Development and Fundamental Understanding of Polybenzoxazine Resins: A Class of Ring-Opening Phenolic Resins that Expand upon Polymerization

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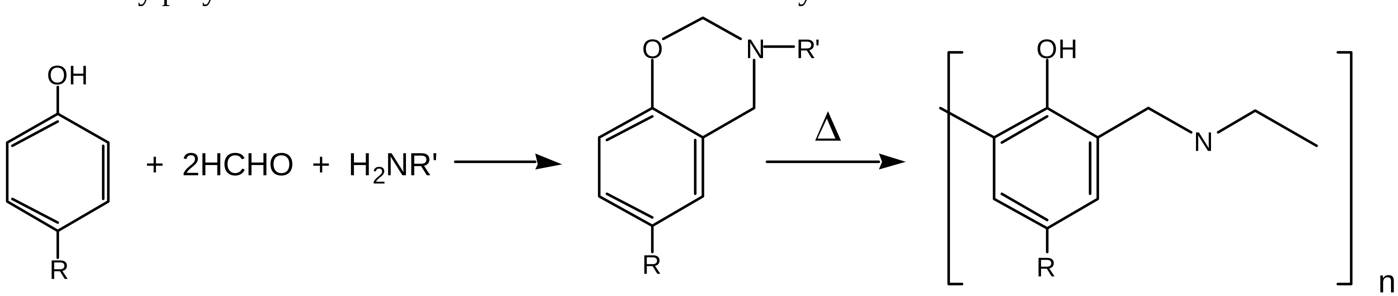
Research Objective: The objective of this project is to develop a new class of polymers that are an alternative to currently commercially available polymers for the aerospace industry. Three main objective of this projects include: development of high performance resins that are comparable or better in fire resistance with the currently available polymers, development of new polymers with improved processability over the currently available polymers through the alternative chemistry, and the understanding of fundamental molecular mechanism of thermal degradation that leads to flammability.

Approach: The key approach of this project is to adopt little known benzoxazine chemistry to develop polymers without resorting to commonly adopted methods of using additives, halogenation, and other approaches (1). The new polymers try to improve char forming characteristics by developing polymer main chains that are inherently suitable for char formation. The benzoxazine monomer is synthesized using three initial compounds of a phenolic derivative, formaldehyde and primary amine as follows. Once benzoxazine resin is synthesized, the resin can be either thermally polymerized with or without initiators and/or catalysts.



The basic chemical repeat unit contains a phenolic and tertially amine units both of which have been considered the chemical group for good anti-flammability characteristics. Benzoxazine resins offer several very unusual properties few polymers are known to exhibit. They include: expansion or near-zero shrinkage upon polymerization (2,3), very high char yield in spite of higher aliphatic content than traditional phenolic resins (4-7), much higher hydrophobicity than epoxies and phenolics in spite of high concentration of hydrophilic groups in the polymer chain structure (2,8), development of high mechanical and physical properties at low conversion, and extremely rich molecular design flexibility (1).

Accomplishment Description: We have successfully developed both ordinary and high performance benzoxazine resins. These laboratory scale materials were first scaled up to tens of pounds in our laboratory. Due to the publicity generated by the FAA conference, benzoxazine resins have received world-wide attention. This lead to a successful formation of Consortium towards Commercialization of Benzoxazine

Resins. In this consortium, the commercially attractive low cost, high performance benzoxazine resins have been studied along with the development of effective polymerization initiators/catalysts. The FAA funds are used to develop high performance polybenzoxazines as well as study fundamental decomposition mechanisms on the molecular level . We therefore achieved detailed molecular understanding of crosslinking mechanisms, the nature of secondary reactions, thermal and thermooxidative degradation mechanisms, understanding of the unified molecular concept of the unusual properties observed (13). Commercial sampling of benzoxazine resins have been initiated by two of our member companies.

Significance: The significance of the current project are three folds. The resins being developed offer high probability for high-volume commercialization as demonstrated already in our Benzoxazine Consortium where sampling-level commercialization has been achieved. Of thousands of new polymers reported through academic study, few reaches commercialization as commercially viable polymers must meet stringent requirement from technical and commercial points of view. Benzoxazine resins seem to have satisfied the severe test thus far. The second significance of the projects is that we have developed a huge class of polymers whose properties ranges from advanced epoxies and phenolic resins to bismaleimides to polyimides. Such wide properties have seldom been reported in any resin chemistry. This will offer rich design flexibility for various applications. Finally, the unusual properties observed in polybenzoxazines are the properties long sought by polymer chemists. However, an important point to note is that all these desirable properties comes without sacrifice of processability. In fact, the processability of benzoxazine resins are superior to the majority of thermosetting resins known today.

Expected Results: We expect benzoxazine resins will receive wide commercial acceptance from the electronic, composite, coating and other industries, many of which have strong implication to the development of aerospace industries. Improved reliability is often very difficult to evaluate as failure takes place slowly. Many of this type of failure is related to shrinking resins that generates residual stress which in time adversely affects adhesion of the resin to substrate. High water absorption will also reduce the performance of the resin as airplanes experience many humidity cycles. All the properties must be satisfied for materials to be used in the aerospace industry in addition to good anti-flammability characteristics. At the present time, no ideal materials exist. However, polybenzoxazine resin seem to have satisfied the highest number of those stringent requirements. We therefor expect that the project under FAA funding will lead to broad and fundamental changes in the materials that are used in airplanes. A few examples include: replacement of highly flammable epoxy and/or polyurethane adhesive for interior decorative by less flammable polybenzoxazine adhesive, insulation of electronic materials as polybenzoxazines have much higher insulating capabilities than epoxy or phenolic resins.

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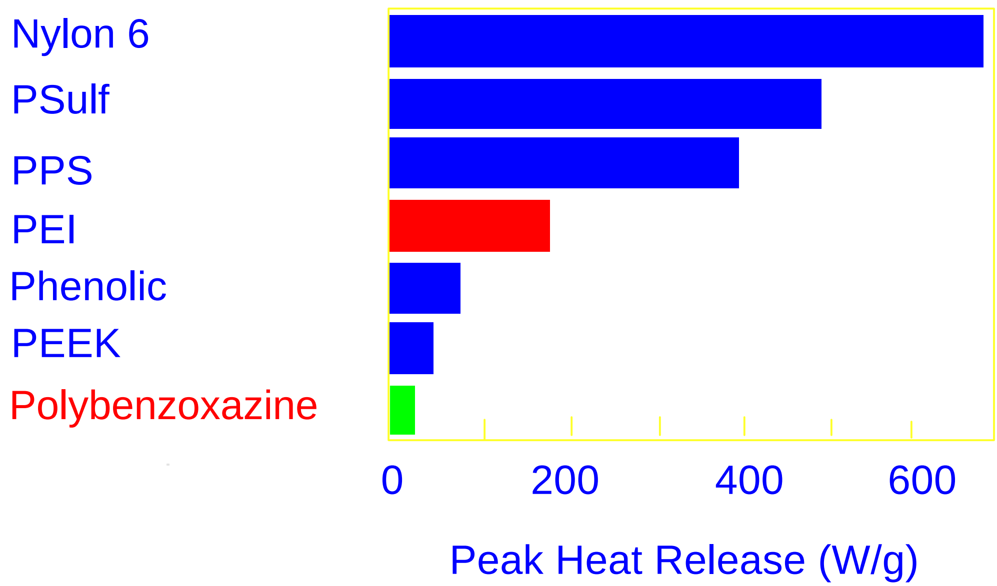
Flammability of High Performance Polymers



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