NOTES

Swelling of Crosslinked Cellulose Film in Water

INTRODUCTION

The moisture sorption property of a textile material is important in determining the comfort during wear of the material. In many cases moisture sorption has been used to study the fine structure of cellulose as exemplified by the work of Richter et al.[1] who determined the degree of crystallinity of cellulose by moisture regain. Gill and Steele[2] have studied the effect of relative humidity on the crease recovery of dry and wet crosslinked cotton and rayon and observed a decrease in moisture regain in the dry crosslinked sample and an increase with samples crosslinked in swollen state. It is possible that in the swollen state some of the original crosslinks due to hydrogen bonding may have been broken. Important contributions to the swelling of crosslinked polymers have been made by Flory[3] based primarily on the swelling of vulcanized rubbery networks by good solvents. The use of the Flory-Rehner equation derived therefrom in the swelling of crosslinked cellulose is precluded by the fact that cellulose is semi-crystalline while the equation is based on completely amorphous networks. White and Eyring[4] had limited success in their attempt to correlate moisture regain of cotton with that predicted from the Flory-Rehner equation. The literature amply demonstrates that crosslinking of cellulose fibers in the dry state greatly reduces their moisture absorption at various degrees of relative humidity as well as from liquid water at constant crosslink densities.

The work presented here is a study of the swelling of crosslinked cellulose film (cellophane) in water as a function of the crosslink density.

EXPERIMENTAL

The regenerated cellulose film used was made by the Dupont Company and had the trade name Cellophane PD-215. The crosslinking reactants were *bis*(hydroxyethyl) sulfone (BHES), obtained from J.P. Stevens & Company, Garfield, N.J. and dimethylol ethylene urea (DMEU), obtained from Rohm and Haas Company, Philadelphia as a 50% solution RHONITE-1. The crosslinking was done by the pad-dry cure method using zinc nitrate as the catalyst for DMEU crosslinking and potassium bicarbonate as the catalyst for BHES treatment. Details on the preparation of the samples and crosslinking have been described by Ibe and Valko.[5] The degree of crosslinking is represented by MCH, the molecular weight between chemical crosslinks. The assumptions and methods of calculating the MCH values can be found in ref. 5. It follows closely the earlier work of Frick et al.[6]

The swelling of cellophane samples in water was determined by wetting the sample in water for 4 hr, blotting between filter paper to remove adherend water, and weighing. This procedure is repeated about four times until a reasonably constant weight is obtained. The wet sample is then bone-dried and weighed. Assuming the specific volume of cellulose as 0.643 cm^3/g and water in cellulose of 1.00 cm^3/g, the volume and weight fraction of water in swollen cellulose was calculated.

The thickness of swollen and dry membranes was measured with a Pratt and Whitney Supermicrometer, Model B, courtesy of Van Keuren Instruments Company, Watertown, Mass. A pressure of 0.5 psi was applied. The area swelling was measured by taking a picture of the dry membrane and the submerged membrane after swelling overnight in water between microscopic slides. Photographs of the samples were taken with Polaroid camera attached to a microscope at a constant magnification of 8.75. The area of the image of the membrane was determined by a planimeter.

RESULTS AND DISCUSSION

The results presented in Table I show the following:

(1) The weight fraction of water in swollen cellulose decreases with increasing crosslink density. It is worth noting that the water content of the film even at the highest degree of crosslinking (ca.

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TABLE I
Swelling of Crosslinked Cellophane in Water, 25°C

Sample	MCH	Wet weight / Dry weight	Weight fraction water	Volume fraction water	Wet area / Dry area	Wet thickness / Dry thickness	Volume Fraction of Water (Calculated from area and thickness)
S_0[a]	∞	2.34	0.57	0.677	1.25	2.05	0.61
S_3[b]	7300	2.20	0.535	0.653		1.89	
S_4	5330	2.09	0.52	0.623		1.80	
S_5	2900	2.00	0.50	0.608		1.69	
S_6	1420	1.92	0.48	0.586		1.50	
S_7	1120	1.67	0.40	0.511		1.38	
X_5[c]	5300	1.93	0.48	0.586	1.20	1.58	0.48
X_7	2400	1.83	0.45	0.560	1.18	1.49	0.44
X_8	950	1.72	0.418	0.530	1.135	1.30	0.32

[a] S_0: pure cellulose.
[b] S_3–S_7: BHES crosslinked samples.
[c] X_5–X_8: DMEU crosslinked samples.

70 g of water per 100 g cellulose) is well above that of the uncrosslinked cotton, which is readily dyable. The observation clearly indicates that reduced swelling cannot alone explain the lack of dyeability of crosslinked cellulose.

(2) The thickness of the unswollen crosslinked film (2.49×10^{-3} cm for sample X_8 with the highest crosslink density) was found approximately the same as that of the unswollen uncrosslinked film (2.54×10^{-3} cm). Since the former contains 8% by weight add-on, its thickness should have increased. However, the measurement was carried out under atmospheric conditions and the reduced moisture regain of the crosslinked sample could have easily balanced out the increased volume in the anhydrous state. A value of 2.5×10^{-3} cm was used in the calculations for the dry thickness. It is probable that the bone dry samples would have been somewhat thinner.

(3) In all samples thickness swelling was much higher than area swelling. However, the anisotropy of swelling decreased considerably with increased crosslink density perhaps indicating that crosslinking has taken place preferably perpendicular to the plane of the film.

(4) The volume fraction of water calculated from the dimensional changes is lower for the crosslinked sample than the volume fraction calculated from the weight changes. This discrepancy can be due to the combined effect of two factors: (a) the water of swelling has in fact a somewhat lower specific volume than 1 cm^3/g used in converting the weight fraction into volume fractions and (b) the bone dry thickness was somewhat lower than the assumed value of dry thickness.

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