

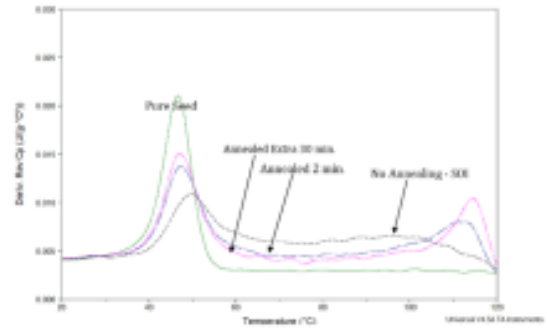
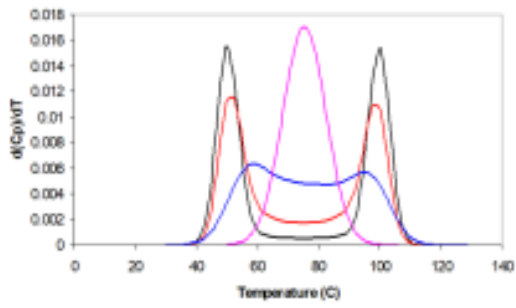
Did you know.....? for January/February 2020

Happy New Year!

This first "Did you know.....?" in 2020 is a follow up to the November-December 2019 edition in which we discussed the interfacial and mixed polymer content in structured (sometimes called core-shell) latex particles. In this edition, we present some thoughts about experimentally measuring the amount of the mixed polymers. Just to remind you, interfacial polymer comes about naturally during the second stage polymerization in the latex particles as phase separation and late stage ripening take place to create the final morphology of the particles. Depending on the reaction kinetics and polymer chain diffusion conditions during the polymerization, we know that the amount of this mixed polymer can be very different from one set of conditions to another. So, many times the particles will contain 3 phases of material - two pure (well, not always so pure) polymer phases and a mixed, or interfacial, phase. Each has certain volumes (masses) that can readily be measured in the DSC. The interfacial polymer is not effectively seen in TEM images, even when chemical staining is applied.

Differential scanning calorimetry is the well-known and widely used technique to measure the glass transition temperatures, Tg's, of polymers. Of course, it also measures the degree of crystallinity in polyolefins, etc. By extension, the DSC thermal signal is also sensitive to mixtures of polymers that have different Tg's. Noting that the glass transition is not a first order thermodynamic change (as are vaporization and freezing - large enthalpic changes at a fixed temperature) thermal analysis of polymers results in significant changes in heat capacity as the temperature increases through the transition region. Thus the DSC generates a signal that, when differentiated, results in a transitional "peak". The maximum in the peak signal is, by common practice, taken as the Tg. As we analyze a dried sample of composite latex particles we should expect to see 3 portions of the curve as mentioned in the above paragraph. While the signals for the 2 pure phases (if present) should be fairly sharp and at or near their expected Tg's, that for the interfacial material will be broad and distributed over the temperature span between those pure phase Tg's, as in the red and black curves in the left hand figure below. Should the composite sample contain no pure first or second stage polymer phase, the DSC signal would be broad and distributed over the temperature range between the pure phase Tg's, as in the blue and pink curves. The sharper pink curve relative to the blue one represents a more homogeneous, mixed polymer state.

A composite latex sample [acrylic seed, styrene(95%)-co-acrylic acid(5%) second stage] is shown in the right hand figure where a highly mixed polymer state is seen in the non-annealed sample. After annealing the sample in the DSC at higher temperatures, more phase separated states result. There is also the possibility of quantifying the amount of mixed polymer by comparing the signals of the original and the completely annealed conditions. These topics are discussed in detail in several of our STEP'n workshops, especially those for latex characterization (STEP 2) and core-shell morphology control (STEP 3). Scientific literature for these subjects can be found in our papers in *J. Polym. Sci.: Part B. Polym. Phys.*, 43, 2790-2806 (2005), *J. Polym. Sci.: Part B. Polym. Phys.*, 49, 1583-1589 (2011), and *Thermochimica Acta*, 568, 20-30 (2013).



As always, we welcome your comments and questions by contacting us via our website, www.epced.com.