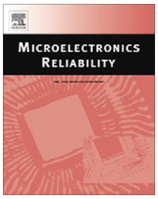
Microelectronics Reliability 51 (2011) 1035–1045

Contents lists available at ScienceDirect

Microelectronics Reliability

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



Modeling mechanical properties of an epoxy using particle dynamics, as parameterized through molecular modeling

Nancy Iwamoto *

Honeywell Specialty Materials, P.O. Box 547, Ramona, CA 92065, United States

ARTICLE INFO

Article history:
Received 18 September 2010
Received in revised form 22 February 2011
Accepted 6 March 2011
Available online 27 March 2011

ABSTRACT

The current paper successively applies molecular modeling and mesoscale modeling to scale mechanical models from an atomistic angstrom level to a sub-micron level and determine modulus, stress/strain behavior and defect formation in an epoxy and epoxy–copper interface. The results will show that molecular modeling may be applied directly to parameterize the bead properties used in the mesoscale model, which scale to the physical properties so could provide a means to understand interface behavior linked directly back to molecular origins.

1. Introduction

The linking of scales from the atomistic to bulk finite element models has been a global goal of modeling for many years. One of the conceptual methods used for such scaling is particle dynamics, which is attractive from the standpoint that discrete elements (the "particles") which follow the classic laws of motion are used to bridge the molecular level and the intermediate mesoscale, and from which material properties may be derived for introduction into continuum models. Such mesoscale methods to link the scales are available, but are often used for phase behavior simulation [1], and to our knowledge have not been used to directly obtain mechanical properties, especially for amorphous materials such as polymers. In addition, in order to successfully scale up from the molecular level, parameterizations should be introduced that represent the correct chemistry of the material. Such parameterizations to make the methods generally useful are sparse. However, particle dynamics (as practiced in Mesocite from Accelrys, Inc.), allows individual tuning of the particle interactions so that parameterization creation and tuning becomes easy to introduce [2].

The philosophy employed to parameterize the mesoscale models has been used to derive properties from molecular models in other papers [3–5], but it is based upon the concept that all properties are derived from a series of interactions. The root of the interaction should be obtainable from the molecular scale, by calculating the interaction of each important molecular interface. It has been found by previous examination that molecular scale models represent the adhesive modulus adequately enough to impact formulation work. And, in cases where the formulations are carefully represented, the modulus is quite accurate. Previous papers on mesoscale modeling [1,2] usually examine smaller functional group units from which to parameterize the particles (or "beads"). However, previous work looking at parameter development for silica particle–underfill interactions [6] suggested that higher averaging across more atoms might be possible in order to parameterize bead interactions. This work was designed to investigate the use of large bead representations of large polymer repeat units in order to see whether a scaling jump in the mesoscale models could be obtained, if consideration is given to the relevant interactions present from the molecular levels and which entities function as groups. For the present case, the repeat unit bead base upon both the base epoxy resin and it is curative was used and the large bead size is appropriate as relatively rigid repeat units are represented.

2. Background: molecular models and the derived mesoscale parameters

The molecular models used in this paper represented an epoxy system which is being characterized by TUDelft, comprising an epoxy novolac cured with bisphenol A [7]; in addition, the interface between the epoxy and copper I oxide was modeled. Both the bulk (unfilled) polymer and the copper interface molecular models applied the CVFF force field supplied within the InsightII/Discover software from Accelrys was used [8]. In a procedure previously used to determine modulus of polymer materials and adhesion in die attach adhesives [5], the molecular model was reduced to the repeat unit structure (epoxy + curative), with the size of these repeat units used to represent the particle–particle or "bead" to "bead" bond size for the mesoscale model. The interaction energies used for the mesoscale model were derived using the procedures to locate modulus using molecular modeling, in which the

---

* Fax: +1 760 788 7109.
E-mail address: nancy.iwamoto@honeywell.com

0026-2714/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.microrel.2011.03.013

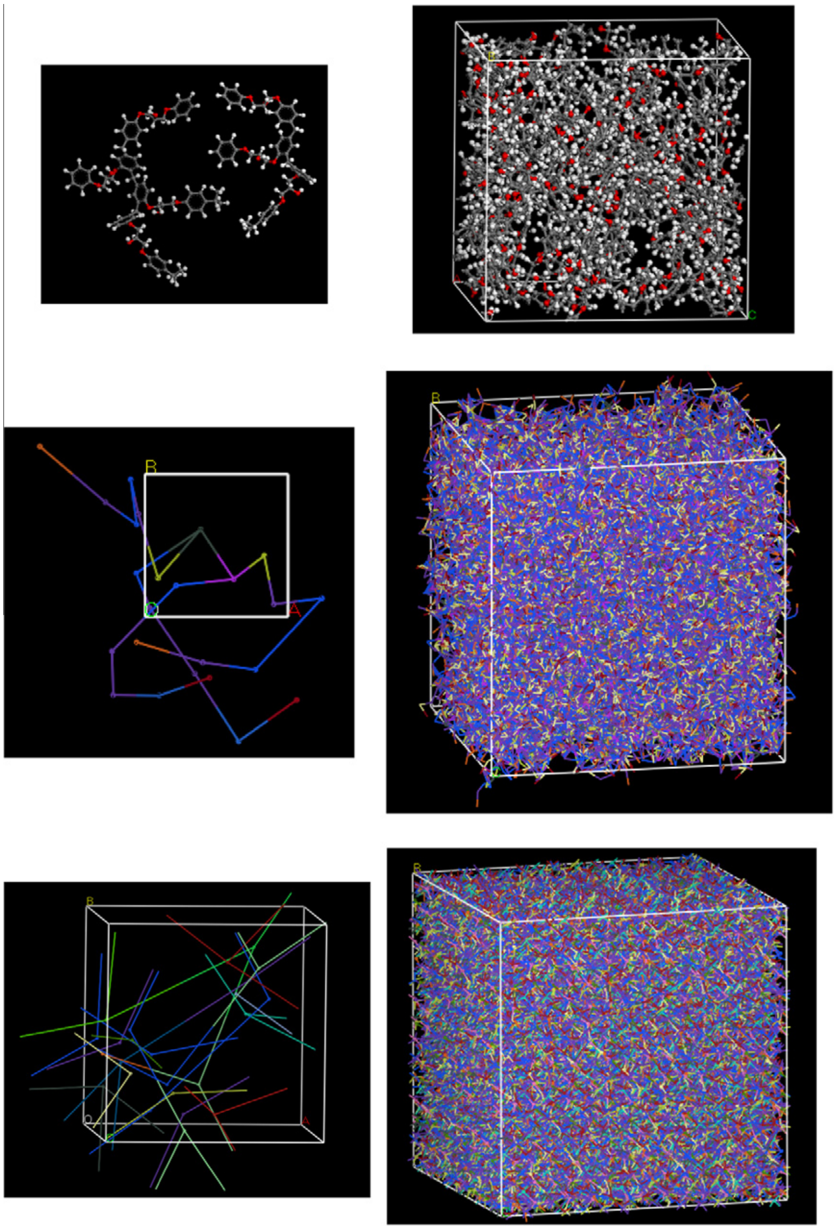


Fig. 1. Model examples. Top: (R) novolac repeat unit; (L) 24 repeat units (MW ~23,400, 24 repeat units). Middle: (R) uncrosslinked mesoscale cell (total MW in cell ~78 M); (L) Uncrosslinked scaled cell (total MW in cell ~78 M).

repeat units (MW ~800) that have been previously minimized together, are given a series of increasing forcing potentials to shear them apart. For each run, the shearing action is then allowed to proceed until the molecules are separated, with the energies proceeding thru a maximum. The initial energy response slope is monitored until a deviation in linear response is found, and the trajectory from this run is used to find the maximum energy change for nonbond parameterization. The maximum energy change upon separation was used for the interaction energies (the nonbond energies) and the average separation distances (after minimization, before strain) between the repeat units was used to estimate the nonbond distances. In a similar manner, the copper (I) oxide adhesive interface was modeled using the same epoxy repeat unit optimized on a single crystal Cu_2O layer (1 0 0 surface) which had been optimized on a fixed copper (1 0 0) surface. Since the parameterizations used were modified from the default MARTINI force field supplied within the software [2,8], an additional improvement would be the determination of the force constants. For the current work the default constants were used. As may be expected additional perfection is warranted for the parameterizations.

Table 1
Modified parameters used in Mesocite (edited MARTINI force field).

	VDW (kcal/mole)	Bond stretch R0 (A)
Epoxy repeat unit	55	24.8
Epoxy–Cu_2O	64	2.1
Cu_2O(Cu)–oxygen terminated surface	90	2.1

The coarse graining of the mesoscale models were generated from polymers derived from the epoxy repeat units and from a crystal surface for Cu_2O. The epoxy and Cu_2O structures were