Studying Degradation Rates of Polymeric Degradable Diverting Agents: A Case Study

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Abstract

There are many applications for hydrolytically degradable polymer in the oilfield industry, including fluid loss control, filter-cake removal, fluid diversion, etc. In a general way, the intended function of diverting agents is needed for a limited period. It is desirable that degradable materials be removed quickly so they do not have any effect on the final fluid flow. One of most favorite applications of these degradable materials is where it is coupled with viscoelastic surfactant in the multi-zone reservoirs with high contrast in permeability in order to create a uniform distribution of stimulation fluids across different zones.

In this study, various tests were conducted to investigate the degrading time of fiber, i.e. hydrolytically degradable polymers. Three commercial fibers evaluated under different parameters such as various temperatures, pressures, effect of salts, and solvents. The goal of this research was to determine effect of each parameters and optimum conditions for each one in case of applicability.

Keywords: Stimulation Treatment, Fiber-Assisted Diversion, Polymer Degradation and Hydrolyze, Multi-Zone Gas Reservoir

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1. Introduction:

In 1932, the oil industry started using hydrochloric acid to stimulate the oil wells. Immediately the problem arose of diverting the acid treatment into desired zone, and over the years the diverting method used; have been dedicated by the reservoirs being developed. The earliest documentation of a diverting agent was in 1936 when a patent was issued by Halliburton for the use of a soap solution. This was a water-insoluble, oil-soluble calcium soap that acted as diverting material for the acid.

Since that time, many diversion methods have been developed and applied because success of stimulation or chemical treatment often depends on fluid placement efficiency and complete zonal coverage. Generally, fluid diversion in categorized into two main groups: chemical and mechanical. Because of difficulties and costs induced from mechanical methods and reservoir conditions, in many areas chemical diversion are in considerable interest.

In this paper, we focus on experimental study of hydrolytically degradable polymers, and evaluation of their degradation time and effect of some chemicals on this parameter. The polymer tested during our experiments, have different crystallinities and composition of chemicals.

Recent introduction of hydrolytically polymer-based diverting agent offer many advantages compared to earlier materials. They can be produced in a variety of shape such as fiber, pellets, flakes, and granular. They are environmentally benign and flow-back fluids containing the degraded byproduct that are none-toxic. For instance, lactic acid is produced from hydrolysis of polylactic acid is naturally present in human body and dairy products. The structure of polylactic acid and its common synthesis pathway from lactic or lactide is shown in Figure 1.
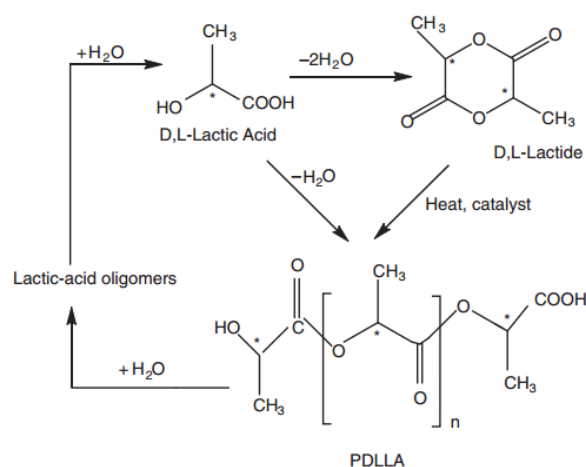

Figure 1: Polylactic acid and its synthesis and degradation

2. Previous works:

After application of first diverter in 1936, many fluid placement methods have been applied over years (Harrison, 1972) and this trend has been continued until present. Particulates such as rock salt, benzoic acid, wax soluble beads, oil soluble resins and sands have significant limitations. Wax soluble beads have limited temperature range, and oil-soluble resins are often not applicable in dry gas and injection well (Glasbergen et al, 2006)

Plenty of researches have been conducted to develop a diverting system that could overcome mentioned flaw backs and limitations. This has been led to developing a novel diverting agent composed of viscoelastic surfactant and a fiber that is essentially a hydrolytically degradable polymer.

Among them, it can be pointed out to work of (Carpenter et al, 1962), (Nitters and Davies, 1989), (Cheng et al, 2007), (Solares et al, 2008), (Potpoenko et al, 2009), (Kalfayan and Martin, 2009), (Fuller and Still, 2010), (Allison et al, 2011), (Quevedo et al, 2012), (Cohen et al, 2010), (Reddy and Cortez, 2013), (Jairo et al, 2010) that tried to develop or modify application this novel diverting system.

Experimental works that have tried to evaluate polymer degradation can be categorized into two main groups. In the first category, effect of different degradation accelerators on different polymer is tested. Some other research, took a constructive step to fabricate a setup in order to evaluate bridging ability of fiber assisted stimulation stages (Potpoenko et al, 2009).

In this work, we tried to apply best experimental procedure to determine degradation time of some available commercial fibers. The application of this novel diversion system is a gas reservoir with a huge contrast in permeability in different producing intervals in south of Iran.

3. The Experiments
3.1. *Experimental Procedure*

To determine the degradation time of fibers, a known amount of fiber was dissolved in $20_{\%}$ $CaCl_2$ solution, the solutions were heated to specified temperature between 6 to 24 hours. Temperature was varied from 93 °C (200 °F) to 135 °C (275 °F). The tests also were performed in presence of mutual solvent and $20_{\%}$ $CaCl_2$ solution to check their effects on polymer degradation rate. After predefined time in each test, solution was passed through 100-mesh sieve and remained residue was dried at oven and finally its weight was measured.

Although the majority of tests condition were the same, but a series of fiber degradation tests were first performed at 194 °F-203 °F with $20_{\%}$ $CaCl_2$ described previously but the degrading

time was too long at low temperature, therefore the temperature was increased to 212 °F- 275 °F. To confirm reproducibility of the data, in case of desire, different tests have been repeated.

Table 1 shows the recipe of solution that applied during polymer degradation tests.

Table 1: Applied Recipe during the degradation tests

Name	/1000 USG	Lab unit
Fresh Water	700	cc
$CaCl_2$	200	gr
Mutual Solvent	100	cc
Fiber	75	lb

4. Results & Discussion

The fibrous component, which degrades as a function of temperature and time also requires the presence of solvents and the small amount of salts to degrade completely.

Figure 1 shows a fiber solution during one of our tests right after mixing (Fig 1.a) and its conditions after passing from 100-sieve mesh (Fig 1.b). As could be seen, a thick film remained on the solution that could be interpreted as bridging ability while pumping in porous media.

In Figure 2, dried residues after polymer degradation in two different tests are shown. As could be seen in Fig 2.a, polymer structure is deformed and some of initial value is hydrolyzed. The same test without mutual solvent is repeated and polymer condition after drying in oven is shown in Fig 2.b. It is clear that rate of polymer degradation in this case is lower and polymer structure is mainly kept as its initial conditions.
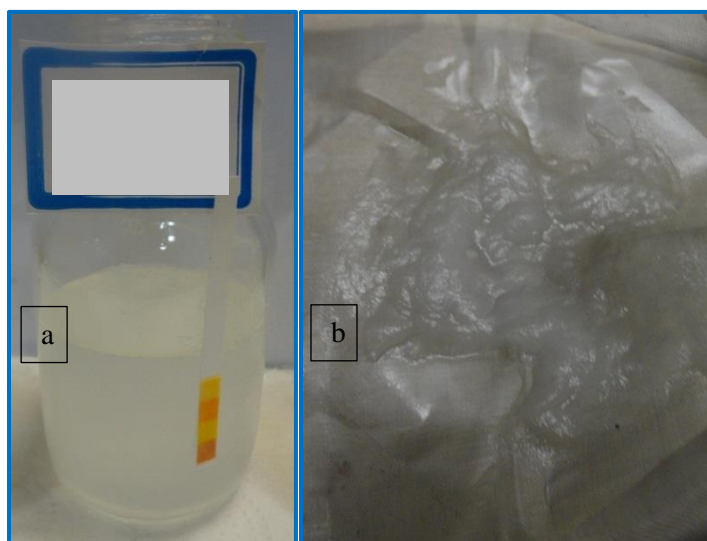

Figure 1: fiber in 10% mutual solvent (right) - fiber after filtering on 100-mesh sieve (left)

Figure 2: fiber in $10_\%$ mutual solvent + $20_\%$ $CaCl_2$ after drying in oven (right) and fiber in $20_\%$ $CaCl_2$ after drying in oven (left)

Table 2 summarizes test results on three commercial fibers available. Effect of temperature, pressure, presence of $CaCl_2$, and mutual solvent as a degradation accelerator is investigated throughout these tests.

Table 2: Summary of Tests Results

		Test Description	Temperature (°F)	Pressure (psi)	Duration (Hrs.)	Remained residue
		Polymer Degradation Test Results				
Sample No.1	a	20% $CaCl_2$	275	300	6	Zero
	b	20% $CaCl_2$	275	800	6	Zero
	c	20% $CaCl_2$	200	800	6	Zero
	d	20% $CaCl_2$ +10% Mutual Solvent	220	__	24	Near zero
Sample No.2	a	20% $CaCl_2$	275	800	6	Zero
	b	20% $CaCl_2$	200	800	6	No change
	c	20% $CaCl_2$	220	__	6	No change
	d	Fresh Water	220	__	6	No change
	e	20% $CaCl_2$	230	__	48	Near zero
	f	10% Mutual Solvent	230	__	48	Near zero
Sample No.3	a	20% $CaCl_2$ +10% Mutual Solvent	220	800	6	Near zero
	b	20% $CaCl_2$ +10% Mutual Solvent	220	__	6	Zero
	c	20% $CaCl_2$	194	__	24	Near zero
	d	10% Mutual Solvent	194	__	24	Zero
	e	20% $CaCl_2$ +10% Mutual Solvent	194	__	24	No change
	f	20% $CaCl_2$ +10% Mutual Solvent	203	__	6	Zero

5. Conclusions

The most indispensable outputs of this study could be summarized as follows:

1. Mutual solvent and $CaCl_2$ acted as degradation accelerator in all cases. It seems that this additive helps to hydrolyze the structure of three available polymers.
2. Pressure has no clear effect on degradation rate of polymer (generally aliphatic polyesters).
3. It seems that hydrolyze process for each polymer has a temperature threshold that in cases lower than it, no degradation happens even in case of lasting test for a long period. After passing this threshold, degradation will increase from 0% to 100% in a noticeable short time.

6. Acknowledgements:

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