# EFFECTS OF THERMAL AGING ON MECHANICAL PERFORMANCE OF PAPER

**B.T. Hotle[1], J.M. Considine[2*], M.J. Wald[1], R.E. Rowlands[3], and K.T. Turner[3]**
[1]*Dept. of Engineering Physics, University of Wisconsin, Madison, WI*
[2]*USDA Forest Products Laboratory, Madison WI*
[3]*Dept. of Mechanical Engineering, University of Wisconsin, Madison, WI*
**contact author: One Gifford Pinchot Drive, Madison, WI 53726; jconsidine@fs.fed.us*

## INTRODUCTION

Confidence in the performance of engineered paper products can be increased through knowledge of how mechanical properties such as strength and stiffness change with exposure to various conditions. The sensitivity of the hydrogen bond dominated structure as well the polymeric composition cause properties to be dependent on factors such as loading rate, temperature, and moisture content. Also, effects from environments present during storage and use can greatly degrade paper properties. A review article sponsored by the European Commission on Preservation and Access summarizes several paper aging studies in which the effects of temperature, humidity, gamma radiation, and various air pollutants on properties were examined [1]. In these studies on the aging of paper materials, the two primary aging mechanisms described are those due to hydrolysis and oxidation, along with the formation of additional cross-links [2]. Degradation of mechanical properties of paper with aging has been measured in the past by MIT fold endurance, tear resistance, and tensile strength, but the underlying mechanisms of changes with aging have not been addressed [3]. Classically, an Arrhenius relationship has been employed with measurements of degree of polymerization (DP) [4]. More recently, time temperature superposition (TTSP) has been combined with the Arrhenius relationship to describe DP along with monitoring of the acid sensitive linkages in cellulose [5]. These techniques allow for more accurate estimation of ambient aging rates, especially since acid detection methods allow for measurements in the ambient range.

A missing element of paper aging research is a description of mechanical performance with aging. Tensile strength cannot be predicted directly from DP measurements [4], and existing models do not represent the effects of aging on strength and stiffness. The primary aim of the present work is to characterize changes of mechanical properties, such as tensile response and dimensional stability, with aging and to develop time-dependent models to describe the behavior of paper components in stamp laminates. This includes understanding the underlying mechanisms of aging, such as changes of fiber properties or inter-fiber bonding, which lead to degradation. This research evaluates the effects of thermal aging on the properties of two different papers using tensile testing to characterize the tensile strength and initial stiffness, along with measurement of the equilibrium moisture content at 50% RH.

## 2B PROCEDURE

**Table 1** – *Aging Conditions*

| Temperature | Times |
|---|---|
| 105°C | 7, 14, 21, 28, 70 days |
| 120°C | 10, 20, 30 days |
| 130°C | 2, 3, 5, 10, 15 days |
| 150°C | 1, 2, 3, 6, 8 days |

The two papers used in this study were a Whatman® filter paper (filter paper) made with 100% cellulose from cotton linters, and a kraft pulp standard wove envelope paper (envelope paper). While aging, materials were placed in stacks inside an oven. The respective temperatures and aging periods are as shown in Table 1. After aging, the mechanical and physical properties, as described below, were characterized.

## RESULTS AND ANALYSIS

Post-aged tensile strengths for envelope paper are plotted in figure 1. Aged strength values are normalized with respect to the un-aged strength values (measurements on control material). Average unaged value for MD strength is 61.2 MPa for envelope paper with standard deviation of 4.9 MPa. The envelope material MD strength demonstrates an exponential decay without an initial increase (Figure 1), while CD strength (not shown) shows an initial increase followed by an exponential decay. Overall, the envelope material shows a greater loss in strength than the filter paper.

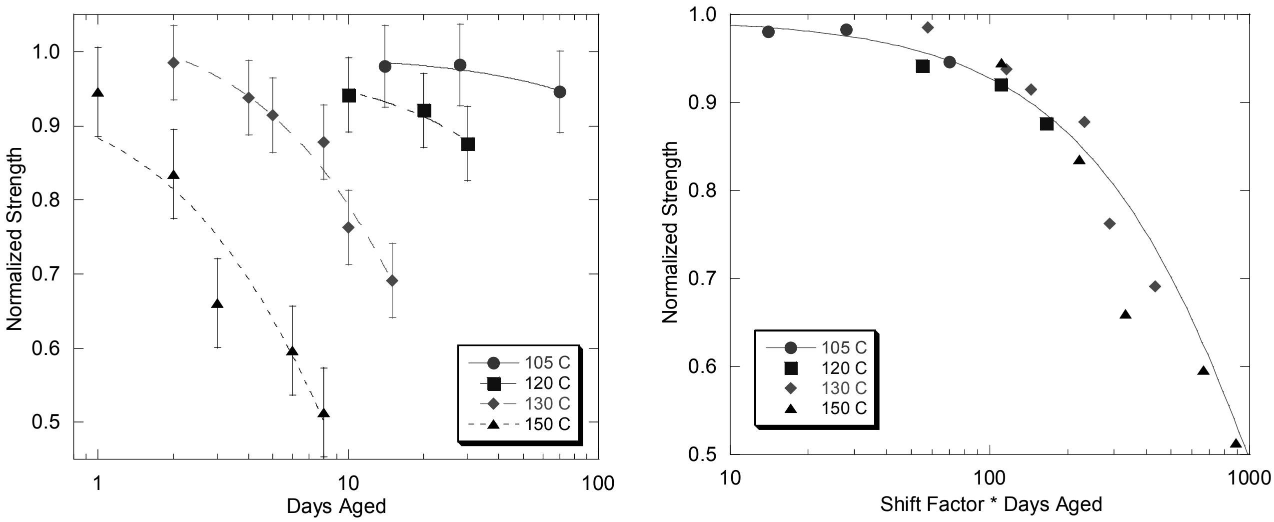


***Figure 1.*** *Plot of normalized strength values of MD envelope paper and resulting time shifted values. The data markers show the mean of 10 measurements at each aging condition, the error bars indicate the standard deviation, and the lines are an exponential fit to the values at each temperature.*

Similar to the method of Ding [5], TTSP was combined with the Arrhenius relationship to analyze the aging rates of the strength data. The Arrhenius relationship describes the degradation rate, $k$, as a function of temperature by:

$$k = e^{-E_a / RT}, \tag{1}$$

where $E_a$ is the activation energy, $T$ is temperature in degrees Kelvin, and $R$ is the universal gas constant. This equation implies that a shift in aging temperature is equivalent to a shift in aging time, and measurements of the rate at various temperatures allows the activation energy to be calculated and used to estimate the aging rate at ambient temperatures. Paper strength data in MD and CD at each temperature were fit with an exponential curve, shown for envelope MD direction in figure 1, a. Curves were shifted horizontally along the logarithmic x-axis by a factor equal to their exponent divided by the exponent of the fit for 105°C (Figure 1, b). This forces the curves to coincide to form the master curve, and the amount each curve is shifted is defined as the shift factor. Each of these shift factors is plotted as a function of inverse temperature in an Arrhenius plot. Since Eq. (1) shows that the rate has an exponential dependence on the activation energy divided by temperature, the slope of the line on the Arrhenius plot can be used to calculate the thermal activation energy.

Unlike strength, a shift-able trend in tensile stiffness with aging temperature is not apparent. Table 2 shows values of normalized initial stiffness at several aging conditions. Average unaged values of stiffness for the filter and envelope papers are 2.60 and 6.14 GPa, with standard deviations of 0.09 and 0.42 GPa. Generally, the results show an increase in stiffness in both material directions for envelope paper, though filter paper exhibits some stiffness loss in MD. Aging at 150°C has a significant effect, increasing stiffness in both materials and directions.

***Table 2.*** *Stiffness of filter and envelope paper at example aging conditions. Values are normalized with respect to unaged set.*

| Condition | | Filter Paper | | Envelope Paper | |
|---|---|---|---|---|---|
| Temperature | Days | MD | CD | MD | CD |
| 105°C | 7 | 0.98 | 1.03 | 1.08 | 1.17 |
| | 14 | 0.96 | 1.02 | 1.01 | 1.15 |
| | 21 | 0.97 | 1.02 | 1.01 | 1.01 |
| 130°C | 5 | 1.01 | 1.03 | 1.08 | 1.18 |
| | 10 | 0.92 | 0.98 | 0.98 | 1.21 |
| | 15 | 0.88 | 1.03 | 1.03 | 1.23 |
| 150°C | 3 | 0.94 | 1.05 | 1.01 | 1.18 |
| | 6 | 1.19 | 1.31 | 1.31 | 1.59 |
| | 8 | 1.23 | 1.30 | 1.44 | 1.67 |

Upon aging, both materials show a significant loss of measured mass for most conditions tested. Table 3 shows the percent mass loss of the materials after aging, with the envelope losing roughly 50% more mass on average.

***Table 3.*** *Equilibrium moisture content loss data.*

| Condition | | Percent Mass Loss | |
|---|---|---|---|
| Temperature | Days | Filter Paper | Envelope Paper |
| 105°C | 7 | 0.05 | 0.08 |
| | 14 | 0.10 | 0.09 |
| | 21 | 0.16 | 0.26 |
| 130°C | 5 | 0.46 | 0.70 |
| | 10 | 0.85 | 0.85 |
| | 15 | 1.01 | 1.67 |
| 150°C | 3 | 0.52 | 0.78 |
| | 6 | 1.59 | 2.33 |
| | 8 | 2.01 | 2.87 |

## DISCUSSION

As mentioned by Gurnagal et al. [2], there are three primary mechanisms of paper aging that have been identified. In the present study, aging was accomplished in a dry oven with temperatures above 100ºC, suggesting that moisture content is low and hydrolysis is negligible. Oxidation was demonstrated by yellowing in color and demonstrating increasingly brittle behavior in tension. This embrittled behavior could be due to shortening of the polymeric chain within the fiber from oxidation along with a reduction in free volume as seen with physical aging [6].

An interesting result was an increase of strength in the filter paper above 105°C and for the CD specimens of the envelope material. Considered with the increases in CD stiffness, this may be evidence of additional cross-linking between fibers as a result of dry thermal aging. In addition, a reduction of equilibrium moisture content may point to additional cross-linking sites, as fiber bonds may occupy former sites of water.

A concern which must be addressed is whether the mechanisms of thermal aging are similar to those which occur naturally. The fact that the filter paper significantly increased in strength in both material directions could be an indication of an artificial mechanism of aging at extreme temperatures such as 150°C. It is likely that removing moisture during aging plays a role in structural changes that occur at high temperatures. It is also noted that interactions between the hydrolysis and oxidation mechanisms may be important [4]. Dry aging is significant, in that it allows quantification of the oxidation mechanism of the cellulose fibers. The question of whether increases in strength and stiffness occur with natural aging processes still remains, though a past article identifies similar effects for naturally aged materials [5]. Regardless of the exact mechanisms leading to changes, the use of measures of mechanical performance as degraded by dry thermal aging should allow the ranking of stability of paper materials.

## ACKNOWLEDGEMENTS

We wish to thank Dan Chen and Chuck Delaney with Stamp Acquisition and Distribution of the United States Postal Service.

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