the PMO homopolymer formed by the open-ring polymerization of dioxolane could not explain the presence of a significant amount of products other than formaldehyde.[33] Because the PMO acid hydrolytic mechanism was relatively simple, the presence of products such as valeraldehyde and butanone could basically be explained by the PMO copolymer hydrolysis. The PMO copolymer was produced by the introduction of oxyalkylene compounds, such as ethylene oxide or 1,3 dioxolane, into the polymerization process; this resulted in a random copolymer, which is more common in the industry because of its resistance to hydrolysis under environmental conditions.[34]

PGA presented a narrow amount of hydrolytic products; this could have been related to glycolic acid and, therefore, to the homopolymeric structure, as indicated by the manufacturer.

CONCLUSIONS
Chromatographic analysis of acid hydrolysis products indicated that the PMO samples were composed by the copolymer once they presented a significant amount of different products other than formaldehyde.

Under test conditions similar to those observed in southeastern Brazilian offshore oil fields, PMO and PGA were not significantly affected by xylene exposition. Therefore, this solvent could not be used to remove those polymers from ICDs after well completion or even in a stimulation treatment.

PMO lost 46.50% of its mass when it was exposed to 15% w/w HCl for 24 h. Despite the fact that it was not completely hydrolyzed, the results indicate that complete hydrolysis would

probably be achieved if the exposure time were extended. However, they also implied that exposure times of longer than 24 h would result in the severe corrosion of the well equipment. Therefore, as neither brine nor xylene had significant effects on PMO, this polymer should not be considered for application in ICDs.

PGA presented the same limitations observed to PMO in terms of acid hydrolysis. It lost 51.40% of its mass, even more than PMO did, but this was still not enough for it to be completely removed from the ICDs. Although the removal of PMO with HCl cannot be recommended in both cases, PGA was highly sensitive to hydrolysis in NaCl brine, too. The relatively slow hydrolysis but extensive mass loss observed in the brine media under the test conditions will allow its use in an appreciable number of oil fields in southeastern Brazil. However, at temperatures above 75 °C, its hydrolysis would be too fast to withstand the well completion process. Therefore, PGA application in ICDs should be limited to oil fields with formation temperatures of 75 °C and below.

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