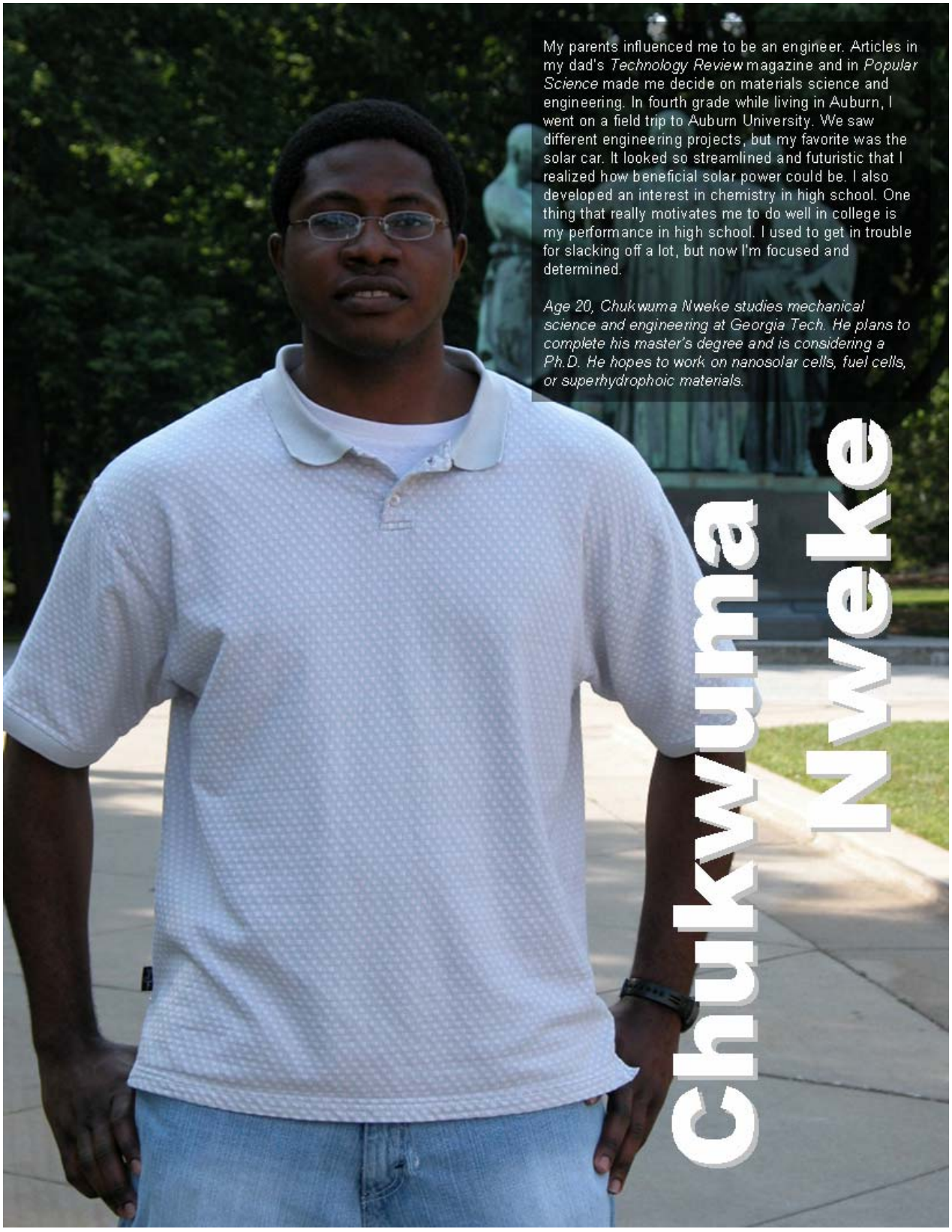

My parents influenced me to be an engineer. Articles in my dad's *Technology Review* magazine and in *Popular Science* made me decide on materials science and engineering. In fourth grade while living in Auburn, I went on a field trip to Auburn University. We saw different engineering projects, but my favorite was the solar car. It looked so streamlined and futuristic that I realized how beneficial solar power could be. I also developed an interest in chemistry in high school. One thing that really motivates me to do well in college is my performance in high school. I used to get in trouble for slacking off a lot, but now I'm focused and determined.

Age 20, Chukwuma Nweke studies mechanical science and engineering at Georgia Tech. He plans to complete his master's degree and is considering a Ph.D. He hopes to work on nanosolar cells, fuel cells, or superhydrophoic materials.

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Targeted Self-healing

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Abstract

The property of self-healing in materials is an important new area of research. Self-healing polymers, specifically, are set to be used in applications ranging from coatings to electronics. Generally, self-healing is a two-part system of catalyst and encapsulated healing agent. When a crack advances through the material, it inevitably passes through and ruptures microcapsules. The healing material spills out, eventually coming into contact with the catalyst. In the ensuing chemical reaction, the liquid healing material cures into a solid. There are many variations of this setup. Research is even being done to scale the microcapsules down to the nanoscale. The smaller capsules promote uniformity, and will allow for damage to be healed on the nanoscale. Another goal for self-healing is to target this functionality to chosen areas. Self-healing polymers are not desired everywhere throughout a material. Thus, tests are being conducted to target self-healing polymers specifically to areas of high strain where cracks are likely to form.

Introduction

The most common mechanism for self-healing in polymers consists of an epoxy matrix with embedded Grubbs' catalyst (bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride) and urea-formaldehyde shelled microcapsules filled with dicyclopentadiene (DCPD).[1] When a crack propagates through the epoxy matrix, DCPD reacts with the ruthenium-based Grubbs' catalyst in a ring-opening metathesis polymerization (ROMP) reaction.[1] The resulting product is a cross-linked polymer network. Another benefit of this system results directly from the microcapsules. The initial toughness of the epoxy matrix is higher than that of a pure epoxy sample due to microcapsule-induced toughening.[1] To scale these microcapsules down to the nanoscale, a slight alteration must be made to the process of microcapsule preparation. In regular microcapsule formation, the prepared chemical mixture is stirred.[2] Depending on the speed of the agitator, microcapsules can be made big or small relative to the microscale.[2] But in order to reduce capsule size to the nano level, a sonication process is used.[3] Current targeted self-healing tests involve experimenting with different patterns of catalyst and microcapsules on the surface of an epoxy substrate. Separate tests have been performed for targeted deposition of the catalyst and the microcapsules. Eventually, these features will be combined in single samples. The catalyst may be written in specific patterns with an underlying sheet of capsules, or the capsules written in an identical pattern. These deposition processes are both accomplished by robotic-controlled deposition.

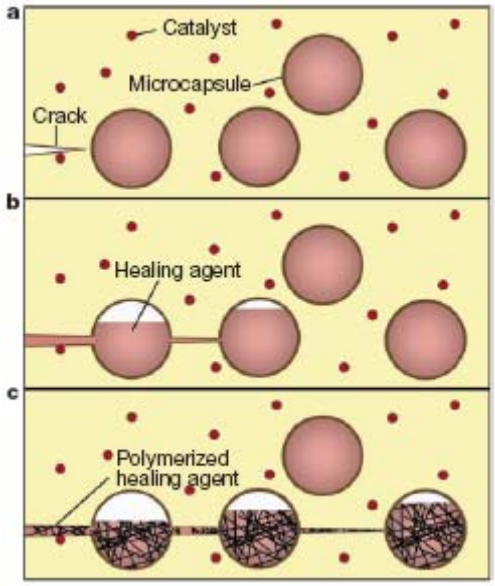
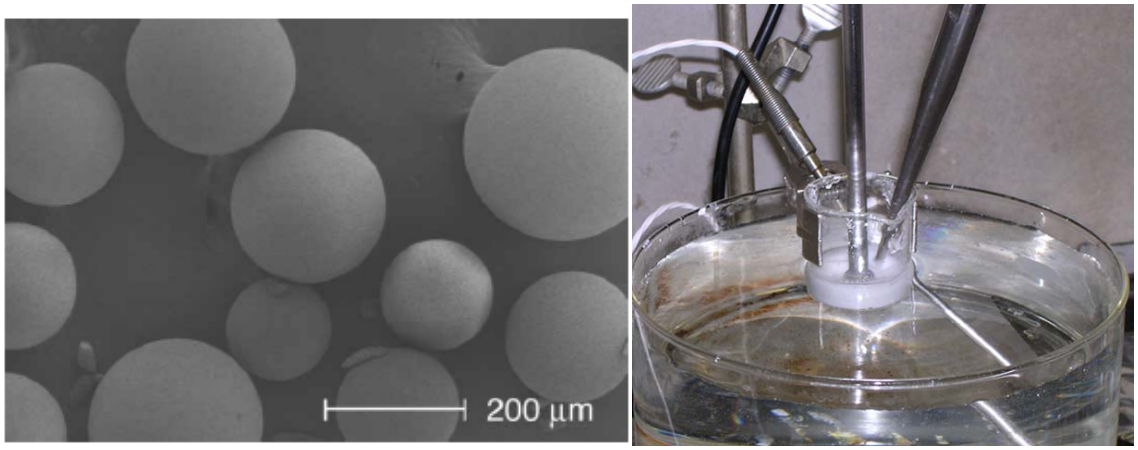


Figure 1: (a) Crack advances. (b) Healing agent spills into crack plane, contacting the catalyst. (c) The polymerization reaction seals the crack.[1]

Background

Preparation catalyst and healing material for use in samples is actually a dual encapsulation method. Rule *et al.* showed that Grubbs' catalyst can be minimized to a 5 weight percentage in a sample by protecting it in wax microspheres. The production of these microspheres involves mixing molten wax and Grubbs' catalyst in aqueous poly(ethylene-co-maleic anhydride) (EMA).[4] Microcapsules can be produced using *in situ* urea-formaldehyde (UF) microencapsulation as shown, for example, by Brown *et al*.[2] The first step for the microencapsulation is the addition of 50 ml of 2.5 weight percentage (EMA) to 200 ml of deionized water. It is then mixed in the range of 300-600 RPM. During mixing, 5.0g urea, 0.5g ammonium chloride (NH_4Cl), and 0.5g resorcinol are added to the solution. At this point, the pH of the mixture must be checked. Providing that the procedure has been followed properly, the pH will fall in the range of 2.6 to 2.8.[2] After adjusting the mixing speed to 300 rpm (if it is not already), sodium hydroxide (NaOH) and HCl are added sparingly until the pH is 3.5. Next, 60 ml of DCPD is added and emulsified. Ten minutes later, 12.667g of formaldehyde is added.[2] Finally, the mixture beaker is covered with foil and left to mix 4 hours at 55 °C.[2] Nanoencapsulation, which will soon be ready for use in targeted self-healing, follows a similar method. A three minute sonication process at 40 percent intensity is inserted before the final 4-hour reaction period to reduce capsule size while surfactant concentration is increased by a factor of two to control clustering .[3]



(a) (b)

Figure 2: (a) Urea-formaldehyde microcapsules containing DCPD [2]. (b) Sonication process of nanoencapsulation with sonication horn shown on the right.[3]

Approach

The direct-write method, also called robotic controlled deposition (RCD), was followed to deposit both the catalyst and the microcapsules. The different patterns were programmed into the RCD to complete this deposition process. Finished self-healing samples are put through a four-point bend test. Patterns were chosen in consideration to the likely direction of crack formation by the four-point bend test. Theoretically, samples with a configuration of a catalyst and/or microcapsules which intersect more cracks will have better healing efficiency.

Results and Discussion

Controlled deposition of both the catalyst and the microcapsules was proven to be possible. Microcapsules prepared at 1800 rpm were deposited as 3% and 10% of an epoxy mixture, respectively. Nozzle pressures were varied between 10 and 20 psi. The nozzle tip diameters used were 200 and 300 microns because these are the smallest sizes which do not result in clumping. To avoid spreading, the epoxy mixture was given 30-45 minutes to partially cure. The direct-write method allowed for the conservation of healing materials and the ability to localize healing properties to the necessary areas.

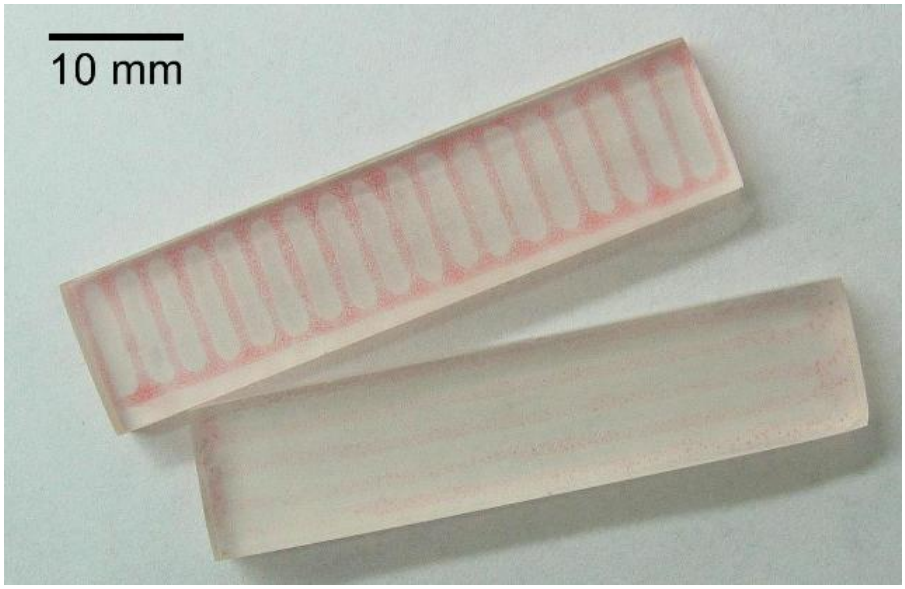


Figure 3: Finished targeted self-healing samples written with catalyst.

Conclusion

In closing, self-healing polymers have successfully been designed to restore a significant portion of the initial toughness upon the development of a crack. Localization of this novel property to specific regions of a material has been accomplished as well. However, challenges in sample characterization remain. More work will be done in the future to demonstrate the effect of targeted self-healing.

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