

## Prepared Contribution

D Page, PAPRICAN

I wish to make a contribution that I believe is relevant to the mechano-sorptive effect(1). In this effect, a sheet under load creeps abnormally when cycled between two relative humidities. With each cycle an extra increment of creep is introduced, so that the total creep after a number of cycles can be many times the creep that would have occurred if the sheet had been maintained at high humidity.

It has occurred to me that there is a similarity between this effect and some observations made 30 years ago on the deuteration of the hydroxyl groups of cellulose(2,3). In that work it was shown that if cellulose (regenerated cellulose, wood pulp or cotton) is deuterated using heavy water, only a certain proportion of hydroxyl groups are substituted (about 60% – in the case of wood pulp). However if the sheet is dried and humidified using heavy water, a further increment of hydroxyl groups are substituted, and if this process is repeated many times eventually all the hydroxyl groups are replaced with deuterium. The authors interpreted these results as follows: during drying hydrogen bonds form within the cellulose and upon wetting some are broken and become accessible for exchange. However, on subsequent cycles, the hydrogen bonds that form are not necessarily the same of those that break during wetting. Thus while the inaccessible groups at any time contribute about 40% of the cellulose structure, they are not always the same hydroxyl groups. The inaccessible regions seem to be in a dynamic, rather than a static equilibrium with the accessible regions.

## Transcription of Discussion

This is a surprising result, since it suggests that, upon drying and rewetting, the amorphous regions of cellulose can migrate through the crystalline regions. Yet this is what the data are telling us.

This phenomenon, interpreted in this way, provides a ready explanation for the mechano-sorptive effect. The stress in paper activates the breakage upon wetting of those hydrogen bonds that are under the greatest shear or tensile strain. Upon drying the bonds that form are those that are under the least strain.

In this way flow can occur upon successive cycles as different highly strained hydrogen bonds fail upon wetting.

It may be noted that this phenomenon will apply to any solid which has two phases in dynamic equilibrium, each of which is accessible to a swelling agent that breaks intermolecular forces. This explains why the effect has been observed in systems that are non-cellulosic and even non-hydrogen bonding.

- (1) Byrd, V L., Tappi 55(11)1612(1972)
- (2) Lang, A R G, Mason, S G., Can J Chem, 38, 373 (1960)
- (3) Sepall, O, Mason, S G., Can J Chem, 39 1944 (1961).

**Mr P T Herdman, Arjo Wiggins R&D Limited, UK**

I think you will find this phenomenon referenced by Corte and Schaschek in the Das Papier publication at around the same time. (Physikalische Natur der Papierfestigkeit. Das Papier, November 1955, p519-530).

**Dr R Shet, Kimberly Clark Corp, USA**

What happens to the X-ray picture of that.

**D Page**

Nothing, because what happens is you get the same crystallinity all the time. It is just that the amorphous regions are migrating, as dislocations move in metal, through the crystalline region. You are getting the crystallisation and re-crystallisation.

**Prof J Roberts, UMIST, UK**

However if you are getting re-crystallisation you might expect it to re-crystallise in the thermodynamically more stable cellulose 2 form rather than cellulose 1.

**D Page**

You might if you have that particular theory of the differences between cellulose 1 and cellulose 2 but some of us don't have that theory.

**R Shet**

Pictures of the structure of amorphous and crystalline cellulose by x-ray crystallography do not agree with this. The crystallite is embedded in the amorphous matrix. According to Dr Blackthorn (case Western University) whole fibre is crystalline and so called amorphous region is on the surface of crystallite.

**Dr L Salmén, STFI, Sweden**

This is an intriguing explanation. Wouldn't you expect that the effect of decrystallisation crystallisation would be manifested as a change, a transition from cellulose 1 alpha to cellulose 1 beta. It is now possible to measure these transitions with for instance NMR. What do you think?

## **D Page**

Not necessarily so, it depends on what you believe is the difference between cellulose 1 and cellulose 2. It is well accepted that on a substrate of a particular structure you can preferentially form that structure on top of it. So it is possible that what you have in effect is a template for the existing crystalline cellulose 1 on which the cellulose is recrystallised. We are only talking here of one or two DP units decrystallising you know, not too many at once.

## **C Soremark, Assi Kraftliner, Sweden**

I was not really aware of the deuterium or heavy water experiment and I don't know if there are any isotopic effects involved in that. I do believe that there is something in what you are trying to describe, we haven't penetrated our model in that much detail yet. There are still some questions left. You say that crystallinity doesn't change at all. In our experiments in the compression creep we obtain a decrease in tensile stiffness and an increase in the hygroexpansion so we are left with some permanent global effects on a more macroscopic scale. Effects caused by increased number of microscopic compressions as a final state.

## **D Page**

I agree that the microcompressions increase because you have shear flow of the matrix between the fibrils. Once you have shear you produce microcompressions and once you've got microcompressions you have dimensional instability. I'm just putting the explanation of the mechanism at a lower level; namely the molecular level.