SYNTHESIS AND CHARACTERISATION OF NOVEL CATALYSTS FOR USE AS SELF-HEALING AGENTS IN EPOXY RESINS

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ABSTRACT

Self-healing polymers typically feature monomer and catalyst either dispersed within a host matrix, or encapsulated within hollow vessels. Unprotected highly active catalysts, sensitive to air and moisture, can readily react with amine cross-linking agents during the cure of reactive prepolymers e.g. epoxy resins. Therefore, catalysts stable to the polymer environment in which they are intended to be used must be developed, in order to remove the requirement for in-situ catalyst encapsulation.
Silver olefin complexes have been shown to be particularly efficient initiators for the curing of epoxy resins. The coordination polymer $\{[Ag(1,7\text{-octadiene})_{1.5}]SbF_6\}_n$, which shall henceforth be referred to as AgOctadiene, is investigated herein for its potential application in self-healing epoxy-based polymers.
Differential scanning calorimetry (DSC) was used to investigate the cure onset temperature of various polymer precursor resins. Tapered double cantilever beam (TDCB) mechanical test specimens were used to investigate thermal activation of the catalyst in the solid state and subsequent healing, results of these tests are presented.

1. INTRODUCTION

Silver olefin complexes have been shown to be particularly efficient initiators for the curing of epoxy resins [1]. AgOctadiene (Figure 1) is investigated for its potential application in self-healing polymer materials. Scope for tuning the behaviour of such coordination polymers through alteration of the ligand is also discussed. 1,7-octadiene was selected as the primary ligand for this study, due to the lability of the Ag-olefin bond and the relative ease of synthesising the quantity required for mechanical testing.
The 'unprotected' silver salt, silver hexafluoroantimonate ($AgSbF_6$), is used as a control initiator.

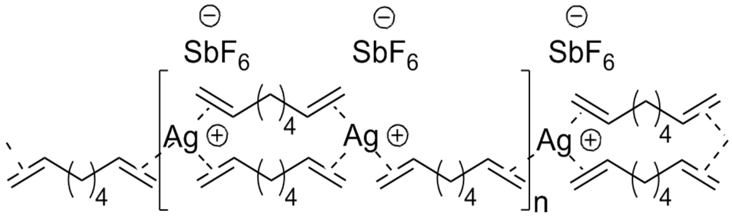

Figure 1: AgOctadiene catalyst.

2. MATERIALS AND METHODS

2.1 Synthesis of {Ag(1,7-octadiene)$_{1.5}$]SbF$_6$}$_n$.

To a solution of $AgSbF_6$ (2 g, 5.83 mmol) in Toluene (15 ml), was added 1,7-Octadiene (2 ml, 1.5 g, 13.5 mmol) dropwise in a nitrogen atmosphere. Solution was stirred at room temperature overnight, yielding an off-white precipitate. Product was isolated by filtration and washed with toluene and pentane prior to drying in vacuo. Product was stored in air in an opaque vial. Elemental analysis: calculated (%): C, 28.32; H, 4.16. Found: C, 27.12; H, 3.93. H^1 NMR (300 MHz, Acetone-d6): δ 1.36-1.47 (m, 4H), 2.04-2.11 (m, 5H), 2.99 (d, 1H), 4.94-5.05 (m, 4H), 5.82-5.96 (m, 2H). C^{13} NMR (75 MHz, Acetone-d6): δ 29.04 septet), 205.4 (s). FTIR (nujol) (cm^{-1}) 3630, 3547, 2928, 2859, 1593, 1459, 1378, 1037, 964, 728, 663.

2.2 Fracture Testing.

Initial and healed strengths were determined using tapered double cantilever beam (TDCB) test specimens, as developed by Beres *et al*. [2]. This geometry encourages continuous fracture toughness values along the central trench section in order to control crack propagation through the catalyst impregnated epoxy. This also allows for use of small amounts of catalyst. A 30 mm, grooved central section, with a 2 mm diameter crack stopper was used in this study. This arrangement leads to termination of the crack so that healing can occur prior to further testing. The geometry of the TDCB specimens is provided in Figure 2.

Testing was conducted on an Instron 3343 test machine equipped with a 1 kN calibrated load cell at a loading rate of 0.3 mm displacement per minute. Benchmark data for the average failure load of a pure EPON 828 / diethylenetriamine (DETA) test specimen were obtained from previous work by Coope *et al.* [3]. Fracture tests were performed on five specimens and average failure load and displacement values of 68.3 N and 0.58 mm respectively were obtained.

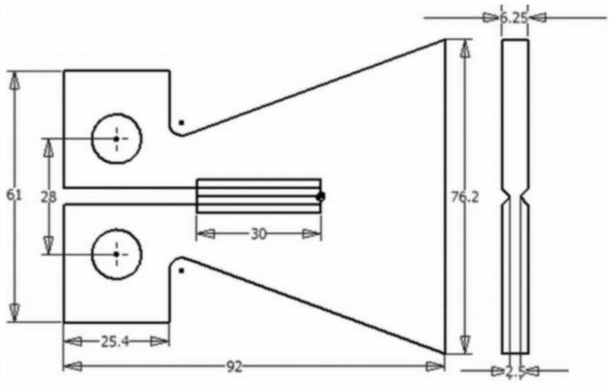

Figure 2: TDCB geometry

3. RESULTS AND DISCUSSION

3.1 Resin Screening.

The effect of dissolved $AgSbF_6$ upon the cure behaviour of various epoxy resins was investigated using DSC in order to determine which resin would be most appropriate for further analysis.
N,N,N,N-tetraglycidyl-4,4-diaminodiphenyl-methane (TGMDA), triglycidyl-*p*-aminophenol (TGPAP), Poly[(phenyl glycidyl ether)-co-formaldehyde] (DEN 431), and the oligomeric diglycidyl ether bisphenol A (DGEBA) (EPON 828) were investigated. DSC analysis showed a single strong exotherm peak due to the presence of $AgSbF_6$ in EPON 828, and the solution displayed no evidence of unwanted reactivity. EPON 828 was, therefore, selected as the primary resin for use in this study.
Synthesis of $\{[Ag(1,7\text{-Octadiene})_{1.5}]SbF_6\}_n$ proceeded as in Barriau *et al*. [1]. The olefin ligands effectively act as protecting groups for the silver ion, supressing its reactivity. The onset of thermal curing of AgOctadiene impregnated EPON 828 was determined by DSC to be 96°C. $AgSbF_6$ initiated curing proceeded at 65°C.

3.2 Healing.

All specimens contained 2.5 pph catalyst dispersed in EPON 828 / DETA (12 pph). Solutions were warmed to 35°C to aid solvation of the catalyst. Catalyst impregnated trenches were cured for 48 hours before being cast into TDCB test specimens. A 2 mm diameter crack stopper was drilled into the end of the trench to discourage complete failure of the specimen. Crack propagation along the trench is encouraged by inserting a sharp notch into the end of the trench. Control specimens containing $AgSbF_6$ (2.5 pph) were also tested. By comparison of the $AgSbF_6$ and AgOctadiene results it was possible to investigate the extent to which the presence of the olefin ligands supressed unwanted reactivity. Monomer delivery occurred by both the use of microencapsulated DGEBA and manual delivery of the resin to the fracture surface. Following monomer delivery, samples were heated for 48 hours to encourage healing. Specimens were then tested again to determine healing efficiency. Results at various temperatures are summarised in Table 1.

Table 1: Summary of healing efficiencies to date

	Healing Efficiency (%)								
Catalyst:	AgOctadiene						$AgSbF_6$		
Monomer Delivery:	Microcapsules			Manual Delivery			Manual Delivery		
Healing Temperature:	45°C	60°C	70°C	45°C	60°C	70°C	45°C	60°C	70°C
Specimen 1	-	54.6	73.5	0	12.7	64	0	-	189
Specimen 2	-	85.3	77.2	0	0	38.6	0	-	144
Specimen 3	-	-	99.1	0	0	94.4	0	-	137
Specimen 4	-	-	53.1	-	0	46.9	-	-	-
Mean	0	70	76	0	12.7	61	0	0	157

Table 1 indicates that the TDCB specimens, catalyst loading, and resin delivery method can result in excellent healing. Inconsistency in results is attributed to variability in the dispersion and particle size of the catalyst as well as the delivery of the monomer. Healing values for control specimens are high because the addition of $AgSbF_6$ appears to significantly reduce the failure loads of pristine samples. This is thought to be due to the highly reactive nature of the unprotected catalyst, which undergoes competing reactions with the amine cross-linking agent, thereby reducing the strength of the resulting thermoset polymer. Also, DSC determined that the onset of thermal curing of EPON 828 due to the presence of $AgSbF_6$ occurs at 65°C, compared to 96°C for AgOctadiene. A higher healing efficiency is expected from the $AgSbF_6$ specimens.

4. CONCLUSION

It has been demonstrated through observation, DSC and TDCB mechanical testing, that $\{[Ag(1,7\text{-Octadiene})_{1.5}]SbF_6\}_n$ is capable of curing epoxy resins both in solution testing and during solid-state mechanical tests.

Thermal activation of both $AgSbF_6$ and AgOctadiene and subsequent self-healing of catalyst impregnated specimens heated to 70°C for 48 hours has been confirmed through TDCB tests. $AgSbF_6$ specimens achieved, on average, a 157% recovery in failure load. AgOctadiene specimens on average recovered 68.5% of their failure loads.

The potential for tuning the activation temperature of coordination polymer-based catalysts through alteration of both the ligand and metal will be investigated in future work.

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