ON THE HEALING MECHANISM OF SOL-GEL DERIVED HYBRID MATERIALS CONTAINING DYNAMIC DI-SULFIDE BONDS

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ABSTRACT

Sol-gel technology is increasingly being used in coatings for corrosion protection and adhesion improvement. So far, the self-healing concept in sol-gel coatings has only been approached from extrinsic healing perspective (i.e. use of nano and micro carriers of corrosion inhibitors) [1]. Despite the benefits of this approach, the damaged area remains open to ambient environment. The implementation of intrinsic healing approaches in sol-gel coatings can thus very well complement current extrinsic ones in order to offer more extended corrosion protection.

In the present work the intrinsic healing sol-gel hybrid systems containing dynamic di-sulfide bonds were developed. The ability of developed systems to restore their cohesion at three different temperatures was evaluated, revealing 70°C as the optimum healing temperature. In order to get a better understanding of the healing mechanisms, dynamic mechanical thermal analysis (DMTA) was complemented by in-situ raman spectroscopy to follow the evolution of the di-sulfide bonds during the healing cycles. Mechanical properties and content of the broken dynamic bonds were found to be the key parameters in the healing performance of the developed systems. Faster healing kinetics at 70°C disclosed the dominating role of the breaking/re-joining of the dynamic di-sulfide bonds in the healing mechanism.

1. INTRODUCTION

Considering the advantageous features of sol-gel chemistry such [2] and the ability of dynamic di-sulfide bonds to be triggered by various stimuli [3], in this work we aim at incorporating dynamic di-sulfide bonds into a cross-linked epoxy matrix through sol-gel chemistry. Upon thermal stimulation, the developed hybrid system is capable of restoring its integrity at moderate temperatures and pressures. The effect of healing temperature on the healing kinetics is presented. Additionally, the healing mechanism is studied using DMTA tests complemented by Raman spectroscopy coupled to a hot-stage.

2. MATERIALS

Hybrid systems were prepared by addition of un-hydrolyzed alkoxy-silanes to the epoxy resin with alkoxy-silane:epoxy resin weight ratio of 1:1. Bis[3-(triethoxysilyl)propyl]tetrasulfide (BS) and (3-Aminopropyl)trimethoxysilane (APS)

were mixed in BS:APS molar ratio of 3:1 and added to the Epikote[TM] 828 based epoxy resin. The mixture was stirred for 3 h at ambient temperature. Ancamine[®]2500 was added as cross-linker with Ancamine:epoxy resin weight ratio of 0.58:1 and the prepared mixture was speed mixed at 2500 rpm for 5 minutes. Pentaerythritol tetrakis(3-mercaptopropionate) (denoted as tetra-thiol) was added in tetra-thiol:epoxy resin weight ratio of 0.56:1 and mixed again for 40 seconds under the same conditions. The resulting mixture was casted using a 600 μm calibrated standard aluminum single blade on Teflon plates and cured for 2 h at 70°C.

3. METHODS

To investigate the cohesive healing, rectangular films of 20 × 10 mm^2 were cut in two pieces. The cut pieces were put 500 μm apart from each other between two glass plates. The ability of the samples to recover their cohesion under constant pressure of 0.03 MPa was investigated at three different temperatures of 50, 70 and 90°C. The cohesion restoration of the samples was monitored using a Leica DMLM microscope in transmission mode. Assuring a uniform thickness of the samples, the changes in gap area as a function of time (A_t) normalized by initial gap area (A_0) was used for calculation of cohesive healing efficiency of the samples.

To study the healing mechanism of the prepared samples, the changes in the storage (E') and loss modulus (E'') as a function of temperature were monitored using a Perkin Elmer Pyris Diamond DMTA analyzer in the range of 20 to 110°C. Samples were tested in a tensile fixture at frequency of 1 Hz, tension amplitude of 10 μm and at a constant rate of heating of 2°C/min.

Moreover, Raman spectroscopy was performed using a U1000 – High resolution double spectrometer from HORIBA Jobin Yvon, with a 632 nm laser at eight different temperatures in the interval of 20 to 90°C with step of 10°C (T_1 = 20°C, ΔT = 10°C, T_8 = 90°C). The temperature of the samples was controlled using a Linkam Scientific Instruments THMS600 hot-stage coupled to the Raman set-up.

4. RESULTS

To study the cohesive healing kinetics, temperature triggered healing of the prepared hybrid systems was performed at three different temperatures i.e. 50, 70 and 90°C. The calculated cohesive healing efficiencies of the samples are plotted as a function of healing time in figure 1. It can be seen that by increasing the healing temperature from 50°C to 70°C, samples were able to restore their cohesion at significantly higher rates. After 10 minutes of exposure to 50°C, the cohesive healing efficiency of the sample was slightly over 70% while heating the same sample for 10 minutes at 70°C led to full cohesion recovery. A further increase in healing temperature to 90°C not only did not accelerate the healing process, but also a slight decrease in healing kinetics was observed.
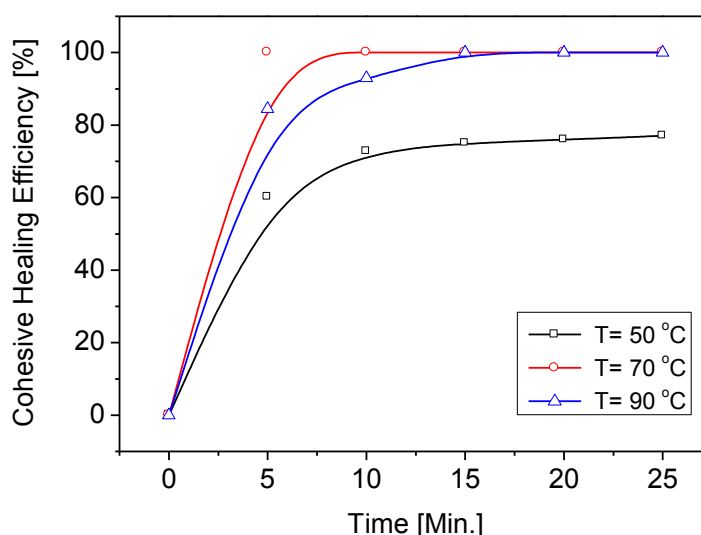
Figure 1: Cohesive healing efficiency versus healing time at three different temperatures.

To further investigate the observed trend, the changes in the storage (E') and loss modulus (E'') of the prepared samples as a function of temperature was measured using DMTA. E' and E'' values at 50, 70 and 90°C were plotted together with cohesive healing efficiency at 10 minutes in figure 2. Figure 2 shows that increasing the temperature from 50 to 70°C lowered the mechanical properties of the hybrid film represented by E'. Furthermore, E'' which is a measure of the viscous phase of the hybrid film showed a decrease by increasing the temperature from 50 to 70°C. Therefore, the faster healing kinetics at 70°C can be attributed to the synergic effect of the reduced mechanical properties and increased chain mobility at 70°C compared to 50°C. A further increase in the temperature to 90°C resulted in higher chain mobility shown by lower E''. However, the mechanical properties represented by E' remained constant. Although higher chain mobility at 90°C should have increased healing rate compared to 70°C, healing kinetics slightly slowed down. To investigate the obtained results, Raman spectroscopy coupled to a hot-stage was employed to follow the changes in the hybrid film in atomic scale. The content of dynamic di-sulfide bonds at different temperatures (which are believed to be responsible for temperature triggered healing) was quantified using peak area criteria (A_{S-S}(T) / $A_{internal\ standard}$(T)) and plotted in figure 2. The obtained results revealed that the content of di-sulfide bonds at 70°C was at minimum level i.e., a higher proportion of the dynamic bonds were broken at this temperature. The decrease in the content of the dynamic bonds at 70°C compared to 50°C is in line with the faster healing kinetics at 70°C. Additionally, the sight decrease in healing kinetics at 90°C compared to 70°C can be attributed to the lower mobility of the system induced by re-joining of the dynamic di-sulfide bonds at this temperature.
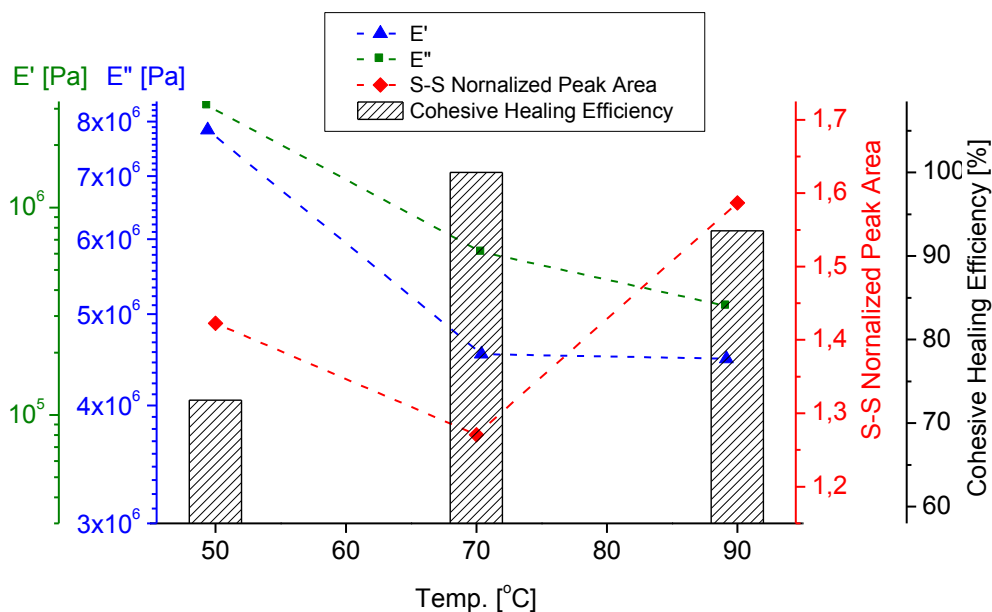
Figure 2. Variations in E' (■), E'' (▲), S-S normalized peak area (♦) and cohesive healing efficiency at t = 10 minutes, versus temperature

5. CONCLUSIONS

Sol-gel based temperature triggered intrinsic healing hybrid systems were developed. Evaluation of the cohesive healing capabilities of the prepared system at three different temperatures revealed 70°C as the optimum healing temperature. Hot-stage Raman spectroscopy together with DMTA results revealed the dominating role of breaking/re-joining of the dynamic di-sulfide bonds in the healing performance of the prepared systems compared to pure viscoelastic behavior.

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