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Kinetics of Cellulose Fiber Degradation and Correlation with Some Tensile Properties to Plan Consolidation or Lining Interventions

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Abstract

In its native state, cellulose is characterized by a high degree of polymerization (DP) and, like most fibrous materials, good tensile properties. However, these characteristics are influenced by several chemical and physico-chemical processes. Some heterogenous degradation phenomena have been investigated in this study by evaluating the effect of light, temperature and acid hydrolysis on two cellulosic materials: flax and cotton. Both separate and combined effects were studied. The degradation reactions, which were evaluated by determining intrinsic viscosity values ($\Delta l/\Delta P$), develop in two steps at different rates. The possible relation between kinetics and yarn tensile properties were also investigated and are of importance in extrapolating useful indications on the future life time of the art object and on the use of consolidation which is an appropriate conservative intervention before lining becomes really necessary.

Keywords

Flexible supports, linen, cotton, kinetics of cellulose degradation, tensile properties, consolidation, lining

Preamble

To project preservation interventions correctly on canvas painting supports, the restorer must first carry out the necessary cognitive investigations on the fibers. The most common investigations[1] do not only offer indications on the type of fiber and the state of conservation (degree of polymerization, biological attack and chemicophysical degradation),[2] but also give essential correlations from which to evaluate the behavioral data of the material (tenacity and ultimate tensile strength) and can also furnish indications on the future life probabilities of the art object; the latter is an aspect of even more relevance to the restorer.

Knowing the type of fiber – and therefore its behavioral characteristics determined from its constituent elements, knowing the cause and the level of degradation, and, finally, knowing the environment in which the work will be kept, one can forecast a reasonable approximation of the future life of the object.

In other words, the restorer is able to hypothesize on the amount of time the work will survive after an intervention which, in the specific case of cellulosic supports, would be consolidation or lining.

The degree of polymerization of the fiber gives some conventional values (it will be recalled that this refers to a small portion of material; the sampling may involve only a few fibers of a single strand from a significant area of the support), but a given value on its own does not automatically justify the necessity of a specific operation;[3] the restorer must evaluate, in the case of each specific work being examined, whether, for example, a degree of polymerization (DP) of 300 warrants a lining or simply a suitable consolidation. In this case the correlation with the tensile properties becomes the determining factor to study.

It is significant to know the environment with which the work has been interacting and with which it will again be interacting, both to obtain a possible dating of the work and, in the planning stage of any possible operation, to forecast how much additional life the restoration will give to the painting.

If consolidation is not carried out, for how much longer can the present behavioral characteristics of the support be counted on? And if carried out? Do the tensile characteristics of the support justify the execution of a lining?

These questions are answered by the present research into the kinetics of degradation.

Introduction

Thermal, hydrolytic, photolytic, photochemical and enzymatic degradation of cellulosic fibers is essentially due to the scission of cellulosic chains, which can be regarded as a number of bonds being broken.

The degradative scission can be followed by measuring the change of the intrinsic fluidity $1/[\eta]$,[4–6] expressed as the inverse of the average degree of polymerization (1/DP). In the literature[7–9] it has been demonstrated that no decrease occurs in the rate at which the chains are being broken.

The random scission of bonds in a linear chain polymer follows a first-order kinetics rate law:

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$$dN/dt = KN \qquad (1)$$

where N is the total number of bonds between monomer units, t is the time and K is the observed rate constant. This relationship may also be expressed in terms of the fraction of the total number of available bonds, $1 - 1/DP_n$, where DP_n is the number-average degree of polymerization:

$$d[1 - (1/DP_n)]/dt = K[1 - (1/DP_n)]. \qquad (2)$$

This equation can be simplified when only a small fraction of the bonds have been broken:

$$\{[(1/(DP_n)_t] - [1/(DP_n)_0]\} = \alpha K't \qquad (3)$$

where α is a measure of the bonds' accessibility and K' is the rate constant for the rate of bonds being broken in the anydroglucose chains. The chain breaking rate follows simple zero-order kinetics.

In zero-order chemical kinetics, an equal number of bonds are broken in a given length of time. Moreover, for a randomly degraded polymer, the number-average degree of polymerization, DP_n, is approximately half of the weight-average degree of polymerization, DP_w, which can be correctly measured by viscosimetry. Therefore, replacing DP_n with $DP_w/2$ in equation (3) and multiplying by a factor of 100, we obtain the expression:

$$100[(2/DP_w)_f - (2/DP_w)_0 = \alpha K''t. \qquad (4)$$

The left-hand side gives the percentage of the initial bonds that have been broken.

In this paper we consider the kinetics of cellulose fiber degradation caused by light, heat and acid-catalyzed hydrolysis (heterogeneous hydrolysis).

As we know well, degradation also causes changes in a wide range of macroscopic properties,[10] e.g. in tensile strength. The decrease of yarn tensile strengths (mainly load breaking and specific stress or tenacity) compared to the $2/DP_w$ changes has been studied.

Experimental

Materials

Raw and bleached cotton and raw flax fabrics were examined. The removal of impurities was carried out by Soxhlet treatments with warm water and petroleum ether for 1 h for each treatment. The fibrous materials were washed several times in distilled water and finally stored in the dark at 20°C, 65% relative humidity (RH).

Heterogeneous acid hydrolysis

Bleached cotton fabric was treated in 1*N* hydrochloric acid at 20°C for different lengths of time. The pH of the solution and the relationship between the weight of cotton and the hydrolytic agent were kept constant . The samples, removed at different times, were washed repeatedly in distilled water at 20°C until free from acid and then conditioned at 20°C, 65% RH.

Exposure to artificial light

10 × 4.5 cm fabric samples were put in standard specimen holders and exposed in a high-pressure xenon arc apparatus (Xenotest Hanau 150 S). The instrument was operated at 45°C, 65% RH, and equipped with Pyrex-glass filters that eliminate UV radiation below 290 nm. These filters simulate the ozone-layer filtering effect of the radiation from the sun.

Thermal degradation

Fabric samples were thermally treated in a laboratory oven at 70°C with 10% RH in dark conditions.

Viscosity determinations

Viscosity was measured in 0.5 M cupriethylenediammine (CuEn) at 25°C with a Sappet viscosimeter. The intrinsic viscosity [η] was determined according to UNI 8282, which partially agrees with ISO 5351/1. Values for the viscosity-average degree of polymerization were obtained by multiplying the intrinsic viscosity by a factor of 1.5.

Tensile properties

Tensile properties (breaking strength, tenacity) were determined on warp yarns extracted from the fabrics and conditioned at 20°C, 65% RH. Their breaking loads were determined at a gauge length of 8.0 cm and a rate of extension of 20 mm min^{-2} on an Instron mod.1122 apparatus. The reported values of the retained breaking strength were based on the breaking load of yarns extracted from untreated fabrics.

Results

If equation (4) is used to follow the overall course of the heterogeneous degradation of cellulosic polymer, it is possible to recognize more distinct stages.[4] The rapid initial stage, not revealed in these experimental conditions, is considered to represent the breaking of a limited quantity of 1,4-β-glucosidic bonds that are particularly sensitive.[11–13]

The second stage proceeds at a slower rate and was attributed to the breaking of 1,4-β-glucosidic bonds located in the amorphous region.[14] The third one indicates that the degradation proceeds at an extremely slow rate, while DP values are approaching the levelling off degree of polymerization (LODP).[15]

In this paper the change in the number of bonds broken in cotton and flax is first examined, under degradation caused by photolysis, heterogeneous acid hydrolysis and thermal aging. DP_w values of the different starting materials at time 0 are reported in Table 1.

Table 1. DP_w and percentage of bonds broken N_t (%)at the break time (t) of degradative actions, photolysis and acid hydrolysis; $N_t = 100[(2/DP_w)_t - (2/DP_w)_0]$

Materials	Degradative action				
	None	Photolysis		Acid hydrolysis	
	$(DP_w)_0$	$(DP_w)_t$	N_t (%)	$(DP_w)_t$	N_t (%)
Raw flax	3,060	340	0.52	–	–
Raw cotton	2,610	380	0.45	–	–
Bleached cotton	2,405	–	–	330	0.52

The degradative scission of cellulosic chains can be considered in terms of two sets of zero-order kinetics: the initial stage (first kinetics) is always the fastest. As is well known, in zero-order kinetics the number of bonds broken is constant in time. In Figure 1 the data are plotted in terms of percentage of the initial number

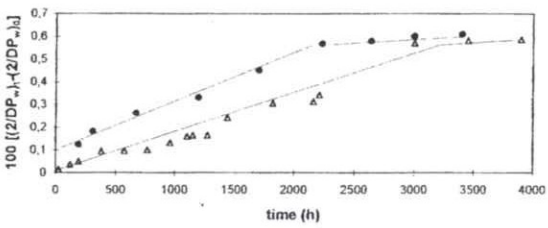

Figure 1. Percentage of bonds broken as a function of time of exposure to xenon arc lamp: ● raw cotton; Δ raw flax

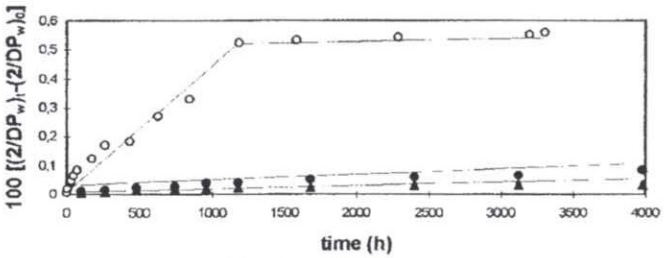

Figure 2. Percentage of bonds broken as a function of time of heterogeneous acid hydrolysis (open symbols) or thermal aging (70°C) (filled symbols): ○ bleached cotton; ● raw cotton; △ raw flax

of bonds that have been broken, $100[(2/DP_w)_t - (2/DP_w)_0]$, versus time of exposure to xenon arc lamp of raw flax and cotton. The first kinetics for raw cotton is faster than that of raw flax, while the second slower stage is characterized by a similar rate for both.

Further, the apparent break occurs when about 0.45–0.52% of bonds have been broken for both cellulosic materials (Table I). The heterogeneous acid hydrolysis (1*N* HCl at 20°C) of bleached cotton exhibits analogous behaviour, with two rates of reaction (Figure 2). These results indicate that the degradation rate of normal 1,4-β-glucosidic bonds is influenced by the accessibility of fibrous material during the different stages of hydrolysis.

As shown in Figure 2, only one rate of degradation is present when raw flax and cotton are thermally treated at 70°C. During the exposure time considered, the thermal aging causes only a small percentage of bonds to be broken (0.03–0.08%); as with photodegradation carried out by exposure to xenon arc lamp, the degradation rate is faster for cotton than for flax. As shown in Figures 3 and 4, a linear correlation between the decrease of the yarn's tenacity, the breaking strength retained and the DP_w changes was found, independently of the degradative action considered. It is interesting to note that these tensile properties also seem to follow two distinct stages, with a break at a value of about 0.35% of bonds broken. This value corresponds to $400 \leq DP_w \leq 450$.

As is well known, the tensile properties of a textile structure such as a fiber depend on the nature and arrangement of the component macromolecules. Tie molecules, linking the microfibrils, are more involved in the mechanical strength of fibers, while "*ciglia*" and folded end chains have less significance. During degradation, the breaking of chains can statistically involve all kinds of macromolecules; when about 0.35% of bonds have been broken, the degradative process has already compromised the action of the tie molecules. Further attack, however,

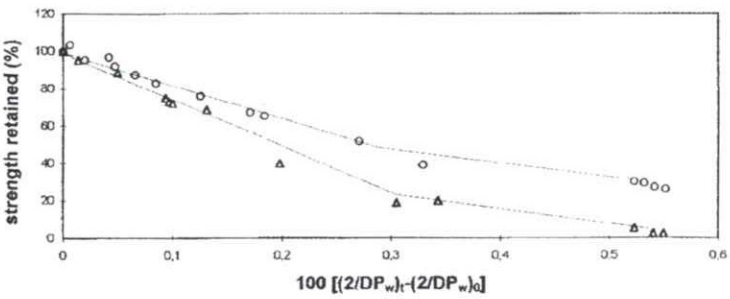

Figure 3. Breaking strength retained by warp yarns as a function of percentage of bonds broken: ○ heterogeneous acid hydrolysis of bleached cotton; Δ photolysis of raw flax

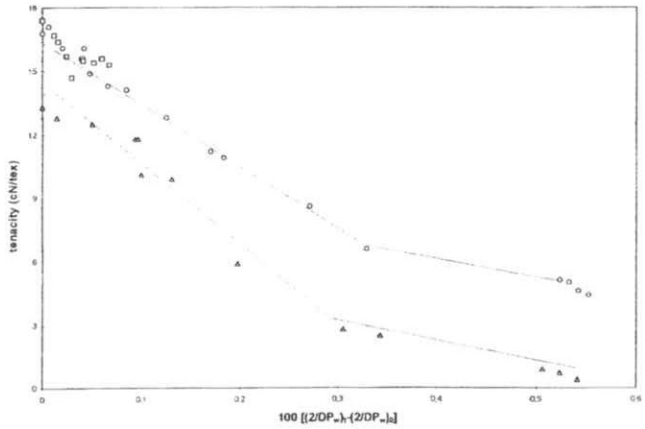

Figure 4. Tenacity of warp yarns as a function of percentage of bonds broken: □ heterogeneous acid hydrolysis of bleached cotton; △ photolysis of raw flax

included in the first step of degradation processes, will affect macromolecules that are less important for the tenacity of the fiber.

Conclusions

These results confirm the data already reported in the literature for the kinetics of degradation of cellulose fibers.[4,11] It was confirmed that degradation carried out by photolysis and heterogeneous acid hydrolysis followed two steps, each represented by zero-order kinetics. During the second step the value of LODP (level of degree of polymerization) is slowly reached. The kinetic rate of cellulosic degradation was slower for flax than for cotton. The main aim of this work was to check the relation between the changes in intrinsic fluidity ($1/[\eta]$) and some macroscopic properties such as yarn tensile strength and tenacity. The data obtained confirm this relation, which could be useful in predicting the durability of cellulose fibers manufactured under known degradative conditions.

Obviously the different values of strength retained in the transition zone between the two rates of decrease in strength shown in Figures 3 and 4 were influenced by the degradation mechanism (photolysis, hydrolysis) and by morphological and structural parameters of cellulosic materials.

On the basis of these results some comments can be made that determine different possible attitudes and operating choices. First of all, the further speed of degradation in supports that have already suffered a loss of tensile property characteristics is such as to ensure a better outcome by applying alternative methods to lining, i.e. consolidation; we know, in fact, that the results obtained are not limited to being positive immediately but the influence on the behavioral characteristics of the painting system go on with aging.

With regard to antique paintings, as we know that the level of degradation will be maintained near to the present value for a very long time, a less problematic intervention project is faced. Much more maintenance and preventive care is foreseen as being needed for contemporary works, with very careful checks on the microenvironment and with preventive intervention on paint films.

The presence of ground and paint films constitutes an element of protection for the canvas, a type of plastering of the support that is shown to be a great help.

A preparation with chalk and bonding agents blocks the macrodeformability of the canvas support and impedes the reciprocal movements between the warp and the weft of the yarn. Therefore only small dimensional variations are permitted and it is from this perspective that the importance of the effects of the consolidating agents on the mechanical properties of the work must be seen. With the right use of consolidation, an improvement in the compactness of the yarn can be anticipated. The material's resistance to lacerations diminishes drastically when reciprocal slip of the yarn warp and weft is impeded. In this way, in a material in which the yarn is not able to slip, the lacerations lead to subsequent breakage of various yarns, while if the same material were to maintain its mobility, the lacerations would be obstructed by the co-operative action of the strick of yarn that is formed perpendicularly to the propagation of the laceration.

Consolidating agents are not able to revive the integrity of the cellulose chain and consequently the degree of polymerization of cellulose. Their action is expressed only at the macroscopic level, anchoring the fiber material, which is reduced to fragments by the degradation, to the yarn.

Moreover, the consolidating agent can be considered suitable if:

- it increases the difficulty of initial elastic deformation of the support, that is if the elastic modulus of the yarn making up the support is increased (by elastic modulus we mean the physical mechanical property that expresses the load-stretch ratio);
- it reduces the deformability that can be caused by the absorption of the relative humidity (synthetic consolidating agents are, for example, generally not very hygroscopic);
- it obstructs the propagation of lacerations in painting supports, so that a not excessively rigid support is preferable.

Therefore, it is of particular importance to select support consolidation interventions using materials that really give to the fiber a protection from stress and suitable behavioral characteristics.

In short, consolidation is an intervention which can prolong the life of a canvas and which limits subsequent degradation. This method must therefore be carefully considered.

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