Thermosetting Polymer based Flexible Synthetic Cement for Successful Zonal Isolation in Thermal Wells - A New Approach

R. Shanbhag, Z. Melrose, S. Nutt, University of Southern California
M. Cleveland, R. Keese, Schlumberger

Abstract: Conventional Portland cements present significant challenges in thermal wells due to a high degree of brittleness, low strength, and inconsistent strength development following set. These challenges are further compounded by progressive degradation of the material with repeated thermomechanical loading. A new, highly flexible synthetic cement based on a thermosetting polymer, that overcomes many of these challenges, is presented. The material exhibits significantly higher strength and lower modulus (thus, a higher elastic strain to failure) than conventional cements and also shows a very high degree of resilience to thermal as well as mechanical fatigue. Further, the material exhibits right angle set and immediate strength development following set.

The material was tested for various mechanical properties in tension as well as in compression. Rheological testing was conducted and the effect of variability in BHCT as well as in initiator concentrations on cure kinetics was determined. A yard test was conducted using conventional oilfield equipment to assess suitability of large-scale deployment of the cement.

Typical compressive strength, tensile strength and compressive modulus values are greater than 8,000 psi, greater than 1,500 psi, and less than 500 ksi, respectively. The density of the material can be modified in the 10.0 to 17.0 pounds/gallon range. In this paper, the 12.0 and 14.5 pound/gallon variations were tested. Poisson's ratio of the material was determined to be 0.27 at 77°F and increases at higher temperatures, showing a very high degree of flexibility. The material

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exhibits a right angle set at a range of temperatures with little variation in set times due to variations in bottom hole circulating temperature and initiator concentration. Further, the strength development is immediate following set in each case. The system also exhibits zero shrinkage upon cure, an important attribute in preventing vent flow.

The high strength and flexibility, high temperature performance, as well as the “set on demand”, zero shrink and “right angle set” properties of the material render it ideal for placement in thermal wells where wellbore integrity is of concern. Further, use of conventional oilfield equipment in placement allows for an easy deployment of this new solution that may solve a number of problems associated with thermal wells.

1. INTRODUCTION

Complete and durable zonal isolation is the foremost goal of the cement job [1] . Failed primary All final manuscripts will be sent through an XML markup process that will alter the LAYOUT. This will NOT alter the content in any way. 2 SPE-SPE-178454-MS-MS cement jobs can lead to Sustained Casing Pressure (SCP) and vent flows, which in extreme cases can have disastrous consequences [2,3]. Well integrity is one of the foremost engineering challenges facing the oil and gas industry that requires additional attention as drilling expands into more demanding environments. Conventional Portland cement systems present a challenge to successful zonal isolation of wells owing to inherent brittleness, limited strength, and low flexibility that can lead to premature failures even in relatively low stress environments. Further, slow development of strength leads to long “waiting-on-cement”[4] times, delaying well completion.

A desirable alternative system would provide greater strength and flexibility along with “ondemand” rapid setting ability. Material systems must meet placement criteria to allow for processing and handling using conventional cementing equipment. Thus, the rheological characteristics as well as predictability of set times of alternative cement materials are paramount.

We introduce a new thermosetting polymer based system, called PRSC 100, which has been developed to address the limitations encountered with traditional oil well cements. The system consists of a suspension of reactive and inert fillers in a blend of thermosetting polymers [5]. Upon initiating the polymerization reaction, the material hardens to form a solid cementitious mass. The time required for the thermosetting polymer to gel and solidify at a given temperature can be controlled by the concentration of the initiator in the suspension or slurry. Material formulations were evaluated for basic mechanical properties, rheological characteristics, and setting kinetics. We will describe the relevant performance of the material in the cured state, as well as its slurry form for compatibility with cementing infrastructure and practices used in the industry.

2. RESULTS AND DISCUSSION

2.1. Mechanical Properties

The density of synthetic cement can be modified in the range of 10.0 to 17.0 pounds/gallon (ppg) through the addition of reinforcing fillers such as hollow glass microspheres and heavy ores. The 12.0 ppg system contained a higher percentage of hollow glass microspheres than the 14.5 ppg variant considered in this study. Mechanical properties of both densities are summarized in Table 1. The compressive stress vs. strain plots of the 14.5 and 12.0 ppg systems respectively are shown in Fig. 1a and Fig. 1b. Tests were conducted in accordance with ASTM C39-12a with a displacement rate of 0.1 inch/ minute. The Poisson’s ratio of this sample was determined using Digital Image Correlation (DIC) using images of the sample recorded during loading. The displacements and consequent strains were calculated along the principal axes. Care was taken to ensure that only displacements during elastic deformation were used. Poisson's ratios of 0.30 and 0.27 for the 14.5 and 12.0 ppg systems respectively are much larger than the value of 0.15 associated with traditional cements [6, 7].

Table 1—Mechanical Properties of PRSC Synthetic Cement.

Property	12.0 ppg	14.5 ppg	Traditional Cement
Compressive Strength (psi)	10,375	10,766	800 – 6,000
Compressive Modulus (ksi)	346.3	295.6	> 1,000
Tensile Strength (psi)	1779	1578	200 -1,200
Poisson's Ratio	0.27	0.30	< 0.20

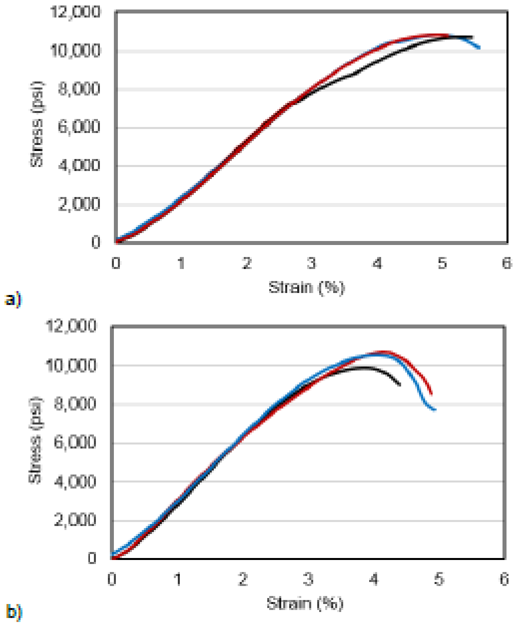

Fig. 1— Compression tests for 14.5 ppg a) and 12.0 ppg b).

While both variants displayed similar compressive strength, the increased compressive modulus and lower Poisson's ratio of the 12.0 ppg system is attributed to the higher glass microsphere concentration in the resin matrix. The low compressive modulus of the matrix material with respect to that of the reinforcing aggregate results in deformation occurring exclusively within the matrix and consequently, the greater volume ratio of fillers reduces overall

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deformation. As would be expected with the same ultimate stress and a higher modulus, the strain to failure is much lower [8].

Fig. 2 shows the material under a compressive load. Failure is preceded by the appearance of bands, henceforth called shear bands, on the outer surface of the cylinder at ±45° to the loading axis. Shear bands are associated with the failure of ductile materials (i.e. Poisson's ratios ~0.30) and not in brittle materials such as cement [9]. The strains are fully recoverable until the material reaches ultimate compressive strength. Also, failure beyond the ultimate compressive strength was gradual rather than sudden and catastrophic, occasioned by the appearance of multiple cracks parallel to the loading axis where circumferential tensile stresses arise normal to the loading axis. This observation is consonant with a tensile strength less than compressive strength, as observed. Note that higher elastic strains (i.e. low modulus and high failure stress) and ductility in the material would prove to be advantageous in a casing material, especially in thermal wells. A further study of failure mechanics of the PRSC system is warranted.

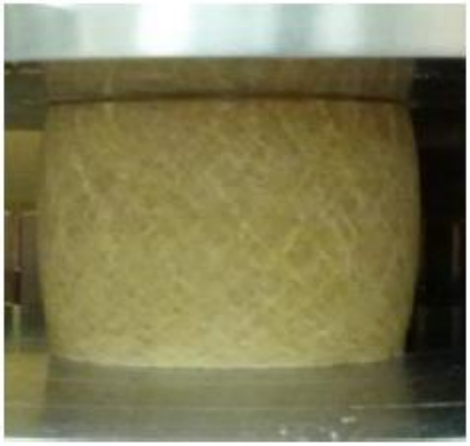

Fig. 2—PRSC under a compressive load

The splitting tensile stress vs. displacement results for the 14.5 and 12.0 ppg variants are displayed in Fig. 3a and Fig. 3b. Tests were performed in accordance with ASTM C496M-11. The average splitting tensile strength of the 14.5 ppg sample was 1,578 psi while that of the 12.0 ppg sample was 1,779 psi. There was minimal scatter in the test data for the 12.0 ppg samples, despite the large volume fraction of hollow glass microspheres. The consistency of displacement-to-failure values in the splitting tension tests suggests the flexible nature of the material. Brittle fracture is typically dominated by the distribution of strength-limiting flaws, resulting in a corresponding strength distribution best characterized by Weibull statistics [9, 10]. A similar statistical distribution in displacement values at failure is also typical of brittle materials. In contrast, the polymer cement exhibits consistent values of strength and displacements at failure.

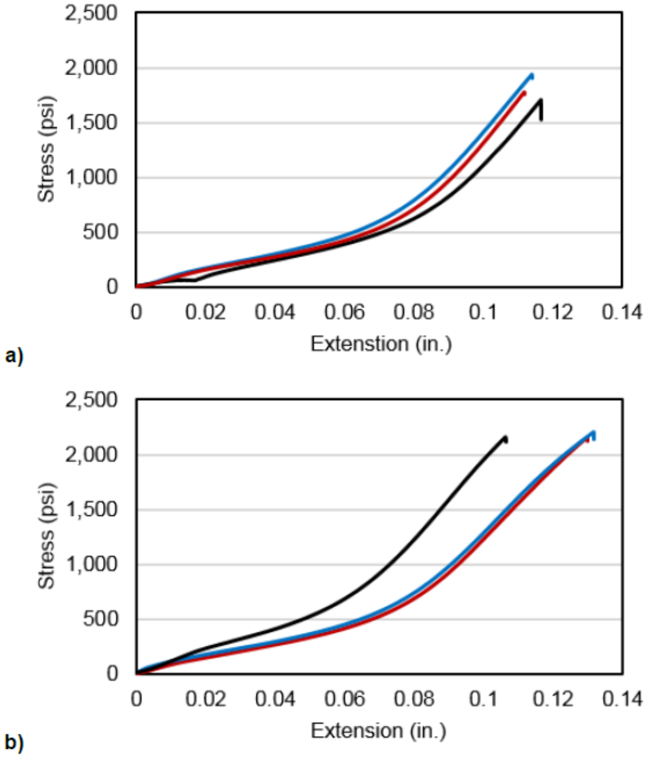

Fig. 3—Splitting Tension tests for 14.5 ppg a) and 12.0 ppg b)

Based on these results, it is evident that while modifying the density using glass microspheres has minimal effect on the ultimate compressive strength, there is significant effect on the elastic modulus and consequently, the strain to failure. Since flexibility is an important criterion for cement performance [11], a more moderate (lower) value of elastic modulus can be desirable, especially with respect to resisting dynamic loads.

The effects of exposure to water and several reagents including 2 molar aqueous solutions of H_2SO_4, NaCl, HCl, NaOH, and crude oil, were investigated for the 14.5 ppg variant. Test coupons of the cured material were immersed in water and the said reagents for two weeks and the ultimate flexural strength was subsequently measured in accordance with ASTM D790. Immersion caused a negligible decrease (<2%) in ultimate flex strength in each case. A separate investigation of creep and fatigue behavior of the material shall be reported in a separate publication.

2.2. Rheological Behavior

Values of the 14.5 ppg slurry at 120°F in an Ofite viscometer with R1B5 geometry are reported in Table 2. The data was analyzed in accordance with American Petroleum Institute (API) Recommended Practice 10B [12]. Shear stress was plotted as a function of shear rate obtained from rotational speeds. Analysis of the data revealed two trends:

Table 2—R1B5 Readings.

Rotational Speed	**Ramp-Up**	**Ramp-Down**	**Average**
300	205	205	205
200	153	179	166
100	112	132	122
60	93	109	101
30	78	89	83
6	63.5	64	63
3	60.8	54.5	60.1
10 second Gel	64.0		
10 minute Gel	64.3		
Temperature (°F)	140.5		

The presence of a yield stress below which $\dot{\gamma} \rightarrow 0$

Shear thinning behavior

This behavior is characteristic of a Herschel-Bulkley Fluid [13] defined by:

$$\tau = \tau y + \kappa \dot{\gamma}\, n \text{ when } \tau > \tau y$$

τ = shear stress

τ_y = yield stress

$\dot{\gamma}$ = shear rate

κ = consistency index

n = power law index

Fig. 4 shows the shear stress vs. shear strain measured for the fluid. Analysis of the data using the above relationship gives a value of 0.696 for n and 3.37×10^{-2} lbf-$s^{n/}$$ft^2$ for κ. Note that these values may not be accurate and in order for the data to be meaningful, the following conditions must be met [1]:

- The fluid must be Newtonian or near-Newtonian
- Bob gap must be at least 10 times the diameter of the largest particle
- There must be no plug flow, thus leading to a uniform change in shear rate across the gap

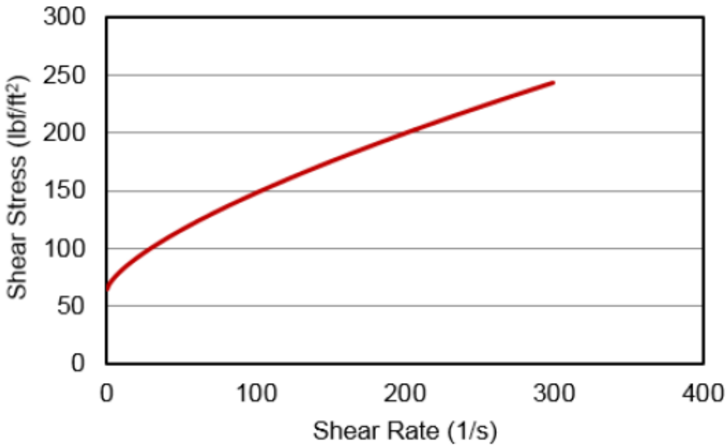

Fig. 4—Shear Stress vs. Shear Rate obtained from R1B5 measurements.

None of these criteria are satisfied with the slurry and test set-up. The slurry is highly pseudoplastic (i.e. viscosity decreases with shear rate) and thixotropic (i.e. viscosity decreases as a function of time at constant shear rate) and thus non-Newtonian. Further, the slurry contains suspended filler particles up to 1000 μm in diameter, whereas with the gap size of 1.17 mm in an R1B5 geometry, only slurries with particle sizes up to 120 μm may be considered homogeneous[14].

Finally, there was evidence of de-homogenization as well as of plug flow in the slurry upon completion of the test. This might be attributed to adhesion between the slurry and the surface of the bob as well as that of the rotor. Alternately, the large particle sizes may be interfering with the development of a shear rate gradient across the cross section of the fluid. Particle migration to one side of the cup interferes with the establishment of a clear relationship between shear stress and shear rate [15]. Appropriate methods for determining the rheological characteristics of the material are needed, as standard oilfield equipment is more suitable for water based cement suspensions and may not be appropriate for this purpose.

2.3. Cure Kinetics

Fig. 5 shows a High Pressure High Temperature (HPHT) consistometer curve for a sample of the 14.5 ppg PRSC slurry at 140°F. The thickening time was defined as the time required for the slurry to reach a consistency of 100 B_c [16]. Thickening time can loosely be understood as the time the material remains pumpable at a certain Bottom Hole Circulating Temperature (BHCT) and can be controlled by adjusting the concentration of the peroxide initiator. Consistometer tests were conducted at atmospheric pressure, 2,000 psi, and 5,000 psi while keeping BHCT and initiator concentration constant. The different pressure conditions seemed to have minimal effect (less than 5 minutes) on the thickening times.

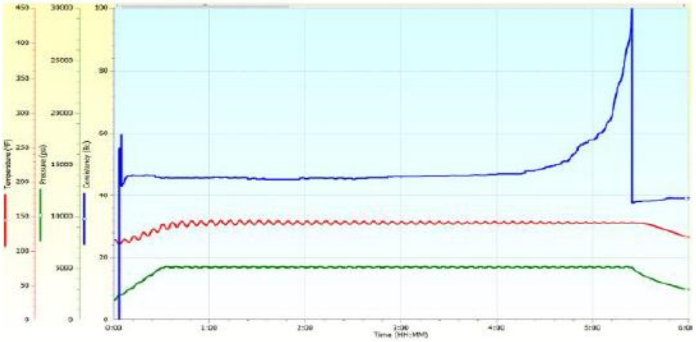

Fig. 5—Consistometer Temperature, Pressure, and Consistency vs. Time.

Sensitivity of thickening time to variations in BHCT and initiator concentrations was determined. The material was tested at BHCTs of 100°F and 115°F with 1.9, 2.1, and 2.3 parts initiator or "kicker"/ 300 parts slurry and it was observed that a 10% change in initiator concentration has an effect of less than an hour on the thickening time. Fig. 6a and Fig. 6b show the consistometer readings and the results are listed in Table 3.

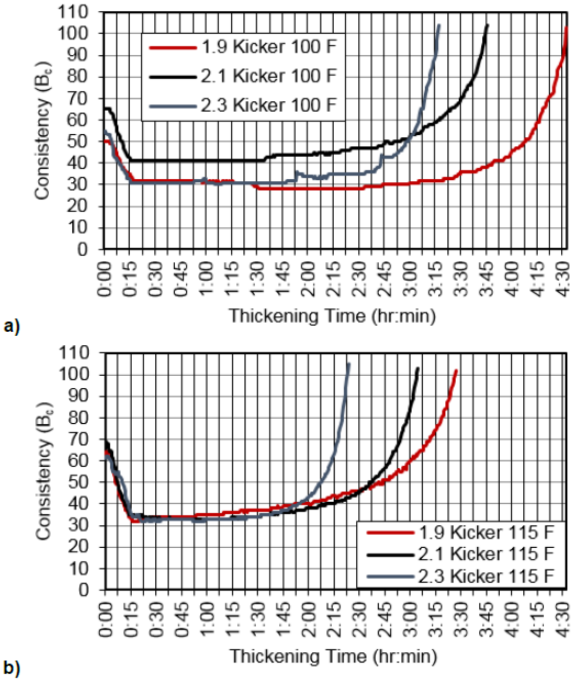

Fig. 6—Thickening times for various concentrations of initiator at 100°F a) and 115°F b).

Table 3—Effect of Initiator Concentration at different BHCT.

Initiator (parts/ 300 parts slurry)	Thickening time at 100°F (hr:min)	Thickening time at 115°F (hr:min)
1.9	4:32	3:26
2.1	3:44	3:03
2.3	3:16	2:23

Setting time is defined as the time to achieve gelation and peak temperature or peak exotherm, whence the material rapidly changes from liquid to solid state. The setting time of the material correlates to the thickening time and is longer than the latter. The PRSC system hardens by a free radical polymerization reaction and the setting time can be determined by plotting the temperature of the material. As the polymerization reaction approaches conclusion, there is a rapid rise in temperature. This temperature rise speeds up monomer consumption and leads to a rapid development of strength, defined as auto-acceleration [17, 18]. Fig. 7 shows a plot of the temperature of the "initiated" slurry in a 90°F environment. The peak exotherm corresponds with the development of strength.

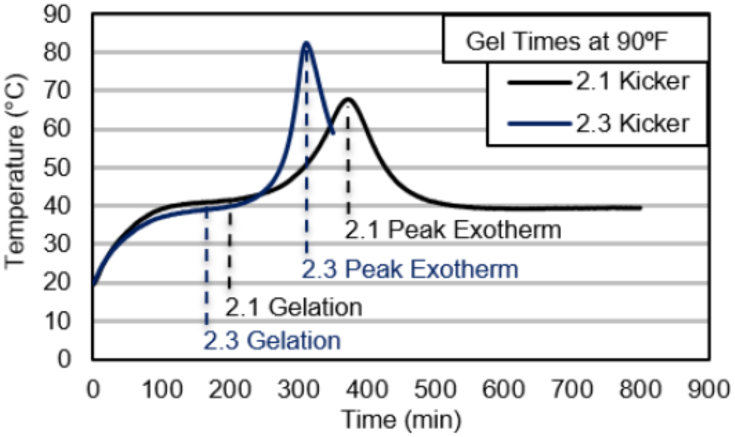

Fig 7—Peak exotherms following gelation.

Strength development is directly proportional to monomer consumption, which in turn is inversely proportional to the residual enthalpy of the reaction [19]. Thus, a differential scanning calorimeter can be used to correlate residual enthalpy to strength development at given bottom hole condition[20] We assert that this method will yield a reliable estimation of strength development as a function of time. The relationship amongst the change in viscosity, gelation, and strength development warrants further study to establish simple testing protocols appropriate for this material.

2.4. Yard Trial

A full-scale yard test was performed on November 20th, 2014 in the Bakersfield yard to simulate a field deployment of the synthetic cement. Fig 8a. shows the offload of twenty barrels of the synthetic cement (Part A) into a Cement Batch Mixer Float (CBF) and circulated and agitated in Fig 8b. prior to the addition of 9.6 gallons of PRSC activator (Part B), a concentration of 2.1 parts of B per 300 parts of A for reference with the laboratory testing. Circulation and agitation with the batch mixer paddles was run for 7 minutes before shutting down to simulate a job failure and test for any strong gelation or thixotropic properties. After 5 minutes of shutdown the centrifugal pumps and paddles were restarted. No issues were observed with gelation and the fluid began mixing as planned. After 5 more minutes of mixing (10 minutes of total mixing PRSC A + B) a sample was taken from the batch mixer sample port and walked over to the cement laboratory for thickening time testing. Samples taken throughout the yard trial were consistent with each other in terms of thickening time.

The equipment was able to be washed up in a quick and efficient manner using the general best practices of the field for washing a cement batch mixer. The use of recirculation, agitation from the CBF paddles and the hose provided on the CBF was sufficient to provide the mechanical energy to clean the batch mixer of any synthetic cement residue. The pump and batch mixer have been sent on several jobs since the yard test and no issues have surfaced.

In conclusion, laboratory testing and the yard trial performed in Bakersfield, California pave the way for future implementation of the synthetic cement system in a well trial. Operationally, the system was able to be executed in a safe, effective manner using equipment available worldwide. The batch mixer was proven to be able to appropriately mix the Part B activator in a reasonable amount of time for operations.

3. CONCLUSION

PRSC mechanical properties hold promise as a solution to several zonal isolation challenges, especially in wells with dynamic thermal and mechanical loads. The flexibility of the material (low modulus and high strain-to-failure), combined with its high strength makes it an attractive alternative to traditional Portland cement in wells that involve dynamic loads and earth movement. The chemical inertness of the material, especially to CO_2, acids, minerals, oils, and alkalis is an attractive attribute that will impart long-term durability. The rheological properties are suitable for large-scale deployment using conventional cementing equipment readily available in oilfields. Also, the set on demand properties with a right angle set and rapid development of strength are of importance when “waiting-oncement” incurs substantial costs, such as in offshore wells. Future applications for the polymer slurry include well remediation and lost circulation prevention.

Work is in progress to more thoroughly characterize the rheological properties of the slurry. Standard oilfield viscometers are designed for near-Newtonian fluids and thus overestimate both the shear stresses as well as the power law exponent for this material. Creep and fatigue behavior of the material, also under evaluation at the time of this publication, will help determine longevity.

Finally, a set of well trials will help better understand practical issues with regards to large-scale deployment.

Fig 8—a) Emptying a tote of PRSC-100 synthetic cement into the CBF and b) high mixing energy in the CBF.

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References:

1. Guillot, D., Nelson, E.: "Well Cementing," Second Edition, Schlumberger, 2006
2. Newman, K., Wojtanowicx, A. and Gahan, B.: "Improving Gas Well Cement Jobs with Cement Pulsation," GasTIPS (Fall 2001) 7, No.3, 29-33
3. Montgomery, C.: "Implications of Cementing for Well Production and Performance," Well Cementing, Second Edition, 2006, Schlumberger, 13-22
4. Jordan, M.E.: "Cement Bond Log: Determining Waiting on Cement Time," SPE 60th annual technical conference, Las Vegas, NV Sept. 22-25, 1985, SPE 14200
5. Shanbhag, R.: "Compositions and Processes for Downhole Cementing Operations," US Patent# 8387695
6. Thiercelin, M.: "Mechanical Properties of Well Cements," Well Cementing, Second Edition, 2006, Schlumberger, 269-288
7. Narayan Swamy, R.: "Dynamic Poisson's Ratio of Portland Cement Paste, Mortar and Concrete," Cement and Concrete Research, 1971, Vol. 1, 559-583
8. Timoshenko, S.P., Goodier, J.N.: "Theory of Elasticity," Third Edition, McGraw Hill, 1970
9. Hosford, W.F.: "Mechanical Behavior of Materials," Cambridge University Press, 2005
10. Suresh, S.: "Fatigue of Materials," Cambridge University Press, 1998
11. Thiercelin, M.J., Dargaud, B., Baret, J.F., Rodriguez, W.J.: "Cement Design Based on Cement Mechanical Response," SPE Annual Technical Conference, San Antonio, TX 5-8 Oct. 1997, SPE 38598
12. API RP 10B-2, Recommended Practice for Testing Well Cements, First Edition, American Petroleum Institute, 2005
13. Herschel, W.H., Bulkley, R.: "Konsistenzmessungen von gummi-benzollosubgen," KolloidZ – 39, 1926, 291-303
14. Guillot, D.: "Rheology and Flow of Well Cement Slurries," Well Cementing, Second Edition, Schlumberger, 2006, 93-142
15. Meeten, G.H., Pafitis, D.: "Granular Fluids Rheometry," Proceedings of Materials Research Society Symposium 114, 1998, 65-74
16. Van Kleef, R.P.A.R., van Villet, J.P.M.: "Improving the Reliability of Cement-Setting-Time Tests by Taking Into Account the Influence of Shear," SPE Drilling and Completion, March 1993, 51-56
17. Tromsdorff, E., Kohle, H., Lagally, P.: "On the Polymerization of Methyl Methacrylate," Makromol. Chem. 1, 169-198, 1948
18. North, A.M.: "The Kinetics of Free Radical Polymerization," Pergamon Press, New York, 1966

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19. Gowariker, V.R., Viswanathan, N.V., Sreedhar, J.: Polymer Science, Halsted Press (John Wiley & Sons), New York, 1986
20. Kessler, M.R., White, S.R.: "Cure Kinetics of the Ring-Opening Metathesis Polymerization of Dicyclopentadiene," Journal of Polymer Science, A: Polymer Chemistry, 2002, 40 2373-2383