METHOD TO STUDY THE CURE KINETICS OF POLY(URETHANE) AS HEALING AGENT FOR SELF-HEALING CONCRETE

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ABSTRACT

Poly(urethanes) (PU) can be used as healing agent to heal cracks in self-healing concrete. Studying the reaction kinetics is however difficult as the PU needs environmental moisture to cure. On the other hand the moisture in the concrete could play a role in the reactions. To monitor the reactions a technique where environmental moisture can reach the sample in a comparable way as in cracks is needed. The crack width usually is in the order of 50-500 µm. For this purpose dynamic mechanical analysis (DMA) with parallel plate geometry was proven to be suited. The PU starts as a viscous mixture but gradually becomes stiffer which is measured via the increase in storage modulus. Differences in reaction kinetics between different types of monomers can be observed in this way. The same methodology will be used to study the effect of the cement matrix on the cure behavior of the PU.

1. INTRODUCTION

Concrete is widely used as construction material due to its high strength, durability, availability and versatility. These properties added to the low production cost and recyclability makes concrete the most commonly used building material in the world. However, concrete is a brittle material and susceptible to many sources of damage, caused by freeze/thaw cycles, drying shrinkage, corrosion, external loading (dynamic or static loading), chemical attacks and other environmental conditions. Cracks, one of various types of damage, not only shorten the service life of concrete structures, but also endanger the structural safety [1], leading to large costs of maintenance and repair. The utilization of self-healing technologies could enhance the service life of concrete structures and reduce the demand for crack maintenance and repair.

Autonomous healing of cracks in concrete by encapsulating healing agents into the matrix improves the healing efficiency of concrete. Upon crack appearance, the capsules break and release their content. In some cases healing agents harden in contact with air or environmental moisture, healing the crack. An example involves filling ceramic or glass tubes with poly(urethane) (PU) [2]. PU has the advantage of having a low viscosity, good matrix bonding, a limited reaction time and low cost in comparison with other systems, such as epoxy or cyanoacrylate [3,4]. An additional advantage for using PU comes from the catalytic effect of the cement matrix on the cure behavior of the PU.
In this work, the study of the cure reaction of PU in controlled conditions of environmental moisture and in a comparable way as in cracks was carried out by means of the use of DMA. The effect of the cement matrix on the PU curing was also studied.

2. MATERIALS AND METHODS

A prepolymer of PU kindly supplied by Recticel was used in this study as healing agent. This prepolymer starts foaming and expanding in moist surroundings. A hardened ordinary Portland cement (OPC) paste was used as cementitious matrix. To study the effect of the matrix on the cure kinetics of the PU, different amounts of OPC powder were added to the PU. This mimics the effect of the crack walls, containing some water or hydroxyl groups, on the cure behavior of the PU. The mixtures were vigorously stirred until homogeneous dispersion, to obtain several samples with different weight ratios. Samples with ten OPC:PU ratios were prepared, as shown in table 1.

<table>
<thead>
<tr>
<th>OPC (g)</th>
<th>PU (g)</th>
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<td>0</td>
<td>100</td>
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<tr>
<td>50</td>
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DMA was carried out with a Perkin-Elmer DMA7 in parallel plates mode to obtain the storage modulus ($E'$) and loss factor (tan δ). Scans were performed at room temperature (25°C±1°C) and at a frequency of 1 Hz for 30 hours. 25 µL of each mixture was placed between the DMA plates, using a piece of open cell foam as spacer to maintain a constant distance between the plates during the experiment. A static force of 200 mN and a dynamic force of 150 mN were used during the measurement to maintain a plate distance of approximately 350 µm. Environmental moisture was controlled by a hand-made reservoir containing a saturated salt solution.

3. RESULTS

Environmental moisture may penetrate into the matrix along the cracks and react with the prepolymer of PU. These conditions were simulated by DMA. Thus, the PU starts as a viscous mixture but gradually becomes stiffer which is measured via the increase in storage modulus. Meanwhile, the loss factor undergoes some changes. The most significant phenomenon is when the gel point is reached and tan δ goes through a maximum. Figure 1 shows the evolution of the storage modulus and the loss factor during a measurement for the sample with 125:50 OPC:PU ratio. An
increase in the storage modulus signal is observed during the scan with a noticeable change in the slope around 750 min. A more evident change is observed in the loss factor signal, in which a maximum is clearly distinguished at 750 min. It should be pointed out that the pure prepolymer (without OPC) did not show any of those changes during the measurement, even in longer experiments of 40 hours, meaning that the presence of OPC increases the reaction rate. Figure 1 also shows the lack of variation in probe position remaining almost constant throughout the experiment at a value close to 350 μm.

![Figure 1: Evolution of probe position, loss factor and storage modulus of 125:50 OPC:PU ratio sample at room temperature.](image1)

The addition of higher amounts of cement to PU led to an increase in cure kinetics, turning into a reduced gelation time. Figure 2 shows the variation of the maximum peak of the loss factor signal as a function of the OPC content. The exponential decay curve generated by the addition of OPC is very clear.

![Figure 2: Maximum peak of the loss factor signal versus OPC:PU ratio.](image2)

According to the results it appears that the presence of humidity or hydroxyl groups in the cement are the responsible for acceleration of PU cure kinetics. However, the use of other techniques should help to clarify this statement.
4. CONCLUSIONS

The development of a new procedure to measure the cure kinetics of a PU was achieved in this study. Variations in storage modulus as well as in loss factor were recorded by means of DMA. Experimental results showed that an increase in the amount of cementitious material added to PU increased the reaction rate, decreasing the gelation time.

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REFERENCES