International Journal of Plasticity 47 (2013) 111–125

Contents lists available at SciVerse ScienceDirect

International Journal of Plasticity

journal homepage: www.elsevier.com/locate/ijplas

Molecular dynamics simulations of compressive yielding in cross-linked epoxies in the context of Argon theory

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ARTICLE INFO

Article history:
Received 15 February 2012
Received in final revised form 25 December 2012
Available online 1 February 2013

Keywords:
A. Yield condition
B. Polymeric material
C. Molecular dynamics

ABSTRACT

Molecular dynamics simulations are performed to study compressive yielding behavior of epoxy-amine cross-linked polymer networks in the low temperature glassy state. The simulations show a sharp drop in stresses after the elastic regime which was identified to occur due to the activation of wedge disclinations. For the first time in literature, both the chemistry and geometry (critical segment length, angles, bond torsions) involved in the molecular mechanism of compressive yielding have been measured. We analyze these results in the context of the Argon theory which is based on a linear elastic model of wedge disclination. The kink distance calculated using this simple theory gives a surprisingly good match to the results seen from the complex molecular simulation. The yield stress versus temperature predictions of Argon theory are directly compared with molecular simulation results. Finally, the use of Argon theory for extracting yield stresses at quasi-static strain rates from high rate molecular simulations is investigated.

1. Introduction

Properties of Epoxy-based thermoset polymers can be tuned towards a variety of applications from stiff binders in fibers for aircraft structures to loose gels for biological membranes. Investigation of the physical origin of such versatile properties is of value in developing polymer networks with multifunctional properties such as superior energy dissipation, impact resistance and adhesion. Glassy epoxies undergo a well-defined yielding behavior under compressive loading. The observed Arrhenius form of exponential temperature dependence of the deformation rate at constant stress prompted early theoreticians to employ viscous flow theory of Eyring (1936). In Eyring's theory, yielding occurs by coordinated flow of molecular segments under the application of stress. However, the theory failed to predict the observed dependence of yield stress with temperature. The theory of Robertson (1966) had many similarities with the theory of Eyring. Robertson also proposed that the yield mechanism was due to increased fluidity under applied stresses although the particular mechanism employed was the conversion of molecules at low energy trans state to a high energy cis state. The model accounted well for the temperature dependence of yield stress around the glass transition temperature but failed at lower temperatures.

Subsequently, attempts were made to understand yield behavior in polymers using ideas from crystal plasticity approaches in metals. Li and Gilman (1970) and Gilman (1968) postulated that deformation occurs by localized coordinated slip rather than by homogeneous shear as in viscous flow theories. In particular, Gilman identified defects in glassy materials in the form of dislocations (involving partial chain displacement) and disclinations (involving chain twisting and kinking). Two separate theories were derived from these ideas: Bowden theory (Bowden and Raha, 1974) and Argon theory (Argon, 1975; Argon, 1973; Argon and Bessonov, 1977), relying on yielding driven by dislocations and disclinations, respectively.

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http://dx.doi.org/10.1016/j.ijplas.2013.01.004

Bowden's theory assumed that yielding starts as a shear patch made by a continuous distribution of dislocations. This model accounted well for the temperature and strain rate dependence of the yield stress closer to glass transition but did not satisfactorily predict yield stress at lower temperatures. Argon noted that disclinations play a larger role in yielding of amorphous polymers. Of the two types of disclinations (chain twisting and chain kinking) proposed by Li and Gilman (1970), Argon chose kinking disclination to be the activating mechanism for yielding. Argon theory performs best at low temperature glassy conditions and has been used to successfully interpret the yield behavior of a large number of epoxy thermosets in Refs. Lee (1988), Yamini and Young (1980) and Cook et al. (1998).

A concise review of molecular theories of plastic deformation in amorphous polymers can be found in Stachurski (1997). During the derivation of these theories, researchers did not have the tools needed to measure or simulate behavior at molecular length scales. With the advent of molecular models and accurate interatomic potentials, it may now be possible to directly visualize molecular mechanisms of yielding. In the case of metallic (crystalline) materials, molecular simulations have allowed detailed study of defect (dislocation) nucleation (Spearot et al., 2007; Kang and Cai, 2010) or structure (Weinberger, 2011; Xu et al., 2013). Unlike crystalline metals, epoxies have an amorphous structure and the process of building such complex cross-linked molecular configurations with realistic properties is challenging and is being currently addressed by several researchers (see review in Knox et al. (2010)). In addition, molecular dynamics involve high strain rates ($> 10^6/\mathrm{s}$) that are seldom seen in many industrial applications. In order to reconcile molecular dynamics results with real experiments, it is important to study strain-rate scaling laws. Of particular interest in this work is the yield behavior at low temperatures where Argon theory has been the most successful. Argon theory proposes a highly localized yielding mechanism that can be tested using MD simulations. In this work, For the first time in literature, molecular dynamics has been used to visualize the yielding mechanisms in cross-linked epoxies and to interpret the molecular parameters involved in Argon theory. Results from Argon theory are then compared with the yield-stress versus temperature predictions obtained from molecular simulations. The utility of Argon theory for extracting the yield stress at quasi-static strain rates from high rate molecular simulations is also investigated. The yield stress obtained from molecular dynamics is then compared to the experimentally measured yield stress (Heinz and Wiggins, 2010) (at quasi-static conditions) recently reported in literature.

2. Technical approach

For this study, a common epoxy was employed: Di-Glycidyl Ether of Bisphenol A (DGEBA). The epoxy and amine monomer structures are shown in Fig. 1. The epoxy molecules were cross-linked (cured) with $4-4'$ diamino diphenyl sulfone (DDS). Each epoxy monomer has two epoxide (oxirane ring) groups, each with a cross-linking functionality of one towards amine curing agents, for a total functionality of two; each DDS monomer has two amine groups, each with a functionality of two towards epoxy molecules, for a total functionality of four. The typical synthetic epoxy to amine stoichiometric ratio is approximately 2:1 or 33.3 mol% amine. Fig. 2 shows polymer formation driven by the bonding of epoxide group in DGEBA and the amine groups in DDS. During formation of a cross-link, the primary amine group reacts with epoxide group forming a bond between nitrogen of DDS and the terminal carbon of the epoxide group. The carbon–oxygen bond breaks between the terminal carbon and the epoxide oxygen forming an alcohol (-OH) link. The cross-linked structure in Fig. 2(a) can undergo further reaction with another epoxy molecule forming a cross-linked molecular structure (Fig. 2(b)). Epoxies used in industrial prepegs show an actual conversion between 70–95% when measured through Near-Infrared (NIR) Spectroscopy (Wang et al., 2003). The conversion percentage depends on the process conditions, most importantly, the temperature and time of curing.

Many approaches have been recently used to build cross-linked polymer network systems with more than 70% conversion rate for use in molecular dynamics simulations. Most of these approaches involve polymerizing unreacted monomer mixtures over time (multi-step) or all-at-once (one-step). In one-step cross-linking (Yarovsky and Evans, 2002; Rottach et al., 2007), sites are randomly selected and pairs of sites within a capture radius are cross-linked together. One-step methods lead to artificially high network strains. In multi-step cross linking (Heine et al., 2004; Varshney et al., 2008; Wu and Xu, 2006) all reactive pairs that satisfy a given length criteria are cross-linked. The length criteria increases with each iteration and equilibration and cross-linking are repeated until desired cross-linking density is reached. Although multi-step methods prevent and relieve network strains, these are computationally intensive. Christensen (2007) introduced a new method to

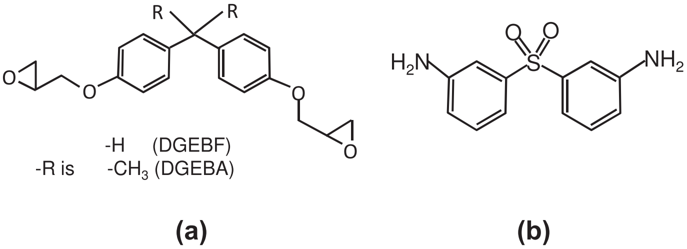

Fig. 1. Chemical structure of epoxy resin. DGEBA and the amine monomer diamino diphenyl sulfone employed in this work.