EFFECT OF MOISTURE AND TEMPERATURE ON THE MECHANICAL PROPERTIES OF PAPER

by

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Abstract

A molecular model involving only hydrogen bond interactions is successful in explaining the effects of temperature and moisture on the elastic modulus of paper. Concepts of glass transitions, free volume, and plasticization help explain the role of temperature and moisture in affecting paper's properties in terms that elicit the importance of paper's macromolecular structure. Ultimate strength properties, inelastic deformations, creep, and rupture, while dependent greatly on morphological and network characteristics, are influenced by temperature and moisture through paper's macromolecular nature and largely through processes that involve the making and breaking of hydrogen bonds. Phenomena involving the combined effects of temperature, moisture, and time are both the least understood in fundamental terms and the most promising in terms of their potential exploitation for developing new papermaking technologies.

Introduction

To the paper physicist, papermaking can be considered a series of complicated processes involving the hydration and dehydration, heating and cooling, and stressing and relaxing of an assemblage of fibers at different stages of consolidation. The combined effects of temperature, moisture, and mechanical stresses on the paper machine not only establish the process conditions for the runnability of a particular furnish, but also, in large part, establish the mechanical and other properties that the finished paper product will exhibit. The properties of the finished product can, in turn, be further modified by exposure to additional changes in moisture, temperature, and stress. Very often, however, an incomplete explanation of the behavior is embellished with a terminology or jargon that hides our ignorance of the basic physics involved. "Horrification," for example, is said to be responsible for the reduction in strength of pulps that have been allowed to dry prior to sheet manufacture. "Latency" removal is said to be enhanced by elevating the temperature of a beaten pulp. And paper is said to exhibit the "accelerated creep" and "premature failure" when loaded in environments of cyclic humidity. All of these, and many more, are examples of phenomena of which we have limited understanding of the physical processes involved.

The separate and combined effects of moisture, temperature, and stress -- all as functions of time -- control the theological behavior of paper by causing changes in both molecular interactions and structure. In order to understand more fully the physics of the phenomena involved, we must examine the nature of the molecular interactions and fiber structural features that control the various theological characteristics of paper.

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The theological behavior of a material may be divided into three general regimes characterized by three portions of the stress-strain curve. The first, linear, portion of the stress-strain curve represents the reversible, or thermodynamic property of the material, i.e., Young's elastic modulus. The second section of the stress-strain curve, showing deviations from linearity, reveals the viscoelastic and partially irreversible flow characteristics of the material. The third portion of the stress-strain curve, containing the rupture point, shows a truly irreversible aspect of the stress-strain process that characterizes the mechanical failure or ultimate strength of the material. As one proceeds along the stress-strain curve, the degree of difficulty in interpreting theological behavior in terms of structural features increases. The initial slope, revealing Young's elastic modulus, must for any material depend upon the average local features of the molecular structure of that material [1]. The point of rupture, on the other hand, may reflect a rather non-average feature of the structure; a defect, flaw or weak point of the assembly. It is clear then that because different structural features control different regions of the stress-strain curve, one region of the curve may respond differently from another to changes in temperature and moisture.

The Molecular Approach -- Factoring Out Structure

There have been two more or less distinct lines of approach to explaining the theological behavior of paper: The structural approach and the molecular approach. The assumption behind the structural approach is that the theological behavior of paper arises from the bending, stretching, and shearing of fiber segments between bond sites as well as the deformation of fibers at bond sites themselves [2]. This approach has included the many network models and deals with the structure of paper on a macroscopic, rather than a molecular, level.

The molecular approach attempts to describe the theological behavior of paper in terms of the molecular structure. Macroscopic stress-strain behavior is assumed to arise from interatomic potentials and the straining of molecular bonds. A strong proponent of the molecular approach to explaining the rheology of paper has been A.H. Nissan, who incorporated into his approach a number of simplifying assumptions to minimize mathematical formalism [3]. The major simplification is that the only interatomic potential that need be considered is that associated with the hydrogen bond, the ubiquitous aspect of molecular structure characteristic of cellulose and other hydrogen-bond-dominated solids. Nissan's molecular approach that emphasizes the importance of the hydrogen bond has been called the theory of hydrogen-bond-dominated solids. (Nissan's many contributions to this theory span a period of the. last 30 years; but the reference cited is the most comprehensive and updates many of the earlier contributions.)

Nissan's hydrogen bond theory that deals primarily with the elastic modulus of paper (and to a lesser extent, the flow portion of the stress- strain curve) sees the hydrogen bond as the predominant average local feature of the structure. It is distinct from structural models in that the elastic modulus of paper appears to be independent of its network structure. In its simplest form, one that assumes isotropy, Nissan's theory states that the elastic modulus of paper is proportional to the cube root of the number of effective hydrogen bonds per unit volume:

$$E = k\,(n)^{1/3} \qquad (1)$$

where E is the modulus of elasticity, n is the number of effective hydrogen bonds per cubic volume and k is the spring constant of the hydrogen bond. This expression states that the density of hydrogen bonds, along with the force constant (k) of the hydrogen bond determine the modulus of the material. Not only is the elastic modulus (E) viewed as independent of the network structure but independent of even the macromolecular structure and the covalent bond structure of the cellulose chain molecule. This idea that the elastic modulus of a material depends only on intermolecular interactions is not new to polymer science. Unfortunately, some fiber scientists are familiar only with cases where elastic properties are determined by the covalent chain structure of the molecules. These cases are those of elastomers (where the entropic configurations of the chain geometry dominate theological behavior at high strains) and textile fibers (where covalent bond characteristics along the chain molecules determine the fiber's axial elastic properties). Polymer scientists, however, understand that the elastic modulus of most polymers in the glassy state is determined primarily by the strength of intermolecular forces and not by the strength and geometry of the covalent bonds along the polymer chains [4]. The exception is the longitudinal Young's elastic modulus of highly oriented materials, such as single fibers, where applied forces can act primarily along covalent bonds of the polymer chains. But even for the case of fibers, the transverse Young's elastic modulus and shear modulus are still largely determined by intermolecular forces.

Intermolecular forces are generally characterized by polymer scientists in terms of the material's cohesive energy density (CED), a measure of the energy needed to separate and remove completely one molecular unit from its neighbors. For small molecules, CED is approximately equal to the heat of vaporization at constant volume, but for polymers it must be evaluated by indirect methods. The intermolecular forces between molecules determine CED, which generally correlates with the elastic modulus of polymers. Tobolsky [5], some time ago, pointed out a simple proportionality between the bulk modulus of polymers and their cohesive energy densities; and Holliday [6] pointed out a similar proportionality between elastic modulus and the CED of polymers. These observations that modulus is determined largely by intermolecular forces expressed in terms of cohesive energy density is very similar in essence to Nissan's suggestion that the elastic modulus of paper depends only on the density of hydrogen bonds, the type of intermolecular force that dominates in hydrogen-bonded materials.

For a highly bonded, unoriented sheet in the limit of zero strain, it is reasonable that the functional structural unit should be smaller than the individual fiber or fiber segment. By selecting the hydrogen bond to represent that structural feature, the characteristics of the hydrogen bond potential and the density of hydrogen bonds determine the elastic modulus seemingly independent of the other aspects of structure. Dodson and Herdman [7] have pointed out that, although Nissan's model cannot be realistic in detail, it provides a sound thermodynamic approach to the physical chemistry of paper. Two properties of paper that the molecular or hydrogen bond approach can help explain in both qualitative and quantitative terms are the effects on the elastic modulus that are caused by changes in either temperature or moisture.

Effect of Temperature on Modulus

Nissan [3] has provided in some detail a derivation of the temperature dependence of elastic modulus. (See also Dodson and Herdman [7] for a concise summary.) Based on a reasonable (Morse function) shape for the hydrogen bond potential, and using data obtained from the dissociation energy for ice, Nissan predicted a temperature dependence for the elastic modulus of cellulose to be

$$d \ln E/dT \sim -4 \times 10^{-3} \quad C^{-1} \qquad (2)$$

This means that the elastic modulus should decrease about 0.4% for every 1 C rise in temperature. Recently Nissan and Batten have rederived this relationship by a more rigorous route using no arbitrary parameters [8]. Using statistical mechanics and the well founded Lippencott-Schroeder potential for the hydrogen bond, they get a value for d ln E/dT approximately equal to $-2.4 \times 10^{-3} C^{-1}$. Nissan [3] compares the predicted value with measured values for a variety of cellulosics and finds the theory reasonably predictive. Values for d ln E/dT obtained from the literature ranged from -1.8×10^{-3} to $-6.3 \times 10^{-3\ C\text{-}l}$ for various cellulosics including paper. Two additional sets of experimental data on paper also give values for the temperature dependence of modulus that support the theoretically derived value. Salmen and Back [9] report that between -25 C and 175 C the elastic modulus of paper decreases at a rate of about 0.3% per degree. From data obtained in torsional experiments, de Ruvo et al. [10] report the relative change in rigidity of paper with temperature to be about -2×10^{-3} C-1.

Effect of Moisture Content on Modulus

The reduction of the elastic modulus with moisture content is another property of paper that is reasonably well described by Nissan's theory of hydrogen-bond-dominated solids. Nissan views the reduction of elastic modulus (E) with increasing moisture as resulting simply from a reduction of the number of effective network hydrogen bonds by the disrupting, competitive action of water. He concludes that the elastic modulus should show an exponential decline with moisture content (m.c.)

$$d \ln E/d (m.c.) = -K \qquad (3)$$

In the region of low moisture contents, below about 5% moisture, the value of K is predicted to be unity. At moisture contents above ~ 5% (and up to saturation), the value of K is predicted to be about 6.7. Nissan obtained this value by combining the ideal of hydrogen-bond- dominated solids with the cluster integral concept of water in order to help explain how one molecule of water added to a cellulosic network seems to disrupt several effective network bonds; i.e., a cooperative bond breaking effect. A value of 6.7 for K indicates that the decrease in elastic modulus is expected to be about 7% for every 1% increase in moisture. Data at low moisture contents are sparse, but for moisture contents above 5%, Nissan [3] has compared the experimental value. of K evaluated from results reported in the literature and, excludinq values obtained from sonic measurements, finds values ranging from 5.7 to 8.2. sonic and other dynamic methods of measurement [11,12] have shown exponential decrease of elastic modulus with increasing moisture content, but give smaller values for K, in the range of 2 to 3.

Factoring in Structural Considerations

Whereas the general features of elastic modulus and how it is affected by moisture and temperature are adequately described by the molecular approach, beyond the initial linear region of the stress-strain curve, structural features other than hydrogen bonds cannot be eliminated from consideration. Fiber morphology and network structure have an effect on all paper properties; and, although hydrogen bonding alone may predominate during the early stages of deformation and easily related to tensile modulus, it is not so easily related to theological behavior further out on the stress-strain curve where other structural features contribute. However, Nissan and coworkers have recently made attempts to relate the plastic or non-linear region of the stress-strain curve to the form of the hydrogen bond potential [13].

As strains become larger, however, the role of other elements of structure necessarily increases. The function of the cellulose chains can be looked upon as providing a framework, a geometric backbone, upon which the hydroxyl groups are arrayed. The morphology and structure of fibers determines how this framework is distributed through space, and thereby, how the hydrogen bonds are distributed. As strains increase, distortions arise not only from increases in interatomic separations. Distortion must involve movement of larger elements of the framework structure. Consideration of larger elements of structure also allows for the treatment of anisotropy, whereas the molecular approach deals easily only with the idealized case of uniform distributions in three dimensions.

One way to factor in the role of polymeric and fiber structure has been through considerations often invoked in polymer research; i.e., glass transitions, free volume, and plasticization. Through such considerations, it is possible to make connections with molecular chain mobility and the effects of both temperature and moisture on the mechanical behavior of paper.

Salmen and Back [14], in their quantification of the effect of temperature on elastic modulus, found a marked decrease in modulus about 200 C that resembled a glass transition. Their analysis of the effect water has on lowering elastic modulus also invoked a plasticizing role for water that seemed to meet the requirements for polymer theory. The glass transition temperature is the temperature at which an amorphous polymer changes from a hard glassy form to a more rubbery form. This transition, and similar secondary transitions, are related to certain movements of polymeric chain segments which become possible at higher temperatures because of thermal expansion and the resultant increase in free volume available. Salmen and Back reasoned that, especially in paper, cellulose is in an incompletely crystalline form, and accompanied by varying amounts of hemicellulose and lignin. These materials in intimate mixture most certainly interact and make the softening point (or points) of the composite fiber material less distinct. Furthermore, the composite's transition temperatures can be reasonably thought to be lowered by the plasticizing action of water.

Kubat and coworkers [15] and de Ruvo and coworkers [10] have also related elastic modulus to volume effects that result from either thermal expansion or hygroexpansivity. Paper's coefficient of thermal expansivity is of the order of $10^{-5}\ c^{-1}$, and is approximately 3 times greater in the cross-machine direction (CD) than in the machine direction (MD). Kubat and coworkers found

that the product of the elastic modulus and the thermal expansion coefficient is constant and independent of the direction (CD or MD) in which the measurements are made. de Ruvo and coworkers verified this observation and also found a similar approximate relationship for the case of swelling. The product of hygroexpansivity and elastic modulus was also almost constant, independent of the direction of measurement. The swelling relationship appeared somewhat improved, however, if the geometric mean of the dimensional swelling was combined with the geometric mean of the elastic modulus in the MD and CD directions. From the similarity of behavior of paper sheets and individual fibers, de Ruvo concluded that the network structure per se has little role in changes caused by temperature or moisture on elastic properties. Instead, response to changes in temperature and moisture are governed by properties and structures intrinsic to fibers and not a result of their network consolidation.

The addition of plasticizing water is qualitatively equivalent to an increase in temperature in that it provides an increase in the free volume available. Expansional strains, caused either thermally or by swelling, are inversely related to elastic modulus.

For reasons of convenience, polymer scientists speak in phenomenological terms of free volume, plasticizers, and glass transitions in order to explain mechanical properties of solids. Such language sometimes obscures the fact that all mechanical properties must have a basis at the molecular level in the cohesive forces holding molecules together. The effects of temperature and water which can be described in terms of increased free volume available are ultimately related to the intermolecular cohesive forces. The mean separation between interacting groups is determined by the balance of attractive and repulsive forces that make up the intermolecular potential energy curve. As the distance of separation between interacting groups is increased, either by thermal expansion or by swelling, the mean attractive force diminishes. This reduced attraction can be viewed as a type of bond-weakening, and, in the limit, as a type of bond-breaking. In this way, the concepts of glass transitions, plasticizers, and free volume afford a means of rationally connecting the mechanical properties of an anisotropic fiber structure to one whose elastic properties may also be described as hydrogen-bond-dominated.

Ultimate Properties

Paper strength properties as evaluated from tests to failure or rupture are more difficult to relate to the structural features of paper. Whereas elastic modulus reflects an intrinsic, average structural feature of a sheet, ultimate strength properties may be dominated by other less general features such as flaws and defects. Nevertheless, strength properties show many of the same correlations with temperature and moisture that elastic modulus exhibits. (Crook and Bennett's survey [16] remains the best overall source of general data on the effects of humidity and temperature on paper's ultimate strength properties.)

The generally held view is that paper strength varies with temperature and moisture content by affecting two basic factors. Page [2] has developed a network theory of tensile strength that identifies and tries to separate the effects of these two factors; fiber-to-fiber bonding, and individual fiber strength. Fiber bonding and fiber strength do not react to moisture in the

same way. Fiber bonding weakens as moisture is absorbed, while individual fibers become softer, more pliable, and stronger [16]. Physical properties that are measures of strength tend to have maxima at low or moderate relative humidity (RH). Properties for which flexibility is of importance will generally increase in value as humidity rises.

Tensile strength, for example, tends to have a maximum at RH between 30% and 50%. Above 50% RH, the tensile strength tends to show a moderate decrease until about 65% RH, when it drops sharply with further increase in RH [16].

Extensibility or strain to failure, on the other hand, tends to increase continuously over the whole range of increasing RH's. Strain to failure may increase over fourfold in going from 20% to 90% RH, an increase among the highest of any mechanical property [16].

Burst strength is a complex property that is influenced by both tensile strength and extensibility; and change in moisture affects the tensile strength and extensibility in opposite directions. Thus, of strength tests, burst shows the least effect of increasing humidity. A typical curve of burst value vs. RH shows little curvature with only a slight maximum between about 40% and 70% [16].

Tear resistance generally shows a continuous increase of between 0.5% to 1% for every percent increase in RH up to about 80% RH. At very high humidities tear resistance also decreases as very weakened fiber-to-fiber bonding allows fibers to slip apart more easily [16].

Fold endurance is a measure of flexibility and tends to show an increase of between 1% and 5% for every 1% increase in RH up to more than 80%. At very high humidities the small tensile load applied to the fold specimen probably becomes limiting and fold endurance, too, drops off near saturation [16].

The effects of temperature on ultimate strength properties tend to be less important than the effects of moisture and are often masked by the small changes in RH or moisture that accompany changes in temperature. Wink [17] has presented a graphical representation of the average effect of temperature on strength of paper while keeping moisture content of the paper constant (by adjusting RH). Over a range of about 30 C, he shows that tensile strength drops about 20%, or at a rate comparable to the loss in tensile modulus. Stretch, on the other hand, shows an increase of about 30%. Tensile energy absorption, being effectively the integration of tensile stress over strain up to failure, shows only modest changes (less than 10%) in the same temperature range.

Time-Dependent Effects

The most challenging unresolved problems in rheology of paper are connected with time effects. Paper exhibits a wide range of time-related phenomena, and the introduction of time into the already complicated inter-relationships of temperature, moisture, and paper structure increases the difficulty. (Kolseth and de Ruvo [18] have recently reviewed the time-temperature-moisture-dependent properties of paper, and their analysis can be considered the most up-to-date and comprehensive in the field.) There are three main areas of study in which

time effects are significant: 1) creep and stress relaxation, 2) duration lifetime/rate-of-loading phenomena, and 3)dynamic mechanical measurements.

Creep and Stress Relaxation

When a sheet of paper is subject to a constant stress, it will deform; and the strain will increase with time. Similarly, if a sheet is strained and held at constant dimensions, the initial stress relaxes with time. Both creep and stress relaxation have been described in terms of kinetics of hydrogen bond breaking [3]. Stressed hydrogen bonds are viewed as less stable than unstressed bonds. As the flickering hydrogen bonds open and close, stressed bonds tend to re-form in unstressed configurations. Because the stress relaxation process is viewed in terms of chemical bond rearrangements, the classical concepts of chemical kinetics apply. Both increased temperature and increased moisture promote both the creep and stress relaxation process [16]. The basic features of creep and stress relaxation of paper in both tension and compression are similar, however, the effects appear to be more serious in the case of compression. One area of intense current research involves the phenomenon of accelerated creep in cyclic humidity conditions [19, 20, 21, 22]. Whereas paper may exhibit creep rate at 90% RH that is several times the creep rate at 35% RH, if the same loaded paper sample is cycled between 35% RH and 90% RH, its creep rate can be over ten times the creep rate shown at the constant 90% RH [19].

Duration-of-load/rate-of-loading phenomena

Paper exhibits two related time-dependent rupture phenomena that influence its load-bearing capacity. If it is stressed to only a fraction of its short-term breaking stress and maintained at the stress over a long enough time, the paper will fail. It has been found empirically that for paper under constant stress, the logarithm of the time to failure varies inversely as the stress level [23]. A related time- dependent phenomena is the rate-of-loading effect. The breaking stress of paper increases as one increases the rate at which it is stressed. If the applied stress is increased linearly with time, the breaking stress increases with the logarithm of the rate of stressing [24]. For this reason, meaningful strength testing always requires a standardized rate of stressing (or straining).

Duration lifetime studies of materials can be aided by the use of a so-called “semiempirical” equation that has been credited to Zhurkov [25].

$$t = t_o \exp [1/kT (U - \gamma\sigma)] \qquad (4)$$

where t is the time to fail, T is the absolute temperature, k is Boltzmann’s constant, σ is the stress, U is an activation energy, and the symbols to and γ are constants.

A form of equation (4) was derived and used years earlier by Coleman to describe the duration-of-load and rate-of-load phenomena exhibited by nylon [26]. In Coleman’s analysis, the equations describing the duration- of-load behavior and rate-of-loading behavior arise from the integration of an equation he derived for the rate-of-creep deformation. Coleman’s fundamental equation, based on Eyring’s rate theory, involves an explicit temperature dependence. (For details see Coleman’s classic paper.) At fixed stress, Coleman’s equation

indicated that increased temperature will decrease a loaded specimen's lifetime, and this behavior has been confirmed for viscose yarn [27] as well as nylon.

Lundberg and de Ruvo [22] (see also ref. [18]) have reported the moisture dependence of duration lifetime for chipboard at three RH's. At a constant stress level, paper at a low RH will support a stress for a longer time before failing than at a high RH. Alternatively, paper at a high RH must be loaded to a smaller stress level in order to equal the duration lifetime of the same paper at low RH. Similar to the case of accelerated creep in cyclic humidity, Byrd [19] has reported the shortened lifetimes in both tension and compression of paper loaded in cyclic humidities. Similar findings were reported also by Lundberg and de Ruvo [22]. Understanding better this phenomenon of accelerated creep-rupture is crucial in the design of packaging and in the structural performance of paper in long-term exposures ty cyclic-humidity environments.

This phenomenon of creep-rupture in cyclic humidity probably arises because of the interference of coupling of two thermodynamically irreversible processes: sorption hysteresis and stress-strain hysteresis. The thermodynamic fundamentals of the coupling of deformation and sorption, the so- called mechano-sorptive effect, was provided by Barkas [28] ; but a complete description of the irreversible thermodynamics involved by the methods of either Prigogine [29] or Osager [30] is lacking. In mechanistic terms, the phenomenon is describable in terms consistent with the theory of hydrogen-bond- dominated solids [31]. During each adsorption leg of a humidity cycle, a "spreading pressure" pries apart two cellulose lamellae and intercalates a layer of water molecules, reducing the number of effective load-bearing elements. The subsequent reduction in humidity fails to reverse completely this process, because the restraining modulus is lower at the higher moisture content, and also stressed bonds have had time to re-form into stress- relaxed configurations. Failure can then be thought to be triggered, as in Coleman's creep-rupture theory, when the strain deformation exceeds a critical strain. A better creep-rupture explanation will probably involve consideration of the accumulation of nonrecoverable work, and the formulation of fatigue lifetime in terms of energy dissipation rather than as a result of a critical strain.

Dynamic mechanical behavior

When paper is subjected to a periodic stress, its strain response exhibits a time-dependent behavior that arises from its viscoelastic nature. If a simple harmonic stress is applied to paper, its strain response is also periodic by lags between the stress. This time lag can be measured in terms of a phase angle, δ, whose tangent is equal to the ratio of loss modulus to storage modulus. Tan δ is a measure of the energy lost due to internal friction generated in the sample during its cyclic deformation. When examined as a function of frequency of oscillation, the internal friction or tan δ exhibits a maximum whenever the elastic modulus undergoes a rapid change. In polymers, the frequencies at which energy losses are maximized have been interpreted as being caused by transitions from glassy to rubbery behavior. The wood polymers, lignin and hemicellulose, have been recognized as essentially thermoplastic polymers whose glass-rubber transitions are both

temperature- and moisture-dependent [32]. For example, whereas isolated dry lignin softens at a temperature close to 200°C, in water its transition is lowered to about 80°C - 90°C. Hemicellulose is even more moisture-sensitive; soften at about 55°C at a moisture content of 23%. The work of Kubat and coworkers [33] and de Ruvo and coworkers [10, 12] has verified that both increased temperature and increased moisture dampen the dynamic response of paper to cyclic stress.

An area of intense research interest has been the effect of changing moisture content on the dynamic loss property of paper [12, 21]. Kubat and Linbergsun [34] first reported that a sudden change in humidity causes a transient increase in mechanical damping and suggested that the damping was associated with the moisture diffusion process taking place in the paper during equilibration. A recent analysis by Back and coworkers [21] has discounted the importance of moisture gradients per se but emphasizes the fact that it is the change of these gradients with time that accounts for the damping effect. Htun and coworkers [12] have studied the dynamic mechanical behavior of paper during drying and attribute the transient damping as well as the increased modulus to the loss of mobility of amorphous components of the cell wall polymers. Understanding the dynamic behavior of paper in transient-humidity environments will certainly aid our understanding of how creep and failure are accelerated by cyclic humidity. whereas dynamic behavior may be explained phenomenologically in terms of chain motions and second order transitions, there is good reason to believe that this time-dependent phenomenon, too, is ultimately governed on the molecular level by the making and breaking of hydrogen bonds.

Temperature and Moisture Effects in Developing Technologies

The influence that temperature and moisture have in affecting the post-manufacture properties of paper is relatively direct. But the temperature, moisture, and mechanical stresses experienced by the fiber assembly durinig the manufacturing process also play important roles in establishing end-product properties. The tensile stresses that the paper web experience in the open draws and the compressive and shear stresses it experiences in press and calender nips, by affecting structure, orientation, and density, clearly have long-term effects on end-product properties.

During the modern papermaking process in which stress, temperature, and moisture are continually changing, their combined effects on structure and properties are profound and poorly understood. Tensile stresses that arise from the combined effects of machine draw and drying- shrinkage add to the other fiber-alignment causes of paper’s in-plane asymmetry. These tensile stresses affect not only dimensional stability, modulus, and strength properties, but also secondary properties such as opacity. The compressive action of a press nip primarily provides the driving force in dewatering the wet web, but also acts to densify the mat. With the advent of steam boxes, high-intensity presses and extended nip presses, the combined action of temperature and stress over time can have profoundly different effects upon the z-directional densification process. Similarly, the application of new technologies, such as press drying, impulse drying, and temperature gradient calendering, involve the combined effects of stress and temperature for periods of time during which the paper’s moisture content is changing. Coupling these new technologies with newer high-yield pulps, whose wood-polymer compositions

are different, has created a fertile field for research. The paper physicist can play an important role in this research by providing an understanding of how temperature, moisture, and the rheological- mechanical behavior of paper interact. This understanding can provide the basis for technological developments.

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