



Design and formulation of soybean oil derived flexible polyurethane foams and their underlying polymer structure/property relationships

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ABSTRACT

A series of water blown polyurethane foams was produced in which polyether polyol content was progressively reduced by the addition of a designed soybean oil derived polyol (SBOP). A sample from each foam was tested for a variety of standard properties and a sample from the same foam was also compression molded into plaques which were tested for elastomer properties. The morphology of the foams and their underlying elastomers was probed by SEM, AFM, DMA, X-ray, FTIR, tensile properties and cyclic stress/strain (hysteresis) experiments. The properties of the polyether control and SBOP containing foams are representative of their underlying polymers. However, foams containing SBOP do not have well developed hard segment organization relative to that of polyether soft segment control foams. Similarly, the SBOP foams do not have as good hard segment organization as the elastomers derived by compression molding the same foams. This suggests that hard segments of SBOP containing foams do not reach thermodynamic equilibrium prior to vitrification during the foaming process. It is possible that this is an artifact of the low equivalent weight (ca. 670 gr/eq) of SBOP which promotes gelation ahead of phase separation. The fact that the elevated temperature modulus is independent of the amount of added SBOP suggests that tensile properties of the foam are not a function of the soft segment crosslink density, but rather the hard segment phase separation. Other foam properties such as airflow and tear strength are shown to be related to the same factors. Improvements in foam properties are achieved by designing the foam formulation to increase phase separation.

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1. Introduction

Substitution of agricultural oils for petrochemically derived feedstocks in polyurethane synthesis has been an area of intense research and development for several decades [1–4]. Much of this work is predicated on the assumptions that petroleum derived feedstocks will be in short supply in the foreseeable future, and that agriculturally derived building blocks will be competent replacements from both performance and economic stand points. Much of the research to date has explored substitution of seed oil derivatives for the polyurethane soft segment and the effect of seed oil derived soft segment on hard segment properties [5–8]. In general, the properties of seed oil derived polyurethanes suffer in comparison to the petroleum derived counterparts [9–12]. After significant attempts at optimization it is clear that performance shortfalls are significant, reflecting intrinsic challenges of

triglyceride structure, and the difficulties inherent with their synthetic conversion to polyols [13,14].

The development of agricultural oil derivatives for preparation of polyurethanes has largely involved the preparation of elastomers [15–18]. There are many fundamental and practical reasons for this. Preparation of foams places an additional layer of complexity on data interpretation since the competitive reaction of isocyanate with water instead of alcohol has a substantial effect on properties [19,20]. Physical properties of foams must then not only be interpreted based on the equilibrium structure, but also the effects of the competitive reactions involved [21,22]. Furthermore, production of foams requires a substantial amount of formulation with surfactants and catalysts whose structure and activity are at best qualitatively known to the researcher, and at worst unknown to the manufacturer [23]. Lastly, a prescribed blowing agent is an additional formulation variable in the production of insulation foams, providing additional complications to understanding polyurethane properties based on the structural variation.

In spite of these challenges, the application of agricultural oil derivatives to rigid polyurethane foams is attractive primarily due to the relatively low hydroxyl equivalent weight providing a high

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glass transition temperature, reduced gas permeability, and rapid gelation required for many insulation applications [24,25]. Until recently, fundamental difficulties stood in the way of technological progress to useable seed oil based rigid insulation foams [26–28]. Recently Macosko et al. [29] developed rigid foam using a soy derived polyol possessing many critical properties required of polyurethane insulation foam, except it showed poor aging of insulation properties due to rapid ingress of nitrogen into the cell structure. Additionally, Macosko et al. [13] explored use of soy derived polyols for making flexible foams from the native triglyceride functionalized via an epoxidation and alcoholysis route. They observed reduction of hard segment organization and, concomitant reduction in properties.

Seed oil derived polyols offer a high glass transition temperature resulting from high crosslink densities required for rigid insulation foams, but this precludes their use in flexible foams. This limitation is unfortunate since 2/3 of all polyurethane foams are in fact flexible foams used in such common applications as furniture cushions, mattresses, carpet underlayments, and automotive seating to name just a few [30]. We have recently presented work showing explicit designs and properties of agricultural oil derived polyester polyols for lubricants [31], and polyurethane elastomers [32] that result in commercial quality materials. In this article we will discuss the application of seed oil derived polyester polyols for application in flexible foam systems. The polyester polyols are created by deconstruction of the native soy triglycerides into fatty acid methyl esters followed by their hydroformylation and reduction to create hydroxymethyl methyl esters (Fig. 1) [33].

The resulting A–B ester alcohols can then be polymerized via transesterification to make polyester polyols with designed hydroxyl equivalent weight, hydroxyl functionality, and viscosity (SBOP following the convention of Ryan et al. [16] and Macosko et al. [13]). Using this technique, polyurethane foams with substantial agricultural oil content can be produced that in many aspects are indistinguishable from polyurethane foams from petrochemical feedstocks. Some of this work has been discussed empirically by us elsewhere [34]. In this article we will provide a fundamental analysis of structure property relationships related to the progressive increase of SBOP composition within polyurethane foams, and provide a basis for distinguishing the effect of SBOP on foam properties versus the underlying polymer from which the foam is comprised.

There is relevant prior information exploring polyurethane foams and their underlying elastomers. Ophir and Wilkes [35] found that polyether based elastomers exhibit superior phase separation to those based on polyesters. Armistead, Wilkes and Turner [36] found that when foams were compression molded into elastomer plaques, the elastomer properties were reflected in the

foam. Moreland, Wilkes and Turner [37] found that relaxation of foams was independent of cell structure and followed the derived elastomer properties. Dounis and Wilkes [38] showed that increasing toluene diisocyanate (TDI) index promotes phase mixing (as opposed to phase separation) and that short range ordering in the hard phase is a maximum at an isocyanate index of 100. Beck and Truss [39] showed that elastomer hysteresis (an inverse relationship to resilience) is minimized by maximizing order and structure of the hard segment. Gaymans et al. [40] showed that foams reflected their underlying elastomer properties. They also showed that hysteresis and compression set increased with increasing urea. Lastly they showed that there are two relaxation regimes (fast and slow mechanisms) and that given adequate time, recovery of a deformed foam is complete. Sonnenschein et al. [41] showed that foam hard segment volume and phase separation consistently correlated to measurable foam properties. In addition they showed that interfacial interactions between phase separated hard segment and soft segment could play an additional role in foam compression set [42].

This article will report on the foam properties and the underlying elastomer properties of polyurethane foams prepared from polyether polyols, and foams made with varying amount of SBOP substituted for the polyether polyol. As much as possible the foam formulations were controlled to allow the least complicated interpretation of the data. The foams were subsequently compression molded into elastomers using a 2-step molding procedure that produced high quality bubble free plaques. Foams and their elastomers were subsequently analyzed by dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), Fourier transform infra-red spectroscopy (FTIR), atomic force microscopy (AFM), tensile, and X-ray analyses. There are several general conclusions drawn from the data 1) foams based on polyether soft segments have properties that are generally well correlated to the underlying elastomer properties 2) progressive substitution of SBOP for polyether soft segments degrades the foam performance in an approximately linear fashion 3) polyurea hard segment is more poorly formed in foams prepared with SBOP, 4) poor hard segment formation in SBOP foams is a kinetic artifact from the foaming process since the derived elastomers exhibit better hard segment organization, 5) SBOP containing foams can have improved physical properties by designing the foam formulation for more optimal phase separation.

2. Experimental

Voronate™ T-80 toluene diisocyanate (TDI) is a product of The Dow Chemical Company. It is an 80/20 mix of 2,4/2,6 TDI isomers. IP 625 is an ethoxylated glycerine and is a product of Dow Chemical

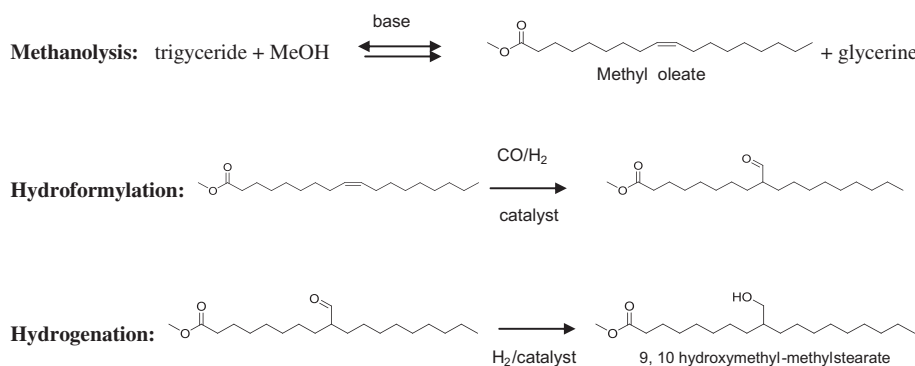


Fig. 1. Reaction path from seed oil triglycerides to derivitized polyester building blocks for making the soft segments of this research. Hydroformylation and reduction permits the methyl hydroxyl groups to form at either olefin carbon i.e. carbon 9 or 10 of methyl oleate.

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