SYNTHESIS AND CHARACTERIZATION OF BIO-BASED EPOXY RESINS FOR COATING APPLICATIONS

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Thermoset resins are widely used as coatings to protect metal substrates from corrosion, as well as primers for precoated steel sheets used in a number of applications, ranging from automotive to household appliances to food packaging [1,2]. Thanks to their good mechanical strength, chemical resistance and excellent adhesion to several substrates, epoxy resins perfectly fit for coating applications, and about 60% of their overall production find application in this field [3]. For example, in food industry epoxy coatings are applied as tin can linings to avoid the direct contact and chemical reactions between food and metal surface. Epoxy resins are specially applied to food cans where chemical resistance is required, i.e. to internal surfaces of cans for aggressive products such as tuna fish, asparagus, spinach, sauerkraut, and tomato paste. Currently, almost the totality of can linings are constituted by diglycidyl ether of bisphenol A (DGEBA)-based resins that can release relevant amount of bisphenol A (BPA) during processing and shelf-life of the product, thereby causing possible migration of BPA into environment. Awareness of this phenomenon is leading global governments to introduce legislation banning the use of BPA-based materials especially in the food industry. Additionally, DGEBA precursors are almost completely derived from fossil sources [4]. Therefore, several research and development efforts are devoted to the replacement of DGEBA with more sustainable alternatives [5]. However, to achieve the required properties in terms of mechanical and chemical resistance, aromatic epoxy resins are needed. Therefore, the development of new platform chemicals from renewable resources for the synthesis of bio-based, low environmental impact epoxy resins for coatings applications is of key interest. So far, the scientific production dealing with bio-based epoxy coatings is still limited. Among the sugar-based derivatives, furanic compounds are particularly suited as epoxy precursors, since the presence of a heteroaromatic five member ring can provide the cured resin with chemical and mechanical resistance comparable to that of the high-performance commercial resins [6–8]. Recently, we have demonstrated that biobased epoxy resins based on 2,5-bis[(oxiran-2-ylmethoxy) methyl] furan (BOMF) cured with methyl nadic anhydride (MNA) possess outstanding thermal and mechanical properties that make them effective alternatives to traditional bisphenol A-based resins [9].

This system can represent a potential substitute of DGEBA-based protective coatings in metal cans. In particular, BOMF/MNA resin and its composites, obtained by the addition of titanium dioxide (TiO_2) nanoparticles, were prepared and tested as tinplate coatings. Incorporation of TiO_2 into epoxy matrix has the potential to improve thermal, rheological, and mechanical performance even at a very low nanofiller content [10–14]. Additionally, nanoparticles, such as TiO_2, can significantly improve anticorrosion performance and resistance against chemical degradation of epoxy coatings [15–19]. Tinplate substrates were coated with the BOMF/MNA based composites. The effect of TiO_2 nanoparticles on processing conditions and overall performance of the resulting coatings was studied through rheological, thermal, mechanical, morphological, and chemical resistance tests. The nanocomposite coatings exhibited remarkable scratch resistance and adhesion properties, and the nanofiller dramatically improved the chemical stability of the coatings. Therefore, these bio-derived epoxy resins are proposed as a valuable alternative for tin can coatings, highlighting the importance of renewable polymers towards a successful bio economy [20].

The cross-linking (or cure) reaction of the epoxides occurs through a mechanism of addition of a nucleophilic agent to the epoxy group. Curing agents for epoxy resins are compounds with active hydrogen atoms such as primary and secondary amines, phenols, thiols, anhydrides and carboxylic acids. Catalysts of the curing processes are, on the other hand, Lewis acids and bases.

In the first part of first PhD year, in order to optimize the crosslinking cycles, crosslinking agents were chosen, including anhydrides and acids.

The selection of care agents was carried out taking into account their reactivity, the non-toxic characteristics, the possible need to operate in the presence of solvents and the technologies used for the coating of the cans. Different formulations were considered, with and without fillers, and / or with different molar epoxide / curing agent ratios.

Kinetic analyzes using DSC, rheology and FT-IR spectroscopy were used for the optimization of crosslinking protocols. All those systems characterized by non-complex polymerization kinetics and with high reaction yields were taken into consideration.
In particular, the thermal and mechanical performances of the cross-linked materials were evaluated. For the thermal properties, thermogravimetric analysis (TGA) were carried out both in an inert and oxidative atmosphere, and DSC tests to trace the glass transition and residual cross-linking temperatures. To determine the mechanical strength, during the second year of PhD, adhesion and elasticity / flexibility characteristics, specific tests will be carried out in accordance with existing standards.
Once the resins have been made and characterized, during the third year of PhD, we will proceed with the realization of coatings on tinplate metal substrates with characteristics similar to those used for the production of food cans. An initial part of this activity, therefore, will concern the development of the techniques for applying bio-derived resins, paying particular attention to the achievement of requirements such as the homogeneity of the thicknesses and the mechanical integrity of the coatings (absence of microfractures and local agglomeration phenomena).
It will also be verified that the biobased coatings made possess physico-chemical properties of high polymers, useful for guaranteeing adhesion to the metal support, adequate porosity, insolubility, chemical inertness, in aqueous environments with high and medium aggressiveness, resistance to high sterilization / pasteurization temperatures. of the food product, resistance to aging during storage for prolonged times. The paint must also have adequate mechanical characteristics, in particular: hardness, abrasion resistance and flexibility. The properties described above contribute to determining both the corrosion resistance of a painted metal / food product system and the possibility that it becomes the site of degradation of the paint film and corrosion of the metal substrate.

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