Polyurethane Technologies for Drilling Lost Circulation and Zonal Isolation

Mario R. Rojas; Nalco Champion an Ecolab Company
Michael Jeffries, David Zielinski, Abdullah Ekin; Covestro.

Abstract

Polyurethanes are widely used in many physical forms such as coatings, elastomeric materials, foams and even rigid structural materials; with applications that widen automotive, clothing, health care, construction and the electronic industries. The versatility of polyurethanes relies on our ability to change their molecular architecture, and the different ways that they can be formulated. The objective of this work is to investigate the feasibility of a novel technology for lost circulation based on a new generation of polyurethane resins. The new materials should provide adequate viscosity for pumpability, sufficient weight to keep well balance during injection, predictable/controllable gelling and curing kinetics, and adequate mechanical properties that allows the cured resin to be drillable.

The slurries were formulated with barite as a weighting agent, a rheological modifier, an initiator and a delaying agent, were used depending on target temperature and weight. Laboratory analyses have been carried out to evaluate slurry gelling kinetics under high temperature and high pressure using different techniques, including consistency (Bc) measurements at 5,000 psi. Mechanical properties such as tensile, compressive strength and sealing pipe test were used to characterize the final resins.

Pumpable times can be tuned to be 3-6 hours for slurry formulations in a range of temperature between 100 and 250 °F, with a weight range of 9 to 14 lb/gal. Compressive strength has been determined to be between 3,000 and 4,500 psi for final cured materials. Pipe sealing tests performed with nitrogen have shown excellent adhesion and isolation with minimal shrinkage.

Introduction

During drilling operations the mud is always in contact with the formation helping to control the pressure in the wellbore and creating a sealing layer (filter cake). This layer prevents the fluid to migrate into the rock and reduces formation damage. In order to control fluid losses, drilling muds are usually formulated with materials that contribute to create the filter cake by two mechanisms: 1. bridging, which involves augmenting the connectivity of the solid particles on the surface of the rock. Typical bridging agents include calcium carbonate and fly ash. 2. Gelling of the fluid at the surface. This means that the fluid creates a gel-like impermeable thin layer along with the bridging agents to seal the surface. Most of these materials are high molecular weight polymers.

However, in extreme cases of fluid loss in rocks with very high permeability, or in vugular cavernous formations and fractures, the drilling fluid may uncontrollably invade further, resulting in formation damage and fluid circulation loss. This ultimately involves stopping the drilling operation and the loss of a significant portion of the drilling mud. The economic impact of wellbore instability -including fluid losses- in oil well drilling worldwide has been estimated to be over one billion dollar annually [1]. In addition, recently published survey data indicates that circulation lost contributes to over 12% for non-productive time (NPT) in rigs in the Gulf of Mexico. These statistics on a worldwide basis, would also translates into billions of dollars of extra cost each year [2].

Currently there are few technologies for severe circulation lost treatment. If the problem cannot be solve by changes in mud formulation or the addition of a concentrated pill (usually removable), the chances of continuing drilling slim down if the fluid loss continues. In such critical cases, the only way to keep drilling is to cement and isolate the vugular areas. However cement can also be a challenging solution since its formulation must be specifically designed for the conditions of the well.

In the recent literature, particularly during the past decade, a couple of studies, including a patent, refer to the use and application of polyurethane based circulation loss material. Boukadi et al. 2006 [3] tested the effects of activator (or catalyst) concentration, pressure, moisture and solvent addition on the kinetics of the reaction and pumpability of the PU foams at temperature between 50-65 °C. The presence of carrier fluids such as diesel was found to be advantageous, except when the solvent amount exceeded 50%, as the physical properties of the final PU become compromised. In most cases, curing times were too fast at wellbore temperature (less than 2 hours). Decreasing activator concentration did slow down the reaction by lengthening the curing time, but with little or no effect on the onset of the reaction. Moreover, below a certain activator concentration, the properties of the foam were also compromised.

Pressure increases showed to improve seal-ability and adhesion of the foam to the porous formation.

Donna Gerrard [4] (MI-Drilling Fluids) holds a patent (WO 2011/070375 A1, EP2510068A1) for a method of treating wellbores with elastomeric gels based on blocked

isocyanates of different unblocking temperatures, and an active alcohol. According to the invention, the combination of the two isocyanates provides a synergistic effect so that the curing time can be adjusted in a way that would not be possible with the individual isocyanates.

This project is focused on developing a PU resin that can be used as a circulation loss material, and be drilled through after setting. Some of the technical requirements of the technology should include:

- Formulation must be mixed in tanks above ground.
- Pumped in drill string, preceded and followed by oil based spacers.
- Moved down the drill string, out drill bit, into formation up to 6 feet.
- Material does not harden significantly until out of drill string and in desired zone.
- Material should harden in 4-8 hours.
- Drilling can resume after this time and material can be easily drilled through.

Experimental

Resins used in the study included 3 polyisocyanates and 3 polyols with molecular weights in the range of 150 to 750 g/mole. Functionality was between 2 and 4. The resins were selected based on their particular properties, especially in terms of reaction kinetics and final mechanical properties. Proprietary catalysts and delayer agents were developed specifically for this application. All formulations were prepared with a 1:1 molar ratio of NCO: OH unless otherwise specified. Three different systems have been evaluated (F1, F2 and F3) designed for a range of 100-200 ºF; and F3HT, a special grade that can be used between 200-250 ºF.

Procedures

To characterize the kinetics of the neat systems, preliminary tests were conducted in 4 oz. bottles in a water bath at the desired temperature (150 and 200 ºF). Empirical measurements were performed: Gel time was recorded as the time at which the formulation would stop flowing if the bottle was inverted. Solid time was recorded as the time at which the sample would not be penetrable by hand pressure with a stirring glass bar.

For formulations with good performance in terms of gelling and curing times, measurements of viscosity at two shear rate (27 and 80 sec^{-1}) were performed as a function of time at the desired curing temperature. For these measurements, a Fann 35A viscometer equipped with a temperature controller was employed, using a combination of rotor/bob/spring (R1/B4/F1), for the desired viscosity range. Caution was taken to stop the test before the formulation would set in the viscometer cup, so the cup/bob could be cleaned.

For further testing and characterization of the best formulations, mixtures of the resins with barite as weighting agent and a rheological modifier for barite suspension were tested in a OFITE high pressure, high temperature consistometer. Pressure was set at 5,000 psi for all the tests. Temperature was set at 150, 200 or 250 ºF depending on the formulation, while heating rate was fixed to 2.5 ºF/min, starting from room temperature. Barite was added to achieve formulation weights between 10 and 14 lb/gal (ppg).

Pipe adhesion/sealing testing was conducted by curing a plug of resin inside a 1.5 inch diameter custom steel pipe apparatus at the desired temperature. After curing, the system was cool down and one side was pressurized with nitrogen, while the pressure on the other side was monitored until there was breakthrough of nitrogen. The length of the resin plug was 3.0 inches. Once the nitrogen surged through the resin or between the pipe walls and the resin, the maximum pressure was recorded.

Compressive strength was measure using a Chandler API Compressive Strength Tester Model 4207. Cubes of 2x2x2 inches were cured for each sample. Testing was done at room temperature with a loading speed of 2,000 psi/min.

Tensile strength was conducted according to ASTM D 412 using an Instron model 5566 with a contact extensiometer at controlled ambient conditions of 23°C and 50% RH. Samples were prepared by casting each polymer system on a mold release coated glass panel after mixing for 30 seconds at 2300 rpm using a Flack Tek DAC 400 model spin mixer. This method of mixing insured a defect free casting at 0.24 in. thickness. The castings were allowed to post cure for 3 days at 20°C and 50% RH and then cut using the appropriate die.

Results and Discussion

Kinetics of gelling and curing

Mixtures of the different compatible polyisocyanates and polyols were prepared, and their approximate gel time and setting time were measured at 150 ºF with different concentrations of initiator (Table 1).

Table 1: Gelling times (GT) and Setting times (ST) for several systems (neat formulations, only NCO: OH).

Systems	GT (h)	ST (h)
F1-1	>10h	>10h
F1-2	5.75	6.75
F1-3	4.25	4.75
F1-4	2.50	3.00
F1-5	1.75	2.25

Gelling time was defined as such time required for the formulation to stop flowing (In a closed 120 ml vial). Setting was defined as the time required for the sample to become solid, this is: it would not be penetrable by a glass bar upon application of hand force. Although these two measurements are just rough estimates of the real gelling and setting points, it provided a relatively good scanning tool for the estimation of how fast the systems would cure, and how much initiator was needed. Under these conditions, optimum gelling times of 4-5

hours were observed, whereas hardening (setting) will take 6.5-8 hours in the same range of initiator concentration.

Ideally polyols and polyisocyanate mixtures are prepared in a 1:1 NCO: OH molar relation so that that there is equal concentration of each functional group in the system to create a crosslinked network. However, in order to test the sensitivity of the reaction to the resin ratio in the mixture, gelling time and setting time for several ratio mixtures were measured at 150 °F and with a fixed catalyst concentration (Table 2).

On the other hand, as it was expected, the resulting resins had significantly different mechanical properties with softer materials obtained in the presence of a polyol excess.

Viscosity can provide more details about the gelling and curing of the polyurethane resins. Viscosity data also provides more accurate information about the handling of the un-reacted mixture and the energy that would take to mix it and pump it down through the drill string.

Table 2: Gelling and setting times for different resin ratios at fixed catalyst concentration (F3 system)

NCO:OH	GT (h)	HT (h)
1.38:1	5.50	6.25
1.18:1	4.25	4.58
1:1	4.25	4.75
1:1.5	4.25	4.91
1:2	5.25	6.00

Figure 1 illustrates how the onset on the reaction (time when the viscosity starts increasing) and the gel time (point at which the viscosity increases asymptotically), may be accurately estimated by this technique. In this particular case, viscosity was measured at two shear rates and at constant temperature. A viscosity above 1,500 cP was considered as the upper limit for practical pumpability. The onset temperature was approximately 120 min and the gelling time 4.25 h. However, the pumpability limit is reached at 225 min (3.75 h). Note that these time estimations are relatively conservative, as it does not account for the time required for the mixture to reach the target bottom-hole temperature, hence, in practical applications it would take a much longer time to gel the formulation as the formulation is slowly warmed up during the pumping process.

The effect of a delaying agent in the kinetics of F2 at 150 °F is shown in Figure 2. Without the addition of the additive the system exhibits an onset at 45 min and a gelling time of approximately 110 min. In practical terms, this system would be unsuitable for any field trial at these conditions. However, upon addition of the delayer at 3.7 wt. %, the onset of the reaction can be delayed to 60 min and the gelling to approximately 150 min (no stiff increase was observed). Further addition of the delaying agent and changes in catalyst concentration provide a set of tuning tools for the reaction, so that the gelling time can be adjusted to suit field requirements.
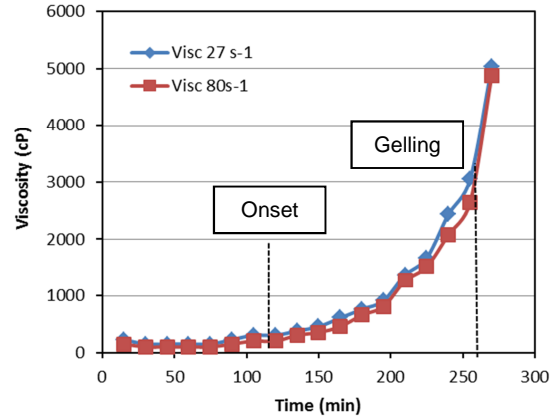

Figure 1: F1 gelling process at 150 °F. Initiator concentration fixed.
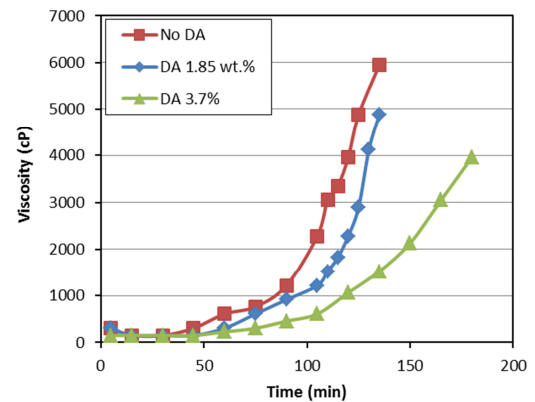

Figure 2: F2 system gelling process at 150 °F with different contents of Delaying Agents (DA). Initiator concentration fixed.

Weighting agents and rheological additives may induce significant changes in the viscosity and kinetics of the formulations. Figure 3 provides an example of these effects. Upon increasing the weight of the slurry to 10 lb/gal and adding enough silica to keep solids suspended; the kinetics of the reaction is drastically decelerated: Onset shifts from 100 to 180 min; and pumpable time from 225 to 400 min (6.7 h).

Consistency measurements were performed for the mixtures considered to have the best performance in terms of gelling time measured by shear viscosity. The consistency (Bc) is an empirical dimensionless viscosity measurement that is widely used to characterize cement slurries, and to estimate pumpable times for real field applications. Values of Bc range from zero to 100. Most companies use a consistency value of 70 or 100 as the threshold for pumpable slurries. Figure 4 shows consistency measurement at 150 °F for formulations based on two different systems with weights of 10 and 14 lb/gal.
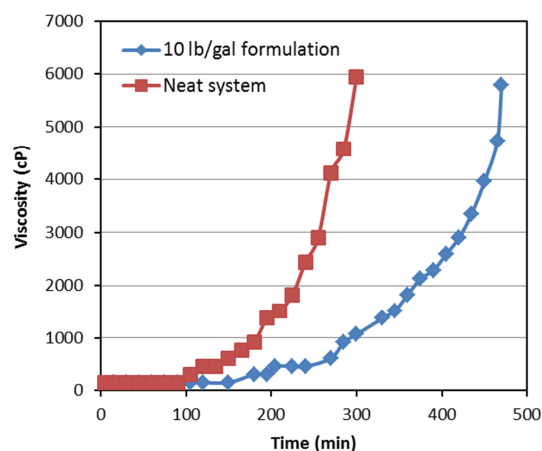
Figure 3: Gelling process at 150 ℉ for F3 with and without barite and silica. Initiator concentration fixed.
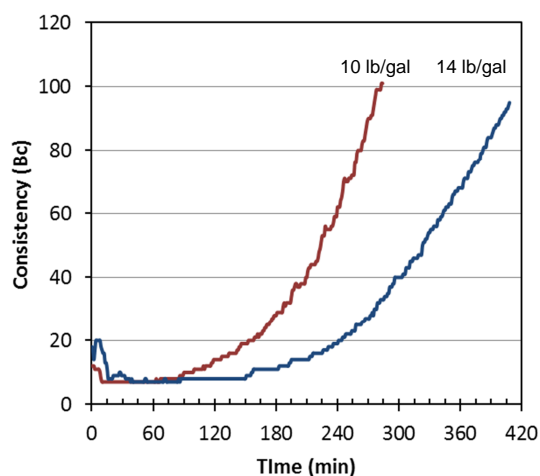

Figure 4: Consistency as a function of time for F3 formulations at 150 ℉ and 5,000 psi and two densities (10 and 14 lb/gal)

As expected, further addition of solids to the formulation decelerates the reaction for both systems. The formulation based on F3 system at 14 lb/gal reaches a Bc~70 after 6 hours. At 10 lb/gal the formulation reaches the consistency threshold after approximately 3.5 hours.

To improve the performance of the formulations, particularly at low solids content, addition of the delaying agent was used for formulations at 200 ℉ (Figure 5). The small amounts of the additive help to extend the pumpability zone for about another hour compared to the system without the delaying agent. Overall this formulation has a pumpable time of about 3 h, assuming temperature reaches bottom hole temperature of 200 ℉ in about 45 min (heating rate of the consistometer was 2.5 ℉/min).

Figure 6 shows the consistency of a formulation particularly designed for 250 ℉. At the testing conditions the pumpable

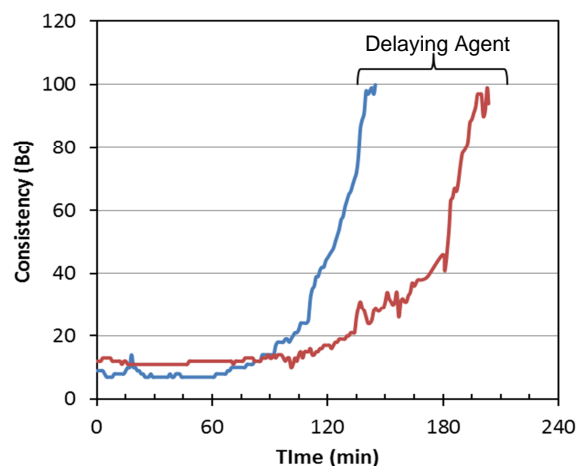time for this system is approximately 160 min approximately, or 2h 40min.

Figure 5: Consistency as a function of time for F3 formulation with and without delaying agent (3.5 wt. %) at 10 lb/gal, 200 ℉ and 5,000 psi. Initiator concentration fixed.
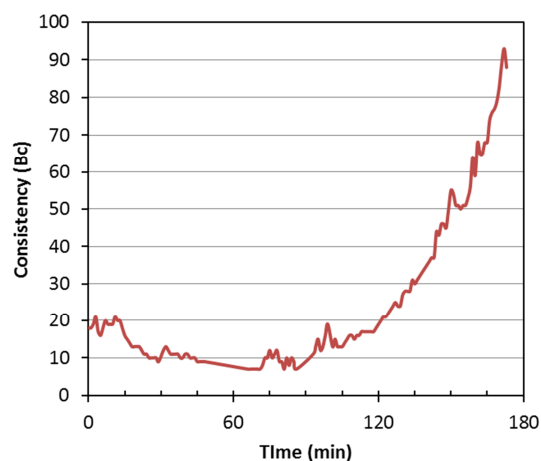

Figure 6: Consistency as a function of time for F3HT formulation (3.5 wt. %) at 14 lb/gal, 250 ℉ and 5,000 psi.

Mechanical Properties

Table 3: Tensile properties of different LCM cured resins (F3) at room temperature according to ASTM 412 Method

Formulation target temperature (℉)	150	200	150	200
Weight (lb/gal)	8.5	8.5	10	10
Tensile strength @ break (psi)	500	576	534	502
% Elongation @ break	140	146	146	116

Table 3 shows a summary of tensile properties for two set of systems designed to be used at 150 and 200 ºF (Based on catalyst and delaying agent content). The properties were measured without barite (neat formulation) and with barite (10 ppg). Results suggest that the tensile properties of formulations for different temperatures (different catalyst, delaying agent content) stay unaffected by these changes. The addition of barite as filler/weighting agent in the range observed does not affect significantly the properties either. At similar conditions, cured cement for well construction typically shows a tensile strength of 133-166 psi [4].

Pipe adhesion test was performed on neat and weighted formulations as an indirect measurement of shrinkage. Also this custom test provides an excellent way to evaluate the bonding of the resin to metal after curing, and the potential performance of the resin as a zonal isolation material to prevent gas migration. Results of the pipe adhesion tests are shown in Table 4.

Table 4: Pipe adhesion/sealing test results for different LCM cured resins formulations (F3), at different weights.

Formulation Target Temperature (ºF)	150	200	150	200
Weight (lb/gal)	9	9	14	14
Maximum Pressure (psi)	128	121	>250	>250

The maximum pressure that the neat resin can withstand is in the range of 121-128 psi. In these systems the failing was always observed between the wall of the pipe and the resin. A channeling effect was observed for neat resin (9 ppg) when samples were watched through light after the test. For the cured weighted systems no maximum pressure or bursting pressure was detected in the range permissible for the equipment (up to 250 psi). As expected, the filler has a positive effect reducing the shrinkage and improving the sealing properties of the resin under these confined conditions.

API compressive strength (CS) measurements follow similar trends (Table 5). The neat material (9 ppg) exhibit the lowest CS, and it was the only material to actually fail completely under the applied load. Filled systems showed enough deformation to sustain the load and they only presented longitudinal cracks (fissures) along the load direction in all four sides. After a period of time, the cubes would almost regain their original shape (See Figure 7). Measurements performed under confined conditions and at bottom-hole temperature would provide further insight into the mechanical behavior of these materials under well stresses.

Table 5: API compressive strength results for formulation F3 at different weights (Formulation target 125 ºF).

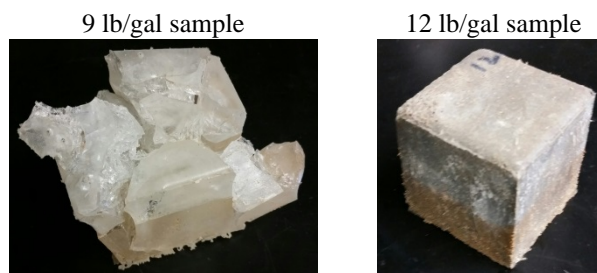| Weight (lb/gal)	9	9	14	14
Compressive Strength (psi)	3,000	4,500	4,500	4,800

9 lb/gal sample   12 lb/gal sample

Figure 7: Compressive strength samples 10 minutes after testing. Longitudinal cracks in 12 ppg sample are not visible anymore.

Conclusions

Novel polyurethane formulations exhibit an adjustable kinetics that can be tune for field applications at temperatures in the range of 100-250 ºF.

Casing sealing, compressive strength and tensile properties suggest that the new technology may be used in critical circulation loss or in situations when mechanical stability is an important issue. The systems are robust enough to changes in temperature, resin ratio and presence of fillers/weighting agents.

References
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