THRUST AREA: BIOBASED PRODUCTS

4.6 — Development of Biobased VOC-free Powder Coating Resin Systems

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In this work we propose to develop biobased powder coatings including epoxy, polyester-epoxy hybrid, and polyurethane powder coating resins using rosin and dipentene as feedstocks. We will collaborate with the Powder Coating Research Group, a member of CB², in this research exploration. In recent years, Zhang’s group has conducted a significant amount of fundamental investigation on use of rosin, dipentene, and other natural chemicals as building blocks in synthesis of epoxies and other thermosetting polymers. The work proposed here is within the continuum of research that is being pursued by the PIs, but it does not overlap with what have been accomplished. Instead, it will greatly benefit from what we have learned and make an extension to a specific application – powder coatings.

Project Objectives. The long-term goal of the proposed research is to develop a viable technology that replaces or partially replaces petroleum-based powder coating resins with biobased counterparts. Specifically, the overall objective of this application is to demonstrate that some natural cyclic compounds are feasible feedstocks in replacing petroleum-based aromatic compounds for synthesis of powder coating resins. This objective will be achieved by: (1) identifying the molecular structures of biobased powder coating resins, (2) investigating the curing behaviors, and (3) determining the primary coating properties of the biobased resin systems. The findings from this study will provide an important guideline in the next step of research that may eventually lead to the development of commercial biobased powder coatings, and set up a framework for developing other biobased polymers.

Industrial Relevance, Need, and Appropriateness for the Center. Since volatile organic compound (VOC) release from traditional coatings is subject to strict government regulations, powder and waterborne coatings have been developed as alternatives to eliminate or reduce VOCs. On the other hand, increasing public environmental concern and awareness of sustainable development has motivated researchers to pursue renewable feedstocks for polymer materials. Current epoxy resins are entirely based on petrochemicals, while polyurethanes based on soybean oil-derived polyols have only found a niche application for foams. Therefore, there is an urgent need for enabling technology to develop cost effective, high performance, biobased epoxy and polyurethane powder coatings. The proposed research is aligned with the interest of the Center for Bioplastics and Biocomposites that aims to bring sustainable solutions for polymer materials including coating resins in collaboration with industrial partners.

Experimental Plan. Besides resisting corrosion and weathering, superior abrasion, impact strength, and hardness are also required for protective coating. For most polymers, the high mechanical performance relies on the inclusion
of rigid molecular building blocks such as aromatic or cycloaliphatic moieties. Among various natural chemicals rosin and dipentene are two important ones with large productions and relatively low price and have found many industrial applications.

Rosin is a resinous exudate from pines, conifers, etc. Rosin acids, which consist of 90% of rosin, are a family of isomeric acids (abietic acid is the dominant component) with a rigid fused ring structure. Dipentene (limonene) is also a readily available cycloaliphatic chemical in a variety of softwood trees, plants, and fruits. Both rosin and dipentene can be conveniently converted to dicarboxylic acid and anhydride (Figure 1). Current polyesters used for polyester, polyester-epoxy hybrid, and polyurethane powder coatings are mainly based on the copolyesters of rigid terephthalic acid (TPA), isoterephthalic acid (iTPA), and trimellitic anhydride (TMA) with neopentyl glycol and trimethylol propane. Our approach is to replace TPA, iTPA and TMA with the biobased alternatives, the Diels-Alder adducts of rosin acid and dipentene with acrylic acid (acrylopimaric acid, or APA) and with maleic anhydride (MPA & DPMA) (Figure 1). Small amounts of the flexible adipic acid and sebacic acid will be added in the synthesis of copolyesters to regulate the balance of molecular rigidity/flexibility and physical properties. For polyester and polyester-epoxy hybrid powder coatings, carboxy-polyesters are needed, while for polyurethane powder coatings hydroxy-polyesters are required. Further, for the powder coating, the resins with high glass transition temperature (Tg > 50°C), low melting or softening point (80-110°C), and melt viscosity are preferred. These requirements demand a fine tune of the stoichiometry of the reactants.

Rosin can also be converted to epoxies which may either serve as base resins for powder coatings or as curing agents for carboxy-polyesters. For example, diglycidyl ether of APA and triglycidyl ether of MPA can be easily synthesized and used as potential curing agents. Further, by manipulating the stoichiometry of epichlorohydrin and APA and/or MPA, rosin-derived epoxies with desirable Tg and softening point for powder coating base resins are likely synthesized. In addition, curing agents can be selected from the commercial products, e.g., triglycidyl isocyanurate, for the curing of rosin-derived carboxy-polyesters. For curing of hydroxy-polyesters, biobased blocked isocyanates will be synthesized. In this effort, diptenene will be first converted to dicarboxylic acid and then to diisocynate. The resulting diisocynate will be blocked with ε-caprolactam.

Curing behavior of the biobased powder coating will be studied by DSC and chemorheology, and the mechanical, dynamic mechanical, and adhesion properties will be evaluated by following ASTM standards. Particularly, the

Figure 1. Rosin and dipentene-derived diacid and acid-anhydride versus their petroleum-based aromatic counterparts.
applications of developed powder coatings will be evaluated with metal cans filled with food simulants under sterilization conditions. The coatings will be tested for their corrosion resistance, adhesion to metal surface, physical deformation during fabrication of the container, thermal and chemical resistances. Transport of low molecular weight additives and unreacted monomers from coatings into food simulants will be tested under industrial food processing and storage conditions.

We do not anticipate any risks and hazards from the proposed research. The polymer synthesis, handling of coatings, sterilization experiments will be carried out in compliance with recommended safety precautions and requirements, as specified by university and regulatory agencies. The PIs have extensive experience with the polymer synthesis, use of food processing systems and analytical instrumentation, and their laboratories are well equipped for conducting this project. We anticipate that biobased coatings on metal cans will be able to sustain chemical environment of foods and high temperatures of sterilization process. If necessary we will chemically modify the coatings.

**Proposed Deliverables.**

- Identify the structures and synthesis methods of biobased resins for powder coatings
- Determine curing behavior of the biobased powder coatings
- Evaluate fundamental mechanical, physical, and adhesion properties of the biobased coatings
- Quantify the level of migrating substances from coatings under high temperature sterilization

**Research Facilities.** For this work a powder coating spray device will be purchased for coatings of metal cans. Otherwise, our labs at CMEC and BSE are well equipped for materials synthesis and characterizations.

**Timeline and Budget.** The fund requested include $35,744 for a PhD student, $13,850 for faculty time, $4,000 for materials and supply, $1,000 for travel, totaling $58,800 (including 10% overhead).

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