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Functionalizing the Surface of Polyethylene

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Background and Motivation

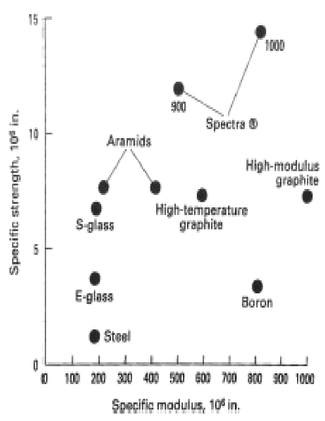
There is a demand in military, industry, and consumer markets for lighter, stronger, and less expensive materials. Ultra-high molecular weight polyethylene (UHMWPE) has a high strength to weight ratio, high impact resilience, and low mechanical wear. However, these materials are not able to create compatible composite structures as they suffer from poor adhesion and delamination due to poor wetting and bonding at the fiber-resin interface. The ability to functionalize these materials would allow for a significant increase in performance of the manufactured composite structures.

The purpose of this work is to chemically modify UHMWPE fibers and fabrics in order to prepare lightweight fibers that are ballistic, wear, and cut resistant. In order to achieve this, carbon-hydrogen (C-H) bond insertion chemistry is utilized, which allows for the polyethylene to be functionalized without compromising polymer integrity. The current method to add functional groups to polymeric fabrics involves methods that often destroy the material, leaving it unusable or incompatible for future use. The method used in this experiment has been proven to work with smaller molecules, such as cyclohexane. Our work will verify that cyclohexane does in fact undergo the carbene addition; we will expand on this proof of concept by using the carbene to functionalize plastic polyethylene discs. Therefore, the goal of this project is prove the concept and then use catalytic C-H insertion chemistry to create an entirely new mode of polymer surface treatment.

Attributes of UHMWPE:

- High modulus
- High yield strength
- High wear resistance
- Relatively low density (appx. 0.925 g/cm^3

Solution: use additive chemical catalysis to modify UHMWPE fiber surface



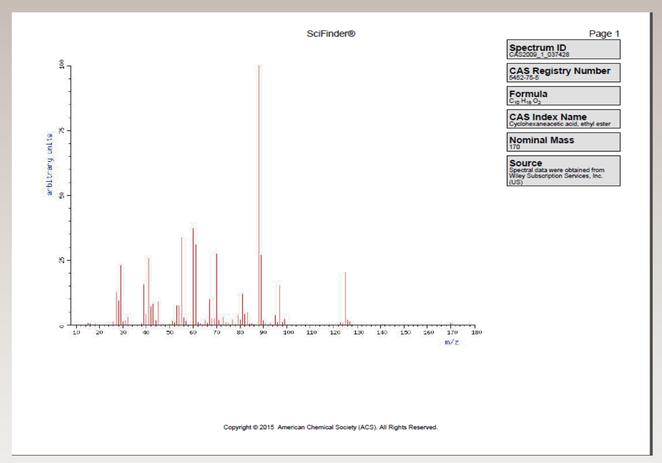
Comparison of typical composite fiber filler strengths

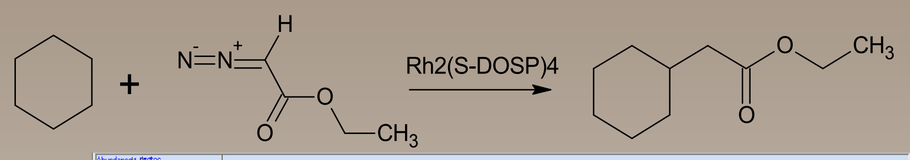
Results and Discussion

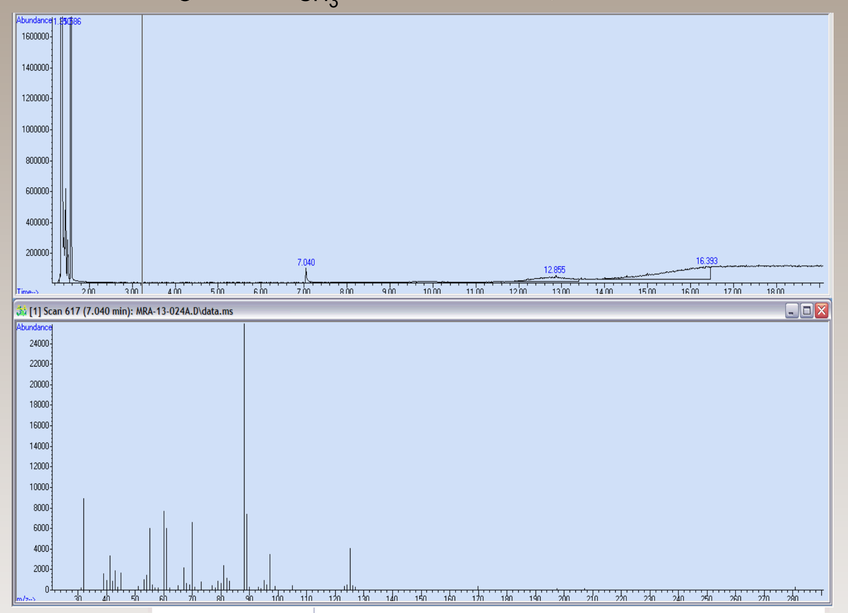
Proof of concept:

The GCMS data shows the product, ethyl 2-cyclohexylacetate, exiting the GC column at the 7 minute mark (a retention time of 7 minutes). The heating profile used was an injection temperature of 250 °C and a column ramping from a start point of 50 °C up to 200 °C .

- The ethyl 2-cyclohexylacetate mass spectrum (below) was obtained from Wiley Subscription Services experimental database (via SciFinder).





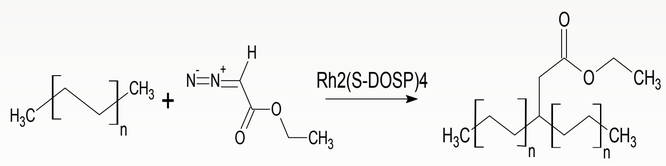


Reactions involving UHMWPE:

Control: carbon NMR of UHMWPE disc

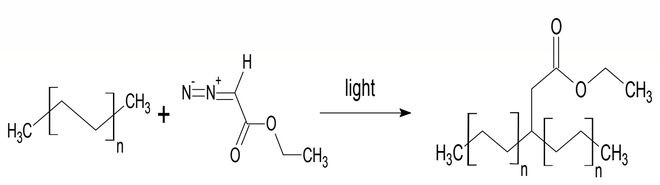
UHMWPE + Rhodium catalyst + ethyl 2-diazoacetate:

- Peak of interest: 172.6 (indicates the carbonyl group on the ethyl 2-diazoacetate)



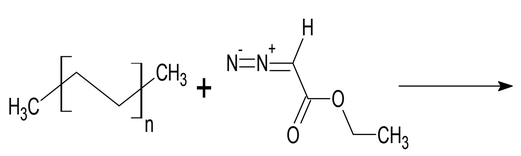
UHMWPE + light + ethyl 2-diazoacetate:

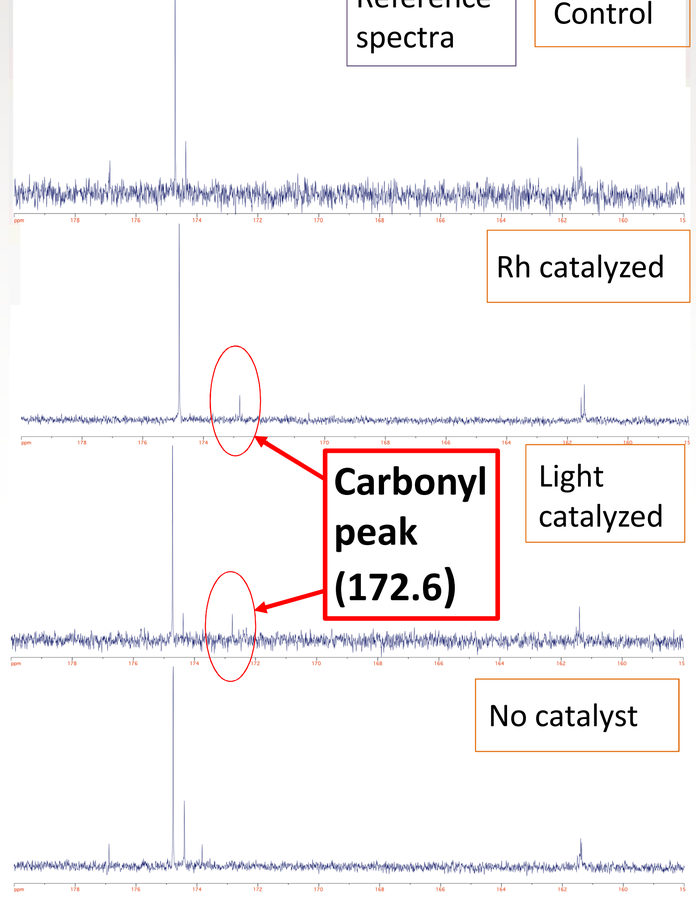
- Has peak at 172.6
- light as a catalyst instead of the Rhodium compound.



UHMWPE + ethyl 2-diazoacetate (no light):

- no reaction
  - No peak at 172.6





^{13}C labeled control reactions

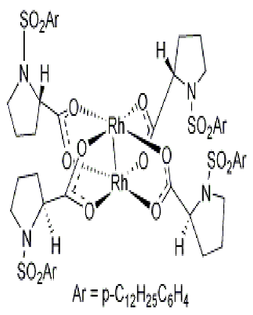
UHMWPE + Rhodium catalyst + ethyl 2-diazoacetate-1-^{13}C :

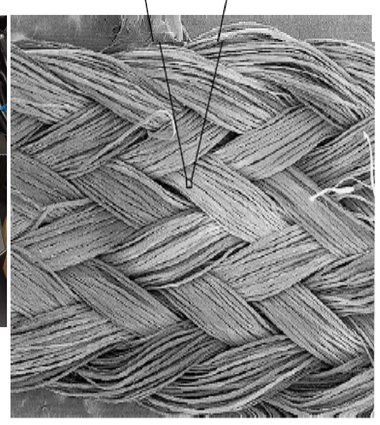
Results: There was a peak at 176.2 but it was the same size as the peak from a previous experiment which used non-^{13}C labeled ethyl 2-diazoacetate, Rhodium catalyst, and UHMWPE.

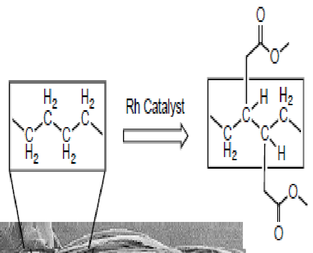
UHMWPE + light + ethyl 2-diazoacetate-1-^{13}C :

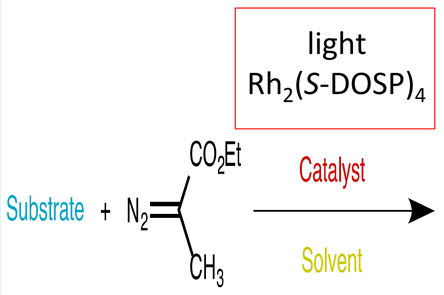
Results: There was a peak at 176.2 but it was the same size as the peak from a previous experiment which used non-^{13}C labeled ethyl 2-diazoacetate, light, and UHMWPE.

Materials and Methods









Summary & Future Directions

- There are conflicting results between those of the ^{13}C labeled control reactions and the promising results that were found with the non-^{13}C labeled reactions
- Further analysis and different characterization methods are necessary to verify if the diazo compound is in fact being added onto the plastic discs

What to do next:

- Analyze the plastic disc with the water droplet test
- Add the ethyl 2-diazoacetate-1-^{13}C to cyclohexane
- Take an NMR of the UHMWPE + ethyl 2-diazoacetate-1-^{13}C (no light)

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