

The Use of Tensile Measurements in Following Cellophane Degradation*

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It has been known for a number of years that cellulose undergoes degradation in alkalis in presence of oxygen. Staudinger and Jurisch¹ have shown that the drop in molecular weight is quite small in the absence of air but substantial if air is present. It appears therefore that oxidation is the principal reaction.

We have repeated Staudinger's experiment both in presence of air and *in vacuo*, using glycerine-free cellophane. The change in DP (degree of polymerization) was followed by measuring intrinsic viscosities, and was compared with the change in tensile strength.

Figure 1 shows that degradation in the absence of air, after a rather fast initial rate, proceeds at a reasonably constant rate. Tensile strength also falls rapidly during the first 24 hr. but decreases gradually afterwards. The two curves follow substantially the same course.

The curves for the aerobic reaction (Fig. 2), on the other hand, are quite irregular. The fluctuations in DP can be explained on the basis of the preferential degradation² and the attendant solubilization of the shorter chains,³ resulting in a higher average molecular weight of the residual polymer.

However, this mechanism cannot explain the fluctuation in tensile strength because it is unlikely that the removal of any material, however small its contribution to the overall structure, could result in an increase of tensile strength. The improved tensile strength would not be surprising if the crystallinity of the cellulose had been increased. Mark⁴ has shown that an increase in crystallinity is accompanied by higher tensile strength. Battista⁵ found that hydrolysis, under mild acid conditions, results in increased crystallinity of cellulose. Our data seem to indicate that the crystallinity, and hence the tensile strength, may similarly be increased in a strongly alkaline environment.

* This work was carried out for the National Aeronautic Space Administration under contract NAS-5-2860.

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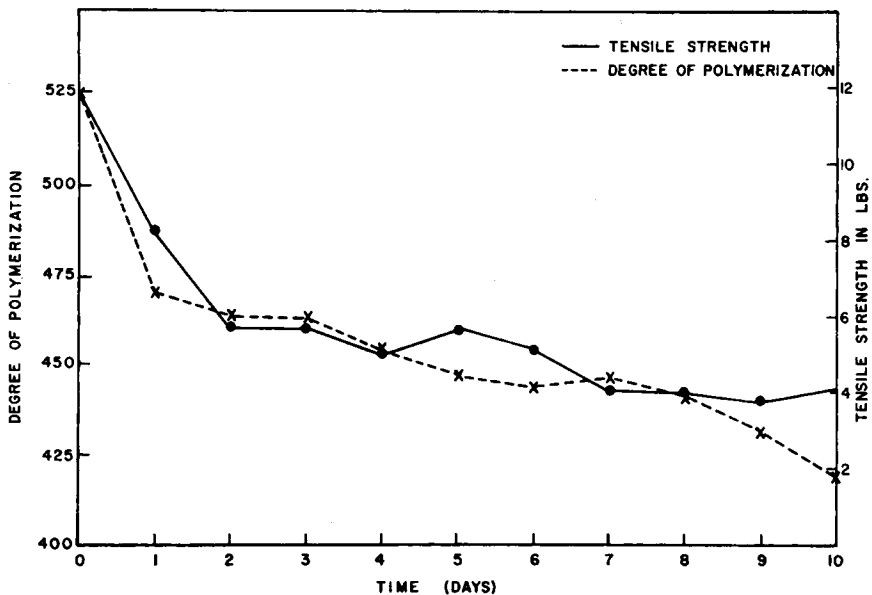


Figure 1. Anaerobic hydrolysis of cellophane in 40% KOH at 90°C.

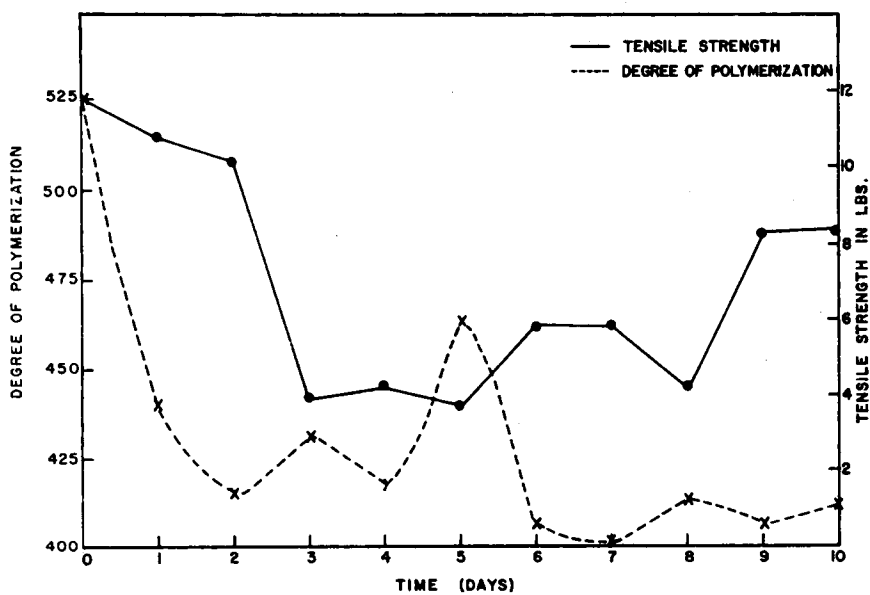


Fig. 2. Aerobic hydrolysis of cellophane in 40% KOH at 90°C.

Experimental

The material was DuPont's PUDO-600 cellophane, 0.0016 in. thick.

Aerobic Hydrolysis. Samples were cut $8\frac{1}{2} \times 4$ in., placed in large test tubes and covered with 40% KOH. The test tubes were covered loosely

to prevent contamination without preventing free access of air. The tubes were then placed in thermostated bath at 90°C . Individual tubes were withdrawn at regular intervals. The samples were consecutively washed with water, acetic acid, and water. When free of KOH, they were dried (1 hr. at 80°C). The samples were then used for intrinsic viscosity measurements (in cupriethylenediamine solution, method of American Viscose Corp.).

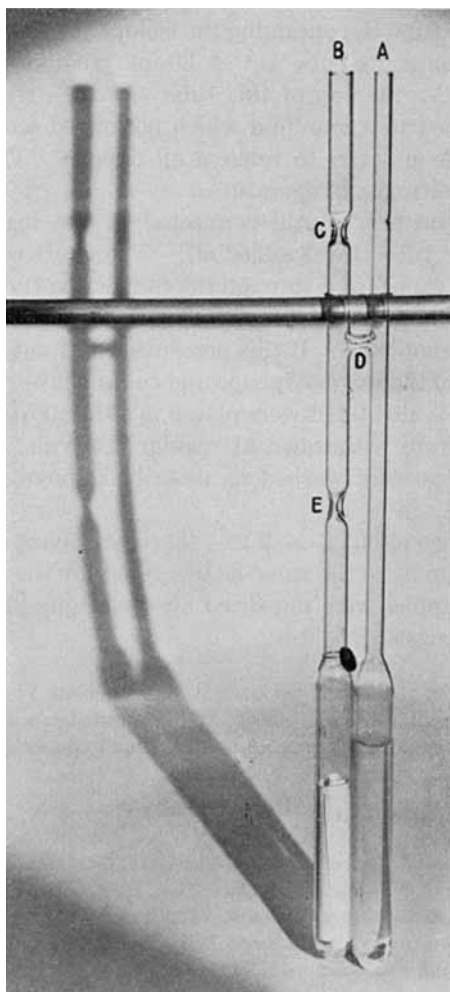


Figure 3.

The samples for tensile tests were also $8\frac{1}{2} \times 4$ in. A number of these samples were clamped in a Teflon frame; several frames were then placed in a resin kettle, covered with 40% KOH, and immersed in a thermostated bath at 90°C . Samples were withdrawn at intervals and washed as above. Test specimens 3×2 in. were die cut from the samples and used, while

still wet, to determine the tensile strength (Thwing-Albert tensile tester, Model 30 FM-24).

Anaerobic Hydrolysis. Samples 3×4 in. were cut by means of a steel die. The samples were placed in one compartment (B) of a double tube consisting of two tubes 18 in. long (A and B), connected by a $\frac{1}{2}$ in. long glass tube (D), about $12\frac{1}{2}$ in. up the side of the tubes A and B (see Fig. 3). The purpose of the short connecting tube is to permit transfer of the alkaline solution from tube A to tube B. Two constrictions (C and E) were now made on tube B, containing the cellophane; one above, the other below the interconnecting tube D. A 30-ml. portion of 40% KOH was poured into tube A; the top of this tube was then sealed. The end of tube B was attached to a manifold which permitted alternate evacuation and sweeping with nitrogen to remove all oxygen. The apparatus was degassed at liquid nitrogen temperatures.

While the apparatus was still connected to the manifold, the upper constriction (C) on tube B was sealed off. The KOH was now allowed to melt and was then transferred through the connecting tube D into tube B.

(The purpose of the double tube was to avoid freezing the solution in contact with the cellophane. If this precaution was not taken, air bubbles clung tenaciously to the wet cellophane and could not be removed.)

A number of the sealed tubes were placed in a thermostated bath at 90°C . Individual tubes were withdrawn at regular intervals, the KOH was removed, the samples were washed as described above and then used to determine the DP.

Tensile samples were cut 3×2 in. The hydrolysis apparatus (double tube) and procedure were the same as described for the DP measurement, except that the samples were not dried after washing but used wet to determine tensile strength.

We wish to thank Dr. Rosser and his associates at American Viscose Corp. for helpful discussions and for significant assistance. We acknowledge with thanks permission from the National Aeronautic and Space Administration to publish this paper.

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Synopsis

Comparisons were made of changes in molecular weight and in tensile strength of regenerated cellulose after exposure to 40% KOH at 90°C ., for varying lengths of time. In the absence of air, both parameters decreased in a fairly consistent manner. In the presence of air, an initial steeper drop was followed by an irregular up-and-down pattern. The theory is advanced that the increase in tensile strength was caused by increased crystallinity.

Résumé

Une comparaison a été faite du point de vue changement de poids moléculaire et résistance à la traction de la cellulose régénérée, après avoir été exposée au KOH 40% à 90°C. pendant des durées de temps variables. En absence d'air, les deux paramètres diminuent d'une façon normale. En présence d'air la décroissance plus prononcée était suivie d'une région de sauts hauts et bas irréguliers. On propose une théorie suivant laquelle l'augmentation de la résistance à la traction était causée par une augmentation de cristallinité.

Zusammenfassung

Die Änderung des Molekulargewichts und der Zugfestigkeit von regenerierter Cellulose nach Einwirkung von 40% KOH bei 90°C durch verschiedene Zeiten wurde verfolgt. In Abwesenheit von Luft nahmen beide Parameter in übereinstimmender Weise ab. In Gegenwart von Luft folgte auf einen steileren anfänglichen Abfall ein unregelmässiger auf- und abwärtsgehender Verlauf. Es wird angenommen, dass die erhöhte Zugfestigkeit durch eine höhere Kristallinität verursacht wird.

Received February 25, 1963