

**EFFECTS OF EXPOSURE TO ELEVATED  
TEMPERATURES ON STRUCTURE AND  
PAPERMAKING PROPERTIES**

**Project 3288**

**Report Two  
A Progress Report  
to**

**MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY**

**May 24, 1978**

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

This report describes two key sets of experiments carried out as part of our investigation of the effects of fine structure on pulp and papermaking properties. In the first set, fibers which were prepared by delignification at low temperatures were immersed in water in pressure vessels and exposed to elevated temperatures typical of commercial pulping processes. The crystallinity of the fibers increased, and with it were correlated an embrittlement and a general deterioration in papermaking properties and absorbency.

The second set of experiments explored the effect of reducing crystallinity on the properties of a commercial kraft pulp. The pulp was treated to attain the maximum possible degree of decrystallization, and its properties were evaluated. The results indicated that the elastic component of the response became dominant. Thus, although the tensile energy absorption and the stretch at failure were almost doubled, an excessive degree of refining was necessary, sheet densities remained relatively low, and the tensile properties of the handsheets were inferior to those from untreated pulp.

It appears that, at least with respect to handsheet properties, the optimum degree of crystallinity is intermediate between the levels attained in the two sets of experiments.

## GENERAL INTRODUCTION

One of the objectives set for this project, and discussed in Report One, is the exploration of the response of pulp fiber properties to changes in molecular organization. Effort in this area has involved investigation of the effects of exposure to elevated temperature, as well as the effects of modifying molecular organization in the pulp fibers by inducing changes in the polymorphic form of the cellulose in the fiber walls. In these explorations two key sets of experiments have established mileposts along the way. The first established that exposure to elevated temperature, as in commercial pulping operations, results in an embrittlement of the fibers which degrades properties inherent in the native fibers. The second set assessed the possibility of reversing this embrittlement by chemical manipulation of the fine structure of pulp fibers. The results of these experiments and some of their implications are discussed in this report.

The report begins with an account of preliminary examinations of the effects of elevated temperature on fiber structure and a description of the studies of paper-making properties which established the importance of these phenomena. These are followed by a discussion of the options that may be available for recovery of superior fiber properties. The option selected for pursuit in the second set of key experiments involves the treatment of commercial pulps to increase elasticity of the fibers, the results are described in the final portion of the report.

Our early work in this area has been outlined in Report One. In essence it demonstrated the possibility of changes in molecular organization of cellulose II upon heat treatment; an increase in the degree of order was observed when mercerized samples were annealed in glycerol (1). In later studies similar effects were observed upon exposing some native celluloses to elevated temperatures. Specifically, it was found

that fibers which are delignified at low temperatures and annealed in glycerol at 160-180°C undergo some increase in ordering at the supermolecular level, which is revealed by changes in the x-ray diffractogram. Measurements on handsheets made from the annealed fibers, as well as from unannealed controls, revealed that the increase in supermolecular order has correlated with its changes in the papermaking properties of the fibers. These results were interpreted in terms of analogies with the behavior of synthetic polymers. Although the glass transition temperature of cellulose is above the temperatures used in the heat treatments, it is very probable that glycerol functioned as a plasticizer and reduced the effective glass transition temperature to one significantly below the treatment temperatures. In order to assess the implications of these observations to papermaking processes a series of experiments which more closely approximated commercial pulping conditions were designed. In these experiments the exposure to elevated temperatures was carried out in water under pressure and involved a temperature cycle which approximated a commercial kraft cook.

The primary focus of the effort was a series of experiments beginning with low temperature delignification and caustic extraction of loblolly pine chips, annealing a portion of the resulting pulp, then characterizing batches of annealed and control pulp with respect to levels of molecular order, papermaking properties, and, to a more limited degree, absorbency. Characterization of molecular order was based on x-ray diffractometry and Raman spectroscopy. Papermaking qualities were evaluated on the basis of variation of properties of handsheets with degree of refining in a Valley beater. Absorbency was assessed by centrifugal water retention at 1000X g and by observing accessibility to dye.

## PULP PREPARATION AND ANNEALING

Loblolly pine was chosen as the wood species for this investigation because it is an important pulpwood and provides a paper with superior strength, and because it has been fairly well characterized. Pin chips were prepared from logs selected to minimize the incidence of compression or tension wood. The chips were subjected to chlorite delignification at 70°C, extracted with caustic to remove hemicelluloses, then washed and screened; the yield before screening was approximately 54%. The procedures are detailed in the Appendix.

A portion of the screened pulp was placed in 316-stainless steel bombs at 22.1% consistency. The bombs were placed in an oil bath, taken up to 170°C, and held for 4-1/2 hours. They were then cooled and the pulp removed and washed. Portions were used in the studies of molecular ordering as well as in the tests of papermaking properties. The degrees of polymerization [DP] were determined viscometrically and were 1225 in the annealed pulp and 1475 in the control, indicating relatively little degradation in the course of annealing. Analyses of the annealing liquors indicated a drop of the order of 1% in carbohydrate content during annealing.

## CHARACTERIZATION OF ORDER

Two different approaches, which provide information on different aspects of the ordering process, were used to monitor changes at the molecular level which attend annealing of the pulp fibers. X-ray diffractograms provide a measure of the level of three-dimensional order, while Raman spectra are sensitive to variations in molecular conformation. Samples of the control and annealed pulps were freeze-dried, from water at 0°C, and pressed into pellets. The pellets were mounted in the x-ray diffractometer and in the Raman spectrometer for characterization.

The results of the characterization studies reflect significant differences between the annealed and unannealed pulps. The most direct evidence is derived from the x-ray diffractograms which are compared in Fig. 1. The widths at half height of the 002 peaks are 2.84 degrees for the control and 2.44 degrees for the annealed pulp; a very significant change in the level of order is indicated. Another feature of the diffractograms which reflects the increased order, is the shift of the 002 peaks to a higher value of  $2\theta$ . Such a change is usually taken as evidence of tight packing, which is made possible by the increased ordering and results in a slight contraction of the average spacings in the lattice.

The Raman spectra were recorded after the pulp samples were bleached in chlorine dioxide. Although minor differences occur in the spectra, most of the major features appear unchanged indicating little change in molecular conformations. It seems, therefore, that the changes reflected in the x-ray diffractograms involve ordering resulting from greater lateral coherence of the molecular chains.

#### PAPERMAKING STUDIES

Portions of the annealed and unannealed pulps were beaten for varying intervals, the Canadian Standard Freeness measured, and handsheets made. The handsheets were then tested for the properties listed in Tables I and II; some of the data are plotted in Fig. 2 to 7. Selected handsheet samples were also examined in the scanning electron microscope.

Examination of the data presented in Tables I and II and Fig. 2 to 7 reveals many indications that the papermaking properties of the fibers have been altered by annealing, generally in an adverse manner. These changes are likely correlated with some of the changes at the molecular level discussed in the previous

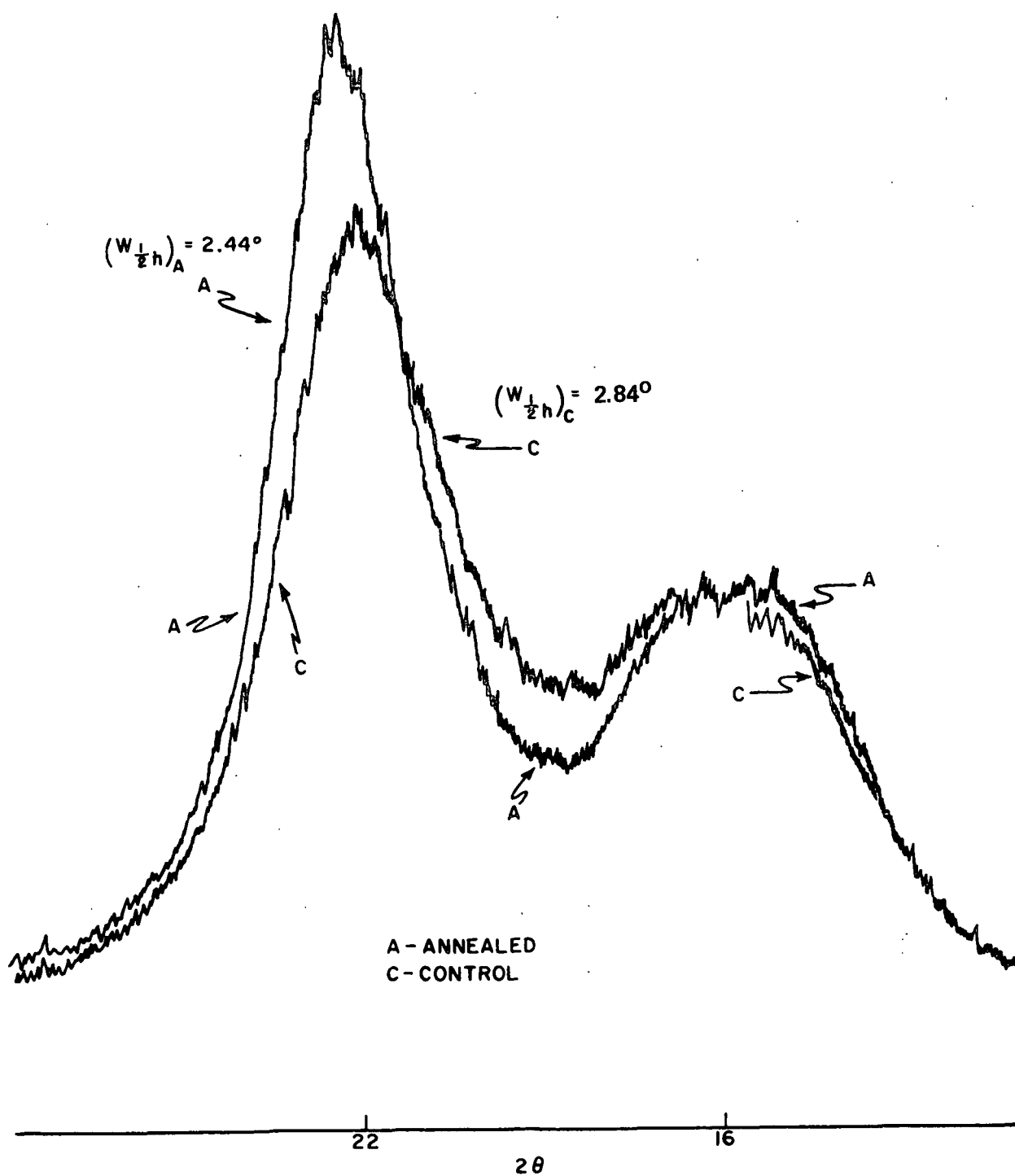


Figure 1. X-ray Diffractogram

section. Causal relations seem obvious in some cases, but they remain somewhat obscure in others.

TABLE I  
HANDSHEETS OF UNANNEALED CONTROL PULP

Beating time, min	0	5	10	15	20	25	30
Density, g/cc	0.656	0.701	0.734	0.756	0.765	0.772	0.747
Burst factor	60.8	70.6	71.9	75.6	78.6	73.7	71.3
Tear factor	114	110	105	98.0	99.5	92.3	98.5
Tensile breaking length, km	8.33	10.2	10.7	11.8	11.4	11.4	11.1
Stretch, %	2.2	2.5	2.3	2.6	2.2	2.1	1.9
Tensile energy absorption, kg-m/m <sup>2</sup>	7.72	10.2	10.5	13.0	10.5	10.1	8.88
Zero-span tensile, break- ing length, km	16.9	17.0	16.7	16.1	16.2	16.4	15.7

TABLE II  
HANDSHEETS OF ANNEALED PULP

Beating time, min	0	5	10	15	20	25	30
Density, g/cc	0.660	0.726	0.754	0.771	0.783	0.829	0.847
Burst factor	29.2	41.2	43.7	46.8	48.6	49.7	49.6
Tear factor	91.2	73.4	67.4	63.9	61.1	56.8	53.6
Tensile breaking length, km	5.94	7.44	8.44	8.97	9.26	9.90	9.61
Stretch, %	0.9	1.0	1.0	1.0	1.0	1.0	0.9
Tensile energy absorption, kg-m/m <sup>2</sup>	4.64	6.66	7.09	7.42	8.02	8.18	7.66
Zero-span tensile, break- ing length, km	12.2	12.8	13.9	14.1	13.8	14.7	14.3

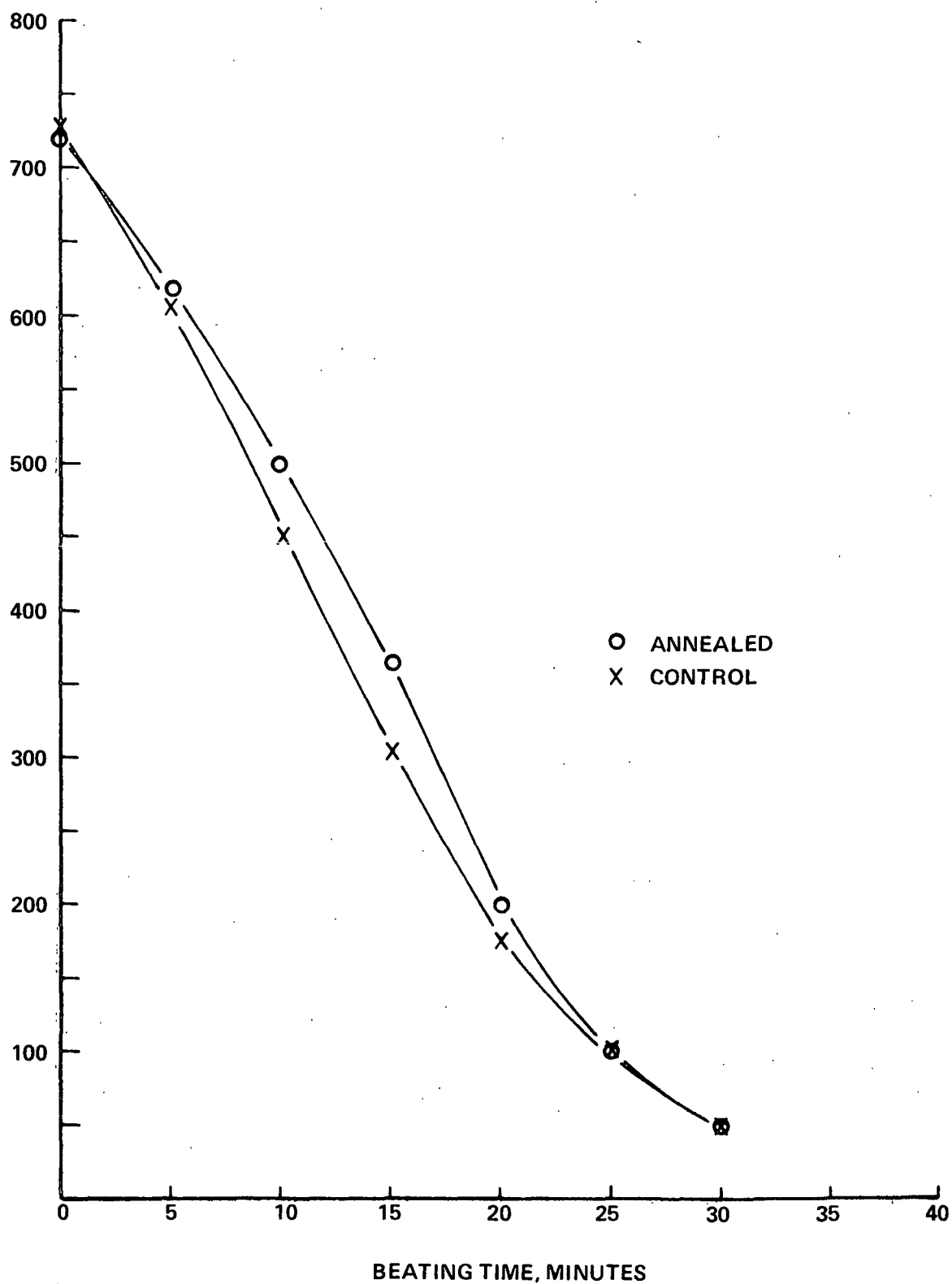


Figure 2. Canadian Standard Freeness

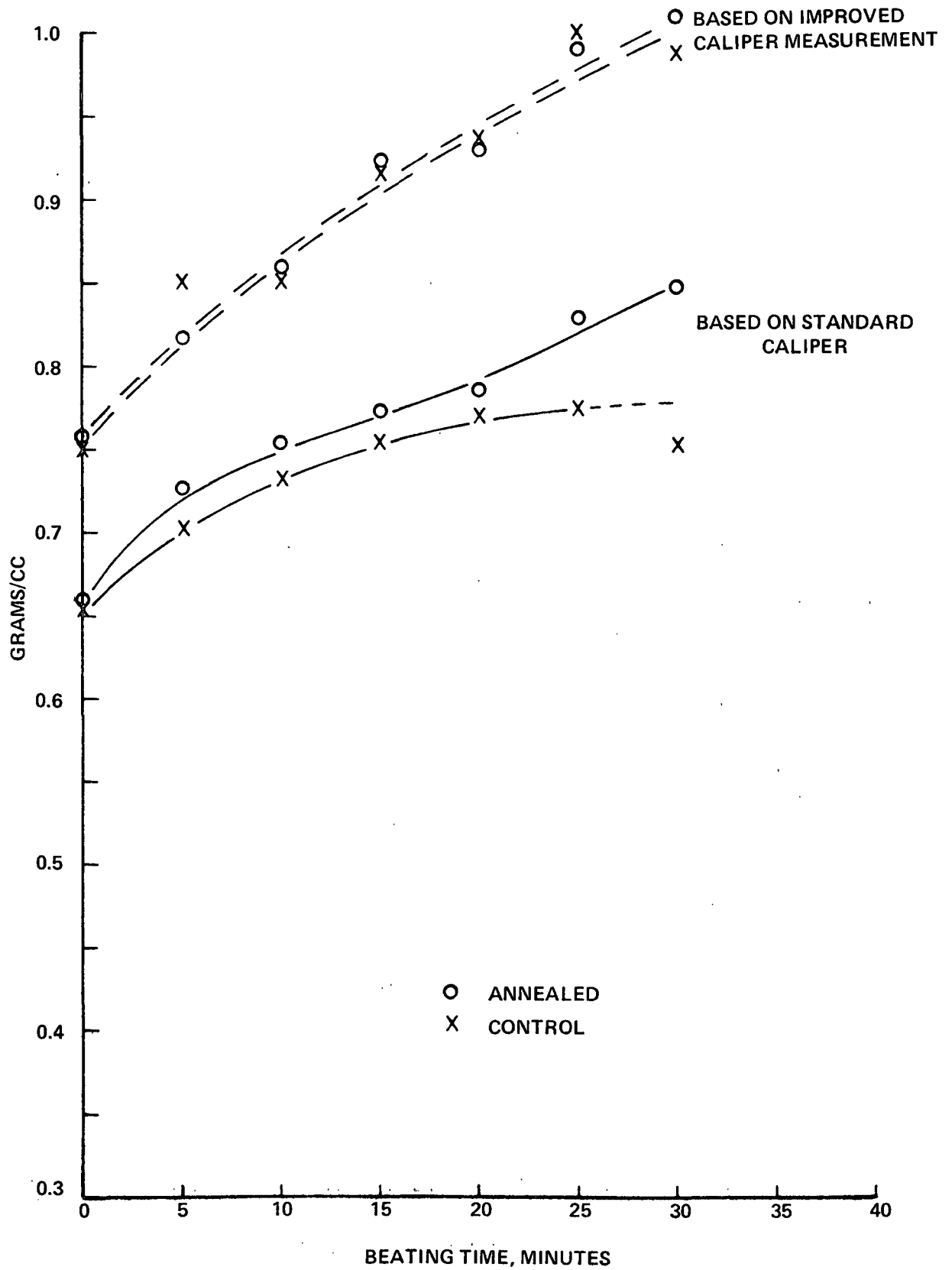


Figure 3. Density

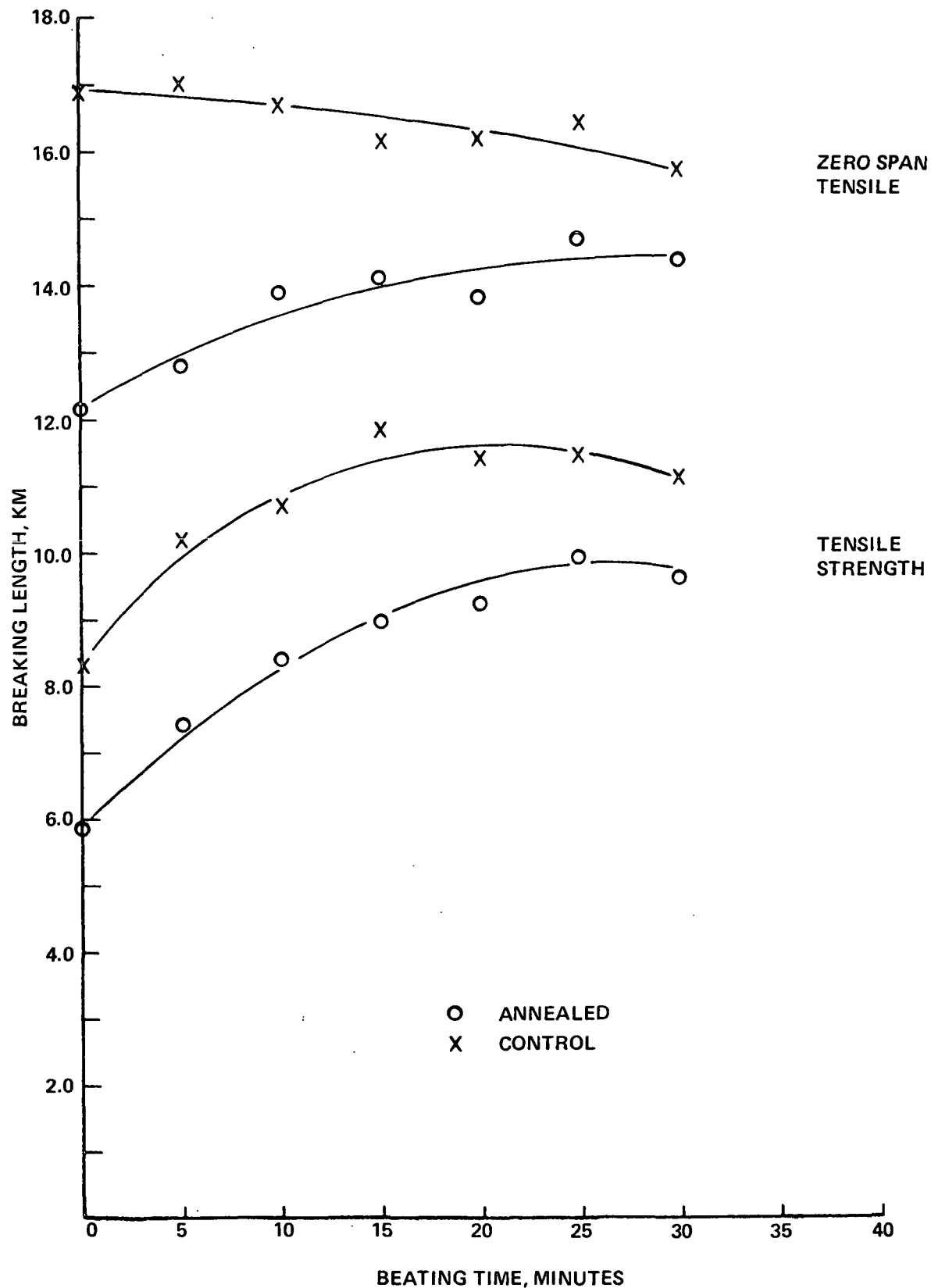


Figure 4. Tensile Properties

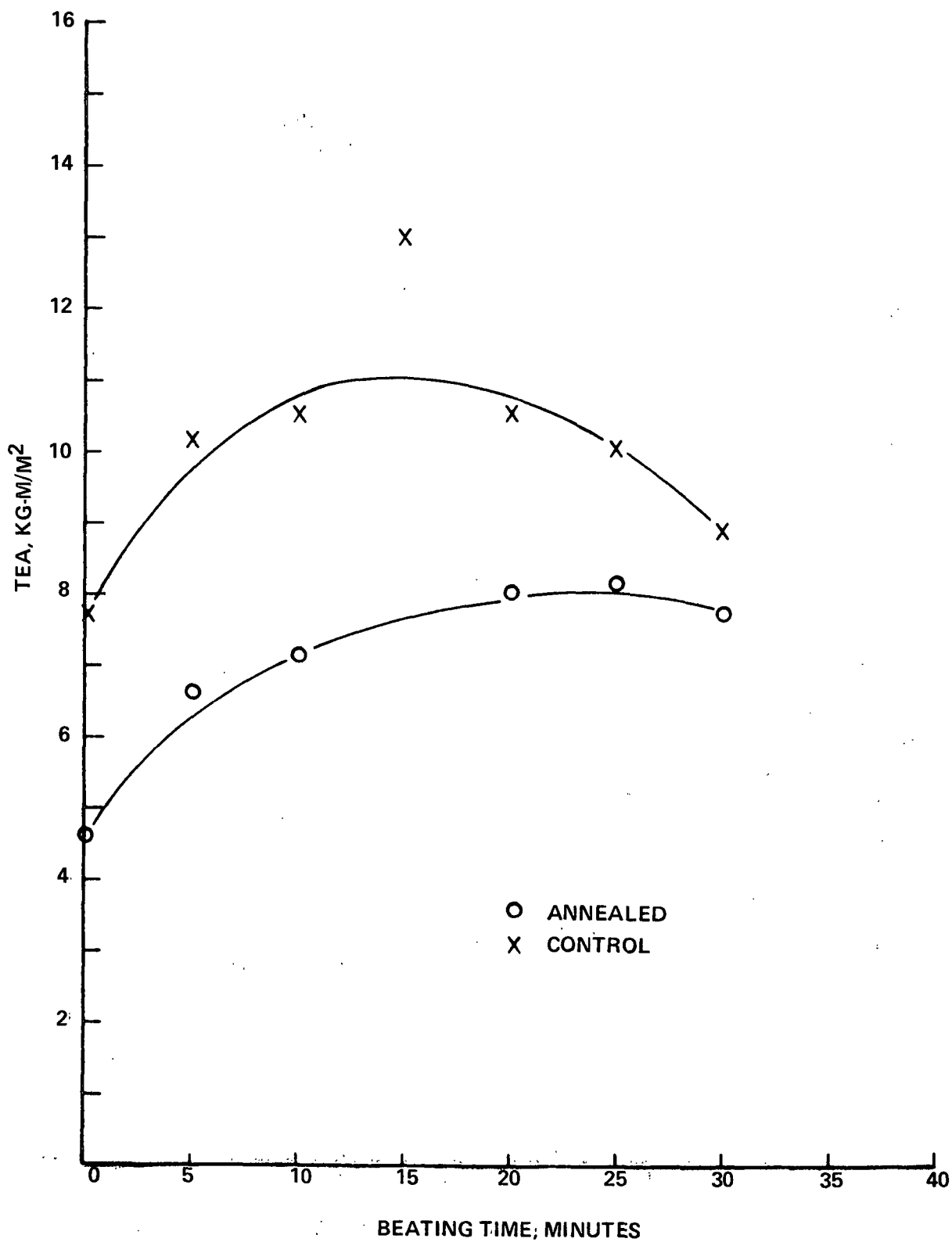


Figure 5. Tensile Energy Absorption

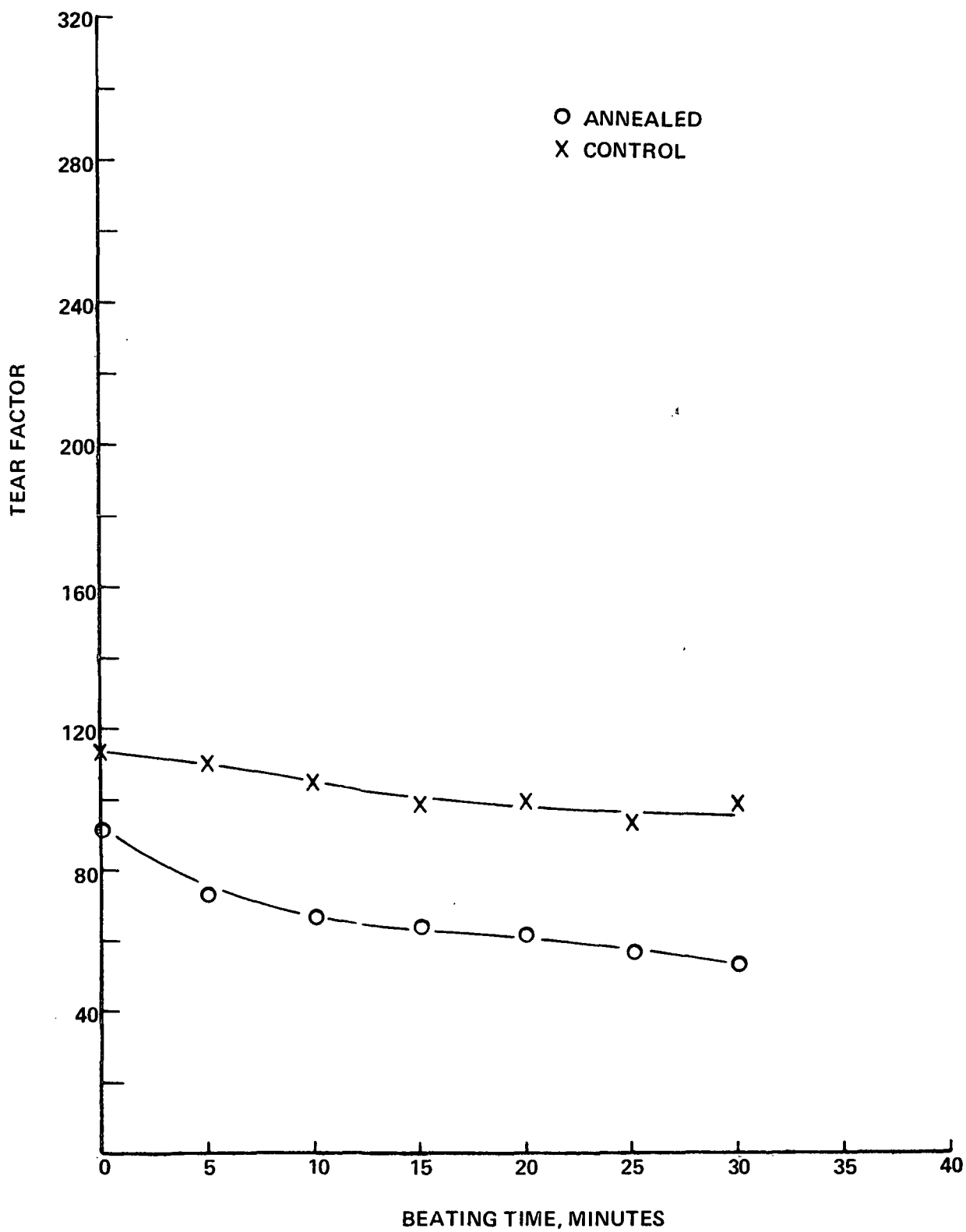


Figure 6. Tear Factor

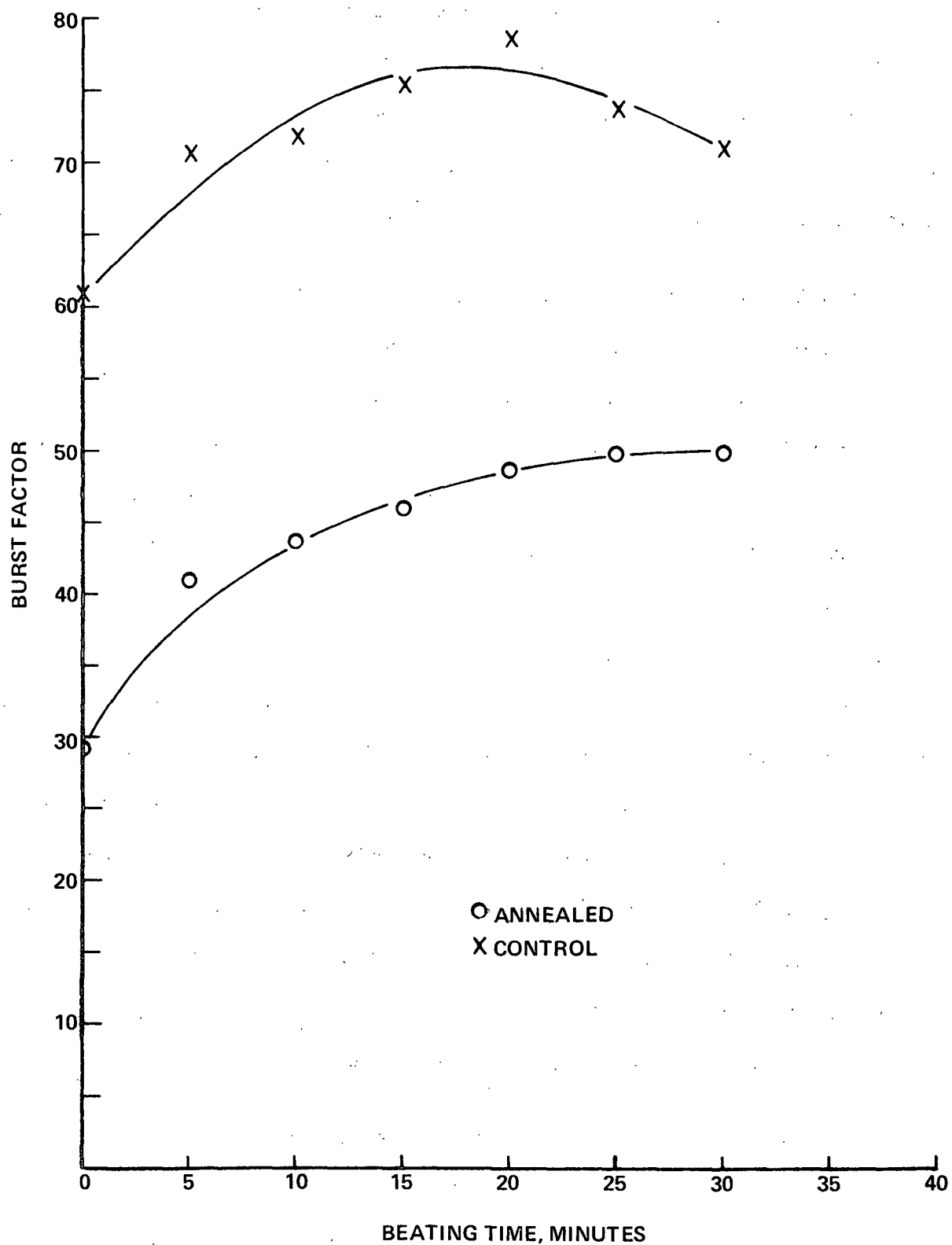


Figure 7. Burst Factor

The most readily rationalized result of annealing is the change in the response to refining. The higher crystallinity of the annealed pulp leads to slower development of the hydration of the fibers and hence to higher freeness at equal beating intervals, Fig. 2. Convergence of the curves at long beating intervals is at a level where freeness is insensitive to differences in filtration resistances.

The density data are shown in Fig. 3. Two sets have been plotted. The first are the values given in Tables I and II, determined on the basis of the standard caliper measurement procedure utilizing a micrometer with metal platens. Because the pattern seemed inconsistent with other results, and because the scanning electron micrograph suggested that the surface roughness may differ between handsheets made from the two pulps, measurements of caliper were repeated using a new procedure, under development by W. Wink (personal communication), wherein the platens have a soft rubber coating. The handsheet densities based on these caliper measurements, which are the other set in Fig. 3, indicate that the difference between the two pulps is within experimental error. Thus the difference which appears in the first set cannot be significant with respect to sheet structure, and it seems plausible to assume that differences between the mechanical properties of handsheets made from the two pulps reflect changes in the mechanical properties of individual fibers and/or changes in the effectiveness of interfiber bonding. Light scattering data on the handsheets from the pulp beaten for 15 minutes indicate only a marginal increment in bonded areas in the handsheets from the unannealed pulp.

The results of the measurements of tensile properties are shown in Fig. 4. Both the tensile strength and zero span tensile strength are plotted as breaking length. It is clear from Fig. 4 that both properties decline with annealing. Since the zero span tensile strength is primarily a measure of fiber strength, it is fair to conclude that the strength of individual fibers has been, on the average, adversely affected by annealing.

While the weakening of individual fibers no doubt contributes to the decline of tensile strength with annealing; it may be only one factor in this decline, however. To develop some indication of the magnitude of the effect, some computations were made on the basis of a simplified form of an equation developed by Page (2) to relate tensile strength to zero span strength and a measure of bonding effectiveness, which is a composite of relative bonded area and bond strength. It was found that the change in zero span tensile did not account fully for the change in tensile strength, indicating that the effectiveness of interfiber bonding has also been reduced by annealing. If on the basis of the density data as well as the measurements of light scattering, it is assumed that the relative bonded area is approximately unchanged, the drop in bonding effectiveness may be taken as evidence of weaker interfiber bonds. Thus it appears that the change in tensile properties reflects decline in both fiber strength and interfiber bonding.

Both the tensile energy absorption, Fig. 5, and the stretch, Tables I and II, decline with annealing. Such changes denote an embrittlement of the fiber; embrittlement is consistent with transformation of significant amounts of amorphous material into the crystalline domain.

Growth of crystalline domains at the expense of amorphous regions generally leads to increases in initial moduli. The moduli of the handsheets from the annealed pulp were 60 to 70% higher than those of the controls.

Both tear, Fig. 6, and burst strength, Fig. 7, are adversely affected by annealing. Though these properties are rather complex functions of fiber and interfiber properties, the changes are consistent with the pattern revealed in the other measurements.

## ABSORBENCY

The measurements of absorbency showed that the ordering process had correlated with it also an adverse effect on this property, which is of considerable practical interest.

The first tests were based on the capacity of the fibers to absorb a dye used routinely in fiber microscopy, Victoria Blue B. In two separate tests, the unannealed fibers took on a deeper blue color indicating greater accessibility to the water soluble dye.

Because unusual optical effects could contribute to the positive results of the dye test, the pulps were also compared on the basis of the centrifugal water tension test commonly used in industrial laboratories to assess the absorbency of fibers. The water retention values at 1000X g were 1.84 for the unannealed pulp and 1.11 for the annealed sample; by this test a kraft fluff commonly used in diapers has a water retention value of 1.07. Thus it appears that the annealing process reduced fiber absorbency to 60% of its original value.

## IMPLICATIONS

It appears that we have identified a previously unrecognized physical process which occurs when fibers are first exposed to temperatures typical of commercial pulping practice. The process can have significant effects on paper-making properties and fiber absorbency.

The studies of supermolecular order indicate that exposure to elevated temperatures leads to conversion of some of the amorphous component of fibers to a more ordered state in a manner closely approximating polymeric crystallization processes. A significant corollary is that pulpwood fibers, in their native state,

are less crystalline than the pulp fibers derived therefrom by common pulping processes. There is no reason to believe that the low temperature delignification can reduce crystallinity relative to the native state.

The papermaking studies have demonstrated that the physical changes, resulting from exposure to temperatures in the range of commercial pulping processes, lead to a general decline of papermaking properties. An important implication of this observation, perhaps the most significant in this phase of the work, is that the performance of pulp fibers is potentially superior to the level realized in current commercial practice. It has generally been assumed that the decline in fiber properties during pulping can be attributed to chemical degradation and the loss of cellulosic matter under typical pulping conditions; the results of the present study suggest that perhaps of equal importance are physical changes which result from exposure to elevated temperatures.

The reduction in the amorphous fraction implicit in increased molecular order provides a rational basis for understanding the changes in fiber properties. Since the amorphous regions are responsible for elasticity in polymeric materials, and ordering imposes greater constraints on the deformation of these regions, it is expected to result in increased rigidity and embrittlement of the fibers; this is indeed the pattern commonly observed with synthetic semicrystalline polymers.

The increased rigidity and embrittlement, postulated as a consequence of ordering, are reflected in the higher modulus and the reduced zero span tensile strength of the handsheets from the annealed fibers. These changes may also be responsible for a hardening of fiber surfaces which in turn could reduce the effectiveness of interfiber bonding.

Though we have focused on thermal environments which occur during pulping, the response of fibers to high temperatures may also be important in other fabrication stages. In the course of papermaking the fibers are exposed to high temperatures again during drying, and the interior temperature of large rolls can remain high for extended periods during storage. Thus the molecular ordering process can continue.

Some evidence for the influence of drying has been developed in recent studies of recycling. When commercial kraft paper was recycled a number of times in an experimental program wherein handsheets were dried against a steam cylinder it was observed that molecular order increased with each stage. It is also generally known that recycled fibers are stiffer and hydrate less readily than virgin fiber. This phenomenon is responsible for some technological problems in recycling.

In his studies of hydrothermal treatment of pulp Lapinoja (3) also found that the exposure to higher temperatures led to a drop in the water retention capacity of the fibers. Both his results and ours are consistent with higher crystallinity, increased rigidity of the structure, and a reduced capacity for hydration during refining. Taken together, these effects suggest a reduction in access to porous structures which are important in commercial technology in the area of chemical modification and derivatization as well as in development of absorbent tissue and personal products.

Finally, it should be noted that the observations made in the present study point to the stability of the cellulose I conformation at high temperatures. This raises questions concerning the general view that the cellulose I conformation in native celluloses is metastable. Theories based on the assumption that native cellulose is metastable imply that annealing of native cellulose should reduce the level of order. Clearly a new understanding of the stability of cellulose I is desirable.

## OPTIONS

The observations reported in the previous section suggest that some departures from current practices might result in changes in the fine structure of pulp fibers which are beneficial to product properties. A number of options are open for further pursuit of this possibility. These can be divided into two groups. The first would be based on the premise of modification of current pulping practice to accomplish the desired objective. The second approach would adopt the strategy of treatment of pulp fibers produced using current technology by application of processes that would reverse the crystallization and the attendant embrittlement of the fibers.

The approach based on modification of current pulping practices itself admits two alternative strategies. One would attempt to achieve the desired objectives by minor modifications of current operating conditions, on the basis of a better understanding of the effects of pulping variables on fine structure. This approach would be most optimally explored in individual pulp mills, where experience in the range of variables possible is available. The results of the present study would provide a basis for characterizing the response of pulp fibers to variations in conditions.

The other approach to modification of pulping processes would involve major changes in pulping technology. Such an approach would introduce consideration of complex criteria above and beyond fiber structure. Explorations based on this approach are necessarily limited, at the present time, to maintaining touch with other ongoing programs seeking new approaches to pulping, and to providing input on characterizing the properties of experimental pulp in terms of the framework developed in the present work.

The second major category, that is the one based on modification of fiber structure in post-treatments of current commercial pulps, is the option that has been selected for pursuit within the framework of the present program. Selection of this option is, in part, based on recognition of the importance of available capacity utilizing current technology. Furthermore, it provides an opportunity for developing a better understanding of the response of fiber structure to different aqueous and thermal environments, apart from the presence of pulping liquors.

In pursuit of the option of post-treatments, a preliminary objective, identified for emphasis, was development of a procedure for reversing the crystallization effect observed in the annealing studies described earlier. It was reasoned that if the crystallization results in embrittlement of the fibers, then reversal of the crystallization process would generate an amorphous component capable of yielding to applied stress in an elastic mode, thus reducing the brittleness of the fibers. Although, in principle, it would have been desirable to attempt to recreate the fine structure that exists in the native fiber, it was felt that an examination of the effect of decrystallization was the logical beginning point.

A series of exploratory studies was undertaken, and a specific method was identified for application to a sample of pulp large enough to permit formation of handsheets for test purposes. The exploratory studies as well as the investigation of handsheets made from the decrystallized pulp fibers are described in the next section.

EFFECTS OF REDUCED CRYSTALLINITY ON PULP  
AND PAPERMAKING PROPERTIES

The approach adopted in pursuit of a decrystallizing treatment was based on studies, outlined in Report One, focusing on the mechanisms of action of mercerizing media. In those studies it was found useful to view the mercerization process as a two-stage response. The first stage involves decrystallization, or conversion from the native lattice to an amorphous form, and the second stage involves conversion of the amorphous material to the cellulose II form. The two stages usually occur simultaneously, or in sufficiently rapid succession, in most mercerizing media that they have generally been regarded as a single process. We have observed, however, in some of our preliminary studies, that under specific conditions it is possible to arrest the transition at a midpoint where the decrystallization has advanced significantly, but the conversion to cellulose II is minimal.

The key to arresting the conversion after the decrystallization step was recognition of the importance of the presence of a threshold amount of water to facilitate the conversion from the amorphous form to the cellulose II form. It was reasoned that if treatments could be developed wherein the amount of water included as a solvent for the mercerizing base was limited to an amount sufficient to facilitate the decrystallization without promoting the further conversion, it would be possible to achieve a decrystallization treatment. Initial studies in this area were undertaken using an organic amine, specifically butyl trimethyl ammonium hydroxide (BTMOH), to achieve the decrystallization. This approach was found to be successful when the BTMOH was dissolved in a mixture of water and methanol. In view of the relatively high cost of the organic amine, a search for a more practical system that could be applied to large enough batches of pulp to permit handsheet testing was initiated. Examination of our earlier work suggested that a system based on

sodium hydroxide dissolved in a mixture of water and methanol might provide the action we sought. Preliminary experiments confirmed that such a system can be prepared in proportions which can decrystallize cellulose.

At this stage in the evolution of the program it was considered desirable to shift emphasis, from exploring the effects of treatments on experimental pulps, to use of a commercial southern pine pulp as the basis for evaluation of the various treatments. A supply of commercial never-dried kraft pulp was obtained. This pulp was used in the development of the proportions of solute and solvents best suited to this application and in the assessment of the effects of treatment on handsheet properties.

In a series of studies utilizing the commercial kraft pulp, it was established that a five-normal solution of sodium hydroxide in a solvent made up of 70% methanol and 30% water provided the maximum degree of decrystallization attainable. The treatment was carried out at a consistency of 3%, and its effect on crystallinity is shown in Fig. 8, wherein the diffractograms of the original kraft pulp and the decrystallized pulp are compared. Although the hint of a peak at approximately  $12^{\circ}$  in the diffractogram of the decrystallized pulp may be associated with trace amounts of the H<sub>2</sub>O polymorph, this is a highly amorphous cellulosic material. In our experience it is difficult to obtain more amorphous materials without going to regeneration procedures under very special conditions.

#### PAPERMAKING PROPERTIES

To assess the effect of decrystallization on papermaking properties, handsheets were made from decrystallized and control pulps after refining for 100, 500, and 800 counts in a PFI mill. The decrystallization resulted in two unanticipated problems associated with the more elastic character of the decrystallized fibers.

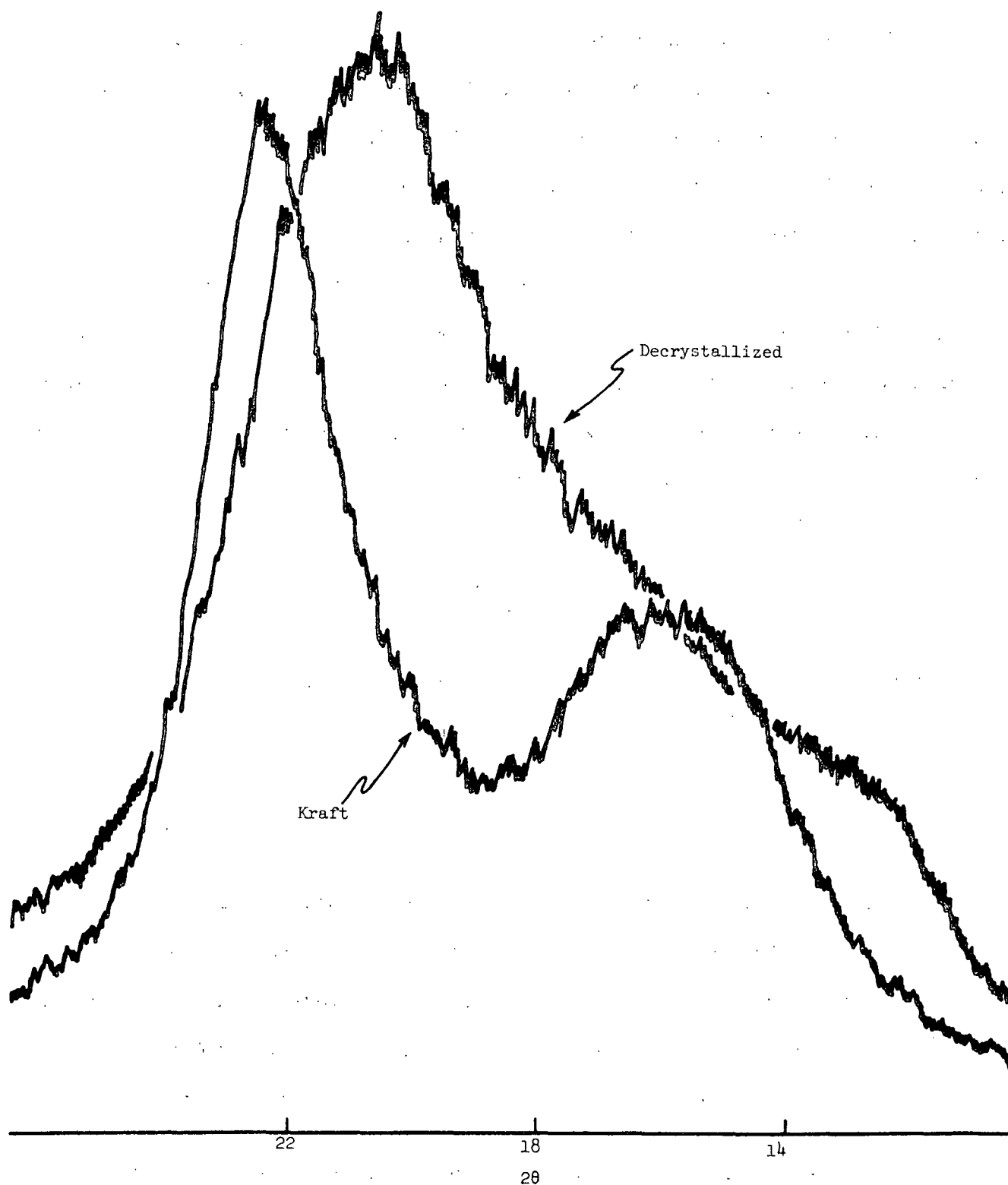


Figure 8. X-ray Diffractograms

The first effect was that the hydration of the fibers developed more slowly during the refining process, probably because more of the mechanical energy was dissipated in elastic, as opposed to plastic, deformation of the fibers. This effect is reflected in the freeness data in Table III. The other unexpected effect that is attributed to greater elasticity is the lower density observed in the handsheets made from the decrystallized fibers; elastic recovery after pressing resulted in a maximum density less than 0.6 for the handsheet made from the decrystallized fibers after 800 counts in the PFI mill. To try to overcome this problem additional sheets were made from the decrystallized pulp after 1100 and 1400 counts. Freeness data on these pulps are also included in Table III.

TABLE III  
CANADIAN STANDARD FREENESS

PFI revs.	100	500	800	1100	1400
Kraft	680	300	180		
Decrystallized	740	570	310		
		570	370	190	100

The handsheet properties are plotted against density in Fig. 9 through 13. Density was selected as the basis for comparison in the present instance, rather than degree of refining, because of the obvious difference in sheet structures indicated by the limited overlap along the density scale. The limited overlap and the density range reflect the problem of elastic recovery after pressing.

The changes in sheet properties as a result of the decrystallization treatment are most interesting; here again some are readily rationalized, while others remain obscure. One property which is readily rationalized is the zero-span tensile strength, which reflects the strength of individual fibers. The indication

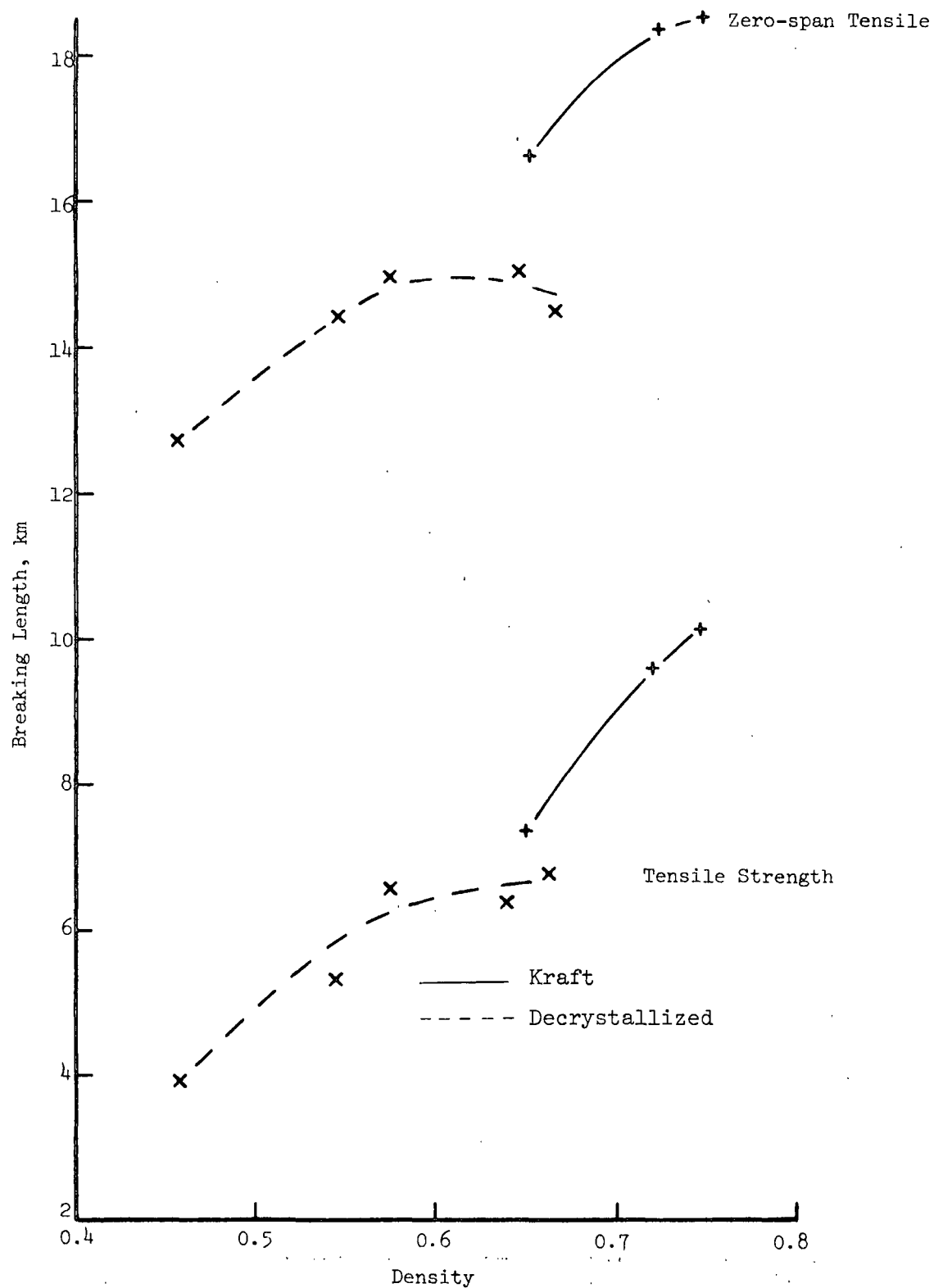


Figure 9. Tensile Properties

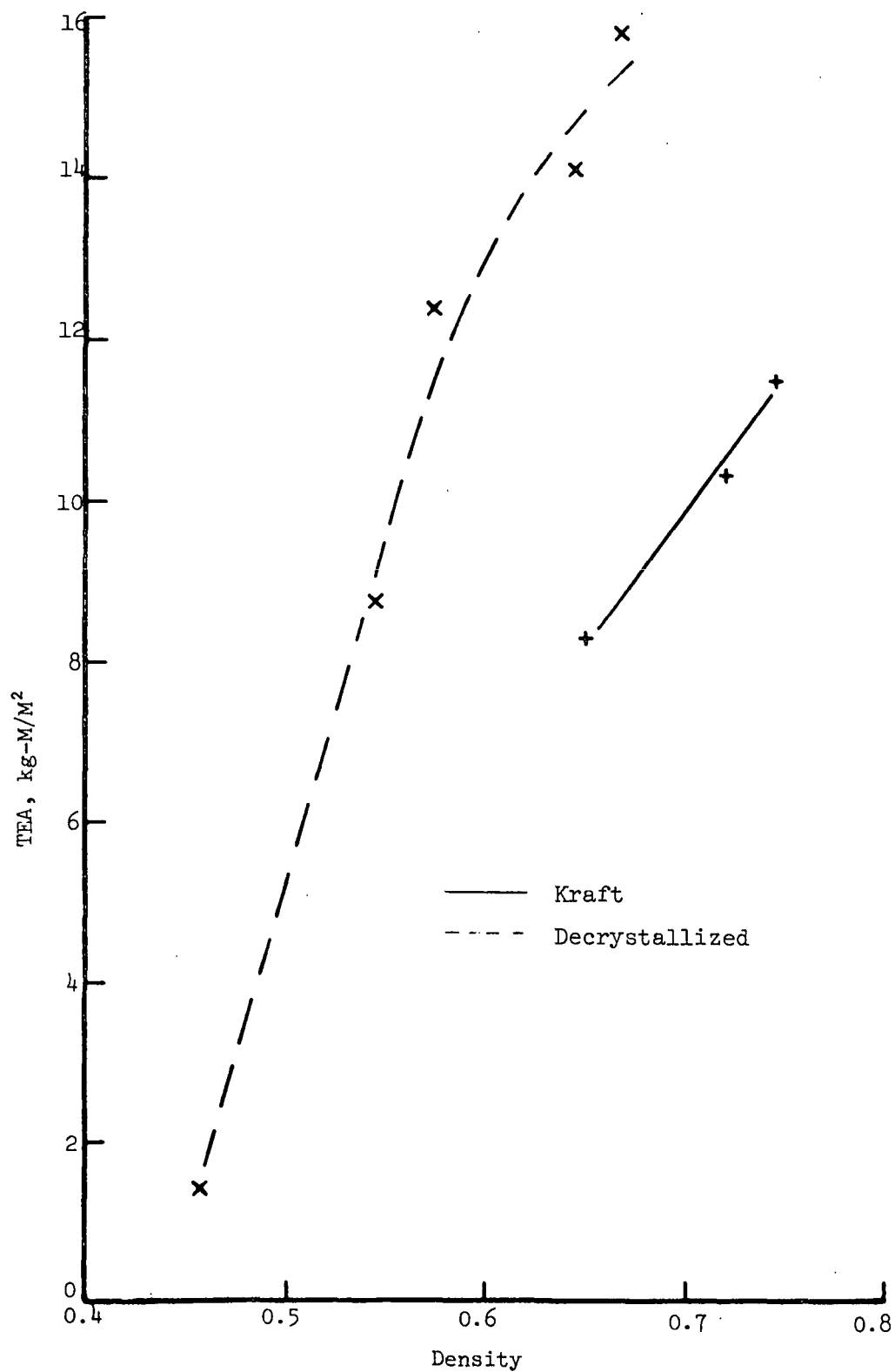


Figure 10. Tensile Energy Absorption

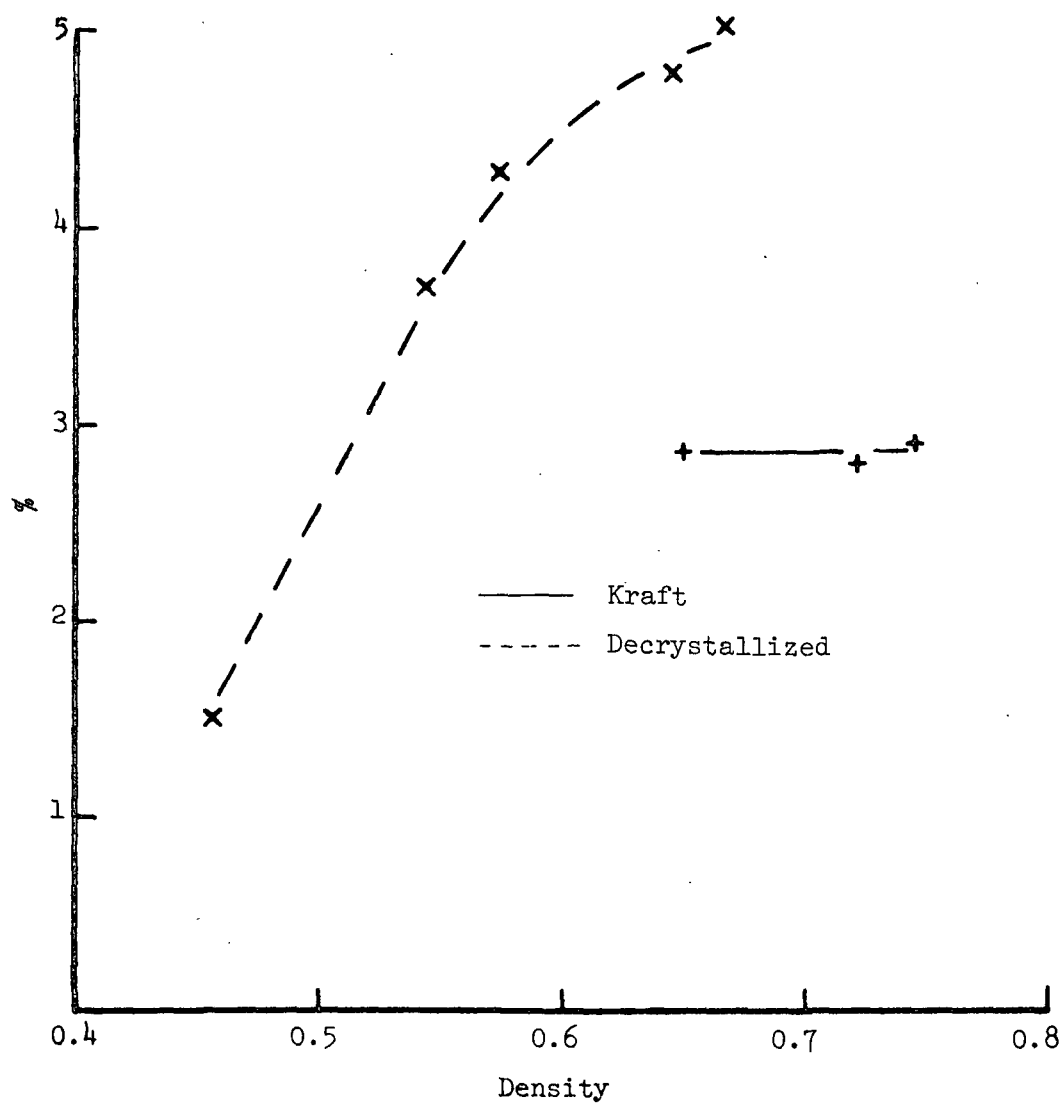


Figure 11. Stretch

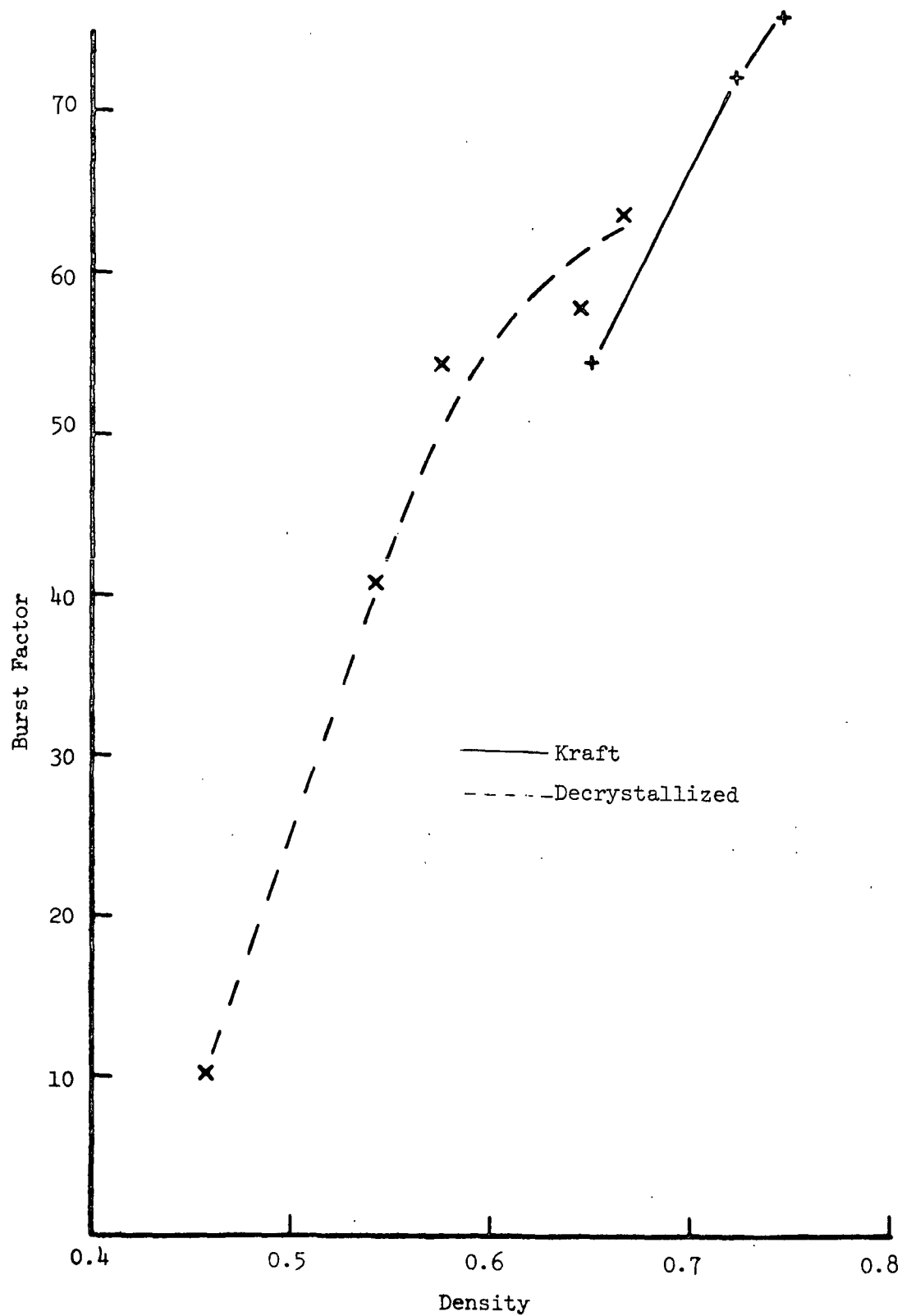


Figure 12. Burst Factor

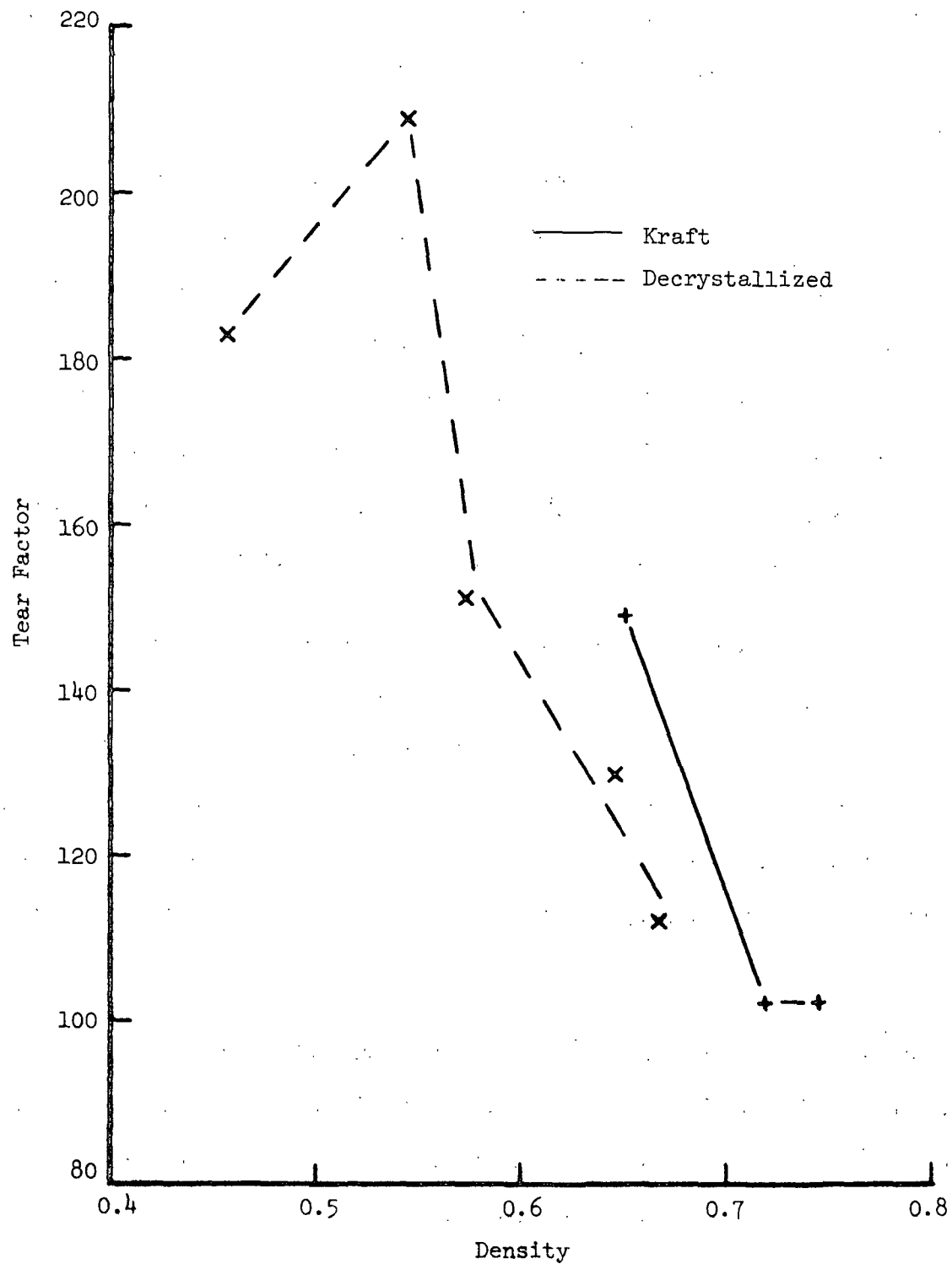


Figure 13. Tear Factor

that it declines with decrystallization is consistent with the likelihood that the elimination of crystalline regions in the fiber is equivalent to elimination of physical cross-linking. It is fairly well established that, particularly in the case of linear polymers, a limited amount of cross-linking can enhance tensile properties, while excessive cross-linking can lead to embrittlement. It would appear that the effect of annealing described in the previous section, is comparable to excessive cross-linking, while the decrystallized fibers have too little. The leveling off of the zero span tensile strength above the density of 0.6 may reflect attainment of a mode where the failure is a measure of the ultimate strength of the fibers, or it may be related to a high degree of damage to the fibers resulting from the excessive refining necessary to attain the two highest sheet density levels.

The tensile strength, also shown in Fig. 9, may reflect the effects revealed in the zero span tests. It is interesting to note that with respect to the handsheets made at the first three levels of refining, the tensile strength would, if extrapolated linearly, fall in the same range as the untreated kraft pulp. This observation reinforces the suggestion made above that at the two highest levels of refining for the decrystallized pulps an excessive degree of fiber damage may be occurring.

The higher tensile energy absorption, Fig. 10, and the higher stretch at failure, Fig. 11, for the handsheets made from decrystallized pulps clearly reflect a substantial increase in the capacity of the sheets to respond in an elastic mode, although the possibility of some contribution due to lower levels of bonding cannot be ignored.

Because of the complexity of the response in the burst and tear tests, Fig. 12 and 13, causal relationships to changes in fiber structure are not readily

identified. It is interesting to note, however, that for both tests, the values corresponding to the handsheet at 800 counts, for the decrystallized fibers, were approximately the same as the values for the original kraft pulp after 100 counts of refining, even though the density of the decrystallized handsheet was significantly lower.

#### OTHER TESTS

Other measures of pulp characteristics which were explored were the absorbency and the scattering coefficients. The two measures of absorbency changed in opposite directions as a result of decrystallization. The equilibrium moisture content had average values of 10% in the decrystallized fibers and 7.8% in the original kraft pulp, a clear indication that decrystallization results in increased access to the internal pore structure of the fibers. On the other hand the centrifugal water retention at 1000 g was 1.34 for the decrystallized pulp and 1.66 for the never-dried kraft. The lower value for the decrystallized fiber may reflect a limit on the degree of compaction of the fibers during formation of the pad for the CWR test. It should be noted that the values of CWR obtained in this series of tests are not directly comparable to those reported above in connection with the annealing study.

The specific scattering coefficient of handsheets from the decrystallized pulp was, on the average, approximately 50% higher than for sheets from the original kraft pulp. Because of the significant difference in sheet structure, it is difficult to distinguish contributions due to increased opacity of the fibers from those due to reduction in the bonded area.

## OTHER STUDIES

In the course of the decrystallization studies, it was noted that the process described above resulted in some loss of hemicellulose content. The loss was approximately 8 to 9% of the weight of the original pulp. This observation raised the possibility that some of the differences in handsheet properties are attributable to the reduced hemicellulose content. To assess this effect, a sample of the kraft pulp was extracted with potassium hydroxide solution at a level sufficient to remove 6 to 7% of the weight in hemicelluloses. Handsheets were made from the extracted kraft pulp and their properties were compared with those described above. It was found that in almost every instance, the changes in the properties of the kraft pulp as a result of extraction with potassium hydroxide were minor variations from the properties of the original kraft pulp, in sharp contrast to the differences shown in Fig. 9 through 13. Thus it is quite unlikely that the difference in hemicellulose content played a significant role in these results.

Another area of fiber modification explored in a preliminary way in connection with the current studies, involved heat treatment of the pulp fibers after the decrystallization process; such heat treatments had previously been shown to induce polymorphic changes. X-ray diffractograms of the heat-treated decrystallized pulp revealed that changes in polymorphic form had indeed occurred. The indication was that significant reversion to the native cellulose lattice or to the cellulose IV polymorph had occurred; for celluloses of such low crystallinity, it is not possible to distinguish the native form from the cellulose I form on the basis of the x-ray diffractograms.

Handsheets were made from the heat-treated decrystallized pulp, and their properties were evaluated and compared with those shown in Fig. 9 through 13. In

general the changes in properties were relatively minor. Some were positive, while others were negative. The densities of the handsheets were somewhat lower than those of the decrystallized fiber at the levels of 100 and 500 counts of refinement, while at the 800 count level the densities were identical. In no case did the pulp react as if it had returned to its original, unmodified, state. The implications of these observations need to be assessed further in conjunction with our future work.

#### IMPLICATIONS

Although we cannot, as yet, define the crystalline structure which is optimum for sheet strength, it is clear from the results reported in this phase of the work that modification of fine structure in order to develop positive changes in fiber properties is indeed possible. Our ability to pursue these possibilities in a systematic fashion is, however, restricted by the limited nature of our understanding of the mechanisms by which the various treatments induce changes in fine structure. It appears that progress in understanding these mechanisms is essential to systematic progress in this area.

It is also clear from the discussions of properties that our understanding of the relation between fiber properties and sheet properties is even more limited. Progress in this area will be a key to implementation of the benefits of modifications of fine structure.

#### PLANS FOR FUTURE WORK

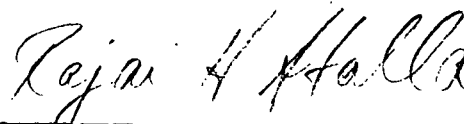
In the coming months we will continue studies of fiber modification, with particular emphasis on establishing the mechanisms of action of the various treatment media, as well as the driving forces which determine the response of the fibers. An understanding of these two factors is essential to systematic pursuit of the broader objectives of the project. As we proceed in our effort, we will pursue leads concerning papermaking properties as they develop.

During the coming months we also plan to bring together the results of our critical reexamination of the literature on the structure of cellulose. These will be incorporated in a review of the state of the art to be transmitted to the membership; particular emphasis will be placed on those aspects which are important to determining fiber properties.

LITERATURE CITED

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A handwritten signature in cursive script that reads "Rajai H. Atalla". The signature is written in dark ink and is positioned above a horizontal line.

Rajai H. Atalla  
Chemical Sciences Division

#### APPENDIX

Two bolts from a 25 to 30-year-old loblolly pine tree approximately 10 inches in diameter were obtained. They were debarked and cut into  $3/4$  inch disks. Compression and juvenile wood were discarded. The remaining wood was cut, parallel to the fiber axes, into pin chips approximately  $1/8 \times 1/8 \times 3/4$  inch. The chips were then extracted by immersion in solvents at room temperature; the solvents were absolute ethanol for 5 days, then 2:1 chloroform: absolute ethanol for 7 days. The extraction was followed by solvent exchange through ethanol to water.

The chips were then delignified for six hours in a sodium chlorite-acetic acid solution: 60 ml acetic acid and 180 g sodium chlorite in 7 liters of water for each 650 g batch of chips. Fresh chemicals were added hourly, and the pH ranged between 3.95 and 4.25.

After delignification the chips were soaked in water, then extracted with 3% NaOH for two hours under a nitrogen atmosphere. The chips were washed (yield was 55%) and screened on a Valley Flat screen fitted with a 0.009 inch slotted screen; accepts were 78%. A portion of the pulp was then annealed in water under pressure at  $170^{\circ}\text{C}$ ; the yield after annealing was 95%.

Viscosities in cupriethylene diamine were determined according to TAPPI T 230 su-66 (pipet method), modified according to Tappi 37, 273 (1954).