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The effect of alkyl chain length on material properties of fatty-acid-functionalized amidoamine-epoxy systems

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ABSTRACT

Polyamine crosslinkers functionalized with pendant fatty acids are commercially used in epoxy coatings in part to enhance water barrier properties for corrosion prevention. However, a systematic understanding of the links between monomer molecular structure and material properties of such systems remains elusive, which limits our ability to design newer and more environmentally friendly coating systems. In this work, the effect of *n*-alkyl chain length in fatty-acid-functionalized polyamines on crosslinked epoxy-amidoamine systems is studied using a combined experimental and simulation-based approach. Both experiments and simulations show that density decreases and volume-expansion coefficients increase with increasing pendant chain length. Furthermore, it is shown that the trends in density and coefficient of volume thermal expansion with chain length obtained from simulations are consistent with an ideal mixing approximation. Interestingly, however, the glass-transition temperature T_g is found to be insensitive to chain length. Molecular simulations reveal that increasing the alkyl chain length from four to ten carbons does not introduce new flexibility mechanisms to the dense thermosets, which explains the T_g insensitivity. This work demonstrates a new way to significantly decrease the density of a thermoset polymer without compromising desirable properties such as high T_g and low coefficient of thermal expansion, and therefore may provide sounder rationale for molecular-based design of epoxy-based coatings.

1. Introduction

Epoxy networks have a wide range of applications and are used as castings, encapsulating materials, adhesives, laminates and in coating formulations [1,2]. They can be made suitable for both high and low temperature applications ranging from −50 °C to +120 °C [3]. Epoxies are typically cured with crosslinkers to form thermosetting polymers which possess enhanced thermomechanical properties, adhesive strength, viscosity, glass transition temperature and corrosion resistance [3]. The properties of a thermosetting polymer critically depend on the type of crosslinker used and specific crosslinkers are chosen to suit specific applications [2].

Among various crosslinkers, amidoamines are preferred in applications requiring moisture resistance, and also cause less skin irritation compared to polyamines [4,5]. Amidoamines have been in use since the late 19th century [1] and are key ingredients in the commercially available formulations Ancamide 500–507 and Ancamide 2029 [6]. However, these

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formulations are poorly structurally characterized and consequently very little is known about their structure-property relationships. This limits our ability to design improved crosslinking agents. A key molecular feature of these formulations, however, are pendant *n*-alkyl fatty-acid chains that cap some primary amine sites that could otherwise crosslink. The effects of alkyl chain length in these crosslinkers on the properties of the polymer and on corrosion performance is not yet known and has hitherto not been investigated. In cases where alkyl chains are part of the internal structure of crosslinkers or epoxy molecules, the effect of increasing chain length has been studied. For instance, increasing the alkyl chain length in aliphatic amine crosslinkers decreases the glass transition temperature T_g and the storage modulus and increases the free volume of the epoxy thermoset [7]. It has also been shown that the glass transition temperature decreases with increase in alkyl chain length in non-epoxy based systems such as polyesters [8], polyetherimides [9], poly-n-alkyl methacrylates [10], *p*-alkyl styrenes, and α-olefins [11]. It is therefore worth determining whether or not increasing pendant alkyl chain length in model amidoamine crosslinkers influences basic thermomechanical properties.

The purpose of this article is to report results of a combined experimental and molecular-simulations based approach to understanding the role of pendant alkyl chain length on thermomechanical properties of thermoset polymers comprising conventional epoxy networks and model amidoamine crosslinkers. Molecular dynamics (MD) simulations have proven to be useful in estimating properties of thermoset polymers and providing molecular-level rationales for structure-property relations [12–20]. The aim here is to systematically investigate this single molecular-level feature using newly synthesized pure amidoamine (AMAM) crosslinkers of varying alkyl chain lengths. These crosslinkers are cured with the diepoxy diglycidyl ether of bisphenol A (DGEBA) and the effect of alkyl chain length on the properties of the resulting thermosets are investigated. The main properties that are addressed here are density ρ, glass transition temperature T_g, and coefficient of volume thermal expansion α. It is shown that an ideal-mixing approximation is sufficient to explain trends in ρ and α with chain length. The T_g was found to be insensitive to n and molecular simulations provide detailed explanations for this behavior.

2. Methods

2.1. Experimental

The epoxy monomer considered here is diglycidyl ether bisphenol A (DGEBA). The crosslinkers considered are and amidoamines (AMAM), derived from diethylenetriamine (DETA) via attachment of one fatty acid chain to a single primary amine site. The AMAM series considered here vary in alkyl chain length n from 0 to 10, and we denote a particular AMAM with a subscript indicating the number of methylenes in the amide moiety. DGEBA and AMAM structures are shown in Fig. 1. DGEBA was acquired from Miller-Stephenson chemicals. DETA, fatty methyl esters (methyl hexanoate, methyl octanoate, methyl decanoate, methyl dodecanoate), and chloroform were acquired from Sigma Aldrich, while magnesium sulfate was acquired from BDH. Polyvinyl fluoride, PVF (Tedlar) was used as release film for making think epoxy/amine films and was acquired from DuPont. All chemicals were used as received.

2.1.1. Synthesis of AMAM crosslinkers

In order to synthesize AMAM crosslinkers of specified chain length, an appropriate fatty methyl ester was reacted with DETA. The synthetic scheme is shown in Fig. 2. Diethylenetriamine (0.467 mol, 48.26 g) was heated to 90 °C and mixed in a two-neck round-bottom flask for 30 min. The ester was then added dropwise to the hot DETA at a 1:10 equivalent ratio

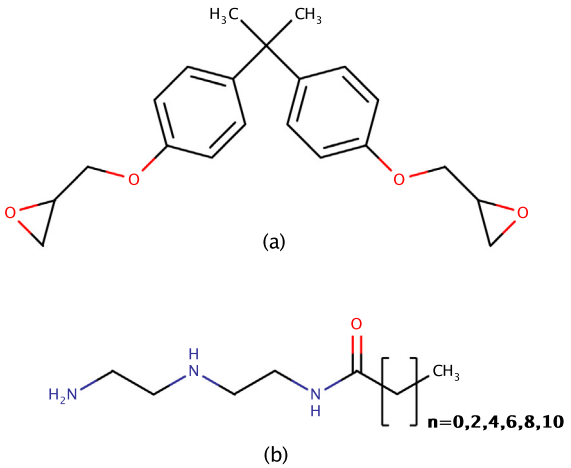

Fig. 1. Chemical structures of (a) DGEBA and (b) $AMAM_n$.