# Compatibility of Curable Resin-Coated Proppants with Breakers in Crosslinked Fracturing Fluids

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ABSTRACT

Curable resin-coated proppant (RCP) is used in hydraulic fracturing treatments primarily as a means of preventing or reducing proppant flowback during post-frac clean-up and production. The RCP is generally placed in the fracture with water based crosslinked fluids. In order to effectively remove these viscous fluids which are detrimental to fracture conductivity from the proppant pack, it is necessary for a reduction in the fluid's viscosity to occur. This reduction in viscosity, or breaking, may occur either (1) thermally (2) with the addition of enzyme breakers, or (3) with the addition of oxidizing breakers, depending on the fluid used and the bottom hole temperature of the well.

Laboratory studies to determine the effects of various commercially available curable RCP's on breaking of commonly used fracturing fluids are presented in this paper. Fluids studied include linear, as well as borate and transition metal crosslinked guar and hydroxypropyl guar. The chemical breakers studied include an enzyme, an oxidizer, and an oxidizer used in conjunction with a free radical initiator. Additionally, the effects of these various chemical breakers on the compressive strength development of the consolidated proppant pack is investigated.

## INTRODUCTION

The use of curable phenolic resin-coated proppants in hydraulic fracturing operations was patented in 1975.<sup>1</sup> Until the last several years its use was primarily limited to the tail-in stages of the job. Recently, however, the use of these proppants has grown, due in part to the acceptance of higher sand concentrations which can result in more proppant flow-back. Many jobs are now pumped with a curable RCP used throughout the entire prop stages of the treatment.

In response to the increasing usage of curable RCP, several investigations have been undertaken in an effort to determine important parameters of the RCP, including: conductivity, crush resistance, compressive strength and compatibility with fracturing fluids.<sup>2-4</sup> The subject of interaction with chemical breakers has undergone only minor investigation. The scope of this earlier work included only linear gel with the conclusion that some significant interactions do occur, and that they should be rectified by using fluids which do not require extensive breaking for clean-up, such as (1) uncrosslinked gels, or (2) thermally degradable crosslinked fluids.<sup>5</sup> Unfortunately, these options may not be feasible in many cases. A series of experiments was performed in order to better understand the effects of the interaction between the RCP's and various breakers. Two widely used curable RCP's, manufactured by two different suppliers were tested and are referred to as RCP-A and RCP-B. RCP-A consists of a dual-coating of phenolic resin with the inner layer pre-cured and the outer layer curable. Each layer comprises approximately 2% by weight for a total resin content of 3.85 - 4.0%.<sup>6</sup> RCP-B consists of a single layer of partially cured thermosetting phenolic resin at approximately 3.5% by weight.<sup>7</sup> The breakers investigated were a hemi-cellulase (enzyme) at  $100^{\circ}$  F, animonium persulfate (oxidizer) with triethanolamine (free radical initiator) at  $100^{\circ}$  F, and animonium persulfate (oxidizer) at  $150^{\circ}$  F. The fluids studied were a 40 lb/mgal linear guar gum, a 40 lb/mgal borate crosslinked guar, a 40 lb/mgal borate crosslinked hyroxypropyl guar (HPG), and a 40 lb/mgal titanate crosslinked HPG. Static and dynamic break tests were run on various combinations of these proppants, breakers and fluids to determine the effect of the curable RCP's on gel breaking time. Compressive strength tests were also performed to determine the ability of the curable RCP to consolidate with varying concentrations of oxidizing breaker.

#### STATIC BREAK TIME TEST PROCEDURE

Base gels were prepared in a Waring Blender<sup>TM</sup> using deionized water with 2% KCl and the proper amount of gelling agent. After the gel was fully hydrated, 8 pounds of RCP/gal of slurry was added to the blender and mixed at high speed for 60 seconds. Crosslinker was then added to the fluids that were to be crosslinked. The slurry was poured into a glass beaker and placed in a water bath at the desired temperature. Viscosities were checked every 15 min using a Chan 35 Viscometer<sup>TM</sup> at 170 sec<sup>-1</sup> (100 RPM's). A baseline was established for each case using no proppant.

# EFFECT OF RCP ON STATIC BREAK TIME

The 40 lb/mgal linear guar at 100°F (Fig. 1) was broken with 2 lb/mgal ammonium persulfate oxidizer and 1 gal/mgal triethanolamine. With no proppant present, this fluid broke to a viscosity of less than 15 cp at 170 sec<sup>-1</sup> in 6 hours, while the 6 hour viscosity for the samples Containing RCP-A and RCP-B were approximately 30 cp. When the same 40 lb/mgal linear guar was broken with 1/8 lb/mgal hemi-cellulase enzyme breaker at 100°F (Fig. 2), the difference in viscosity between the broken fluid with and without RCP was only 2 cp at 170 sec<sup>-1</sup>. At a temperature of 150° F (Fig 3), the 40 lb/mgal guar with 3 lb/mgal ammonium persulfate maintained a viscosity of 23 cp at 170 sec<sup>-1</sup> in the presence of RCP-A and RCP-B and only 16 cp at 170 sec<sup>-1</sup> in the fluid with no RCP.

When the 40 lb/mgal guar was crosslinked with a borate complexing agent, the effects of the RCP on break time became even more pronounced. At 100° F, using 2 lb/mgal ammonium persulfate and 1 gal/mgal triethanolamine(Fig 4), the crosslinked fluid without any RCP degraded to a viscosity of less than 15 cp at 170 sec<sup>-1</sup> in 5 hours, while RCP-A and RCP-B still had viscosities of 45 cp and 52 cp respectively. At 150° F with 0.5 lb/mgal ammonium persulfate breaker (Fig 5), the prop-free fluid had broken to 16 cp at 170 sec<sup>-1</sup> in 6 hours, while RCP-A and RCP-B remained at 45 and 51 cp respectively.

Similar results were observed with 40 lb/mgal borate crosslinked HPG. Using 3 lb/mgal ammonium persulfate and 1 gal/mgal triethanolamine at 100°F (Fig 6), the control fluid was down to 15 cp at 170 sec<sup>-1</sup> in 3 hours and 15 minutes. At that point, the fluid containing RCP-A was still at 48 cp and the fluid containing RCP-B was at 49 cp. This trend continued through the end of the test at 6 hours when the control fluid was 7 cp, RCP-A fluid was 33 cp and RCP-B fluid was 34 cp at 170 sec<sup>-1</sup>. In tests at 150° F with borate crosslinked HPG using 0.25 lb/mgal ammonium persulfate (Fig 7), the viscosities of the RCP laden fluids were again approximately double that of the control fluid.

# DYNAMIC BREAK TIME TEST PROCEDURE

Fluids were prepared by the same method used for the static break test procedure. In this case, however, the RCP was sheared in a blender prior to its addition to the fluid in order to introduce a significant amount of free colloidal sized resin into the fluid. This was done so that the proppant could be sieved from the sample, enabling it to be placed on a Fann  $50C^{TM}$  high temperature rheometer for dynamic viscosity determination. Although the RCP was not actually in the fluid during testing, the breaker did have some opportunity to react with the proppant prior to sieving the fluid. More importantly, the free resin that was removed from the RCP surface remained in solution in the frac fluid to react with the breaker.

## EFFECT OF RCP ON DYNAMIC BREAK TIME

A 40 lb/mgal HPG crosslinked with a delayed titanate was tested at  $150^{\circ}$ F (Fig 8). The breaker used was 1.0 lb/mgal ammonium persulfate, resulting in a broken viscosity of 14 cp at 170 sec<sup>-1</sup> in 6 hours for the fluid exposed to no RCP, and a viscosity of 26 cp for the fluid exposed to RCP-A and 29 cp for the fluid exposed to RCP-B after the same elapsed period of time. At the end of six hours, the fluids containing the RCP were still not totally broken, with viscosities remaining at 27 - 29 cp.

#### COMPRESSIVE STRENGTH TEST PROCEDURE

Samples of proppant laden slurry were prepared by the same method used for the static break tests. The prepared fluid was poured into a pressurized test vessel (Fig 9) and placed into a heating jacket at the desired test temperature and pressure. No confining pressure was imposed on the samples at that point. After 2 hours, the bottom valve of the test cell was opened, allowing the floating piston to displace the fluid through a 325 mesh stainless steel screen. As a result, confining pressure was applied to the sample, which was cured under these conditions of temperature and pressure for the specified time. The cured samples were carefully removed from the test cell and allowed to cool for one hour. They were then placed in a controlled rate load cell and crushed to determine the compressive strength of the consolidated proppant pack.

## EFFECT OF RCP ON COMPRESSIVE STRENGTH DEVELOPMENT

A 40 lb/mgal borate crosslinked HPG containing 8 lb/gal of RCP-A was tested at  $180^{\circ}$  F for 24 hours. Tests were performed with incremental increases in chemical breaker from 0 - 10 lb/mgal, for RCP-A (Fig. 10). Compressive strength of the proppant pack decreased from 320 psi with no breaker, to 220 psi with 10 lb/mgal of oxidizing breaker.

#### CONCLUSIONS

1) When linear guar is broken with ammonium persulfate oxidizing breaker, the broken viscosity is 30 - 100% higher in the presence of curable RCP than in proppant free fluid.

2) When hemi-cellulase enzyme breakers are used to break linear guar, the difference in broken viscosity between RCP laden fluid and clean fluid is minimal.

3) When borate crosslinked guar and HPG are broken with ammonium persulfate oxidizing breaker, the broken viscosity ranges from 55 - 220% higher in the presence of curable RCP.

4) For all of the fluids studied, the reduced efficiency of ammonium persulfate oxidizing breaker in the presence of curable RCP becomes more pronounced as the temperature decreases.

5) The magnitude of the decreased breaking efficiency of ammonium persulfate oxidizing breaker is approximately the same for both the dual coated RCP-A and the partially cured RCP-B.

6) Some decrease in the compressive strength of the consolidated RCP pack does occur as the amount of ammonium persulfate oxidizing breaker is increased, however, even with breaker concentrations as high as 10 lb/mgal, acceptable strengths can be obtained.

#### RECOMMENDATIONS

Recent studies have shown that unbroken fracturing fluids can lead to significant decreases in fracture conductivity. This damage becomes even more substantial due to an increase in the polymer concentration which occurs from fluid loss during pumping and at fracture closure.<sup>8</sup> This phenomenon, when coupled with the reduced effects of oxidizing breaker in curable RCP packs, could result in reduced fracture conductivity. New encapsulated breakers have proven effective in reducing the conductivity damage by releasing amounts of ammonium persulfate breaker sufficient to break the polymer concentrated in the fracture after closure, without destroying the fluid's viscosity during proppant placement.<sup>9</sup> This same encapsulated breaker technology would allow for complete breaking of fluids containing curable RCP by increasing the ammonium persulfate concentration without compromising the fluid's ability to place the proppant. Since some decrease in compressive strength was noted for the curable RCP packs with high ammonium persulfate concentrations, care must be taken to insure that sufficient strength to prevent flowback will be obtained.

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 Figure 6 - 40 #/mgai borate crossinked HPG + 3 #/mgal AP oxidizer +1 gai/mgal TEA at 100°F



at 150°F

