Evaluation of the efficiency of copolymers of methyl methacrylate and vinyl acetate synthesized by emulsion polymerization for control of aqueous filtrate loss

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ABSTRACT: One of the main problems faced while drilling oil wells is loss of fluid to the rock formation. This loss can be reduced with the use of chemical additives called filtrate controllers, which must be tailored to the specific characteristics of the rock formation and drilling conditions. In this study, copolymers made of methyl methacrylate-*co*-vinyl acetate were synthesized by the emulsion polymerization technique, the most efficient technique to obtain copolymers with widely differing reactivity ratios. The products were characterized and evaluated for filtrate reduction efficiency, in the form of an emulsion and a polymer suspended in water. The filtrate reduction percentage, on the order of 80%, increased with higher concentration of vinyl acetate. The use of the polymer suspended in water caused only a slightly greater reduction in filtrate loss than that produced by the respective emulsion. However, other important advantages are associated with the suspended formulation: lower optimal concentration (~ 8.5 g/mL), formation of extremely discrete filter cake particles and better logistical aspects, since in the case of emulsions, the volume of material that must be transported is much greater. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42191.

INTRODUCTION

Drilling fluids perform a series of important functions to prevent problems that arise during the well drilling process.[1–3] The use of one or more additives in these fluids will depend on the type of drilling and the reservoir characteristics. In the case of extremely deep wells, the use of more than one additive is generally necessary, including polymers with high molar mass and bentonite clays to form filter cake to reduce infiltrations.[2–7] Various additives are used in these fluids to reduce infiltrations. The resulting fluid must be able to form a thin film with low permeability, but if this is not well controlled, the rock formation can suffer various damages.[8–12] Recent studies have shown the possibility of using microspheres of poly(methyl methacrylate-co-vinyl acetate) synthesized by polymerization in suspension to reduce filtrate, evidencing the contribution of vinyl acetate to the compacting of the spheres to assure the formation of a thin filter cake with high efficiency. However, the polymerization technique used in these studies produced materials with low vinyl acetate content, since the difference of the reactivity ratios of the two monomers is very large: vinyl acetate, $r_1 = 0.015$, and methyl methacrylate, $r_2 = 20$.[13,14] Besides this, there is a need for high correlation between the particle size of the fluid and the pore size of the rock formation. The microspheres should have diameters on the order of 10 μm, which requires rigorous control of the polymerization process, mainly when using the above two monomers.[13] Therefore, the emulsion polymerization technique can be a good alternative to obtain this type of copolymer containing a higher concentration of vinyl acetate and particle sizes in the desired range (>10 μm).

When using emulsion polymerization with hydrophobic monomers, the system is initially composed of the aqueous phase, composed of micelles containing a dissolved monomer and monomer droplets stabilized by the emulsifier used.[15] The final product has the form of a latex, with particles in the size range of 0.1–1.0 μm.[16–24] The stability and nucleation of these emulsions depend on kinetics parameters, such as temperature and quantity of initiator.[15] In emulsion polymerization, the type of reactor has a strong influence on the properties of the final product, such as the particle size distribution and composition of the copolymer. In this type of polymerization, it is possible to prepare the product in batches or semi-continuously. When using the batch mode, the composition depends on the difference in reactivity and the solubility in water of both monomers.

In the semi-continuous mode, it is possible to produce copolymers with the desired chemical composition only if the reactor is feed into the system during the reaction with a more reactive monomer.[25–28]

In this study, poly(methyl methacrylate-co-vinyl acetate) copolymers were synthesized by emulsion polymerization and tested as filtrate controller in aqueous fluids. The influence of the concentration and composition of the polymers, as well as the aspect of the product (emulsion bulk and recovered solid polymer) on the performance of the fluids samples was studied.

EXPERIMENTAL

Materials

To synthesize the poly(methyl methacrylate-co-vinyl acetate) in emulsion, we used methyl methacrylate (MMA) and vinyl acetate (VAc), as received, supplied by Cia Química Metacril (Candeias, Brazil) and Vetec Química Fina (Rio de Janeiro, Brazil), respectively. Potassium persulfate ($K_2S_2O_8$), sodium lauryl sulfate (SLS) and sodium bicarbonate ($NaHCO_3$), supplied by Vetec Química Fina, were dissolved in water and used respectively as initiator, emulsifier and buffer. Distilled and deionized water (QUIMIS system) was used as the dispersant medium and 95% ethanol P.A. ACS, supplied by Vetec Química Fina, was used to precipitate the emulsions.

For the filtrate reduction tests, we used an HPHT filter press and ceramic disks supplied by Fann Ins. Co. (Houston, USA), with average pore diameters of 3 and 10 μm, to simulate the pore sizes found in rock formations. Xanthan gum (Kelsan SCD polymer), supplied by Kelco Oil Field Group (Houston), was used to produce an aqueous dispersion with viscosity similar to that of a typical drilling fluid.

Synthesis of the Polymers

The polymers were obtained by free radical initiation using the emulsion polymerization technique. Potassium persulfate ($K_2S_2O_8$), sodium lauryl sulfate (SLS) and sodium bicarbonate ($NaHCO_3$) were dissolved in water at 0.97, 4.9, and 0.97%wt/vol, respectively, using 300 g of the monomers for each 600 mL of water. The total mass of vinyl acetate and 30% of the mass of methyl methacrylate, established for the reaction, were added in advance, and then the remaining 70% of methyl methacrylate was added to the system during the initial polymerization process, at a rate of 1 mL/min.[26] For calculation of these ratios, we used densities of 0.945 g/cm^3 and 0.934 g/cm^3 for methyl methacrylate and vinyl acetate, respectively.[29] The polymerization was carried out at 80°C and stirring of 260 rpm for 6 h. At the end of the polymerization, part of the emulsion was precipitated in ethyl alcohol and dried in a heated chamber at 60°C for 48 h and the other part was stored for the filtrate control tests.

Characterization of the Polymers

Composition. The composition of the copolymers was determined by nuclear magnetic resonance of -^{13}C (NMR) in a Varian Mercury VX300 spectrometer operating at 75 MHz, using 5 mm test tubes containing the copolymers dispersed in deuterated tetrachloroethane (TCE). The calculations were carried out using the areas under the peaks referring to the carbonyl of the methyl methacrylate (177 ppm) and that of the vinyl acetate (169 ppm). The results were expressed in terms of mass composition.

Size and Size Distribution of Particles. The average size and size distribution of the emulsified polymer particles were measured by light scattering using Zetasizer Nano Series- Malvern equipment. The particle size analysis requires refraction index and absorbance data of the samples. Then, initially the emulsions refraction index and absorbance at 633 nm were determined using Abbe B&C 32400 refractometer and Varian Cary 50 UV-vis spectrometer equipment, respectively. The average size and size distribution of the solid copolymers particles obtained after precipitation were determined in Malvern Zetasizer Micro equipment. This equipment allows the particle size determination in range of 0.3–300 μm.

Determination of the Solids Content of the Emulsions. In order to measure the solids content of the emulsions, a determined sample volume was frozen in the freezer compartment of a domestic refrigerator and then lyophilized for 24 h at a temperature of 100°C, using Liofilizador K 105 Liotop, the mass of powder obtained was determined.

Thermal Stability. The thermal stability of the polymers was evaluated using a TA Instruments Q500 thermogravimetric analyzer (TGA) in the temperature range of 20 to 700°C with a heating rate of 20°C/min, under nitrogen atmosphere.

Glass Transition Temperature. The glass transition temperature (T_g) of the polymers was determined using a TA Instruments Q1000 differential scanning calorimeter, with work temperature range of −20 to 200°C and a heating rate of 20°C/min, under nitrogen atmosphere. For the poly(vinyl acetate) sample the work temperature range was of −80 to 80°C.
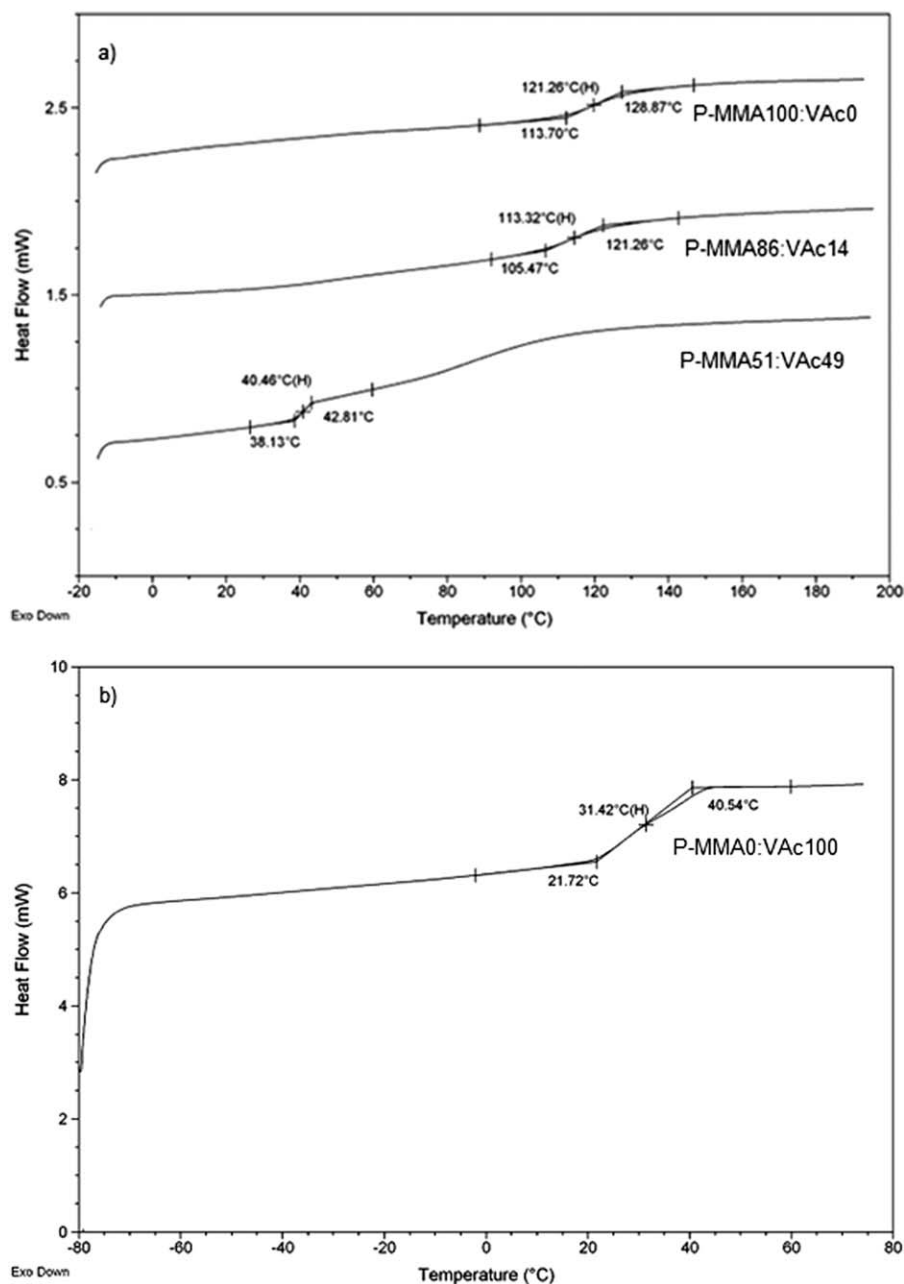
Reduction Filtrate Tests. In the reduction filtrate tests, the samples were used in the original emulsion form (as obtained from the polymerization), as well as in the powder form. The amount of xanthan gum in aqueous dispersion was varied in order to maintain constant its final concentration in the fluids at 0.14% wt/vol, to perform the filtrate control testing. The xanthan gum dispersion was prepared under stirring for 20 min using homogenizer Hamilton beach machine and, then, it was kept at rest for a period of 24 h. In the case of fluid containing polymer such as powder, the fluid remained this period of 24 h under magnetic stirring. The analyses were carried out at room temperature and pressure of 100 psi. The test consisted of three steps: (1) passage of 160 mL of the aqueous xanthan gum solution through the ceramic disk (V_1); (2) passage of 160 mL more of the same fluid through the disk (V_2); and (3) passage through the disk of 160 mL of the aqueous xanthan gum fluid containing the synthesized polymer (V_3). The volumes from each step were recorded after 30 min. V_1 was discarded and the results were expressed in terms of percentage of volume reduction (%VR) by applying the following relation: $[(V_2 - V_3)/V_2] \times 100$. The tests were run in duplicate.

Observation of the Disks Before and After the Performance Tests

The ceramic disks were observed visually and photographed before and after the filtrate control tests. They were also

Table I. Composition, Solids Content, Glass Transition Temperature, and Thermal Stability of the (Co)Polymers

Sample	Theoretical mass composition (MMA/VAc)	Actual mass composition calculated (MMA/VAc)	Solids content (g/mL)	Glass transition temperature, T_g (°C)	Thermal degradation onset (°C)
P-MMA100:VAc0	100/0	100/0	200	121	154
P-MMA86:VAc14	80/20	86/14	250	113	187
P-MMA51:VAc49	50/50	51/49	262.5	40	186
P-MMA0:VAc100	0/100	0/100	250	31	-

Figure 1. Glass transition temperature for the samples: (a) P-MMA100:VAc0, P-MMA86:VAc14, and P-MMA51:VAc49 and (b) P-MMA0:VAc100.
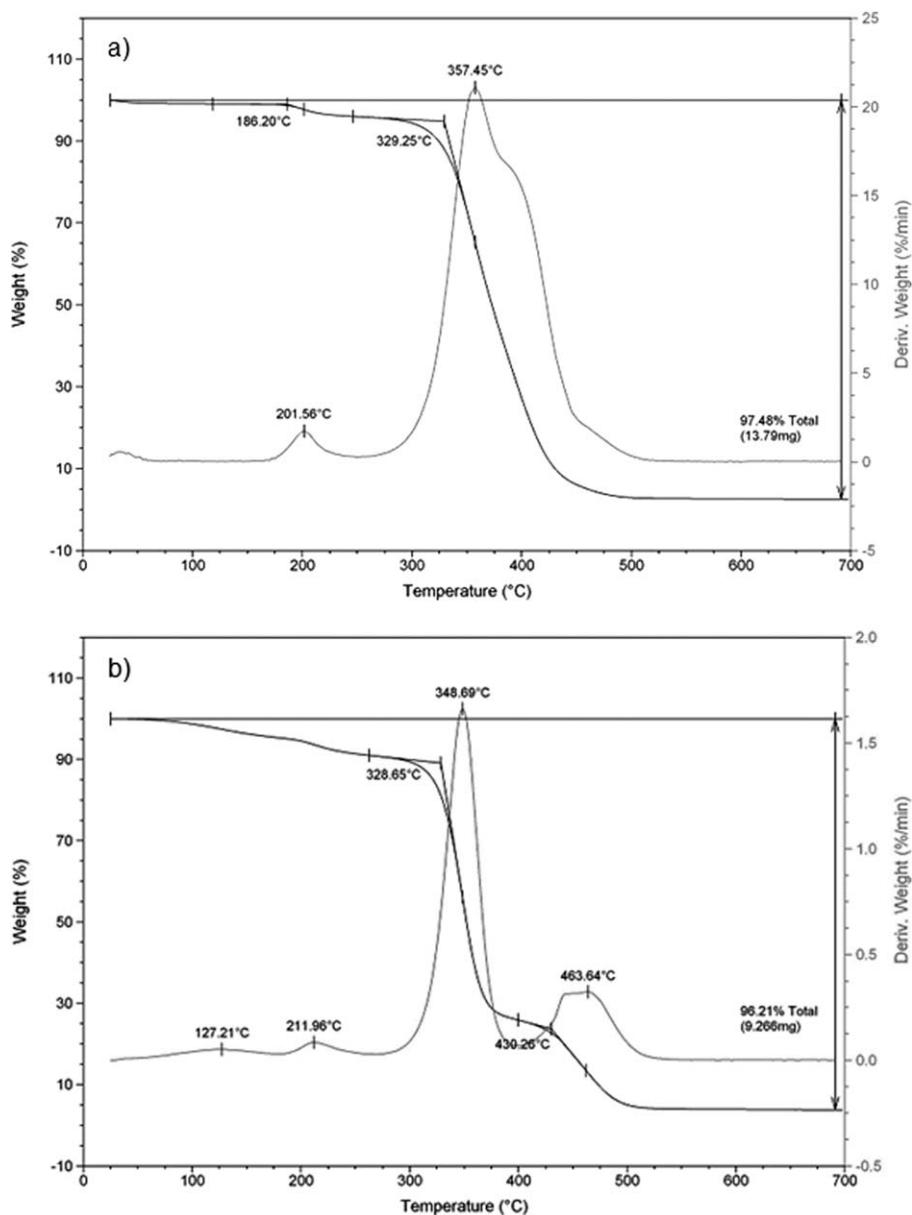
Figure 2. Thermal stability for the samples: (a) P-MMA51:VAc49 and (b) P-MMA0:VAc100.

observed by scanning electron microscopy (SEM) using a Jeol JSM- 5610 L microscope, after gold sputtering, using magnification of 50 to 500x and scale bar of 500 μm.

RESULTS AND DISCUSSION

Copolymers of methyl methacrylate (MMA) and vinyl acetate (VAc) were obtained using the emulsion polymerization technique. This enabled obtaining copolymers with vinyl acetate content near those used in the feed, as shown in Table I, since the entrance of the monomer in the micelle is random, so the reactivity ratios are no longer the most important factor to establish the distribution of the comonomers in the copolymer.[26] The conversion ratios of the monomers to polymers varied from 70 to 90% for all products reactions; these data were used to calculate the amount of polymer used in the

performance tests in order to allow a correlation between both forms: emulsion and powder.

The incorporation of vinyl acetate (VAc) led to a reduction of the glass transition temperature of the poly(methyl methacrylate) from 121°C to 113°C and 40°C, respectively, for VAc content of 14 and 49%wt (Table I). This indicates larger elastomeric character of the material containing higher vinyl acetate content, since the poly(vinyl acetate) T_g is 31°C. The Figure 1(a) show the DSC curves for P-MMA100:VAc0, P-MMA86:VAc14 and P-MMA51:VAc49 samples, respectively. The DSC curve of the P-MMA0:VAc100 sample was not included at same figure due to the lower temperature range(−80 to 80°C) needed to perform the analysis.The Figure 1(b) show the DSC curve for P-MMA0:-VAc100 sample.

Table II. Particle Size Distribution and Average Particle Size of the Emulsions

Sample	Particle size distribution ranges (nm)		Average particle size in the smallest size range (%)
E-MMA100:VAc0	11.7-190	2305-6439	50
E-MMA86:VAc14	7.5-295	2669-6439	54
E-MMA51:VAc49	6.5-220	2669-6439	50

Thermogravimetric analysis (TGA) was performed to verify the materials thermal stability as shown in Figure 2(a) for the sample MMA51:VAc49. The vinyl acetate content incorporated in the molecule did not reduce the polymers thermal stability, however the onset degradation temperature was increased by about 20°C in relation to the pure poly(methyl methacrylate) (Table I). This makes the material suitable for using as filtrate reducer in drilling fluids where the wellbore temperature can reach 80°C. The poly(vinyl acetate) sample showed weight loss at temperatures below 80°C [Figure 2(b)], probably due to the water volatilization in this temperature range, as result of an inefficient drying process of the sample, which would not be detrimental to the application intended to this material.

Table II shows the polymer emulsions particle size ranges and the average particle size calculated for the size distribution in highest volume percentage. The average sizes (∼50 nm) and the particle size ranges detected for E-MMA100:VAc0, E-MMA86:-VAc14, and E-MMA51:VAc49 samples were very close to each other. The Figure 3 shows that these samples exhibited two particles distributions: broad distributions in the range of smaller particle sizes with the highest volume percentage (11.7–190, 7.5–295, and 6.5–220 nm for E-MMA100:VAc0, E-MMA86:-VAc14, and E-MMA51:VAc49, respectively) and another distribution with very small volume percentage, in a range of 2305–6439 nm. The range of larger particles can be related to few precipitated particles visible to the naked eye, observed in the testing cuvette. This bimodal particle size distribution might
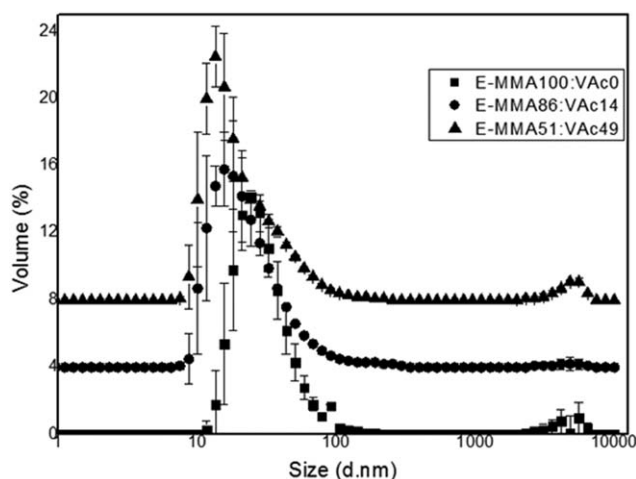
Figure 3. Particle size distribution for E-MMA100:VAc0, E-MMA86:-VAc14, and E-MMA51:VAc49 samples.
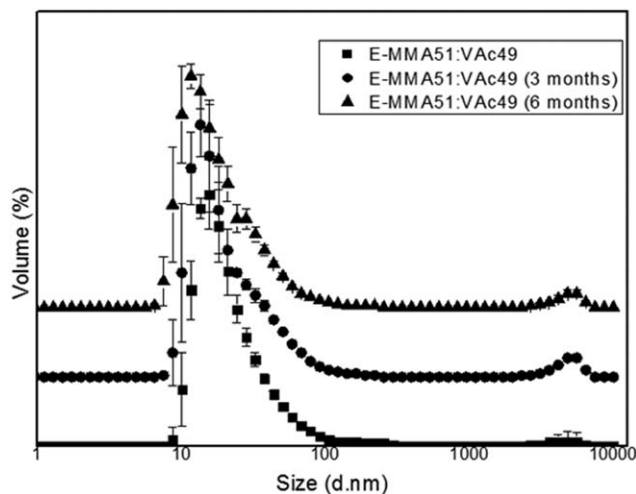
Figure 4. Stability for the emulsion E-MMA51:VAc49 sample.

have occurred due to the use of semi-continuous feed in the reaction during the process.[26–28]

The emulsions stability was also evaluated during six months and, no significant variation of the average size and size distribution was observed. The Figure 4 shows the size distribution curve for the emulsion E-MMA51:VAc49, in which the stability of the emulsion as function of time could be confirmed.

The particle sizes of co(polymers) recovered from the emulsion were also determined. In this case, the average size was ∼86 μm for P-MMA100:VAc0 and P-MMA86:VAc14 samples, while the sample P-MMA51:VAc49 was considerably larger (∼120 μm). This can be attributed to the greater agglomeration of the particles caused by the higher content of vinyl acetate in the copolymer.

Table III shows the results of filtrate reduction of the emulsions, obtained in ceramic disk of 10 μm pore size. The first test was conducted only with the emulsion E-MMA100:VAc0, taken directly from the reaction bulk in ceramic disks having pore sizes of 3 and 10 μm. In both cases the filtrate reduction percentage in relation to pure water was zero, meaning the emulsion passed directly through the disks without any retention. Since a thickener agent is often used in a typical drilling fluid formulation, the other tests were carried out in xanthan gum dispersion.

The polymeric emulsion volume used in the testing fluid (emulsion plus xanthan gum dispersion) was varied to produce fluids with different polymer concentration, in order to evaluate the influence not only of the co(polymer) composition but also of its concentration on the filtrate control results. For this, the solids content of the synthesized polymeric emulsion was calculated (Table I). It is important to highlight that the xanthan gum dispersion volume was fitted according to the polymeric emulsion volume, to keep the total testing fluid volume to be performed at 160 mL, which is the work volume of the filter press used. The xanthan gum concentration in all testing fluids was the same, i.e., 0.14%wt/vol (0.224 g in 160 mL).

It can be observed in Table III, that the E-MMA100:VAc0 fluid was initially tested in a concentration of polymer of 10%wt/vol,

Table III. Filtrate Reduction Test Results for the Emulsions with Addition of Xanthan Gum (Constant Gum Concentration of 0.14% wt/vol)

Sample	Concentration of polymer in fluid (%wt/vol)	Filtrate reduction percentage (10 μm disk) (% ± 3)
E-MMA100:VAc0[a]	20	Zero
E-MMA100:VAc0	15	Zero
E-MMA100:VAc0	10	27
E-MMA100:VAc0	5	26
E-MMA100:VAc0	1.6	46
E-MMA100:VAc0	1.3	63
E-MMA100:VAc0	1	65
E-MMA100:VAc0	0.8	52
E-MMA86:VAc14	1	70
E-MMA86:VAc14	0.8	57
E-MMA51:VAc49	1	78
E-MMA51:VAc49	0.8	70

[a] Since the xanthan gum was dispersed in pure water, this test, with 0 mL of xanthan dispersion, was performed only with the polymer emulsion.

Table IV. Filtrate Reduction Tests with the Polymer Precipitated from the Respective Emulsions (Fluid Containing 0.14% wt/vol Xanthan Gum)

Sample	Concentration of polymer in fluid (wt/vol %)	Filtrate reduction percentage (10 μm disk) (% ± 3)
P-MMA100:VAc0	0.6	61
P-MMA100:VAc0	0.8	76
P-MMA100:VAc0	1	72
P-MMA100:VAc0	1.3	62
P-MMA100:VAc0	1.6	57
P-MMA100:VAc0	10	43
P-MMA86:VAc14	0.8	79
P-MMA51:VAc49	0.6	66
P-MMA51:VAc49	0.8	82
P-MMA51:VAc49	1	79
P-MMA51:VAc49	1.3	65
P-MMA51:VAc49	1.6	62

while the typical filtrate controller concentration used in drilling fluids is 13.25 g/L, that is, 1.3%wt/vol. This means that the concentration tested was far higher than that used commercially. Therefore, we prepared fluids with varied E-MMA100:VAc0 concentration in the range of 0.8 to 15%wt/vol. The best performance, 65% filtrate reduction, was observed for the system with 1%wt/vol concentration. It seems that the performance in filtrate reduction increases as decreasing the polymer concentration. It was also observed for tests conducted with 3 μm disk: filtrate reduction of 47% was obtained with 5%wt/vol concentration, while the reduction was 22% when using 10%wt/vol of the polymer.

The E-MMA86:VAc14 and E-MMA51:VAc49 samples were then tested at the optimal concentration observed for E-MMA100:VAc0 fluid (1%wt/vol) and in the lower concentration evaluated

(0.8%wt/vol). In these cases, the best results were also observed at the concentration of 1%wt/vol. When holding the polymer concentration constant and comparing the performance results, it was observed an increase in filtrate reduction efficiency with higher vinyl acetate content in the copolymer: 65, 70, and 78%, respectively, for E-MMA100:VAc0, E-MMA86:VAc14, and E-MMA51:VAc49 samples at 1%wt/vol. This is due to the greater elastomeric characteristic of the copolymer as increasing vinyl acetate content, and due to the pressure imposed in system (100 psi) the compaction on the disks pores occurs more effectively. For these systems, the best performance occurred at a slightly lower concentration than that used commercially.

Because of the difficulties related to logistical questions, the polymers were recovered from the emulsion and evaluated as a suspension in water, since they are insoluble in this solvent. The polymer precipitated from emulsion MMA100:VAc0 (P-MMA100:VAc0) was first tested at concentrations similar to those in the assays with the emulsions, using a 10 μm disk. The
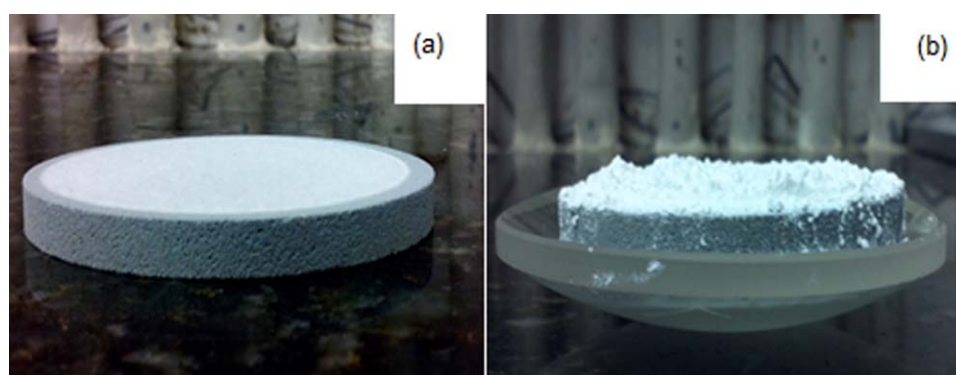
Figure 5. Images of the 10 μm ceramic disk after the filtrate control test with: (a) P-MMA51:VAc49 (0.8% wt/vol) and (b) P-MMA100:VAc0 (10% wt/vol). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
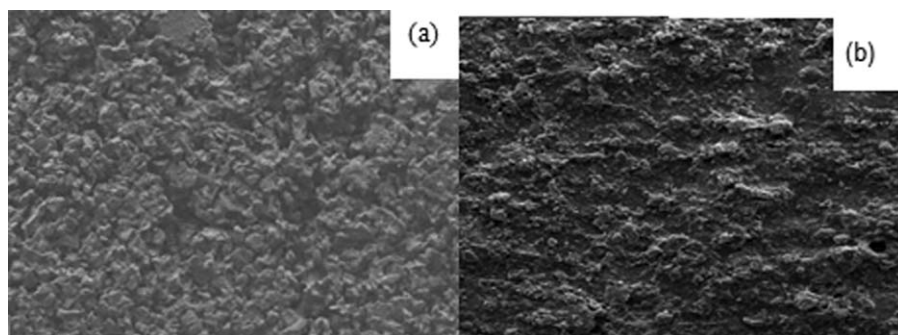
Figure 6. Scanning electron micrographs of the 10-μm disk: (a) before the filtrate control test and after with (b) P-MMA51:VAc49 (0.8% wt/vol) with magnification of 50×.

xanthan gum concentration was also maintained constant (0.14%wt/vol). The results are reported in Table IV. The optimal concentration observed was 0.8%wt/vol, causing a filtrate reduction of 76%, slightly better than that of the emulsion and at a lower concentration. This behavior was repeated for the all polymers recovered from the other emulsions P-MMA86:VAc14 and P-MMA51:VAc49 at 0.8%wt/vol. The performances of the polymers suspended in water were, respectively, 76, 79, and 82% for P-MMA100:VAc0, P-MMA86:VAc14, and P-MMA51:-VAc49 samples at 0.8%wt/vol, compared to 65, 70, and 78% for the respective emulsions at the optimal concentrations of 1% wt/vol. Once again there was an influence of the vinyl acetate content in the copolymer on the filtrate reduction. The difference in performance of the samples containing 14 and 49% wt of vinyl acetate was relatively similar.

The Figure 5(a,b) shows the photos of the disk after the filtration test for P-MMA51:VAc49 (0.8%wt/vol) which presented the best performance in the filtrate control test and for the P-MMA100:VAc0 (10%wt/vol) which presented lower performance when compared to other samples of P-MMA100:VAc0 in lower concentrations, respectively. The results showed it seems that when part of the particles of the fluid can penetrate the disk pores, under the pressure imposed on the system, and other part provide the formation of a thin film as filter cake [Figure 5(a)] leads a better filtration efficiency.

The scanning electron microscope (SEM) images enabled observing not only the external filter cake, but also the penetration into the disks pores.

Figure 6(a,b) show micrographs of 10 μm disks before and after the filtrate reduction tests with P-MMA51:VAc49 samples (0.8%wt/vol). The micrograph of the virgin disk [Figure 6(a)] clearly shows its porosity. For sample, for the P-MMA51:VAc49 (0.8%wt/vol), which presented the best filtrate reduction efficiency (82%), the formation of the external filter cake is very discrete. In this case, the polymer penetrated the disks pores, forming a highly efficient internal barrier, able to minimize one of the problems of the drilling process, which is instability of the borehole wall. This problem can be provoked by the formation of a very thick filter cake.[3] These results associated with those on performance indicate that the suspended polymer system has the greatest industrial potential, besides the advantage related to the logistical aspect.

CONCLUSIONS

Polymerization by emulsion with incremental addition of the most reactive monomer (MMA) produced copolymers of MMA-VAc with vinyl acetate content near those used in the feed. Increasing the vinyl acetate content from 14 to 49%wt caused a sharp decline in the glass transition temperature, but this effect was less intense in the filtrate reduction tests. The filtrate reduction percentage, on the order of 80%, increased with higher vinyl acetate content and varied with the concentration of the polymer used, and an optimal concentration was determined for both polymer in emulsion and suspended in water. The polymer suspended in water caused only a slightly greater filtrate reduction than that produced by the respective emulsion, but other important advantages should be considered: lower optimal concentration ($\sim$ 8.5 g/mL), the formation of an extremely discrete filter cake, and the logistical advantages, in the case of emulsions, the volume of material to be transported would be extremely higher.

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