Polymer 68 (2015) 1–10

Contents lists available at ScienceDirect

Polymer

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

Curing dependent spatial heterogeneity of mechanical response in epoxy resins revealed by atomic force microscopy

Amir Bahrami [a], Xavier Morelle [b], Lê Duy Hông Minh [a], Thomas Pardoen [b], Christian Bailly [a], Bernard Nysten [a, *]

[a] Institute of Condensed Matter and Nanosciences - Bio-and Soft Matter (IMCN/BSMA), Université catholique de Louvain (UCL), Croix du Sud, 1/L7.04.02 - 1348, Louvain-la-Neuve, Belgium

[b] Institute of Mechanics, Materials and Civil Engineering - Materials and Process Engineering (IMMC/IMAP), Université catholique de Louvain (UCL), place Sainte Barbe, 2/L5.02.02 - 1348, Louvain-la-Neuve, Belgium

ARTICLE INFO

Article history:
Received 21 February 2015
Received in revised form
29 April 2015
Accepted 30 April 2015
Available online 12 May 2015

Keywords:
Epoxy resin
Atomic force microscopy
Crosslinking density

ABSTRACT

The local mechanical properties of partially cured epoxy resins based on tetraglycidyl methylene dianiline (TGMDA) are proved to be heterogeneous at the nanoscale with the degree of heterogeneity decreasing when the crosslinking density increases. The fully cured resin can be considered homogeneous on both the nano- and macroscale. These conclusions are supported by a comprehensive statistical analysis of AFM-based local mechanical properties measurements, which reveal changes in the modulus distributions from multimodal to monomodal. Furthermore, the histograms of adhesion force and energy dissipation exhibit decreasing fluctuations with increasing degree of curing. The surface topography of all samples is very flat at the nanoscale, which indicates that the observed features are not the result of surface irregularities. The existence of differently cured domains due to local fluctuations in the curing kinetics is proposed as the origin of the observed properties contrast.

1. Introduction

Understanding the molecular structure and the properties of epoxies at the micro- and nanoscale in relationship with the mechanical performances has drawn the attention of many researchers since the 1960s [1,2]. Among others, significant efforts have been devoted to address the question whether the molecular structure and properties of epoxies, as a function of scale, are homogeneous or not. In order to generate optimal mechanical and physico-chemical properties, epoxy resins are mostly processed in a highly crosslinked state. Hence, the natural expectation about the molecular structure and resulting properties is a high degree of homogeneity. However, definite confirmation of this expectation is not straightforward and has prompted numerous researches on the subject.

Early structural analyses were performed with the help of electron microscopy on epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) and triglycidyl ether of glycerol (TGEG) crosslinked using various curing programs [3,4]. These studies mostly evidenced a nodular morphology with a length scale between 5 and 60 nm for highly cured resins and related this finding to heterogeneities in the molecular structure due to differences in local crosslinking state. Later, however, other groups raised doubts about these results using structural characterization techniques like small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) [5–7] on DGEBA-based epoxies cured with amine agents. It was claimed that, as a matter of fact, the molecular structure of epoxies and the crosslinking distribution within the cured structure is homogeneous and argued that the previous electron microscopy findings were probably influenced by imaging artifacts due to sample preparation or to the electron interactions with etched surfaces. Nevertheless, there are other proofs of the existence of structural heterogeneities in the literature based on SAXS [8] analysis or comparative studies using both SAXS and SANS [9], which confirmed the presence of a structural heterogeneity on similar epoxy systems. These contradictions highlight the difficulty to reconcile evidences gleaned from different techniques, especially from SAXS and SANS.

* Corresponding author. Tel.: +32 10 473104.
E-mail addresses: amir.bahrami@uclouvain.be (A. Bahrami), xavier.morelle@uclouvain.be (X. Morelle), DuyMinh.Le@soprabanking.com (L.D. Hông Minh), thomas.pardoen@uclouvain.be (T. Pardoen), christian.bailly@uclouvain.be (C. Bailly), bernard.nysten@uclouvain.be (B. Nysten).

http://dx.doi.org/10.1016/j.polymer.2015.04.084
0032-3861/

Addressing the question from a different angle, other researchers hypothesized that if there is any sort of structural heterogeneity in cured epoxies it should be reflected in the physical and mechanical properties. Mijovic et al. [10–12] measured at different temperatures the fracture toughness and dynamic mechanical properties of DGEBA with different curing agents, curing and postcuring programs. They assumed the existence of a heterogeneous nodular morphology with different crosslinking states and established a relationship between the morphology of the fracture surfaces observed by transmission electron microscopy (TEM) and the mechanical properties. In another work, Wu et al. [13] studied the effect of the curing program on the elastic modulus, fracture toughness, impact resistance and glass transition temperature (T_g) of epoxies based on DGEBA crosslinked with two different linear diamines. The morphologies characterized by SAXS were related to the bulk properties.

An epoxy network builds up progressively and passes through partial crosslinking stages with rubbery or glassy dynamics before reaching the maximum crosslinking density [14]. A better understanding of the structure and properties of epoxies must take into account the network formation kinetics. Furthermore, partially cured epoxies have important industrial applications that justify more attention to the link between their molecular structure and their physical as well as mechanical properties, which is the reason why the effect of partial crosslinking on the morphology and properties of epoxies and the progressive network build-up of these resins have been addressed by several authors [15–18].

A survey of previous researches on epoxies shows a lack of comparability among the studies due to the widely different chemical compositions as well as curing and sample preparation schemes. Free surfaces, interfaces formed with different substrates or fracture surfaces were the most widely used sample preparation methods to study various resin systems with a wide variety of crosslinking degree. The experimental plan in each research was adapted to specific needs, which explains also the diversity of approaches and results. Furthermore, most of the previous works were concerned with the relationship between the molecular structure homogeneity and the *macroscopic bulk properties*. Nowadays however, the increasing application of epoxies in many high-tech fields like nanocomposites, or thin adhesive films, asks for considering the *local properties* and their relationship to local scale homogeneity as a central question in this field. A better understanding of the mechanical properties of epoxy resins at the local scale is indeed becoming essential in nanoscience and nanotechnology. Heterogeneities in the local mechanical response can also lead to so-called back stress effects or kinematic hardening which shows up during cyclic loading with a key effect on fatigue resistance properties [19].

Advanced scanning probe microscopy techniques constitute a very attractive approach to unravel local mechanical properties. Early efforts have mostly used tapping-mode atomic force microscopy (TM-AFM) analysis on fractured or etched epoxy surfaces to image the surface topography as well as the phase signal. A nodular morphology was observed on height and phase images taken from the free surface, interface and bulk samples for different epoxy systems [20,21]. The authors suggested the existence of structural heterogeneity at the scale of 75 nm in the case of a bulk sample. Other authors [22], however, studied similar systems and defined a criterion for the presence of a heterogeneous structure based on the difference between the observed features in the height and phase images. Kishi et al. [23] reported an inhomogeneous microstructure in DICY-cured epoxies and related the AFM images to bulk mechanical and physical properties, e.g. fracture toughness, ductility, solvent resistance and heat resistance. Contrast in phase images in AFM tapping-mode is indeed influenced by the local material properties [24–27] and can, in principle, be used as a tool for the detection of heterogeneities in mechanical properties. However, the interpretation of phase images is complicated by the fact that they are also affected by surface physico-chemical properties such as adhesion as well as by the topography. Hence, the observed signal must first be deconvoluted into its various contributions before it can be ascribed to local mechanical heterogeneity.

Recently new AFM modes have been developed for mechanical property mapping, involving the HarmoniX™ mode [28–32], the Peak-Force Quantitative Nanomechanical Mapping (PeakForce-QNM) [33] and the contact resonance [34,35] modes. The aim of these modes is to perform in real-time the decomposition mentioned above by separately measuring different properties like adhesion force, energy dissipation and modulus. Most of these techniques are based on recording and analyzing the force versus distance curves (f–d curves) that result from very shallow indentation of the surface by the AFM tip, as explained later in the experimental section. Haba et al. [36] exploited Peak-Force QNM to study the morphology and mechanical properties of a DGEBA-based epoxy cured with different agents. They used two different tapping forces as well as two different tip sizes in order to verify the possible presence of a nodular morphology and an associated heterogeneity in the mechanical response. Through comparison with typical amorphous polymers, they concluded that epoxies show no heterogeneity in mechanical properties at the local scale and that the observed nodular morphology is essentially an AFM imaging artefact erroneously called “tip convolution”.

The present work aims at clarifying the link between the progressive network build-up of epoxies and the resulting morphology as well as the local mechanical properties homogeneity by using an advanced AFM mode on a well-controlled and representative resin system. The commercial RTM6 epoxy system used as matrix for high performance composites in aerospace applications has been chosen. A range of bulk samples with partial and full curing has been systematically prepared. As flat as possible surfaces were prepared with the help of ultramicrotomy in order to avoid artifacts due to other sample preparation methods, e.g. fracture surfaces, which might be influenced by preferred crack propagation pathways, or chemically etched surfaces, which might alter the true resin structure. High resolution mapping of topography combined with high sensitivity mechanical property mapping were performed using the HarmoniX™ mode. A detailed analysis of topography as well as a cross-correlation of property maps was performed in order to rule out the possible contribution of surface artifacts to the measured properties and to establish a solid relationship between morphology and local mechanical properties.

This analysis shows that the distribution of moduli on stiffness maps changes from bimodal for partially crosslinked samples to monomodal for the fully cured resin. The AFM-extracted modulus for the later sample nicely compares with that obtained from macroscopic tensile tests [37]. These results demonstrate how the homogeneity of the resin local mechanical response changes as a function of crosslinking degree. This is an important result in the context of the current controversies in the literature about epoxy resins opening to several perspectives in the deep understanding of complex mechanical properties such as plasticity initialized by shear transformation, fracture and fatigue influenced by back stress effects.

2. Experimental

2.1. Materials

The experiments have been performed on a premixed epoxy system under commercial name HexFlow® RTM6 supplied by