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PNNL-32903

Self-Healing Polymer-Modified Cements for Ambient-Temperature Applications

May 2022

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

We present two novel polymer-modified cement formulations which can self-heal cement microfractures at ambient temperature. The polymers used are either commercially available boric acid gel (BAG) or a synthesized polymer MBA-BDA.

Summary

This report summarizes the progress of developing polymer-modified cement formulations. The polymers used are either commercially available or synthesized in house. Results show two formulations (commercial boric acid gel BAG and as-synthesized polymer MBA-BDA), both with potential to bring about room-temperature self-healing to conventional cement.

Acknowledgments

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1.0 Project Approach, Results, and Accomplishments

The structure of BAG is shown in ***Figure 1*** (0.1-0.4 mm particle size). Two batches of cement samples with and without 1.5wt % BAG polymer were prepared, and the initial compressive strength was tested which is denoted as C_{s0}. After the initial compressive strength test, the sample was aged at room temperature for at least one week under 100% humidity and then measured again, the strength is denoted as C_{s1}. C_{s0}/C_{s1} is the recovered ratio of compressive strength. The results show that 1.5 wt% BAG in cement can recover the cement strength by 82.5% and control sample only recovers by 7.2% (**Table 1**).

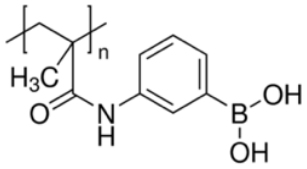

Figure 1 *structure of boric acid gel (BAG)*

The rheology test of the cement slurry with 1.5 wt% BAG shows lower plastic viscosity (better workability) than conventional cement in the first two hours of hydration and similar plastic viscosity to conventional cement then after (see **Figure 2**).

Table 1 *Recovery test of compressive strength*

Samples	C_{s0} *(psi)*	C_{s1} *(psi)*	C_{s0} $/C_{s1}$
Control	3109	225	7.2%
Control+1.5wt%BAG	5405	4458	**82.5%**

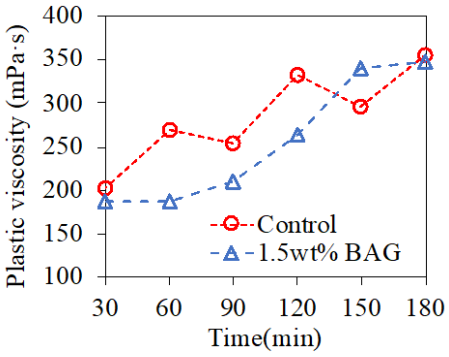

Figure 2 *Plastic viscosity of cement W and W/O 1.5 wt% BAG*

The structure of the MBA-BDA copolymer is shown in **Figure 3**. The MBA-BDA copolymer was synthesized at 35°C for 24 hours in the presence of MeOH/H_2O. Then acetone was added to precipitate the copolymer product. After waiting overnight and MBA-BDA polymer can be achieved in the precipitated phase. The solvent was removed, and the MBA-BDA polymer was rinsed 5 times with acetone followed by vacuum drying at 50°C for 48 hours. The final product is a glassy polymer and can be made into powders easily with pestle and mortar.

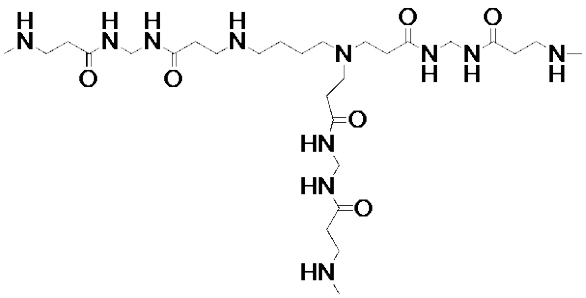

Figure 3 *structure of N, N-methylene-bis-acrylamide (MBA) and 1,4-butanediamine (BDA) copolymer*

Figure 4 (a) to (d) shows the self-healing processes of MBA-BDA polymer at room temperature. The polymer plate was made with MBA-BDA powders and heated to 100 °C and then pressed to a round plate. At room temperature, the broken polymer plate can heal itself multiple times. A cement sample containing 10 wt% MBA-BDA seems to self-heal after 24 hours when it is cracked in two pieces (**Figure 4**(e)).

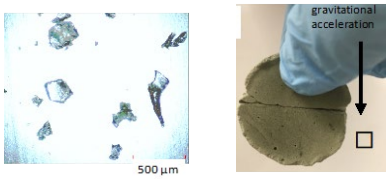

Figure 4 *(left)crushed MBA-BDA glassy polymer under the microscope; (right) 10wt% MBA-BDA cement after healing. T=room temperature*

2.0 Conclusions

This work reports on two promising polymers for the formulation of self-healing polymer-modified cement at ambient temperature. The first polymer, BAG, can recover the cement compressive strength by more than 80% after the first damaging event and it will be subjected to additional damage/healing cycles. Its slurry viscosity is lower than or equal the control sample in the first three hours of hydration, which suggests good workability. The second polymer, MBA-BDA, also shows potential as an additive to bring about self-healing capability to cement (Figure 4(e)) though quantitative mechanical tests are required.

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