



Toward a computational and experimental model of a poly-epoxy surface



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ABSTRACT

A model poly-epoxy surface formed by the reaction of DGEBA and EDA is studied by the combination of experiments and DFT calculations. A special synthesis protocol is presented leading to the formation of a surface that is smooth ($S_a < 1$ nm), chemically homogeneous, and that presents a low-defect density ($0.21 \mu\text{m}^{-2}$), as shown by AFM characterizations. Then, XPS is used for the determination of the elemental and functional groups' surface composition. DFT allows the identification and assignment of individual bonds contributions to the experimental 1s core-level peaks. Overall, we demonstrate that such a model sample is perfectly suitable for a use as a template for the study of poly-epoxy surface functionalization.

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1. Introduction

Poly-epoxy polymers are widely implemented in three families of applications: adhesives, paints, and composite materials [1]. The latter, such as epoxy/C fibers composites are increasingly found in a wealth of devices and parts in the fields of leisure (skis, rackets, boats, golf clubs, etc.), or transports, aeronautics and space (cars, aircrafts, satellites, etc.), to name but a few. These composite materials possess stiffness and Young's modulus that compare well with metallic alloys but with a much lower chemical reactivity and density. Therefore, they allow mass reduction and a large increase of parts durability.

Replacement of metallic or ceramic parts by polymers often requires surface functionalization in order to acquire optical, electrical, magnetic, biomedical, esthetic, or chemical properties. The main drawback when it comes to coat or to graft the surface of polymer-based composites comes from the very low surface energy of such materials once polymerized. This leads to a poor wettability rendering painting or gluing difficult, and resulting in poor adhesion. The surface energy of poly-ether ether ketone (PEEK) or poly-epoxy is approximately $40\text{--}50 \text{ mJ/m}^2$ to be compared to

approximately 500 mJ/m^2 for aluminum. Moreover, the polar component (due to H bonding) is as low as $6\text{--}7 \text{ mJ/m}^2$ which inhibits the use of simple functionalization protocols [2–4]. Hence, a large number of particular protocols has been described or patented, where the increase of reactivity and roughness is sought. A selection amongst the wealth of publications can be found in Refs. [5–16].

Such protocols or methods that have been used until now remain empirical despite the resulting improvement of the targeted properties and/or the extension of the durability of the material. Therefore, the need exists to access the basic mechanisms which control the surface functionalization of polymers and to control them so as to achieve satisfactory functional properties and adhesion. By subscribing in this perspective, our approach aims at describing the nucleation and growth of metallic thin films on polymer surfaces, by using an integrated method where all the elementary mechanisms are taken into account. The first step in this frame – object of the present study – is to obtain a model of the polymer surface, both experimental and theoretical, at the atomic/molecular level. Such a model will serve as a template for further surface treatments, including pretreatments, molecular grafting, or application of films and coatings. It is worth noting that, to the authors' knowledge, no such a theoretical surface model exists, most likely because of structural disorder and a lack of experimental inputs.

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Regarding our objectives, specifications of such an experimental model polymer surface include:

- A 100% polymerization after curing to be comparable with calculations, where total polymerization is assumed.
- A low surface arithmetic roughness, namely $R_a < 1$ nm to make sure that we can observe nano-islands or nano-clusters of a given thin film. Otherwise, they would be hindered by roughness.
- A very low defect density to avoid heterogeneous nucleation at defects.
- Chemical homogeneity to make sure that calculation models where homogeneity is assumed are representative of the tracked chemical reactivity. Also to make sure that chemical composition is independent on the analyzed surface area corresponding to a given probe size.

Our experimental approach is based on the method described in [17,18] for forming model poly-epoxy surfaces. It consists in the polymerization of the poly-epoxy in an Ar gloves box at ambient temperature for at least 24 h, followed by a post-curing at elevated temperature (polymer-dependent). Gu et al. [17] synthesize samples from a stoichiometric mixture of DGEBA + 1,3-di(aminomethyl)-cyclohexane, with a small amount of toluene for decreasing viscosity and favoring an homogeneous stirring (7 min). Samples are then stored for 24 h at ambient temperature, and post-cured for 2 h at 130 °C in an air furnace. Characterizations of the free surfaces are performed by atomic force microscopy (AFM) in Tapping[®] mode. Surface roughness and phase contrast are determined. It is shown that samples synthesized in an Ar glove box show a lower surface roughness than those prepared in ambient conditions, and that they are homogeneous in composition. Kansow et al. [18] use a similar method with the aim of characterizing the formation of Al, Cu, Ag, and Au films by physical vapour deposition. DGEBA reacts with diethylene triamine in low excess at 55 °C under controlled atmosphere, before it is left for 48 h at ambient temperature. At this step, polymerization rate is about 75%. Completion is achieved by post curing for 1 h at 120 °C. Surface roughness is about 1 nm.

Theoretically, our greatest challenge is to circumvent the description of the disordered/amorphous structure and to limit the number of atoms. To that end, we start with a small macromolecule made from the reaction of bisphenol A diglycidyl ether (DGEBA) with ethylenediamine (EDA) (61 atoms). Even for this moderately complex system, the analysis of the experimental core-level XPS spectrum is not trivial and can lead to incorrect conclusions. The help of accurate theoretical tools is thus needed and density-functional theory (DFT) is usually used for computing XPS core-level shifts in the case of small organic or inorganic systems. The application of this theoretical method to large systems, e.g. polymers, is a challenge but it is established that experimental spectra are directly related to the electronic states obtained from calculations on smaller model molecules. For instance, Endo et al. presented a comprehensive analysis of the XPS 1s spectra for polymers using the negative of the energy of molecular orbitals [19,20]. More recently, they used the ‘transition state’ theory [21] for the calculation of the core electron binding energies [22,23]. Following this work and in a first approach, we compute the molecular orbitals energies on model molecules as preliminary input for the assignment of experimental XPS spectra of the investigated polymer.

We complement these results in the different DGEBA + EDA system by implementing a more detailed description of surfaces by AFM and XPS characterizations complemented by DFT calculations. The paper is organized as follows. Experimental and computational

details are given in Section 2, followed by results in Section 3. Conclusions and perspectives are presented in Section 4.

2. Experimental and computational details

2.1. Synthesis

We use a stoichiometric mixture of DGEBA (DER 332, Dow Chemicals, $n=0.03$) and EDA (analytical grade, purity >99.5%, Sigma Aldrich). The mass of DGEBA (m_{DGEBA}) is fixed to 5 g. The mass of EDA m_{EDA} is thus determined following Eq. (1).

$$m_{\text{DAE}} = \frac{f_{\text{DGEBA}}}{f_{\text{DAE}}} \times \frac{M_{\text{DAE}} \times m_{\text{DGEBA}}}{M_{\text{DGEBA}}} = 0.43 \text{ g} \quad (1)$$

where M_{DGEBA} is the molar mass (348.52 g/mol) of this DGEBA and f_{DGEBA} is its functionality (2), and M_{EDA} is the molar mass (60.10 g/mol) and f_{DAE} is the functionality (4) of the EDA. We assume that no etherification occurs.

The mixture is then mechanically stirred (in an Ar glove box when specified) for 7 min before it is poured into different molds or deposited as a thin droplet on aluminum foil. Polymerization is then allowed for 48 h at ambient temperature, followed by a post curing of 2 h at 140 °C. For roughness comparison, we consider the following poly-epoxy surfaces formed:

- At free surfaces, surfaces ref. either epoxy^{Air} or epoxy^{Argon}.
- At the interface with a 1 cm × 1 cm × 0.2 cm silicone mold, itself molded on a Si wafer for transferring atomic flatness. Interfaces ref. SiO_{Si}/epoxy^{Air} or SiO_{Si}/epoxy^{Argon}.
- At the interface with a 1 cm × 1 cm × 0.2 cm silicone mold, itself molded on polystyrene (PS). Interfaces ref. SiO_{PS}/epoxy^{Air} or SiO_{PS}/epoxy^{Argon}.
- By mechanical polishing up to a ¼ μm with diamond paste. Surfaces ref. polished^{Air}.

Interfaces formed in the same molds but in air or Ar show different roughnesses (shown hereafter). This is the reason why SiO_{Si}/epoxy^{Air} and SiO_{Si}/epoxy^{Argon}, and SiO_{PS}/epoxy^{Air} and SiO_{PS}/epoxy^{Argon} are differentiated.

2.2. Bulk characterizations

Differential scanning calorimetry (DSC) is used for the determination of the glass transition temperature (T_g) of the poly-epoxy under investigation. We use a DSC 204 Phoenix Series (NETZSCH) coupled with a TASC 414/4 controller. The apparatus is calibrated against melting temperatures of In, Hg, Sn, Bi, and Zn, applying a +10°/min temperature ramp. Samples are placed in aluminum capsules. Mass is measured with an accuracy of ±0.1 mg. We choose to report the onset $T_{g\text{-onset}}$ temperature.

Fourier transform infrared spectroscopy, FTIR (Frontier, PerkinElmer equipped with a NIR TGS detector), is performed in transmission in the 4000–8000 cm⁻¹ range. 16 scans are collected for each analysis with a resolution of 4 cm⁻¹. We monitor the characteristic epoxy band (combination band of the -CH₂ of the epoxy group) at 4530 cm⁻¹ with increasing polymerization time, and after post curing treatment. The reference band is the combination band of C=C with aromatic -CH at 4623 cm⁻¹ [24]. Peak areas are then used for calculating the conversion rate (X_{eNIR}) of epoxy groups, following Eq. (2).

$$X_{\text{eNIR}} = 1 - \frac{(A_{\text{epoxy}}/A_{\text{reference}})_{t=t}}{(A_{\text{epoxy}}/A_{\text{reference}})_{t=0}} \quad (2)$$

where A_{epoxy} and $A_{\text{reference}}$ are the peak areas of the epoxy and reference groups, respectively.

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