Synthesis of epoxy resin with catechol performance enhancers

Casey Busch

Mentored by Dr. Daniel B. Knorr Jr. and Dr. Ngon Tran

Introduction

Structural adhesives are used in various military applications such as equipment repair and structural bonding. Most adhesive applications require a surface pre-treatment, which often involve silane coupling agents. These agents are susceptible to hydrolysis, are expensive, are time consuming to apply, and are short-lived. Therefore, the discovery of a versatile adhesive that does not require a surface treatment would be beneficial for military applications (Knorr et al., 2016). An additive was incorporated into an adhesive with the goal of improving adhesion performance and eliminating the need for a surface treatment by introducing catechol-containing molecules into the adhesive. Catechol was chosen because it has shown the ability to promote bonding between its hydroxyl groups and a variety of surfaces. This bond must be strong to produce a durable adhesive. The catechol-containing additives used were dopamine, tyramine, and 3, 4-dihydroxybenzaldehyde. Through nuclear magnetic resonance (NMR) analysis and lap shear strength tests, adhesive mixtures with each additive were examined to determine which produced the most successful adhesion without a pre-surface treatment.

Methods and Materials

Figure 1: Layup of aluminum coupon on Teflon™ sheet with shims and weight for balance. Coupon is on the left and shim is on the right.

Figure 2: The preparation and environmental conditioning of lap shear specimens. Individual coupons placed in a test tube for 2 weeks fully submerged in deionized water at 63 °C.

To synthesize the adhesive mixtures, the different catechol sources (0.28 wt%) were added to D230, a curing agent, in a round bottom flask, and heat was applied to obtain a homogeneous solution. After adding bisphenol A diglycidyl ether (DGEBA), a resin, the resulting adhesive was degassed for 10 min to remove bubbles. The reaction solution was heated at ~35 °C until the desired viscosity was obtained for lap shear assembly.

The single lap joints were prepared according to ASTM D1002. Coupons of 2024T3 aluminum were cleaned with acetone to remove greasy debris, polished with Scotch Brite™ to remove some of the oxide layer, and grit blasted to improve mechanical interlocking adhesive binding. The adhesive was poured on the coupons, and a combination of shims and weights were used to obtain the desired bondline thickness (Fig. 1). The samples were cured under nitrogen, at 100 °C, for 18 hours. After curing, a band saw was used to divide the coupons, and the rough edges were smoothed using a belt sander. The lap joints were either

Methods and Materials (cont.)

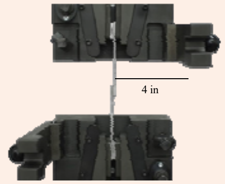


Figure 3: Lap shear measurements with Instron model 1125 testing machine.

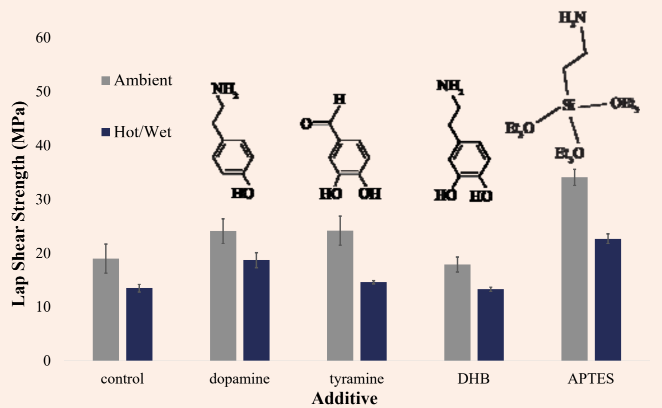
placed under vacuum prior to dry testing or completely immersed in a 63 °C deionized water bath for 2 weeks prior to hot/wet testing (Fig. 2).

An Instron model 1125 was used to measure load (N) as a function of distance pulled vertically (Fig. 3) for each lap joint. The lap shear data are important for evaluating the effects of the additive on the adhesive

Results

The average shear strengths of adhesive formulation containing dopamine, tyramine and 3,4-dihydroxybenzaldehyde (DHB) additives are shown in Figure 3. Only dopamine displayed adhesive improvement in both dry and hot/wet conditions. Specifically, dopamine enhanced adhesive shear strengths by 27% for dry conditions and by 39% for hot/wet conditions compared to the no additive control. Tyramine displayed adhesive improvement only under dry conditions compared to the no additive control, and this improvement was statistically similar to that of dopamine. Lap shear data of DHB demonstrated no improvement in both dry and hot/wet conditions compared to the no additive control. Based on a 2-sample *t*-test, there were no adverse effects on adhesive performance by any of the additives compared to the no additive control. The adhesive strengths of the best performer, dopamine, were 29% less under dry conditions and 36% less under hot/wet conditions compared to the APTES surface treatment standard.

Effects of Catechol Additives in Adhesive



Graph 1: Comparison of adhesive performance of formulations with additives to the formulations without additive (e.g. control) and the industrial surface standard (APTES). Included are standard deviation error bars from a sample size of 10 coupons per condition.

Results (cont.)

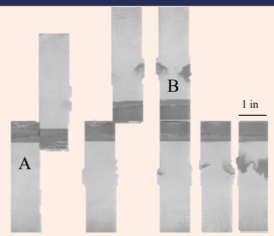


Figure 4: A sample that displays (A) cohesive failure and (B) adhesive failure.

Analysis on types of failures displayed mainly adhesive failure, a clean break between the aluminum surface and the adhesive, and cohesive failure through bonding, a shattered break across the adhesive (Figure 4). Results show 100% of the ambient data were adhesive failures while 63% of hot/wet conditions resulted in cohesive failure through bonding.

Conclusion

Overall, the lap shear experiments demonstrate that catechol-containing additives are a promising strategy for enhancing epoxy adhesive performance without a surface treatment. Shear strengths significantly improved under dry conditions and under hot/wet conditions for dopamine. Lap shear data of tyramine, which has one less hydroxyl group compared to dopamine, suggest that catechol is important for the observed adhesive performance of dopamine under hot/wet conditions. The lap shear data of DHB, which has a different functional group (i.e., aldehyde) compared to that of dopamine (i.e., amine), shows that the functional group of the catechol-containing molecule is also very important for adhesive performance. Analysis of failures on samples indicate that the additive does not significantly improve adhesion compared to the no additive control. While the lap shear data of catechol-containing additive at 0.28 wt% are not as great as that of the industry surface treatment standard (e.g. APTES), these studies suggest that further research (e.g. increased additive amounts) with catechol-containing additives may lead to higher adhesive performance without surface treatments.

References

Knorr, A. B., Tran, N. T., Gaskell, K. J., Orlicki, J. A., Woicik, J. C., Jaye, C., . . . Lenhart, J. L. (2016, April 7). *Synthesis and characterization of aminopropyltriethoxysilane-polydopamine coatings.* Retrieved March 1, 2017, from http://pubs.acs.org/doi/abs/10.1021%2Facs.langmuir.6b00531.

Subcommittee D14.80 (2010). *ASTM D1002-10, Standard test for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal),* ASTM International, West Conshohocken, PA. Retrieved April 24, 2017 from https://www.astm.org/Standards/D1002.htm.

Acknowledgments

I would like to thank Drs. Dan Knorr and Ngon Tran for supporting me with my senior capstone project. Special thanks to Dr. Ngon Tran for incorporating meaningful chemistry and learning experiences into a short time to provide me with the most beneficial experience. I also want to thank Mr. Davis for being a supportive, assisting advisor. Last, thanks go to the SMA staff for providing me with the best educational experience.