

Discovering the Cause of Haze in Clear Polymers

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Introduction

SAN resins are random, amorphous copolymers of styrene (S; $C_6H_5CHCH_2$) and acrylonitrile (AN; CH_2CHCN) monomers. These materials are used in such applications as automobile instrument lenses and clear housings or covers for small appliances and other applications where one would like high clarity materials. Recently a performance problem was encountered with respect to subtle haze that was present in some SAN materials. Several analysis techniques were applied to attempt to find the cause of the haze, including looking for particles by visible light and a fractionation technique that is sensitive for the detection of crosslinked particles. Although none of these methods suggested a cause, laser light scattering suggested that if the haze was caused by particulates, the latter had to be 50-500 nm in size. Using scanning transmission x-ray microscopy we were able to prove that the haze was caused by phase segregation arising from AN composition drift. No other technique was able to identify the problem owing to the phase size and the lack of any solubility differences

Scanning transmission x-ray microscopy (STXM) uses differential absorption features in near edge x-ray absorption fine structure spectroscopy (NEXAFS) as a contrast mechanism. This provides STXM with an excellent chemical contrast and capabilities for identifying microscopic phases in polymers. With a spatial resolution approaching 50 nm, this technique was well suited to identify the nature of particulates, which cause the haze problem in the SAN.

Experimental Details

Two samples of SAN were analyzed. One was SAN that exhibited the haze issues and the other was a similar material that was clear. These samples were ultramicrotomed to produce thin sections about 100 nm in thickness.

The STXM analyses were performed using the microscope on beamline BL 7.0.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. This facility has been described previously [1]. X-rays produced by the undulator are energy selected (resolution $\sim 3000 E/\Delta E$; slits = 50 μm entrance and 50 μm exit) by the spherical grating monochromator, focused

onto the sample with Fresnel zone plate optics and light transmitted through the sample is down-shifted into the visible and detected using a photomultiplier tube. The sample is scanned in x and y using piezo-ceramic positioning to build up an image on a pixel-by-pixel basis. Spectra can be obtained in microprobe

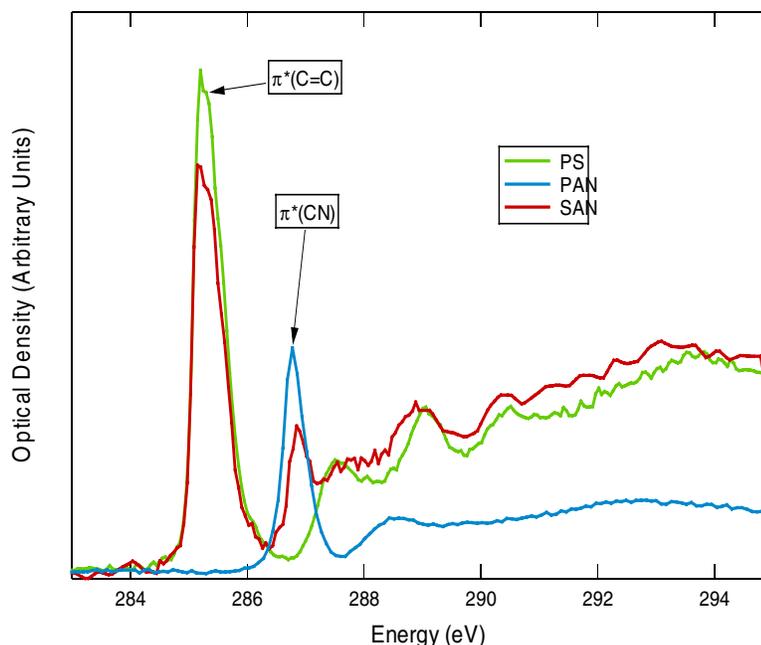


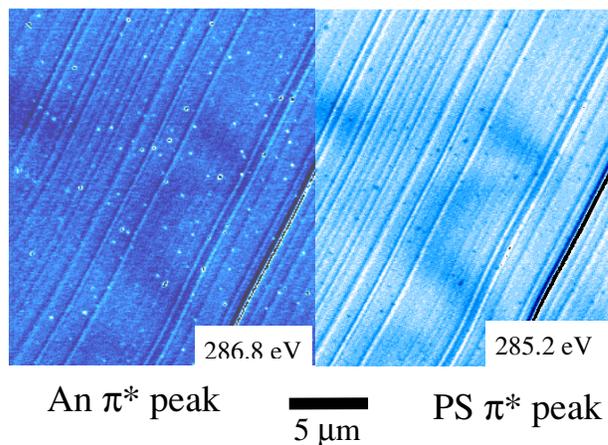
Figure 1. Comparison of the NEXAFS spectra of PS, PAN, and SAN.

fashion by pointing the beam at a spot of interest and scanning the wavelength or defocusing the microscope to cover a larger area. Since the focusing optics are highly chromatic, the focal distance of the zone plate must be scanned during a spectral scan, which leads to pointing errors on the order of one μm in a 40 eV scan. Alternatively, one can acquire images (or a single line scan) at a series of different energies and recover spectra at every pixel of the image. Realignment of the images to each other in software after the acquisition is then useful for minimizing the pointing errors. These spectral acquisition methods we call image stacks or linescans [2].

Results

Figure 1 presents NEXAFS spectra of Polystyrene (PS) polyacrylonitrile (PAN), and a spectrum of SAN from this work. The most intense peak in the PS spectrum occurs at 285.2 eV and is assigned to a transition of $\text{C}(1s) \rightarrow \pi^*(\text{C}=\text{C})$. The most intense peak in the PAN spectrum occurs at about 286.8 eV and is due to a transition of $\text{C}(1s) \rightarrow \pi^*(\text{C}=\text{N})$. Both of these peaks occur in the spectrum of SAN and their relative heights can be used as a gauge of the relative proportion of styrene (S) and acrylonitrile (AN) based units in the finished polymer [3].

Figure 2 compares images of the hazy SAN material recorded at different photon energies, chosen to



correspond to the energy of the NEXAFS peak maxima for the styrene and the acrylonitrile moieties (285.2 and 286.8 eV respectively). At the lower energy (285.2 eV) phases which contain a higher percentage of S will be darker than those with higher AN content. At the higher energy just the opposite relationship holds. The striations that are visible running from bottom left to upper right of each image are thin sectioning artifacts. In these images a second phase which consists of small particles 1-200 nm in dimension can be seen. This is the size of particles predicted by light scattering, which could be responsible for the haziness. When we obtain images at the same energies, from the competitive material, no evidence of particles was observed at either energy (not shown).

Figure 2. STXM Images of the hazy SAN recorded at 286.8 eV (right) and 285.2 eV (left) which correspond to the major peaks for acrylonitrile and styrene respectively.

To complete the analysis we measured stack spectra of the SAN sample and obtained spectra from the matrix phase and the small particulate phase. The spectra from both phases match that expected for SAN, but the spectra for the particles, had a slightly smaller AN peak indicating that the particles were S rich. The images in Figure 2 confirm that the particles are styrene rich, since when the image is obtained at the energy of the S peak, the particles become darker than the surrounding phase and there is a contrast inversion at the energy of the AN peak.

Conclusions

The hazy SAN was found to contain a dispersed second phase of particulate like material which appeared to be styrene rich SAN. Because the second phase was not picked up in experiments intended to detect gel particles, we must conclude that the second SAN phase has a similar molecular weight to the matrix and that the difference in AN content has resulted in phase segregation.

Acknowledgements

The STXM analyses were performed at the Advanced Light Source in Berkeley, CA on BL 7.0.1. We thank Stephen Urquhart for providing the NEXAFS spectrum of polyacrylonitrile. We thank George Meigs (ALS staff) for excellent help in setting up the beamline and microscope and for help in resolving computer issues during the analyses. The ALS STXM was developed by T. Warwick (ALS), B. Tonner (UWM) and collaborators, with support from the U.S. DOE under contract DE-AC03-76SF00098. The zone plates at ALS were provided by Eric Anderson of CXRO, LBNL.

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This work was supported by The Dow Chemical Company.

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