



ORAL COMMUNICATION 1

EPOXY PRECURSORS BASED ON ISOSORBIDE: FOR WHICH APPLICATIONS IN THERMOSETTING MATERIALS?

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INTRODUCTION

Epoxy monomers may be reacted either with themselves through anionic or cationic homopolymerization, or with a wide range of co-reactants (hardeners) including polyfunctional amines, acids, anhydrides, phenols, alcohols, and thiols. Epoxy thermosets are mainly used in diverse industrial applications requiring superior strength, excellent adhesion, good chemical resistance, and excellent performance at elevated temperatures. Due to that, they are used in coatings, electrical/electronic laminates, adhesives (including structural adhesives), flooring and paving applications, and high performance composites. Control of properties and also processing is usually based on the selection of the appropriate epoxy precursors or combination of monomers, on the selection of curing agents and associated reaction mechanism, and on the addition of organic or inorganic fillers and components. New markets for structural composites in automotive parts or wind turbine blades are new challenges for epoxies.

The most popular epoxy monomers are those derived from the industrial reaction of bisphenol A, BPA with epichlorohydrin, ECH in the presence of sodium hydroxide. The structure of the major product, diglycidyl ether of bisphenol A, DGEBA and its condensed forms is dependent upon the stoichiometry of the reactants. An easy way to obtain a partially bio-based DGEBA is to use commercially available ECH from bio-based glycerol. For BPA, the problem is more complex. The aromatic ring of BPA is particularly suitable since it confers a good thermal resistance to epoxy networks. Unfortunately, BPA has been known to have estrogenic properties [2] and its negative impact on human health and the environment necessarily implies focusing research on the substitution of BPA, especially since some countries have recently banned the use of BPA in food contact materials. Renewable molecules and derivatives of biomass can be sources of alternatives to epoxies from BPA. Epoxy precursors can be prepared from a lot of renewable resources: tannins, lignin, vegetable oils, terpenes, and polysaccharides, or others [3].

Many epoxy pre-polymers obtained from bio-based aliphatic polyols such as vegetable oils, glycerol and sorbitol are commercially available and are mainly aliphatic glycidyl ether types. Interest in the production of 1,4:3,6-dianhydrohexitols, especially isosorbide, 1,4:3,6-dianhydro-D-sorbitol (DAS), has been generated by potential industrial applications such as the synthesis of polymers. As already shown by Fenouillot et al., [4] isosorbide is a non-toxic and chiral molecule which also brings stiffness to polymer chains such as polyesters, polycarbonates, and polyurethanes. In this presentation we will focus on this molecule as an epoxy precursor. Even if it is possible to find old patents [5,6], a lot of recent patents [7-11] and many papers have been devoted the past 10 years to isosorbide-based epoxies as safe and renewable alternatives to petroleum-based BPA epoxies [12-18]. But from our knowledge, up to now there is no direct industrial synthesis an application. And so, it is now time for an evaluation, and it was the subject of our collaborative work.

RESULTS

1- Precursors synthesis

The reaction of ECH with natural aliphatic polyols, bearing both primary alcohol and/or secondary alcohol groups is not trivial. Indeed, this reaction generates new alcohol groups, which are also reactive toward ECH [19]. Unlike the reaction between phenol groups and ECH, the hydroxyl groups resulting from the reaction between the polyols and ECH show reactivity fairly similar to that of the starting polyols. This thus implies multiple additions of ECH onto the same alcohol, which is then not able to undergo intra-cyclization. This can explain the chlorine content since these -Cl atoms are not situated in the α -position and so no cyclization into epoxide is then possible. This in fact reveals that the expected structures are idealized structures since other byproducts containing -Cl atoms are also obtained. As an example most of commercial products based on sorbitol contain about 10-20 wt % Cl. In the case of isosorbide, the -Cl content is much lower but remains slightly higher than that of polyphenols. Our first aim was to prepare a well-defined diglycidyl ether of isosorbide, DGEDAS. In the frame of our work, Roquette has developed a new process able to give a practically pure DGEDAS as demonstrated by NMR analysis and equivalent epoxy measurements [20].

2- Epoxy networks.

The cross-linking reaction was performed with (cyclo)aliphatic amines and anhydrides with different curing schedules but similar to those used for DGEBA with the same hardeners. The T_g 's of networks synthesized from DGEDAS were always lower than those of the corresponding DGEBA-based networks, but with higher rubbery moduli. However, the main problem to solve is the water uptake of the networks which deteriorates the properties, as it can be from 10 and up to 50% bw. Our work was focus on coatings and adhesives applications. The trials were focused on the study of various formulations in order to optimize the mechanical properties and to decrease the water uptake of the DGEDAS formulations.

CONCLUSIONS

Our point of view is that DGEDAS alone cannot be considered as a renewable drop-in solution to replace petroleum-based BPA epoxies. However we have identified promising DGEDAS formulations leading to a good compromise regarding the mechanical properties and the water uptake. Details will be presented during our communication

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