The Deterioration of Newsprint and Implications for Its Preservation

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Introduction

The preservation of newsprint and other acidic wood based paper objects presents challenges particularly in assessing the physical and chemical condition of the materials and the urgency of treating or copying them. The consideration of chemical and mechanical properties of papers gives a good indication of material lifetime. Mechanical testing of typical newsprint shows that lifetimes of about 100 years are common, and chemical testing shows that the effects on the surface of the fibers are more important than the eventual loss of strength of the fibers themselves.

Much of the information we have about history, science, culture, and civilization for the last 500 years is stored in paper-based formats. Unfortunately, changes in the technology of papermaking in the 19th century rendered the survival of much of the recorded information of a hundred year period problematic.

As its use spread in Europe from the late 1400s, paper was traditionally prepared from rag fibers of cotton or linen. Such paper was quite stable, and many books and documents not subjected to physical or environmental abuse have survived in quite good condition. The demand for paper eventually exceeded the supply of rags, and the use of other sources of cellulosic fibers such as straw and grasses was explored.

It was not until the late 19th century, however, with the development of mechanical equipment and chemical processes capable of converting wood to pulp that the most abundant source of cellulose could be exploited. Decades later, the relative impermanence of paper produced by these processes became evident (1). The inherent acidity of the wood, chemical processing, and additives such as rosin accelerated the breakdown of cellulose. Many wood pulp based books and documents degraded to the extent that they literally fell apart.

Once this was realized, more permanent papers were used for important purposes, but "ephemera" such as newspapers, magazines, and paperback novels continued to be printed on acidic paper. Because of the perception (often encouraged by the preservation industry) that all such papers and documents of this era are in imminent danger of turning to dust, many institutions have initiated programs to discard original objects such as newspapers usually, but not always, after converting them to other formats such as microform or digital files (the permanence of these will not be addressed here). The necessity and wisdom of such programs have been questioned (2).

The research reported here was conducted in order to understand better the processes causing the damage, the rate of these processes, and to provide information to make more informed decisions regarding the necessity or urgency of replicating or discarding acidic wood pulp based paper materials.

Methods

We tested newsprint that was stored under a variety of conditions. These included specimens from one source stored for up to 20 years in the laboratory at 40 to 50% RH and 21°C (conditions typical of the general environment of many museums and archives). The remaining newspapers were obtained from sources such as flea markets, garages, and shops and had been stored in uncontrolled environments.

Specimens were selected using no criteria other than that they showed no obvious environmental damage with mold or staining. Microscopic examination confirmed the newspapers were composed of wood based pulps with no rag content.

Mechanical tests were performed with screw driven tensile testers as previously described (3). We used full stress-strain measurements rather than techniques such as fold endurance or zero span testing. These other tests were developed by industry for measurement of durability, not of permanence. Durability is the ability to resist change during use, while permanence is the ability to resist change when not in use.

Fold endurance measures the number of times a paper sample can be folded to a specified angle under a specified force. It is a pragmatic test for which samples exhibit changes in results earlier in the aging process than for other physical tests. However, the results indicate more a measure of utility than of permanence. It is the opinion of the authors that fold endurance testing underestimates the ability of a paper object to be handled.

Zero span tests involve pulling apart samples with no initial gap between the grips used to hold the sample. This is meant to be a measure of fiber strength, but interpretation suffers from the fact that few fibers are aligned in the direction of the test. As will be shown below, bulk damage to the fibers is not the primary factor in the loss of integrity of the paper.

Uninked areas of newspapers were sampled at the edges and inked areas sampled near the center of the papers.

Stress-strain measurements were conducted with small increments in strain with sufficient time between increments to allow stress relaxation to occur. Such equilibrium stress-strain measurements minimize time-dependent behavior, and the results are more relevant to the physical and mechanical effects of routine handling. Breaking strain, breaking strength, stiffness, plasticity, and elasticity are derived from such measurements and relate more directly to chemical properties than the results of other tests. Stress-strain measurements are necessary for modeling behavior of materials and composites subjected to environmental changes or specialized storage environments (4).

Data was gathered for three specimens from each inked and uninked area, in both the machine and cross directions of the newsprint, for a total of twelve specimens of each newspaper.

Gas chromatographic analyses of monomeric and oligomeric saccharides were performed after aqueous extraction and a two-step derivatization to convert carbonyl groups to oximes and to trimethylsilylate reactive hydroxyl groups as described previously (5). Identification of components was made by comparison of retention times with standard samples. Concentrations were determined by comparison of peak areas with that of an internal standard (O-phenyl-β-D-glucopyranose).

Results and Discussion

Mechanical testing of samples stored under laboratory conditions showed that there was very little change in mechanical properties over the 20 year interval. The breaking strain exhibited little change over this period both in the inked and uninked areas as well as in the machine and cross directions.

The color of the newspapers stored in the laboratory had however turned yellow, a condition often misinterpreted as indicative of a weakened material.

Specimens of newspapers from uncontrolled environments were tested similarly. Figure 1 shows the breaking strains for inked and uninked samples in both directions for all the samples.

The plot clearly shows that the breaking strains decrease with time until they are less than the elastic limit, measured at 0.004 strain, and then become too fragile to test. This occurs at about 120 years of age.

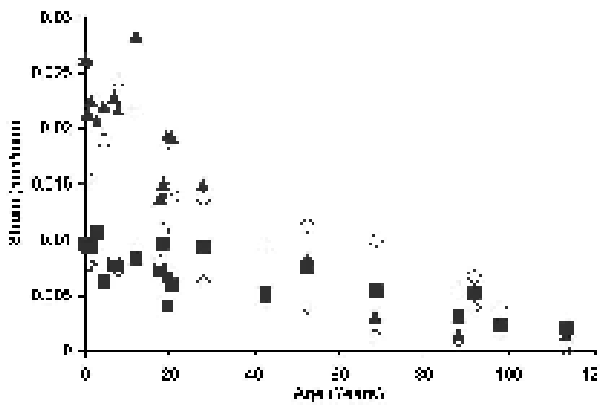

Figure 1. Breaking strains of newsprint samples as a function of age. Data is for both inked and unlinked areas, and in both the machine and cross directions of the samples. Data in cross direction, open circles are inked, solid triangles are uninked; in machine direction, open diamonds are inked, solid squares are uninked.

Papers fail the so-called “double-fold test” (in which a corner is folded to see if the paper breaks) when their breaking strain is less than about 0.01, depending on the thickness of the paper (5). Thin papers such as newsprint would pass the test even with breaking strains of less than 0.01. Failure of the double-fold test was noted for samples more than 80 years old. However, all of the newspapers tolerated routine handling with the exception of the final 113 year old specimen.

It has been shown previously that the concentration of soluble carbohydrates (mono- and oligosaccharides) in paper increases in samples subjected to accelerated aging as hydrolysis of cellulose and associated materials such as hemicellulose occurs, and that the increase in concentrations correlates with a loss of mechanical properties (6).

Similar trends were also noted for naturally aged samples (5). The concentrations of xylose and glucose in the newsprint samples generally increase with age for papers from the last hundred years (Fig. 2). Older papers had increased levels of saccharides compared to new papers, but did not fit in with the trends of papers produced later.

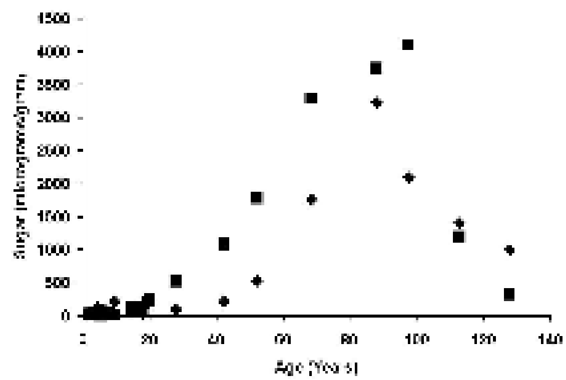

Figure 2. Concentrations of xylose and glucose in newsprint samples plotted as a function of age. Xylose is represented by squares and glucose by diamonds. Both exhibit a clear increasing trend with age for papers up to a hundred years old. Older papers break the trend, but still exhibit increased levels of saccharides compared to younger papers.

This break in the trend may be due to different storage conditions or more likely to changes in papermaking technology. The concentrations of xylose are greater than that of glucose in almost all samples. This indicates that the hemicellulose xylan, the primary source of the xylose, is more easily hydrolyzed than cellulose, the primary source of the glucose, since xylan is present in smaller quantities than cellulose.

Hemicelluloses in the paper fibers account for the large amounts of xylose present. Xylan, the major hemicellulose component present in wood, is composed primarily of xylose. Arabinose is associated with the xylose in xylans,

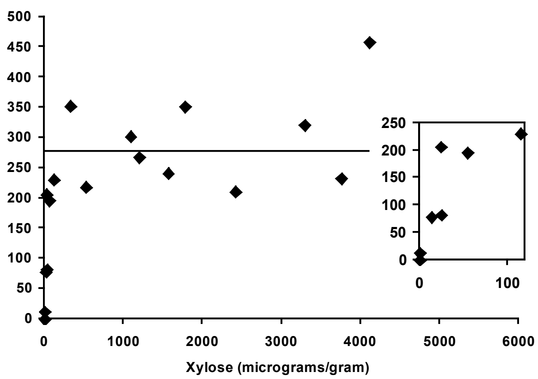

Figure 3. Concentration of arabinose in newsprint samples plotted as a function of xylose concentration. The insert shows a rapid initial increase in arabinose levels reaching a limiting value before significant amounts of xylose appear.

generally as a terminal group or single unit side group (7). Figure 3 shows the relationship of the concentrations of xylose and arabinose. The more sterically accessible and thus more readily hydrolyzed arabinose terminal and side-chain units are cleaved first as the hydrolysis of the xylan proceeds. Significant amounts of xylose and xylose oligomers appear only after the concentration of arabinose reaches a limiting value. It is interesting to note that no arabinose dimer or trimer was detected, confirming that arabinose occurs as isolated units rather than as multi-unit segments of the polymer.

The relationship of the soluble glucose concentrations to the structural behavior of the paper is illustrated in Figure 4. The glucose concentration increases as the breaking strain of the paper decreases. A power function fitted to the data is shown. The breaking strain drops initially with a small rise in glucose, and as the breaking strain reaches the elastic region of the paper (strain < 0.004), the glucose concentration increases rapidly.

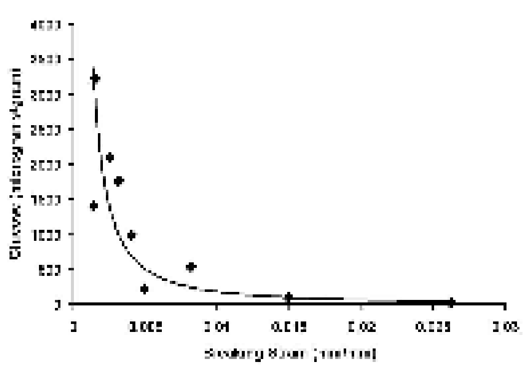

Figure 4. Glucose concentrations of the samples plotted as a function of the cross-direction breaking strain. The glucose concentration rises and the breaking strain decreases as hydrolysis takes place during aging.

That small amounts of glucose correspond to large decreases in the breaking strain indicate that much of the initial hydrolysis occurs at the fiber surface, reducing the fiber-fiber interactions responsible for the strength of the paper. Small amounts of hydrolysis at the surface of the fibers will have a disproportionate effect on the mechanical properties. The fit is the more remarkable since both the initial compositions and breaking strains of these papers as well as their environmental histories are unknown and variable.

Similar power curve relationships were exhibited when the concentrations of glucose, its dimer and trimer, and xylose were plotted against the breaking strain.

The data for wood based papers show that other associated carbohydrates are more susceptible to hydrolysis than the cellulose. In particular, the arabinose terminal and side groups in the xylans hydrolyze much faster than the xylose in the backbone of the xylan. Xylose and its oligomers, in turn, are produced at a faster rate than hydrolysis products of the cellulose, i.e. glucose or glucose oligomers.

Even though hydrolysis of the cellulose backbone is relatively slow, the ability of the paper to plastically deform decreases rapidly as even small amounts of glucose are produced. This indicates that the hydrolysis of cellulose occurs disproportionately on the surface of the fiber, where it has a much greater effect on the fiber interactions and properties of the paper. By the time the paper fibers themselves become significantly degraded, the paper has already lost much of its physical integrity.

The mechanical data presented here show that wood pulp newsprint typically has a useful lifespan of about a hundred years. Storage in controlled conditions should extend this lifespan by excluding pollutants and avoiding excursions to conditions of elevated temperatures and relative humidities that accelerate chemical deterioration processes. Storage at lower temperatures would also increase the lifespan. For example, based on activations energies of 21-24 kcal/mol for hydrolysis at various positions along the cellulose chain (6), storage at 0˚C would increase the lifespan by at least a factor of ten.

In addition to such "passive" approaches as modifying the storage environment, there are more active techniques to increase permanence. These range from deacidification and alkaline buffering for papers that are acceptably strong to reinforcement with a stronger and more stable layer. The least intrusive technique required to stabilize the paper is preferred. These approaches will not restore the paper to its original state, but will help to slow or prevent further deterioration. They can be expensive and time-consuming.

A final option for papers that cannot be saved is to copy them and discard the original. This is obviously a last resort. What is not obvious is when it is necessary. While the number of books and documents produced on impermanent paper is large, many of these are still in usable condition.

The Deterioration of Newsprint and Implications for Its Preservation, continued

The data presented here show that the degradation process is a slow continuous one, and that materials in salvageable states will remain that way for years. The remaining lifespan of even very degraded papers can be extended by lowering the temperature. The stress-strain data also indicate that criteria such as the double fold test overestimate change when applied to cultural material and indicate failure long before actual catastrophic failure.

Collections may be copied and discarded because of lack of suitable storage space or lack of funding to treat them, but their imminent demise should not be used as an excuse for such actions.

References and Notes

1. A history of the increasing awareness of paper deterioration and the determination of its causes can be found in S. Roggia, Ph.D. dissertation, Columbia University (1999) http://palimpsest.stanford.edu/byauth/roggia/barrow/) and references therein. The perspective of William Barrow, who publicized the problem, can be found in W. J. Barrow, R. C. Sproull, *Science*, 129, 1075 (1959).

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3. M. F. Mecklenburg, Ph.D. dissertation, University of Maryland, College Park (1984).

4. For a general description of modeling environmentally induced stresses, see M. F. Mecklenburg and C. S. Tumosa, in *Fiber Composites in Infrastructure; Proceedings of the First International Conference on Composites in Infrastructure* ICCI'96 Tucson, Arizona, H. Saadatmanesh, M. R. Ehsani, Eds. (Univ. of Arizona, Tucson, 1996), pp. 956-971; see M. F. Mecklenburg, M. McCormick-Goodhart, C. S. Tumosa, *Journal of the American Institute for Conservation*, 33, 153 (1994) for application to paintings and photographs.

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8. We thank Joseph A. Coles for assistance in microscopy and Marion F. Mecklenburg and Martha Goodway for helpful conversations.