Addition of Polyurethane to Portland Cement

A.E. Martinelli*, D.M.A. Melo, F.M. Lima, U.T. Bezerra, E.P. Marinho, D.M. Henrique
Programa de Doutorado em Ciência e Engenharia de Materiais - PDCEM
Universidade Federal do Rio Grande do Norte, Natal, RN, Brazil.
(* corresponding author, aemart@uol.com.br)

Keywords: Portland, polyurethane, well cement.

Abstract

Portland cement is by far the most important binding material used in both civil construction and oil well cementing. However, especially in the latter application, its brittle nature impairs its ability to withstand dimensional changes due to thermal gradients (RT to approximately 200ºC), typical of heavy-oil recovery operations. This often results in extensive cracking of the cement sheath and debonding of the cement-casing interface, which leads to loss of zonal isolation, gas migration and production of water and oil through the well annular. Portland-Polyurethane composites have been formulated and tested in an attempt to improve the deformation ability of the cement during thermal cycles without affecting the pumping behavior or high-temperature resistance of the material. Preliminary results confirmed that the addition of small contents of polyurethane considerably improved the plasticity of the cement in approximately 50% as well as decreased porosity and permeability. No significant changes were observed in the rheological behavior of the composite slurries with respect to plain Portland cement.

1 Introduction

Few cement materials have been as widely used in oil wells as the Portland cement. Its properties allow the formulation of cement slurries capable of withstanding wide ranges of pressures and temperatures commonly encountered during secondary recovery of heavy oils [1]. Nevertheless, defects can be formed in the cement sheath both upon primary cementing and during the production period of the well. In both cases, remedial operations are necessary to slow down crack propagation and prevent structural failure of the sheath. In particular, oil recovery by steam injection involves temperatures as high as 200ºC and pressures between 10 and 65 Kgf/cm², causing brittle fracture of the cement sheath due to thermo-mechanical mismatches between Portland and casing steel [2]. Although Portland cements depict considerable compressive strengths, they are not resistant to high tensile loads [3]. Therefore, new developments to Portland-based slurry formulations may necessarily include additives to improve the deformation ability of the cement so that its mechanical properties allow the cement sheath to withstand thermal cycling and steam injection. Appropriate materials should depict higher tensile strengths and plasticity along with lower stiffness compared to plain Portland (Fig. 1) and yet retain thermal stability to temperatures as high as 250°C. Polyurethanes are polymers resistant to temperatures as high as 300°C. They are obtained by the polycondensation of polyol and polyisocyanides and are potential candidates to be added to Portland slurries in an attempt to improve the required properties both for primary and remedial cementing [4].

The performance of a cement slurry basically depends on the properties of the cement powder, especially particle size distribution, chemical and phase composition, in addition to other meaningful aspects such as water-to-cement ratio, nature and contents of additives, and energy and order of mixture [5]. In this scenario, the present study focused on determining the rheological and mechanical behavior of composite cements using experimental techniques and procedures recommended by the American Petroleum Institute in order to establish the potentiality of adding polyurethane to Portland-based slurries.

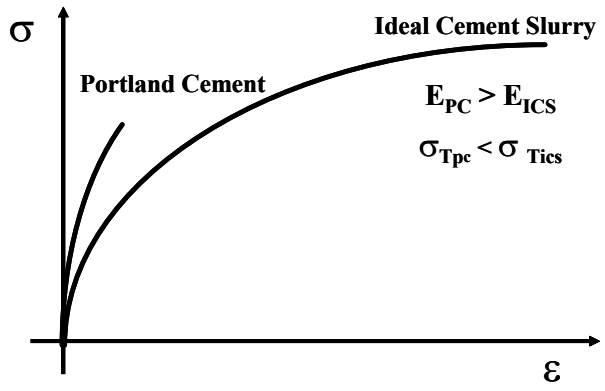


Figure 1: Schematically tensile strength vs. strain curve depicting aimed behavior for a oil-well cementing material as compared to that of Portland.

2 Experimental Procedure

2.1 Materials

Composite slurries were prepared from mixtures of Portland cement and polyurethane. Two types of polyurethane, referred to as A100 and W2366, were tested in the preparation of aqueous solutions, which were further added to the cement slurry. The chemical composition and physical properties of the polyurethanes and cement batch used herein are summarized in Table 1.

Table 1: Selected properties and composition of base materials.

Special Portland Cement	Oxide (wt%)		
	SiO_2		20.53
	Al_2O_3		4.09
	Fe_2O_3		3.22
	CaO		61.13
	SO_3		2.83
	MgO		3.37
	Na_2O		0.09
	K_2O		0.93
	Free Lime		1.32
	Loss on ignition		1.61
	Fineness (Blaine) (cm^2/g)		2762.15
Polyurethane Aqueous Solution		**A100**	**W236**
	Total fraction of solids (%wt)	35.0	40.0
	Particle Load	Anionic	Anionic
	Particle Size	Colloidal	Colloidal
	pH at 25ºC	7.0 – 9.0	7.0 – 9.0
	Density (g/L)	1.1	1.1
	Tg (ºC)	77	-27

2.2 Preparation and characterization of slurries

Two series of mixtures – referred to as A (Portland + PU A100) and B (Portland + PUW236) in addition to a plain Portland reference composition, R, were prepared according to API specification 10B [7]. The composition of each slurry is listed in Table 2.

Table 2: Composition of test slurries.

Slurry tag	Mass of Cement (g)	Mass of water (g)	Contents of Polyurethane (wt.%)
R	792.0	349.0	–
A	786.0	342.4	1.0
B	786.0	342.4	1.0

In the preparation of the cement slurries, polyurethane aqueous solutions were added to the cement mixing water. The resulting slurry was mixed at 4000 rpm for 15 s and 12000 rpm for 35 s using a Chandler model 30-60 mixer. Full homogenization was achieved by stirring the slurry for 20 min in a Chandler 1200 atmospheric consistometer. Rheological parameters were obtained using a rotating coaxial cylinder viscometer Chandler model 3500.

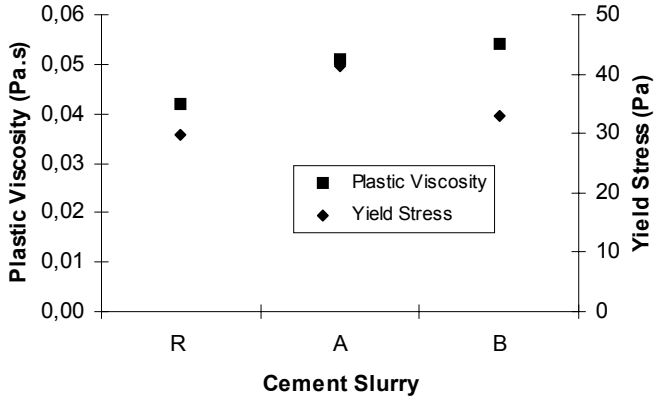
Samples from each composition were cast into 50 x 50 x 50 mm moulds for strength tests. The moulds were immersed in water for curing during 8, 24, 48 and 168h at 38ºC. Compressive strength tests were carried out using a Shimadzu Test Machine AG-I. The loading rate was set to 71.9 KN/min [7]. Strength values reported herein correspond to the average of three specimens. Cylindrical samples (50 mm in diameter and 100 mm in height) were also cast for diametral tensile strength tests. The samples were cured for 7 days and tested at a compressive loading rate of 0.025 KN/min using the same equipment described above [7]. Microhardness tests were also carried out using a Shimadzu system.

The permeability of the composite cements to N_2 at 100 psi was estimated by curing cylindrical samples (38 mm in diameter and 78 mm in height) for 7 days. A Ultraperm 2000 permeabilimeter was used to that end. Finally, microstructural evaluation of hardened slurries was also carried out by observing thin sections of cured slurries under an optical transmitted light microscope.

3 Results and Discussion

3.1 Rheological Behavior

The addition of polyurethane increased both the plastic viscosity and yield stress of the composite slurry with respect to the standard Portland composition (Fig. 2a). The polymer remained in the aqueous fraction of the mixture, which was not consumed in the hydration reactions of the Portland cement. As it can be seen from Fig. 2b, the changes in the rheological behavior corresponding to the addition of polyurethane did not cause any significant departure from reference levels recommended by API standards for well cementing, i.e., maximum plastic viscosity of 0.055 Pa.s and yield stress between 14.4 and 33.5 Pa. Minor deviations from these ranges are not deleterious to cement performance and, if necessary, can be further adjusted by small additions of dispersants.



(a) (b)

Figure 2: Rheological Properties of Portland and composite slurries.

3.2 Mechanical Properties of Cement Slurries

Although the addition of polyurethane slightly decreased the compressive strength of Portland cement, improved tensile strength and reduced stiffness could be observed (Figure 3). This results in an increase in the plastic behavior of the cement and improved toughness.

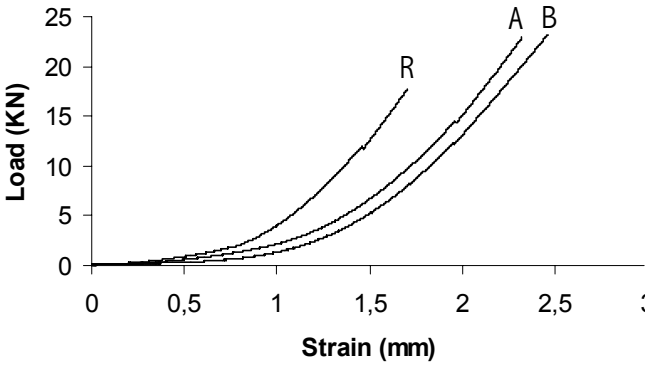


Figure 3: Compressive strength (left) and tensile load vs. strain (right) for Portland and composite hardened slurries.

As materials become less brittle by means, for example, of the addition of plastic reinforcements in composites, their hardness tends to decrease. In order to verify this aspect, microhardness tests were carried out. As it can be seen from Figure 4, addition of polyurethane to Portland significantly reduced the microhardness of hardened slurries by up to 34.5% for composition A and 35.7% for composition B with respect to plain Portland. This implies the action of polyurethane is not restricted to the aqueous component of the system, but it interacts with the microstructure of the cement increasing its plasticity and toughness and reducing stiffness and microhardness [8].

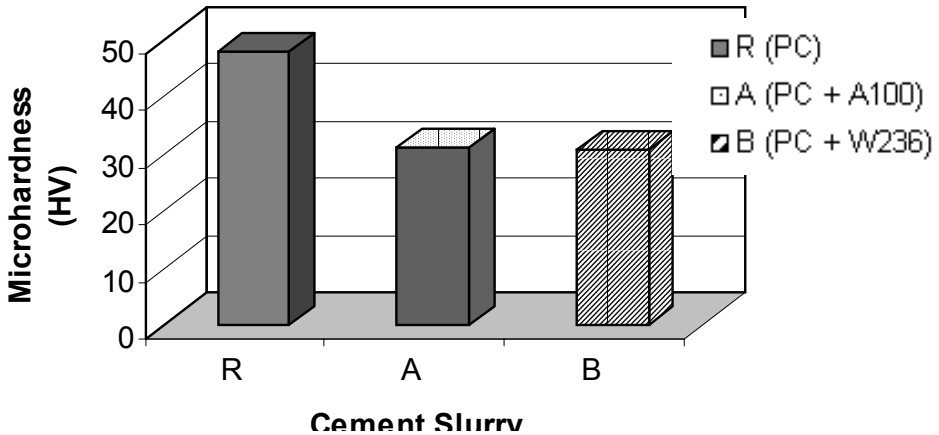
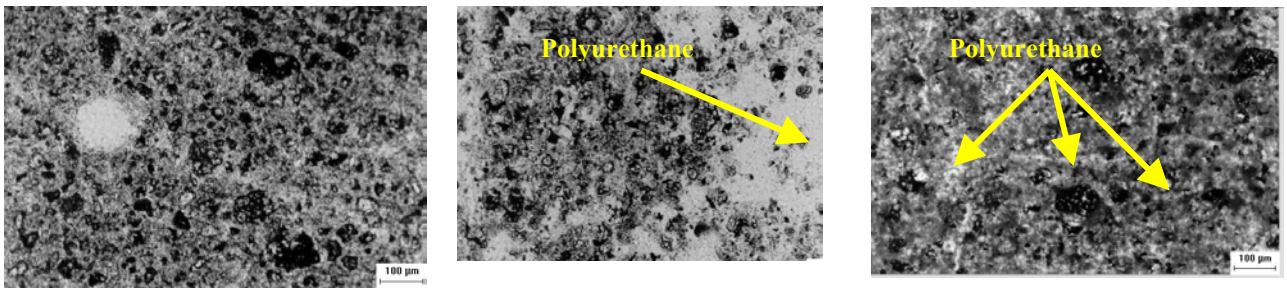


Figure 4: Microhardness of Cement Slurries.

3.3 Microstructure and permeability.

The microstructure of plain Portland and composite samples are shown in Figure 5. The reference sample depicted significant porosity homogeneously distributed over the entire visible area. Addition of A100 polyurethane resulted in a denser but inhomogeneous microstructure (Figure 5b) characterized by unreinforced areas. On the other hand, composites with W236 polyurethane were characterized by reduced porosity and homogeneous distribution of the reinforcement.



(a) (b) (c)

Figure 5: Optical images of samples (a) R, (b) A (PC + A100) and (c) B (PC + W236).

Denser cement microstructures imply reduced permeability to fluid and gases. The presence of polyurethane particles in the capillaries of the Portland hydrated structure allowed permeability values below 2 mD for composite samples, as shown in Figure 6. This feature is particularly important to isolate gas zones, which are especially encountered in Northeastern Brazil. Gas migration though the annulus of the well is a deleterious effect both from an economical standpoint as it reduces controlled production and from safety reasons.

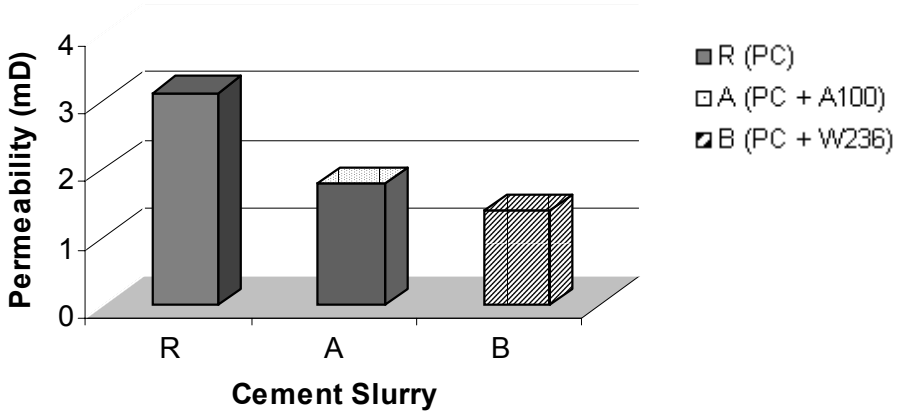


Figure 6: Permeability values of plain Portland and composite samples.

4 Conclusions

The present study was carried out to assess the effects of adding polyurethane to Portland cement aiming at improved mechanical properties and adequate rheological behavior. Addition of small contents of polyurethane improved the tensile strength and reduced the stiffness of the material. Polyurethane deposits in the porosity characteristic of Portland hardened samples creating a denser microstructure of reduced permeability. Although changes in the rheological behavior and compressive strength were noticed, they do not affect either the performance or the pumping characteristic of the cement. Composite slurries consisting of Portland and polyurethane are potential candidates to be fully tested to be used in oil well cementing.

Acknowledgments

The authors acknowledge the financial support granted by the National Research Council of Brazil, CNPq, and Crompton Ltd. for supplying the polyurethane used in this work.

References

[1] Toutanji, H.A., Bayasi Z., Effect of curing procedures on properties of silica fume concrete, Cem. Concr. Res. 29 (1999) 497– 501.

[2] Salem, T.H.M. Electrical conductivity and rheological properties of ordinary Portland cement–silica fume and calcium hydroxide–silica fume pastes. Cement and Concrete Research 32 (2002) 1473–1481.

[3] TAYLOR, H.F.W. Cement Chemistry, 1992.

[4] Wen T.C., Wang, Y.J., Cheng, T.T., Yang, C.H. The effect of DMPA units on ionic conductivity of PEG–DMPA–IPDI waterborne polyurethane as single-ion electrolytes. Polymer 40 (1999) 3979–3988.

[5] Heikal, M., Aiad, I., Helmy, I.M. Portland cement clinker, granulated slag and by-pass cement dust composites. Cement and Concrete Research 32 (2002) 1805–1812.

[6] Targan, S., Olgun, A., Erdogan, Y., Sevinc, V. Effects of supplementary cementing materials on the properties of cement and concrete. Cement and Concrete Research 32 (2002) 1551–1558.

[7] Specification for cements and Materials for Well Cementing, API specification 10A, twenty-second edition, January 1, 1995.