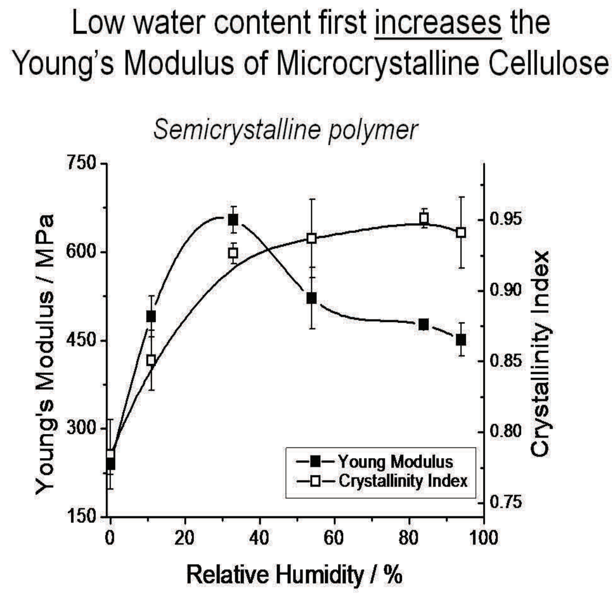
Polymer-based composites
as means of control of product performance for bioactive compounds

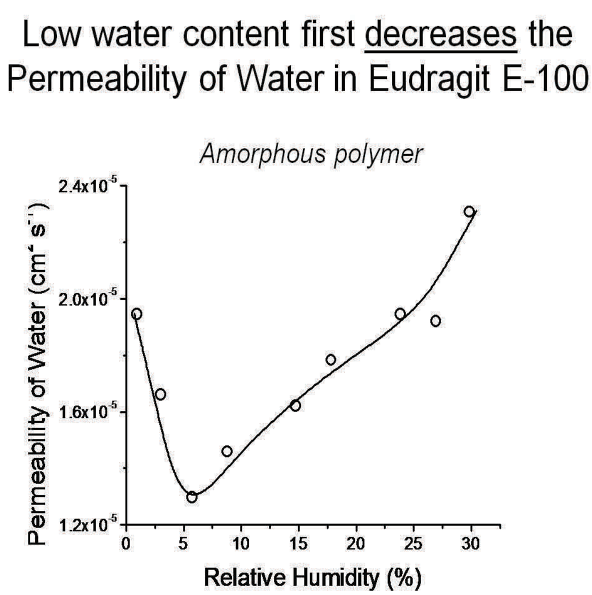
Antiplasticization

The interactions of water with polymers such as microcrystalline cellulose and starch present an effect that has received little attention. Water is a known plasticizer of these materials, having the effect of softening them. However, low water levels of the solvent have the exact opposite effect: antiplasticization. This means that small amounts of water actually harden the polymer before higher moisture levels begin to soften it. This phenomenon is actually widespread, it also occurs with other polymer-solvent combinations, such as those used in packaging. The adjacent figure shows how there is a range in the water content for microcrystalline cellulose (MCC), where its compacts are stronger than those having either higher or lower levels of water.



Is the Young's modulus the only property where this type of effect is observed?

Not by a long shot (*Tablets & Capsules* 2007, **5**, 22-33). In fact, this phenomenon is quite common and amazingly easy to reproduce in the laboratory, hence in practice, with different properties. We have found a similar effect on the permeability of water. There is a water level where the ability of water to permeate through the MCC compact is minimum, slower than in either dryer or wetter matrices. The practical implications of this phenomenon can be significant in cases where the presence of water is a concern. While being more difficult and more expensive, water removal to complete dryness may not be as effective as an optimally selected low moisture level.



The figure to the left shows the permeability of water vapor in the polymer Eudragit E-100 as a function of relative humidity (RH). With sorbed water acting as a plasticizer, the common expectation is that permeability ought to increase as the amount of water present increases. This is indeed the case, with the notable exception of the first portion of the curve. When water is present at very low levels, it depresses permeability before greater concentrations begin to increase it.

Antiplasticization is a rather general phenomenon with important implications to pharmaceutical products. You can readily see it in the mechanical, transport and structural relaxation properties of pharmaceutical polymers. Even though it is not widely recognized in the pharmaceutical field, this is a remarkably persistent phenomenon, whose impact goes beyond the physical properties of pharmaceutical materials and formulations. Antiplasticization is observable in the drug release performance of some formulations (*Colloids Surf. A*, **331**, 25-30 (2008).

A plasticizer can actually increase the glass transition temperature (T_g) of a polymer.

The figure to the right shows that low levels of water increase the Tg of Eudragit E100 (*Water Properties in Food, Health, Pharmaceutical and Biological Systems: ISOPOW 10*. Wiley-Blackwell, 2010, pp. 401-409). This means that at low levels, the plasticizer arrests molecular mobility. The significance of this finding has more to do with what is happening below the glass transition temperature than during its measurement. When we measure the Tg, we heat the sample, thus weakening (if not overcoming) the intermolecular interactions. If our polymer has a Tg in the order of 100°C (the boiling point of water) for example, there is little chance we are going to see the arrested mobility that took place when the same mixture was at 25°C. We can see the increase in Tg of Eudragit E100 because the Tg is close to room temperature. However, the decrease in molecular mobility would still take place even if the Tg were near 100°C. A glass transition measurement does not tell us much of what is happening at temperatures far away from