

## New Filtrate Loss Controller Based on Poly(methyl methacrylate-co-vinyl acetate)

Rita de Cassia P. Nunes,<sup>1</sup> Renata V. Pires,<sup>1</sup> Elizabete F. Lucas,<sup>1</sup> Angelo Vianna,<sup>2</sup> Rosana Lomba<sup>2</sup>

<sup>1</sup>Federal University of Rio de Janeiro (UFRJ), Institute of Macromolecules (IMA), Laboratory of Macromolecules and Colloids for Petroleum Industry (LMCP), 21941598 Rio de Janeiro, Brazil

<sup>2</sup>Petrobras/CENPES, Cidade Universitária, 21941915 Rio de Janeiro, Brazil

Correspondence to: R. d. C. P. Nunes (E-mail: ritapessanha@ima.ufrj.br)

**ABSTRACT:** The drilling of petroleum wells requires the use of suitable drilling fluids to ensure efficient operation without causing rock damage. Specific polymers have been used to control infiltration during drilling, to reduce operational problems. In this study, spherical microparticles of poly(methyl methacrylate-co-vinyl acetate) were synthesized (by suspension polymerization), characterized, and evaluated in terms of their performance in controlling filtrate loss of aqueous fluids. A filter press test with ceramic disk, simulating the rock, was used. The performance of the synthesized materials was compared with commercial polymers. It was observed that the performance of the material is directly associated with the relation between particle size and pore size of the rock specimen. Furthermore, for a suitable particle size, the rubbery characteristic of the material produces a more efficient filter cake, for filtrate control. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40646.

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### INTRODUCTION

The process of oil well drilling requires the use of suitable drilling fluids to ensure fast and secure operation without formation damage.<sup>1</sup> In this context, chemicals are added to drilling fluids to act specifically as: thickeners, filter loss reducers, clay swelling inhibitors, drag reduction agents, lubricants, and dispersants. Among such additives, polymers have been used in drilling fluids since 1930.<sup>2–4</sup>

To reduce filtrate loss, the drilling fluid must be able to produce thin membrane with low permeability in well walls called filter cake.<sup>2</sup> Filtrate loss reducing agents are selected considering their ability to form an effective filter cake.<sup>5–9</sup> The filtrate and the thickness of cake are two parameters routinely measured to evaluate drilling fluids in terms of filtrate loss control.<sup>1</sup> If these parameters are not adequately controlled, some problems can arise, such as excessive invasion of fluids in geological formations and reduction of the well diameter.<sup>10,11</sup> Starch, bentonite, and sodium carboxymethyl cellulose have been used as filtrate loss controller.<sup>12</sup>

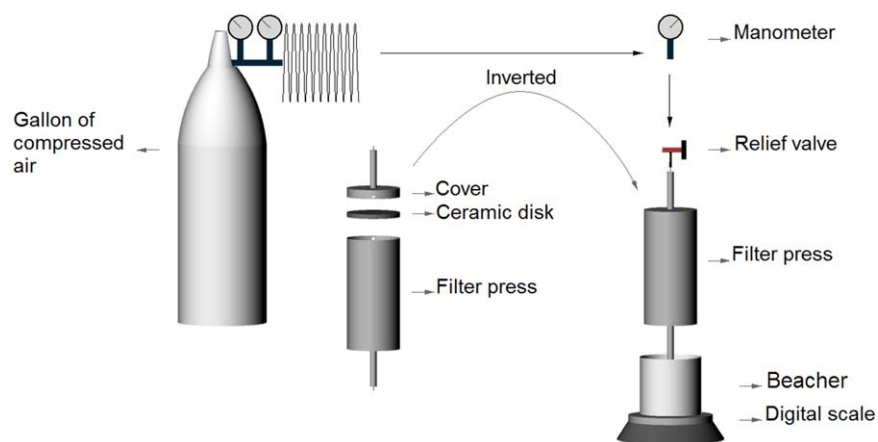
Due to the variety of well drilling conditions, such as temperature, pressure, and rock formation characteristics, specific additives for filtrate loss control must be developed. In general, particles are more effective than films, because films are formed

on the well wall while particles fill up the pores rock. However, it is expect that the effectiveness could be improved if using deformable particles that create a nonpermeable cake.

Also, fluid loss control additives have been produced for use for both drilling and cementing.<sup>4,13,14</sup>

Polymers can be produced by different techniques.<sup>15</sup> Suspension polymerization is widely used industrially due to its advantages, such as easy temperature control during the reaction and the possibility of producing spherical particles, porous or not, with diameters in the range of 50–1000  $\mu\text{m}$ .<sup>16,17</sup> The particles produced by this technique can be used in chromatographic separation, water treatment, enzyme immobilization, and vascular embolization.<sup>18–21</sup> The suspension polymerization technique has been used to produce poly(methyl methacrylate) (MMA), which has high Young's modulus. On the other hand, spherical particles of poly(vinyl acetate) (PVAc), which has a relatively low Young's modulus, are not produce by this technique.<sup>22–24</sup>

In this work, spherical microparticles of poly(methyl methacrylate-co-vinyl acetate) (PMMA-VAc), prepared by suspension polymerization, were evaluated in terms of their performance to control filtrate loss of aqueous fluids. The influence of copolymer composition and particle size on the additive performance was investigated.



**Figure 1.** Schematic representation of filtrate controlling apparatus. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) and vinyl acetate (VAc), supplied by Cia Química Metacril—Candeias, Brazil and Vetec Química Fina—Rio de Janeiro, Brazil, respectively, were used as received. Benzoyl peroxide (BPO), supplied by Vetec Química Fina (Rio de Janeiro), was used as the polymerization initiator at a concentration of 1% in ratio to the total concentration of monomers. Gelatin 240 Bloom, supplied by Theorberg Imp. Exp (Rio de Janeiro), was used as stabilizer at 1.25% in aqueous phase of the reaction. Two commercial samples were used as reference for filtrate control: sodium lignosulphonate supplied by Borregaard Ligno Tech (São Paulo) and two commercial latex samples, named Latex A and Latex B, supplied by Lanxess Elastômeros do Brasil (Rio de Janeiro). Ceramic filter disks were supplied by Fann Ins. Co. (Houston), with mean pore diameters of 10, 60, and 90  $\mu\text{m}$ . Xanthan gum (Kelsan SCD Polymer), supplied by Kelco Oil Field Group (Houston), was used to produce an aqueous dispersion to achieve viscosity similar to the drilling fluid.

### Polymer Synthesis

The copolymers were obtained via free radical suspension polymerization. The aqueous phase was prepared by dissolving 1.3 wt/vol % of gelatin in water at 60°C. The organic phase was prepared by dissolving 1 wt % of BPO in the monomer. The organic phase was added, under mechanical stirring (IKA 20RW), to the aqueous phase at a concentration of 40 wt/vol %. Nitrogen was bubbled in the aqueous suspension for 2 min. The polymerization was carried out at 80°C and 400 rpm for 4 h. The beads were washed thoroughly with distilled water to remove the stabilizer, until the filtrate was soluble in water. The beads were then size classified using hydraulic sieving (Retsch AS-200), with sieves of 45, 75, 150, and 355 mesh. After that, the material was dried at 60°C for 24 h.

### Polymer Characterization

Polymer samples were characterized in terms of: copolymer composition, morphology, bead size distribution, thermal stability, and glass transition temperature. Some samples were also characterized by dynamic mechanical analysis. The performance

of the materials as filter loss reducers was evaluated by an apparatus as shown in Figure 1, containing a ceramic disk of specific average porosity.

**Copolymer Composition.** The spectra were obtained from a  $^{13}\text{C}$  nuclear magnetic resonance spectroscope (Varian Mercury VX300) at 75 MHz, using 5 mm tubes containing the copolymer dispersed in deuterated chloroform. For calculation, it was used the ratio of the areas centered at 177 ppm and 169 ppm, related to the molar ratio of carbonyl group of methyl methacrylate and vinyl acetate, respectively. The results were expressed in terms of mass composition using for that molar mass of methyl methacrylate (100 g/mol) and vinyl acetate (86 g/mol).

**Morphology.** The samples were observed on a glass slide using diffuse back lighting. The photomicrography was obtained by a Nikon Coolpix 5400 digital camera coupled to the microscope.

Ceramic disks were observed by scanning electron microscopy using a Jeol JSM-5610 L after gold coating, with zoom 50 and 500  $\mu\text{m}$  ruler.

**Bead Size and Size Distribution.** The synthesized samples were analyzed with a Malvern Zetasizer Micro (size range: 0.3–300  $\mu\text{m}$ ), which requires lens alignment with a beaker containing distilled water. Commercial samples of lignosulphonate and latexes were analyzed in terms of particle size and particle size distribution by using a Malvern Zetasizer Nano series that requires the refractive index and absorbance at 633 nm of each sample. The refractive indexes (1.3353 for lignosulphonate and 1.4695 for latexes) and absorbances (1.2119 for the lignosulphonate and 2.2796 for latexes) were determined by using an Abbe B&C 32400 refractometer and a Varian Cary-50 ultraviolet spectrometer, respectively.

**Thermal Stability.** The thermal stability was evaluated by using a TA Instruments Q500 thermogravimetric analyzer, in a temperature range from 20 to 700°C, at a heating rate of 20°C/min, under nitrogen flow.

**Glass Transition Temperature.** The glass transition temperatures ( $T_g$ ) were determined in a TA Instruments Q1000 differential

**Table I.** Reaction Yield and Characterization of Polymers in Terms of Composition and Glass Transition Temperature

Sample	Theoretical composition MMA : VAc (mol : mol)	Real composition MMA : VAc (mol : mol)	Yield (%)				$T_g$ (°C)
			45–75 ( $\mu\text{m}$ )	75–150 ( $\mu\text{m}$ )	150–355 ( $\mu\text{m}$ )	>355 ( $\mu\text{m}$ )	
MMA100 : VAc0	100 : 0	100 : 0	23.1	41.0	27.3	8.6	121
MMA94 : VAc6	80 : 20	94 : 6	13.5	44.4	17.0	25.1	112
MMA91 : VAc9	70 : 30	91 : 9	7.5	21.2	35.2	35.2	108
MMA92 : VAc8	60 : 40	92 : 8	6.2	34.1	47.4	12.3	111
MMA90 : VAc10	40 : 60	90 : 10	12.7	34.0	52.0	1.3	104
Latex A	-	-	-	-	-	-	-44
Latex B	-	-	-	-	-	-	-47
SLigno	-	-	-	-	-	-	19

SLigno, sodium lignosulphonate.

scanning calorimeter, in a temperature range from  $-20^\circ\text{C}$  to  $200^\circ\text{C}$ , at a heating rate of  $20^\circ\text{C}/\text{min}$ , under nitrogen flow.

**Dynamic Mechanical Analysis.** Some copolymer samples were analyzed in a TA instruments Q800 dynamic mechanical analyzer at a frequency of 1 Hz, in a temperature range of  $-50$  to  $150^\circ\text{C}$ , under nitrogen flow. The specimens were prepared by pressing (15 psi) the sample in a mold at about  $200^\circ\text{C}$  for 2 min.

**Acid Resistance.** The samples and sulfuric acid 20% were kept in contact for 24 and 72 h under magnetic stirring. The samples were analyzed by optical microscopy at 0, 24, and 72 h.

#### Polymer Performance as Filter Loss Reducer for Drilling Fluids

For the performance test, the copolymer samples and sodium lignosulphonate were dispersed in water (respectively, 2.12 g and 77.4 g in 160 mL of water) and the latexes were used as received, exhibiting solid content of 96 g/160 mL in both samples. The MMA sample was also dispersed in an aqueous fluid prepared with xanthan gum at 5.7 g/L, using the same microsphere concentration as that in pure water. Three different average porosities of the ceramic disk were used: 10, 60, and 90  $\mu\text{m}$ .

The test consisted of five steps: (1) passage of distilled water and recording of mass flow; (2) passage of polymeric fluid; (3) passage of distilled water and recording of mass flow; (4) passage of sulfuric acid 20%; and (5) passage of distilled water and recording of mass flow. The mass flow data recorded for distilled water in step (3) compared with the data from step (1) indicate the performance of the polymeric fluid as filter loss reducer, while the mass flow data in step (5) reflect the ability of acid to clean the disk, restoring the flow. When the test was carried out with polymer added to the xanthan gum dispersion, steps (1) and (3) were conducted with xanthan dispersion, and steps (4) and (5) were not carried out. Three types of aqueous dispersions were evaluated, one containing PMMA-VAc (samples synthesized in the laboratory), another containing sodium lignosulphonate and the third consisting of commercial latex samples.

The fluids were pressured at 100 psi. The mass flow was determined by relating mass, measured on a balance, and time,

measured with a chronometer. The results were exhibited as a plot of mass flow against time<sup>25,26</sup> and as mass flow reduction (MFR) percentage, expressed by  $[(\text{water mass flow} - \text{fluid mass flow})/\text{water mass flow}] \times 100$ . The tests were carried out in triplicate, by choosing, for the same sample, disks exhibiting similar water mass flow.

## RESULTS AND DISCUSSION

The results and discussion are presented in two parts: sample characterization and performance evaluation for filtrate loss control.

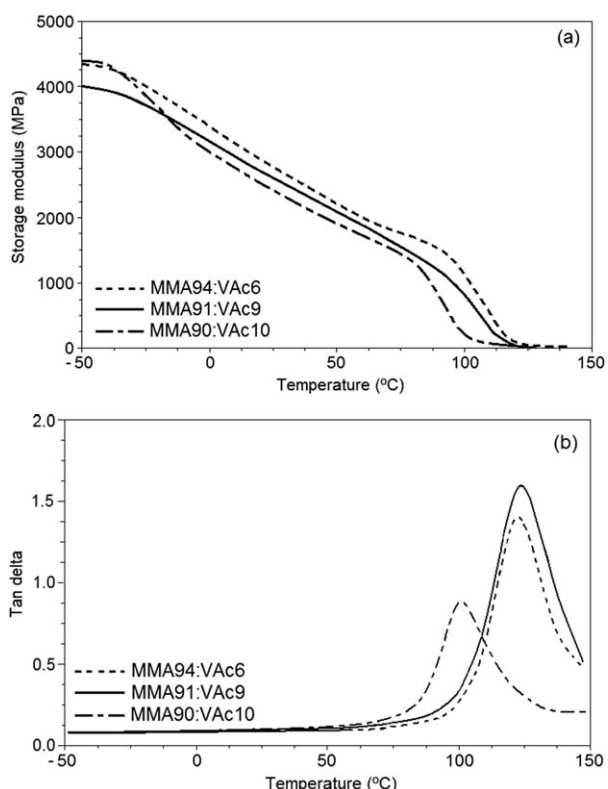
#### Characterization of Polymer Samples

Table I presents the mass composition results for the synthesized copolymers and the glass transition temperatures for all samples. As expected, the VAc content in the copolymer is less than that in the feed because of the reactivity ratios of monomers used: 0.015 for VAc and 20 for MMA<sup>27</sup> and also because the monomers were fed at the same time. Despite that, the aim of the work was achieved since copolymers presenting different compositions were obtained, varying from 0 to 10 mol/mol % of VAc.

The reactions showed higher yields in the particle size range of 75–150 and 150–355  $\mu\text{m}$ . As known, the size and size distribution of the beads can be controlled by changing, among other parameters, the stirring protocol and the type and concentration of stabilizer.<sup>28</sup>

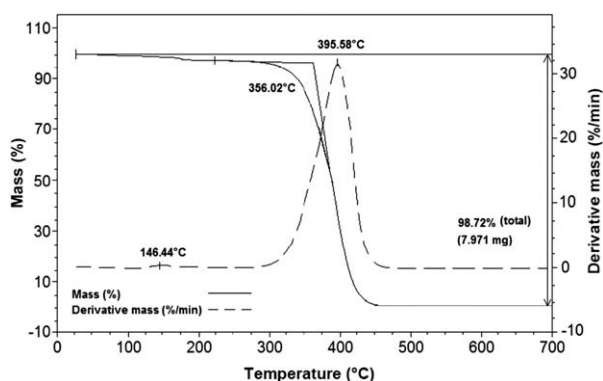
Also as expected, the glass transition temperature of materials decreased with increasing vinyl acetate content in the copolymer. The  $T_g$  decreased from  $121^\circ\text{C}$ , for pure PMMA, to  $104^\circ\text{C}$ , for the MMA90 : VAc10. The latex samples exhibited very low  $T_g$  ( $-44$  and  $-47^\circ\text{C}$ ). This result is in agreement with the chemical structure of the polymer which contains butadiene, so that the polymer exhibits easier chain mobility than the MMA/VAc copolymers.<sup>29</sup> The  $T_g$  determined for the sodium lignosulphonate sample was  $19^\circ\text{C}$ .

The dynamic mechanical analysis was carried out to evaluate the variation in Young's modulus as a function of MMA/VAc copolymer composition. The essays were run only for samples

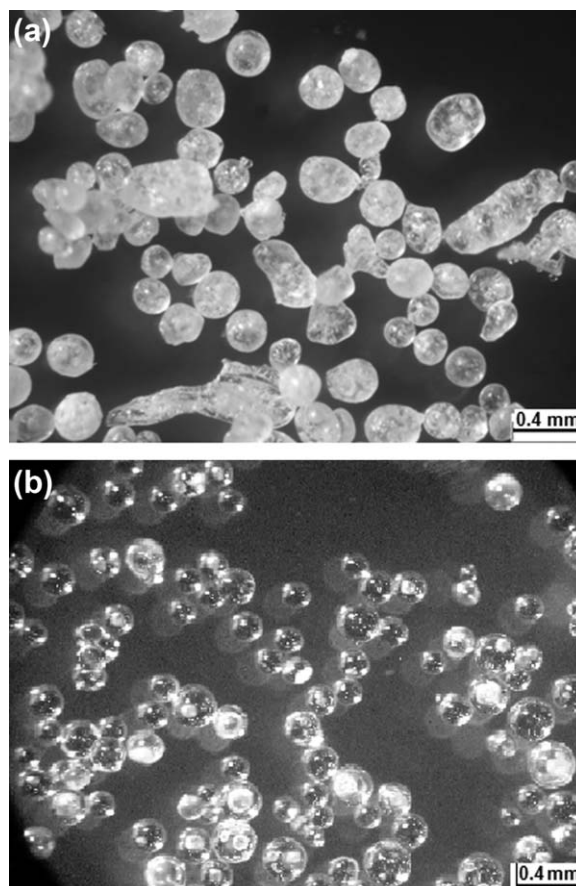


**Figure 2.** Dynamic mechanical results of MMA-VAc copolymers: (a) Storage modulus and (b)  $\tan \delta$ .

MMA94 : VAc6, MMA94 : VAc9, and MMA90 : VAc10. Figure 2(a) shows the reduction of storage modulus as a function of increasing amount of VAc in the copolymer. At room temperature, the storage moduli are around 2600 MPa, but these values are even lower at higher temperatures: for example, at 80–90°C, the temperature range in many oil wells, the storage moduli drop to about 1500–900 MPa, becoming the polymer particles less rigid, mainly for the sample MMA90 : VAc10. The  $T_g$  results obtained from the  $\tan \delta$  versus temperature plot [Figure 2(b)] are in agreement with those obtained by DSC.



**Figure 3.** Thermal stability of poly(methyl methacrylate-*co*-vinyl acetate) (91 : 9).



**Figure 4.** Optical micrographs of the copolymers: (a) MMA90 : VAc10 and (b) MMA94 : VAc6.

The thermal stability of the samples is very important for controlling filtrate loss in oil wells, where temperatures can reach relatively high values ( $\leq 80^\circ\text{C}$ ).

All MMA/VAc copolymers exhibited no significant mass loss below  $200^\circ\text{C}$ , as shown in Figure 3 for the PMMA-*co*-PVAc 91 : 9. This means that no chemical degradation is expected in the oil well. The commercial latexes presented good thermal stability: the maximum rate of degradation happened at about  $450^\circ\text{C}$ . Although some mass loss was observed around  $100^\circ\text{C}$ , it was probably due to water volatilization, because the product consists of an emulsion. This does not prevent the application of these samples for filtrate loss control. On the other hand, sodium lignosulphonate is more unstable, starting to lose mass at  $30^\circ\text{C}$ .<sup>30</sup> Among the materials analyzed in this work, sodium lignosulphonate is the only one susceptible to chemical degradation under application conditions.

Except for MMA90 : VAc10, the morphologies of the MMA/VAc copolymers (Figure 4), observed by optical microscopy, were identical: spherical shape characteristic of suspension polymerization. The behavior exhibited by the MMA90 : VAc10 sample can be attributed to the higher VAc content (10 mol %) in the copolymer and the relatively high (60 mol %) VAc amount in the feed. This sample was not tested as filtrate loss reducer. Sodium lignosulphonate also exhibited spherical morphology,



**Table II.** Particle Size and Size Distribution of MMA/VAc Copolymers Fractions After Sieving

Sample	Particle size distribution <sup>a</sup> ( $\mu\text{m}$ )								
	(45–75)			(75–150)			(150–355)		
	D(0.1)	D(0.5)	D(0.9)	D(0.1)	D(0.5)	D(0.9)	D(0.1)	D(0.5)	D(0.9)
MMA100 : VAc0	49.2	82.3	155.7	79.5	113.5	171.3	128.1	181.1	235.8
MMA94 : VAc6	52.6	78.4	125.1	86.6	122.4	178.4	128.2	172.2	220.3
MMA92 : VAc8	52.4	73.7	107.6	84.9	133.8	212.7	146.5	216.8	272.0
MMA91 : VAc9	47.2	68.1	109.6	87.3	125.8	199.3	150.5	193.8	247.0
MMA90 : VAc10	47.5	77.3	135.7	95.7	140.2	211.9	164.6	202.0	244.3

<sup>a</sup>Obtained by mastersizer micro analyzer.

but the size of the spheres was smaller than that of the MMA/VAc copolymers.

Table II shows the results of particle size and size distribution of MMA/VAc copolymers. The analyses were done for each fraction obtained after sieving the material. The results were expressed in terms of D(0.1), D(0.5), and D(0.9), which indicate the highest size presented by 10%, 50%, and 90% of the sample, respectively. Considering that the sieving is a physical process susceptible to the sieve quality and to the particle aggregation after separation, and that the master size analysis is an analytical procedure using calibration standards, the values obtained by both methods are in good agreement. In general, the MMA/VAc copolymers presented similar average particle sizes.

Because it was not possible to analyze the particle size of the commercial samples by Mastersizer Micro, it was used a Zeta-sizer Nano particle size analyzer. Sodium lignosulphonate in water exhibited particle size range of 2–8 nm and sodium lignosulphonate in water containing sodium chloride (0.8% p/v) and iron chloride (49.2% p/v) showed particle size range of 400–1500 nm. The results obtained for the latex samples were 20–70 nm for latex A and 7–18 nm for latex B. The commercial samples had much smaller particle sizes than those observed for MMA/VAc copolymers.

#### Acid Resistance

After being in contact with 20% sulfuric acid, the samples did not exhibit any variation in shape or size, indicating their high resistance that acid. This result is not so good for the purposes of this study, because we expected to be able to remove the filter cake from the rock formation when desired by applying acidic fluid.

#### Performance Evaluation as Filtrate Loss Controller

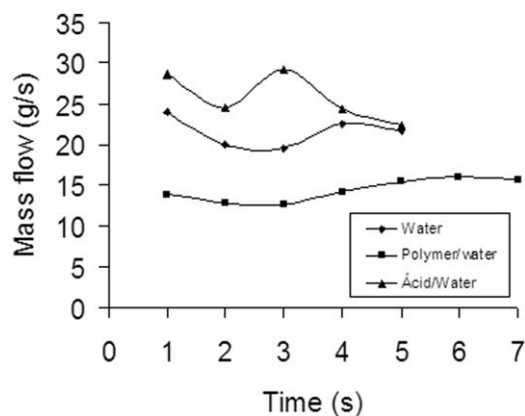
Figure 5 shows the plot obtained for the MMA91 : VAc9 sample through ceramic disk of 60  $\mu\text{m}$  and the mass flow after using acid fluid. Concerning the effect of 20% sulfuric acid, most of the tests using MMA/VAc copolymer showed the same behavior, that is, the mass flow increased compared with the original flow. Although this was a desirable result, because it indicates that the flow can be restored, it was unexpected because the acid was not able to attack the polymer samples as discussed

before. So, an assay using 20% sulfuric acid through a virgin disk was performed and an increase of 150% in the mass flow was achieved. This means that the acid erodes the ceramic disk, which increases the mean pore diameter, making it easier to recover the polymer from the disk, even though the acid is not able to attack the polymer particles.

All performance results, expressed in terms of MFR percentage, are summarized in Table III.

Sodium lignosulphonate in water did not show good results as filtrate loss reducer when tested using disks of 10  $\mu\text{m}$ . The same sample in salt water exhibited reduction of 27% and 0% in 10 and 90  $\mu\text{m}$  disks, respectively. This suggests that fluids containing lignosulphonate pass through the pores of the disk and there is no retention of material to form the filter cake, because the particle size (2–8 nm and 400–1500 nm) is much smaller than the disk's pore diameter (10 and 90  $\mu\text{m}$ ).

Although the particle size of latex A ( $\sim 40$  nm) and latex B ( $\sim 10$  nm) are in the same order of magnitude as those of sodium lignosulphonate, there was a reduction of mass flow when passing the latex samples through the 10  $\mu\text{m}$  disk (a reduction of 72% and 67% for latexes A and B, respectively). This is probably because the solid content in the latex samples is higher than that in sodium lignosulfonate. Latex A, with larger particle size than Latex B, could promote a higher reduction in the mass flow. So, this sample was also tested using the



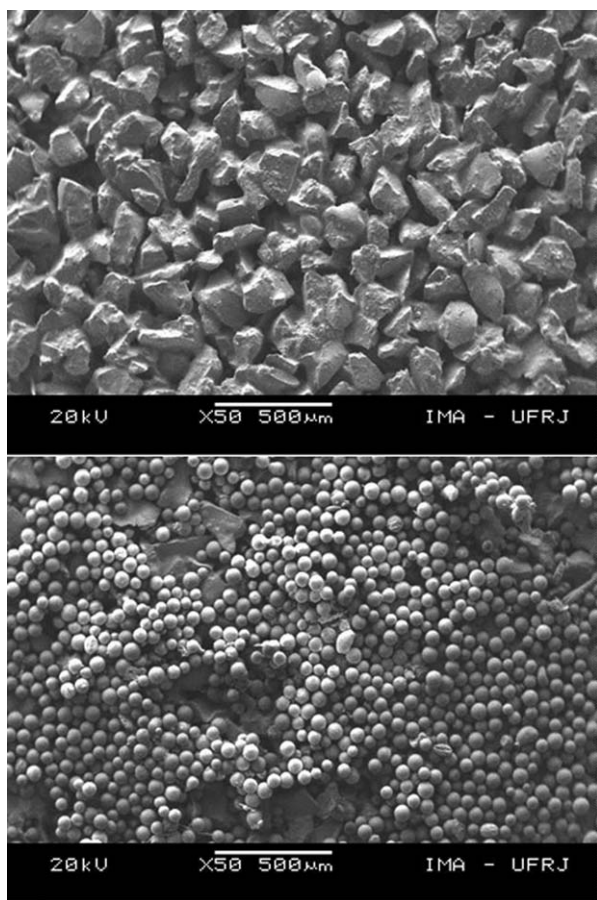
**Figure 5.** Filtrate reduction test of the polymer MMA91: VAc9 (disk 60  $\mu\text{m}$ ).

**Table III.** Mass Flow Reduction Percentage of the Fluids Using Ceramic Disks Exhibiting Mean Pore Diameter of 10, 60, and 90  $\mu\text{m}$ 

Sample	Mass flow reduction (%)		
	10 $\mu\text{m}$ disk	60 $\mu\text{m}$ disk	90 $\mu\text{m}$ disk
SL in water	9	-	-
SL in salt water	27	-	Zero
Latex A	74	68	18
Latex B	70	-	-
MMA91 : VAc9	Zero	30	15
MMA92 : VAc8	Zero	20	12
MMA94 : VAc6	Zero	16	9
MMA100 : VAc0	Zero	11	7
MMA100 : VAc0/XG	Zero	62	20

SL, sodium lignosulphonate; XG, xanthan gum.

60  $\mu\text{m}$  and 90  $\mu\text{m}$  disks, and the results showed that the performance decreased for the 60  $\mu\text{m}$  disk (63%), while no MFR at all was observed when using the 90  $\mu\text{m}$  disk (0%). This can be explained because pore size is much larger than the particle size of the additive.



**Figure 6.** Electron micrograph of ceramic disk (60  $\mu\text{m}$ ) before (above) and after (below) passing aqueous fluid containing MMA91: VAc9 (45–75  $\mu\text{m}$ ).

The MMA/VAc copolymers were tested in 10, 60, and 90  $\mu\text{m}$  ceramic disks, using particle sizes in the range of 45–75  $\mu\text{m}$ , which are more compatible with the pore size of the disks (Table II). The tests performed through the 10  $\mu\text{m}$  disk did not present any MFR, probably because the (co)polymers' particle size is much larger than the average pore diameter of the disk. For tests with the 60  $\mu\text{m}$  disk, MMA100 : VAc0, MMA94 : VAc6, MMA92 : VAc8, and MMA91 : VAc9 were used. The results showed that the performance increases as the material becomes more rubbery, when keeping the average particle size of the resin similar to that of the disk pore size: sample MMA91 : VAc9, which contains 9% VAc and has average particle size of 68  $\mu\text{m}$ , showed better performance in reducing flow (MFR = 30%) than the other samples evaluated, which have less VAc content. It seems that the higher VAc content of MMA91 : VAc9 can contribute to more effective compaction of the resin in the disk. In order to confirm that this sample is able to form a filter cake as desired, scanning electron microscopy was used to observe the resin in the pores of the disk after testing. Figure 6 shows the photomicrographs of the 60  $\mu\text{m}$  ceramic disk before as after using resin MMA91 : VAc9 (45–75  $\mu\text{m}$ ). The porous characteristic of the disk and the spherical particles inside the pores can be observed.

The same behavior was observed for the tests using the 90  $\mu\text{m}$  ceramic disk: higher VAc content in the copolymer led to better performance. However, the performance in MFR was only about half than that obtained when using the 60  $\mu\text{m}$  ceramic disk. It seems that the majority of microparticles passed directly through the disk pores, because that their sizes are much smaller than the pores (Table II): in the case of the 60  $\mu\text{m}$  disk, more spheres are able to penetrate into the pores, blocking the flow more effectively. The effect of the copolymer particle size was confirmed when carrying out a test with sample MMA100 : VAc0, having a particle size range of 75–150  $\mu\text{m}$ , and using the 90  $\mu\text{m}$  ceramic disk. In this case, no significant performance was observed because almost all particles were too large for the disk's pore. The resins in pure water exhibited worse performance than Latex A. Nevertheless, consideration must go to the solid contents in each case: the resin concentration (1.3%) used in the tests was significantly lower than that in the latex sample (60%).

Because water-based drilling fluids are prepared with a thickener, three tests of MFR were carried out with sample MMA100 : VAc0 (45–75  $\mu\text{m}$ ) added to a xanthan gum dispersion. The behavior in function of pore size was the same as observed in the tests conducted with polymer in pure water, that is, the performance increased in the following order 10  $\mu\text{m}$  < 90  $\mu\text{m}$  < 60  $\mu\text{m}$ . No performance was observed for the 10  $\mu\text{m}$  disk. A slight increase was observed for the 90  $\mu\text{m}$  disk, varying from 7 to 20%, and a significant increase could be noted for the 60  $\mu\text{m}$  disk: MMA in pure water reduced the mass flow by 11%, whereas MMA in xanthan gum dispersion reduced it by 62%.

## CONCLUSIONS

The performance of the spherical resins based on PMMA-VAc is closely related to their particle size range and to the pore size of the rock. Particle sizes much smaller than the pore size do not

form the desirable filter cake to block the entrance of fluid into the rock. On the other hand, particle sizes much larger than the pore size are not able to penetrate into the rock pores. This suggests that the best size range corresponds to that in which the largest particle size is similar to the average pore size of the rock. Moreover, it seems that the resins presenting lower modulus are able to better compact in the rock, enhancing the performance of the filter cake.

In comparison with the commercial latex samples, the resins are able to achieve similar performance for filtrate control using lower amounts of polymer. Besides that, the resins present advantages related to logistics, storage, and fluid preparation process.

The potential use of the resins for filter loss control was confirmed by the high performance achieved when the microspheres were added to the xanthan gum dispersion.

#### ACKNOWLEDGMENTS

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