

## Why, After All, Are Chitosan Films Hydrophobic?

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Chitosan has a molecular structure very similar to that of cellulose, except that one of the –OH groups on each repeating unit (at the C2 position) is replaced by an amine group. Since chitosan has abundant water-loving groups and is soluble in weakly acidic aqueous solution, one might expect films prepared from casting of chitosan solutions to be hydrophilic. Experiments have shown wide variability, often indicating a hydrophobic character of the chitosan films. A 2008 article by Cunha *et al.* presented evidence suggesting that the apparent hydrophobicity was attributable to impurities. However, not all the evidence was consistent. In particular, extraction of chitosan film with methanol failed to increase the polar component of surface free energy. It is proposed in this editorial that the explanation can be found in a differing water-affinity of chitosan polymer segments, depending on their orientation. This explanation, if valid, is consistent with differences in the hydrophilic or hydrophobic character of different crystalline faces of cellulose.

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### Startling Findings Presented in 2008

A fascinating article by Cunha *et al.* (2008) considered possible ways to explain a wide divergence in the contact angles of water on the surface of chitosan films. They pointed to evidence that part of the explanation may involve hydrophobic contaminants in the material, *i.e.* extractives. The polar component of surface free energy was increased greatly when chitosan pellets were extracted using a series of methanol/water solutions of increasing methanol content, and finally by pure methanol. The authors concluded that the relatively hydrophobic nature of chitosan films, formed by evaporation of aqueous cast films, can be attributed to hydrophobic impurities that come to the surface during film preparation.

One aspect of the study, however, did not appear to have a full explanation. That is, when the extraction experiments were repeated in the case of cast chitosan films rather than pellets, the same extraction procedures were very ineffective with respect to increasing the polar component of surface free energy. The latter was evaluated by contact angle experiments, using principles explained by Owens and Wendt (1969). Cunha *et al.* (2008) attributed this surprising finding to the entrapment of hydrophobic monomers within the structure of the solid chitosan during its drying. In other words, they proposed that such molecules not only were able to express their hydrophobic nature, effectively covering the surface, but also they remained embedded into the chitosan with sufficient depth as to resist extraction. As a partial demonstration of this theory, it was found that the polar component of surface free energy on the chitosan films became much greater following scraping of the film surfaces.

## A Proposed Way to Explain the Results

Some similarly puzzling results, also involving hard-to-explain contact angles, were published in 2006, and this time the polymer in question was cellulose (Yamane *et al.* 2006). These researchers compared cellulose prepared in different ways, including regeneration from cuprammonium hydroxide or from ionic liquid solution. The authors found a strong correlation between the measured water contact angles and the orientation of the cellulose crystals in the surface films. The authors explained these results by proposing that different phases of cellulose crystals end up facing outwards depending on the conditions of regeneration. In addition, post-treatments by exposure of the cellulose to either a non-polar liquid or to highly polar glycerol were found to influence the resulting surface energy and degree of polar nature of the surfaces. Consistent with these findings, there has been discussion among scientists regarding a possible dual character of cellulose, involving both hydrophilic and hydrophobic aspects (Glasser *et al.* 2012).

It is known that during gradual drying of a polyelectrolyte film from aqueous solution it is possible for relatively non-polar polymers or their segments to migrate to the air-water interface (Khayet and Essalhi 2015). As in the case of the extractives mentioned at the start of this editorial, such migration achieves an arrangement that is thermodynamically favorable – providing a relatively low-energy surface facing the air. What is not known is whether a chitosan molecule is able to so arrange its orientation at a film surface during drying to achieve such effects. What would be required would be an orientation of those chitosan molecules at the surface of the film such that most of the polar groups, including both the amine and hydroxyl groups, are facing inwards or parallel to the surface. The formation of hydrogen bonds might be expected to drive such a reorientation during drying. One would anticipate extensive hydrogen bonding of all or most of these groups in various inter- and intra-molecular associations. Presumably, the absence at the chitosan film surface of groups capable of hydrogen bonding could account, at least in part, for the often-observed relatively hydrophobic nature of chitosan films (Cunha *et al.* 2008). The reported effects of scratching the film surfaces (Cunha *et al.* 2008) might be attributed to bringing about exposure of other, more hydrophilic crystal faces, as well as exposure of polar groups present within the chitosan.

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