

Synchrotron Based Surface Science to Probe Polymeric Interfacial Regions

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Introduction

Synchrotron based X-ray absorption spectroscopy was utilized to probe the chemistry and structure of polymers in interfacial regions, including the interfacial composition of filled epoxy composites, and the surface orientation of polymer films. Polymer interfacial properties can be very different than their bulk properties, due to variations in chemical composition, molecular orientation, mobility, crystallinity, and microstructure near the interface. Due to current trends in device miniaturization coupled with increasingly complex material formulations, the interfacial properties of polymers play a critical role in device performance as well as the performance of many general materials systems such as adhesives, encapsulants, foams, filled polymers, and coatings. To understand and control reliability and aging issues associated with polymer interfaces it is important to understand on a fundamental level what controls the properties, structure, and composition of polymers near the interface. This requires advancing measurement technology capable of assessing polymer interfacial properties with improved chemical resolution, spatial resolution, and chemical sensitivity when compared to current techniques.

Methods and Materials

Sandia National Laboratories and the National Institute of Standards and Technology (NIST) have engaged in collaboration to develop an advanced interface science beam-line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Both laboratories have committed capital funding and personnel resources to the beam-line. While this beam-line is currently under construction, research is conducted at an existing low energy Near Edge X-ray Absorption Fine Structure (NEXAFS) beam-line (U7A).

The currently available NEXAFS beam-line has an energy range of (180 to 1200) eV, enabling the core level transitions in low Z elements (carbon, nitrogen, oxygen, and fluorine) to be explored. A second beam-line will be improved and rebuilt at the NSLS with higher-energy NEXAFS and X-ray Photoelectron Spectroscopy (XPS) capability with an energy range of (1000 to 8000) eV. The synchrotron light source provides high intensity and variable energy incident radiation, which will enhance signal, peak resolution, and depth-profiling capabilities compared to standard laboratory instruments.

Results

Fig. 1. shows a schematic depicting the principles of NEXAFS. The sample is exposed to tunable plane polarized, monochromatic X-ray radiation from a synchrotron light source. In these experiments, the incident radiation is scanned over the carbon K-edge region, an energy range from (280 to 330) eV. X-rays are preferentially absorbed by the sample when the incident radiation is the appropriate energy to allow the excitation of a core shell electron to an unoccupied molecular orbital. During electronic relaxation, Auger electrons and characteristic fluorescence photons are released. These

electrons can only escape from the top surface of the sample (1 to 10) nm. The photons are detected from approximately 100 nm within the sample. NEXAFS has elemental sensitivity because the characteristic binding energies of the carbon, nitrogen, oxygen, and fluorine core electrons are well separated. In addition, due to the well-defined energy gap associated with a core shell / unoccupied orbital transition, NEXAFS is also sensitive to the bonding characteristics¹.

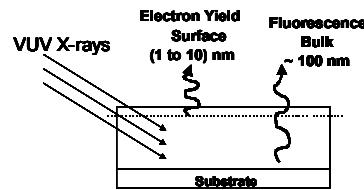


Fig. 1. A schematic depicting the principles of NEXAFS.

NEXAFS was utilized to provide insight into the fracture behavior of alumina filled epoxy resins. The interaction between the polymer and filler, and the properties of the polymer-filler interfacial region can impact the material properties of the composite. Fig. 2. shows the carbon K-edge NEXAFS spectra of the fracture surfaces for a series of epoxy composites loaded with 18-micron aluminum oxide filler from Sumitomo (AA18).

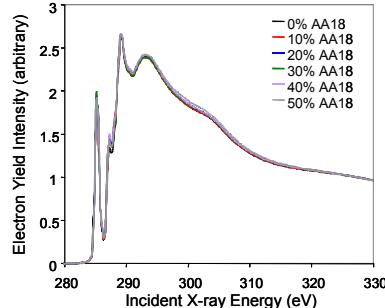


Fig. 2. Carbon K-edge electron yield spectra for a series of epoxy composites with varied volume percent filler loading.

The peaks present in the NEXAFS spectra represent different types of carbon bonding. The epoxy monomer in the resin contains phenyl rings, whereas the amine hardener is a linear polymer chain with no double bonds. Therefore, the C1s \rightarrow $\pi^*_{C=C}$ transition near 285 eV can be utilized to investigate changes in chemical composition at the fracture surface. Interestingly the carbon chemistry of the fracture surface is independent of the filler loading. This indicates one of two scenarios for these composites: a) the fracture occurs in the bulk polymer even at the high filler loadings or b) the composition of the polymer – filler interfacial region is the same as the bulk polymer. NEXAFS data on the oxygen K-edge combined with scanning electron microscopy images of the fracture surfaces indicate that fracture occurred at the alumina-epoxy interface,

meaning the interfacial composition of the epoxy resin is the same as the bulk composition.

Because the incident synchrotron radiation is polarized, NEXAFS can also be utilized to probe molecular orientation. Fig. 3. shows a schematic of a poly(styrene) monomer. The C1s $\rightarrow \sigma^*_{C-C}$ transition is oriented with the polymer chain backbone. The C1s $\rightarrow \sigma^*_{C-H}$ transition is oriented perpendicular to the chain backbone. A pendant phenyl ring is normal to the chain backbone and contains a C1s $\rightarrow \pi^*_{C=C}$ transition that is perpendicular to the phenyl group and parallel to the chain backbone. Since the incident X-ray radiation is polarized, with the electric field vector perpendicular to the direction of the light propagation, measuring the NEXAFS spectra at different angles can be utilized to investigate the orientation of these absorption transitions.

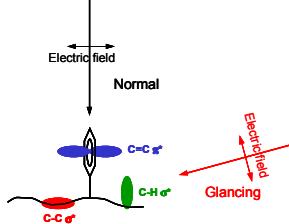


Fig. 3. A schematic of a polystyrene molecule and the various orbital transitions that can be probed with NEXAFS.

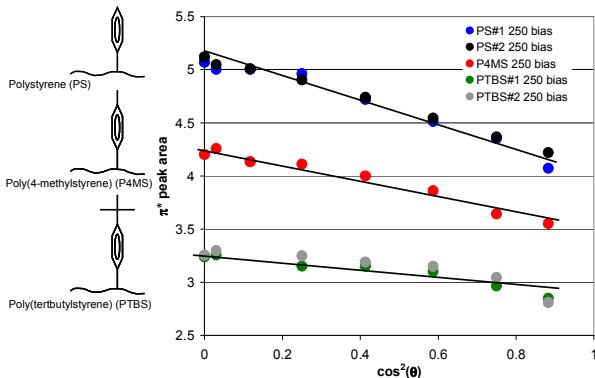


Fig. 4. NEXAFS spectra as a function of angle for poly(styrene), poly(4-methylstyrene), and poly(4-tertbutylstyrene).

Fig. 4. plots the C1s $\rightarrow \pi^*_{C=C}$ peak area for a series of poly(styrene)-like polymers as a function of the angle of incidence for the incoming radiation. Before integration, the spectra were pre and post-edge jump normalized. When the $\cos^2\theta$ is zero, the incident radiation is normal to the film surface. When $\cos^2\theta$ approaches 1, the incident radiation is in glancing mode relative to the film surface. Three polymers were investigated, poly(styrene), poly(4-methylstyrene), and poly(4-tertbutylstyrene). For each polymer, at the normal angle the C1s $\rightarrow \pi^*_{C=C}$ transition is stronger than in the glancing mode, indicating that nominally the phenyl groups are oriented perpendicular to the film surface. However, as the functional group of the ring becomes larger, the orientation is less pronounced (the decrease in peak area when moving from normal to glancing angles). Poly(styrene) has a stronger angular dependence than poly(4-methylstyrene). The least angular dependence is with poly(4-tertbutylstyrene), which has the bulkiest pendant group on the styrene ring. Steric effects from a bulky pendant group on the ring may hinder surface orientation. The electron yield detector bias was set at 250 eV, so that only electrons with energy near the characteristic carbon Auger electrons are collected. These electrons escape from the top

monolayer of the polymer surface, since the carbon Auger escape depth is approximately 10 Å. Therefore, the electron yield spectra are extremely surface sensitive.

The variable low to high-energy beam-line that is currently under reconstruction will have a high energy XPS detector on the end-station. One important advantage of high-energy synchrotron based XPS is the tunability of the incident X-ray radiation. If the incident X-ray energy is varied, then the kinetic energy of the ejected electron also changes. This allows improved depth profiling capability over typical laboratory based XPS. Fig. 5. shows the “universal curve” describing the effective attenuation length of an electron as a function of the kinetic energy of the electron². Laboratory based XPS often operates near the minimum of the curve (red circle) where the attenuation length of the electron is only a few monolayers. Operating near this minimum makes XPS extremely surface sensitive, where contamination layers can interfere with analysis. With synchrotron based XPS, the energy can be tuned up the universal curve (blue circle) to escape depths near 10 monolayers. A larger portion of the signal will originate from below the contamination layer allowing studies of the desired underlying interfacial region and buried interfaces. In addition, the energy can be tuned up and down the universal curve allowing nondestructive depth profiling.

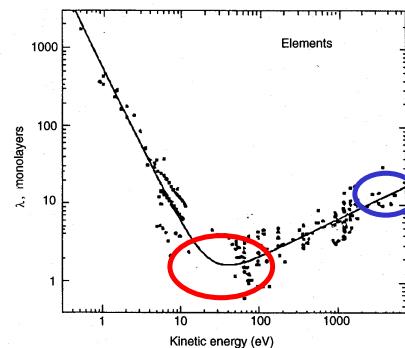


Fig. 5. The “universal curve” plotting the attenuation length of an electron as a function of the kinetic energy².

Conclusions

Sandia National Laboratories and NIST have engaged in collaboration to refurbish an existing beam-line at the NSLS to conduct NEXAFS and XPS with an incident energy range of approximately (1000 to 8000) eV. In addition, research is ongoing with an existing lower energy NEXAFS beam-line (U7A), which has been utilized to study a variety of interfacial issues with polymers including the fracture surfaces of filled composites and the surface orientation of thin polymer films.

References

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