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The Fracture of Toner Due to Paper Swelling

Lorraine C. Vander Wielen, Joel C. Panek, and Peter H. Pfromm

ABSTRACT

Improvements in the deinking of toner-printed paper have been hampered by a lack of understanding of the mechanisms occurring during recycling processes. These mechanisms are difficult to study largely due to the complexity of the toner-paper system. To analyze the initial step of repulping, this work focused on the fracture of the toner layer resulting from paper swelling. We first observed an isolated system of toner printed on paper that is immersed in water, then examined whether these results were apparent after repulping.

Observations with a light microscope at 40X showed that significant fracture of toner can occur due to paper swelling upon immersion of toner-printed paper in water (no mechanical agitation). Below the glass transition temperature of the toner, fracture was evident; however, above this temperature, fracture was virtually nonexistent. This is due to the change of the toner from a brittle to a rubbery material at its glass transition temperature. The pH did not appear to have a significant effect on the toner fracture due to paper swelling. The effect of temperature on material properties was also apparent in the repulping experiments. In addition, the repulping experiments indicated that paper swelling controlled mainly the largest particle sizes, while mechanical action in the repulper controlled the smaller sizes.

Effective deinking of photocopies and laser-printed paper has proven elusive, largely due to the properties of the toner that forms the image. Toners are thermoplastic-based dry inks that are applied to paper using electrophotography. This process produces an irregular layer of toner on the paper surface that varies in thickness and is typically more a porous structure than a continuous film. In this work, we are considering the toner and paper to be a two-layer composite consisting of a toner polymer on a cellulosic substrate **(Figure 1).** In this simplified context, the events occurring in the repulping process that lead to the breakup of the toner layer may be more clearly understood.

The first step in deinking of wastepaper is repulping, in which the paper is disintegrated by immersing the furnish in water and applying mechanical forces. This produces a fiber slurry from which toner can be more easily removed in subsequent separation processes **(Figure 2).** In this slurry, toner is primarily found as flat particles with a wide size distribution. The particles may or may not be detached from the fibers [1,2]. Removal of toner particles has been shown to be influenced by their size and shape, as well as retention of toner particles to fibers [2-7]. The sizes of toner particles resulting from repulping have been shown to be related to the composition of the toner, the printing process used, and the deinking conditions [1-9]. It has been suggested that these factors influence the cohesiveness of the printed layer, thereby affecting the extent to which the printed layer fractures into smaller particles.

The toner layer will fracture into smaller particles when a mechanical stress acting on the toner exceeds the toner's fracture strength. The stress acting on the toner may originate from swelling of the paper and from the mechanical forces that are applied in the repulping step. The magnitude of these stresses will vary with the materials and the system conditions. The strength of the toner layer depends on the material properties of the toner and its physical structure. In the following sections, we will further discuss the origins of the stresses and strength of the toner.

Paper Swelling

When toner-printed paper is immersed in water, the paper readily swells due to water sorption. However, the toner remains virtually unchanged by water. Because the toner is fused to the paper surface, it resists swelling of the paper, which leads to mechanical stress in the toner. The toner may respond to the stress by detaching from the paper, cohesively fracturing, or remaining attached **(Figure 3).** The response is determined by the cohesive strength of the toner and the adhesive strength of the toner to the paper. When the stress exceeds the cohesive strength of the toner, the toner will fracture into smaller pieces.

Mechanical Action of the Repulper

A second mechanism leading to fracture of the toner is the mechanical energy input in the system. The mechanical forces in a repulper include direct mechanical forces (paper hitting rotors), fiber-fiber shear forces, shear stress from differences in flow velocity, attrition, and mechanical shearing between two plates [10]. Higher consistencies and longer pulping times produce more smaller particles, due to the forces acting on the toner [2-4,7,8]. The degree of toner fracture will be influenced by the magnitude of these forces and the strength of the toner layer.

Fracture Strength of Toner

The fracture strength of the toner is determined by its material properties and physical structure. In this work, we are addressing the material properties, though it is recognized that the physical structure, particularly the thickness and the porosity of the layer, plays a very significant role [4].

The material properties of toner are largely determined by the polymeric binder. Toner consists of a polymer binder (5590%) and pigment (5-40%), as well as other additives. Due to the properties of the polymer binder, temperature can have a significant effect on the properties of the toner **(Figure 4).** Below the glass transition temperature (T,) of the polymeric binder, toner behaves as a brittle solid. It is stiff and resists stress, but fractures at relatively low strains. Above its glass transition temperature, toner becomes rubbery. It is flexible and shows little resistance to stress, but elongates significantly before fracture. **Figure** 5 shows that the brittle toner below T_g will preferentially fracture.

This work compares the significance of paper swelling during the initial immersion step with the significance of mechanical action during repulping on the fracture of a continuous line of toner into particles. Initially, we addressed the effect of temperature and pH on the fracture of toner that occurs due to paper swelling upon immersion of toner-printed paper into water. Next, we investigated the size of toner particles resulting from high-consistency laboratory repulping. The repulping work included an experiment that decoupled the mechanisms of paper swelling and mechanical action.

EXPERIMENTAL

Paper Swelling

The toner used for this work was Xerox Dry Ink Plus, which consisted of a styrene-acrylate polymer, carbon black pigment, zinc stearate, and amorphous silica. The glass transition temperature of this toner is 56±2°C. A pattern of lines was photocopied (Xerox 5042 photocopier) onto standard copy paper (20 lb. alkaline copy paper stored at 50% relative humidity). Each line was approximately 20 mm long by 0.28 mm wide and estimated to be 10 to 20 microns thick. The use of a line simplifies the detection and quantification of fracture. For uniformity of results, the data reported here were collected using lines printed along the cross direction of paper only. All copies were made using the same photocopier so that the thickness of the toner layer and the degree of fusing would be consistent.

The samples were immersed in water at various temperatures and four different pH levels (water temperature ± 1°C, pH adjusted with hydrochloric acid (6N Baker analyzed) and sodium hydroxide (0.16% VWR)). The samples were immersed for 5 minutes, removed, and immediately placed under a light microscope at 40X. Upon submersion in water, cracks in the printed line formed **(Figure** 6 and 7). Fracture is defined here as a crack detected across the width of the line. The distance between cracks was measured using OPTIMAS image analysis software (Optimas Corp.). Ten samples from two sheets of paper were analyzed at each condition. From each sheet, a sample was selected from each of the four corners and from the center. The average number of cracks per millimeter of printed line was then calculated.

Repulping

Toner-printed samples were repulped at 11% consistency in a LaMort laboratory pulper (LaMort, France) with a Helico rotor. Each sheet of paper was printed with 55 lines that were 147 mm long by 0.28 mm wide (3.8% area coverage or 38,000 ppm) with the same photocopier used for the paper swelling experiments. 1.0 kg of the printed paper was torn into sections, then added to 9.5 L of deionized water. Repulping was done at pH 6.5 and pH 11, and at temperatures below and above the toner's T,. The pH of 6.5 is the natural pH of the system, while pH 11 was reached by adding aqueous sodium hydroxide. The temperature of the below T_g experiments began at room temperature (25°C), and increased by 10 to 15°C during repulping, still well below T,. The temperature of the above T_g experiments began at 70°C (water was heated before paper was added). The temperature decreased by 6 to 7°C during these experiments, but did not drop below the T,. Repulping was done for 10 minutes on the low setting (900 rpm) for a power input of 4600 kW per ton.

Table I describes the four sets of repulping experiments. In the first two sets, the paper was immediately repulped, one above the toner's T_g (Exp. A) and one below the T_g (Exp. B). Both these sets were done at two pH levels. In the second two sets (Exps. C and D), the paper was allowed to soak in the water for 80 minutes, then repulped. Experiment C consisted of soaking the paper in water at room temperature, heating the paper and water above the toner's T_g, then repulping above the T,. Experiment D consisted of soaking the paper in water at room temperature, then repulping below the T,.

Handsheets were made from samples of the pulp on a Büchner funnel using grade 4 15 qualitative filter paper. The image analysis program Spec*Scan 2000 (Apogee Systems, Inc.) was used with a Hewlett Packard Scan Jet 3C scanner to measure the black particles appearing in the handsheets. The detected particles were classified into size categories ranging from 0.007 to 1.00 mm”. Particles smaller than 0.007 mm” were not reported because they could have slipped through the filter paper that was used to form the handsheets. All but the outer 1 .O cm of the 15.0 cm diameter handsheets were analyzed.

RESULTS AND DISCUSSION

Figures 6 and 7 show that cracks became visible in a line of toner upon immersion of toner-printed paper in water. These images are typical of the cracks that formed, including the many long cracks that extend across the width of the line and along its length, in addition to smaller cracks that were barely detectable.

This indicates that paper swelling is fracturing the toner. However, it may be possible that these cracks are already present in the line of toner prior to immersion, rather than created from paper swelling. Swelling of the paper may simply increase the size of the cracks and allow the cracks to be seen more easily. Under 40X magnification, cracks in the toner became visible only after being immersed in water at 23.5°C. These cracks were not apparent prior to immersion in water and were no longer detectable when the sample was dried. Thus, it is clear that cracks are visible only when the paper is in the swollen state. However, samples that were immersed in 70°C water did not show a significant number of cracks (an effect of the toner being rubbery rather than brittle, which will be discussed later). If the cracks were already present before any swelling, these samples should have shown a similar number of cracks to those at 23.5°C. The fact that samples immersed in water at 70°C did not display significant cracking shows that the observed fractures were created by swelling of the paper.

The cracks were observed to occur preferentially along the machine-direction of the paper, regardless of the orientation of the lines relative to the paper **(Figures** 6 and 7). This appears to be the result of greater cross-directional swelling of the paper, which leads to cracks that are perpendicular to the greater strain. Studies have shown that paper swells 1.2 to 3 times more along the cross-direction than the machine-direction [11].

The significant effect that temperature has on fracture is clearly shown by the dramatic decrease in the number of cracks that form as the temperature reaches and exceeds the T_g **(Figure 8**). The change in fracture behavior can be explained by the change in material properties of the toner. Below the T_g, the toner is brittle. When the paper swells, the brittle toner fractures. Above the T_g, the toner behaves as a rubbery, more flexible substance. The rubbery material stretches with the swelling paper, rather than fracturing. This shows that the material properties of the toner are important to determining the amount of fracture that occurs.

In this system, the pH did not have a significant effect on the amount of fracture due to paper swelling **(Figure 8**). This indicates that the pH change did not affect the degree of paper swelling and the material properties of the toner significantly enough to affect fracture. The paper swelling is not expected to be affected much by pH. In this study, the toner was printed on copy paper made from fully bleached chemical pulps. Measurements of the water retention value of bleached chemical pulp indicate that the pH does not have a significant effect on fiber swelling [123. The effect of pH on the toner will depend on the base polymer. In this case, the toner polymer appeared inert to changes in pH.

The repulping experiments gave evidence that the results of the paper swelling experiments allow some predictions even after the more intense repulping process is applied. The paper swelling experiments showed that more fracture occurred below the T_g than above because the toner is more brittle **(Figure** 8). The repulping experiments showed that fewer large and more smaller particles are formed below the T_g than above **(Figures** 9 **and 10).** Basically, large particles are broken into more smaller ones as a direct result of the toner being more brittle. Also, both the paper swelling and repulping experiments showed that pH does not have a significant effect **(Figures 8 and 11).** These repulping results agree with the work of Berg *et al.* [3].

In order to determine whether paper swelling contributes to the final particle size distribution after repulping, we separated the effects of swelling from repulping by changing the toner from brittle to rubbery between these steps. This experiment, C, consisted of soaking the toner-printed paper in water below the T_g of the toner, then repulping it above the T,. The toner is brittle (below T_g) in the soaking step and rubbery (above the T,) in the repulping step. The premise is that paper swelling will produce significant fracture, while repulping should produce relatively less fracture. The extended soak used in Experiment C is not expected to have any other effects on the particle size distribution, as indicated by the similarity of the results from Experiment B (short soak and repulping below T_g) and Experiment D (extended soak and repulping below T_g) **(Figures** 12 and 13).

The results indicate that the two mechanisms become dominant in different particle size ranges. Paper swelling governs the size distribution of the largest particles, while mechanical action breaks the larger particles into smaller ones. Experiment C (soaking below with repulping above the T,) resulted in fewer small particles than Experiment B (repulping below the T_g) **(Figure 12).** This is because the particles were more rubbery in the repulping step and did not break into smaller particles as easily. Fracture occurred during soaking; however, only the brittle toner (below T_g) broke down to a greater extent during repulping. On the other hand, Experiment C (soaking below the T_g followed by repulping above) resulted in fewer large particles than Experiment A (repulping above the T_g) **(Figure 13).** This is because the particles were more brittle in the soaking step and broke into smaller particles prior to repulping. Even though the repulping was done at the same conditions, the fracture that occurred during soaking was evident in the final particle size distribution.

In short, the toner basically starts as a continuous line that is broken into smaller particles. It appears that paper swelling can break up this line only to an extent; thus, it produces only larger particles and essentially no smaller ones. Mechanical action will break these large particles into smaller and smaller fragments, depending on time and energy input. Under intense repulping, all the larger particles would likely fracture, and the effect of paper swelling would become less obvious. However, the repulping energy input used here is already quite high, so that the swelling fracture mechanism is likely to be significant in industrial practice. The size of the particles in all these steps is influenced by the properties of the toner, particularly whether the toner is brittle or rubbery.

CONCLUSIONS

This work demonstrates the significance of paper swelling as a mechanism of toner fracture and the importance of the toner’s material properties. Paper swelling creates stress in the nonswelling toner. Below the toner's glass transition temperature (T,), solid toner is brittle and cohesively fractures. However, above the T_g of the toner, the toner is rubbery and very little fracture occurs. The pH did not have a significant effect on the fracture of toner in this system, indicating that the pH did not significantly affect the strength of the toner or the paper swelling.

The repulping experiments also showed the importance of material properties. The brittle toner (below T_g) is broken down into a greater number of smaller particles than the rubbery toner (above T,). The effects of initial paper swelling are evident even after the more intense repulping step. Ultimately, paper swelling governs the size of the large particles, while mechanical action breaks these large particles into smaller ones.

These results indicate that a quantitative study of a simplified model system will yield results that can be applied to the actual toner-paper system. This will be valuable in determining the effect of toner properties on the particle size distribution.

ACKNOWLEDGMENTS

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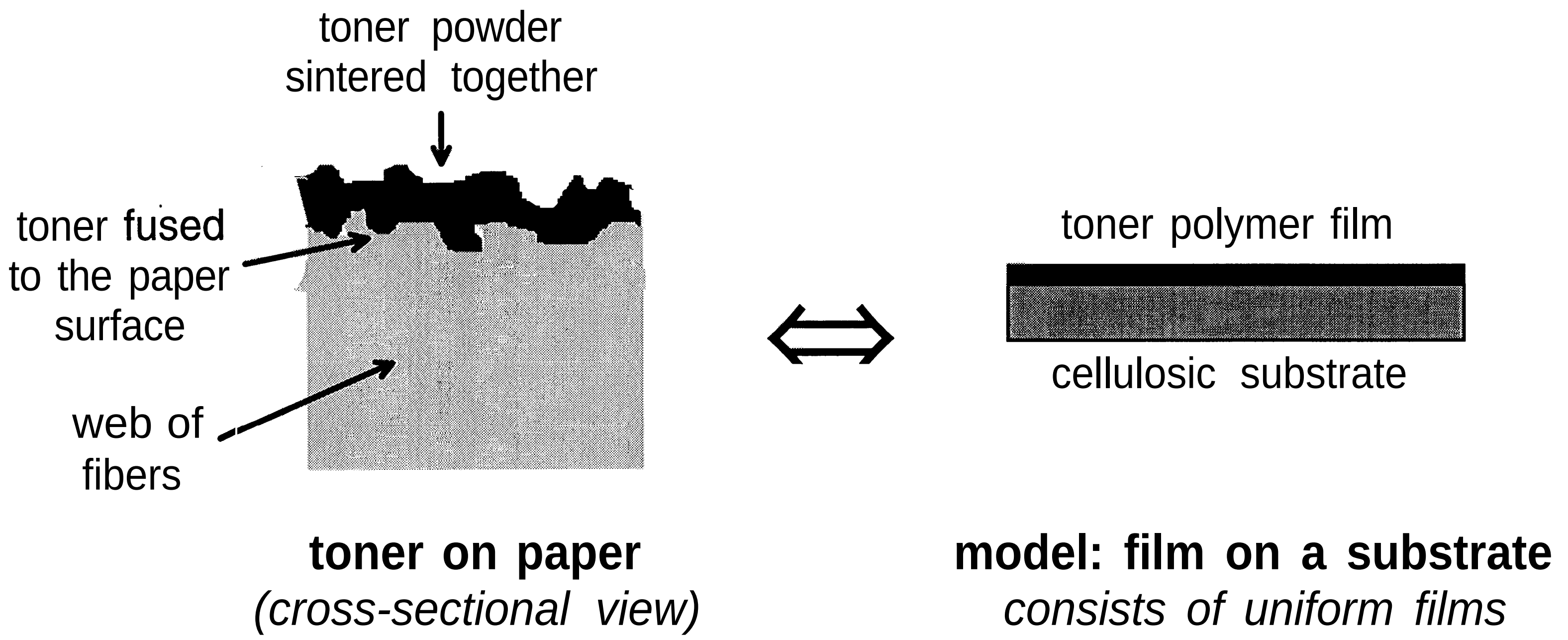
Experiment	soaking below T_g	soaking above T_g	repulping below T_g	repulping above T_g
A		X		X
B	X		X	
C	X - long soak			X
D	X - long soak		X	

A: paper was soaked (brief) and repulped at temperatures above the toner's T_g
B: paper was soaked (brief) and repulped at temperatures below the toner's T_g
C: paper was soaked for an extended time (80 min.) at temperatures below the toner's T_g and repulped at temperatures above the toner's T_g
D: paper was soaked for an extended time (80 min.) and repulped at temperatures below the toner's T_g

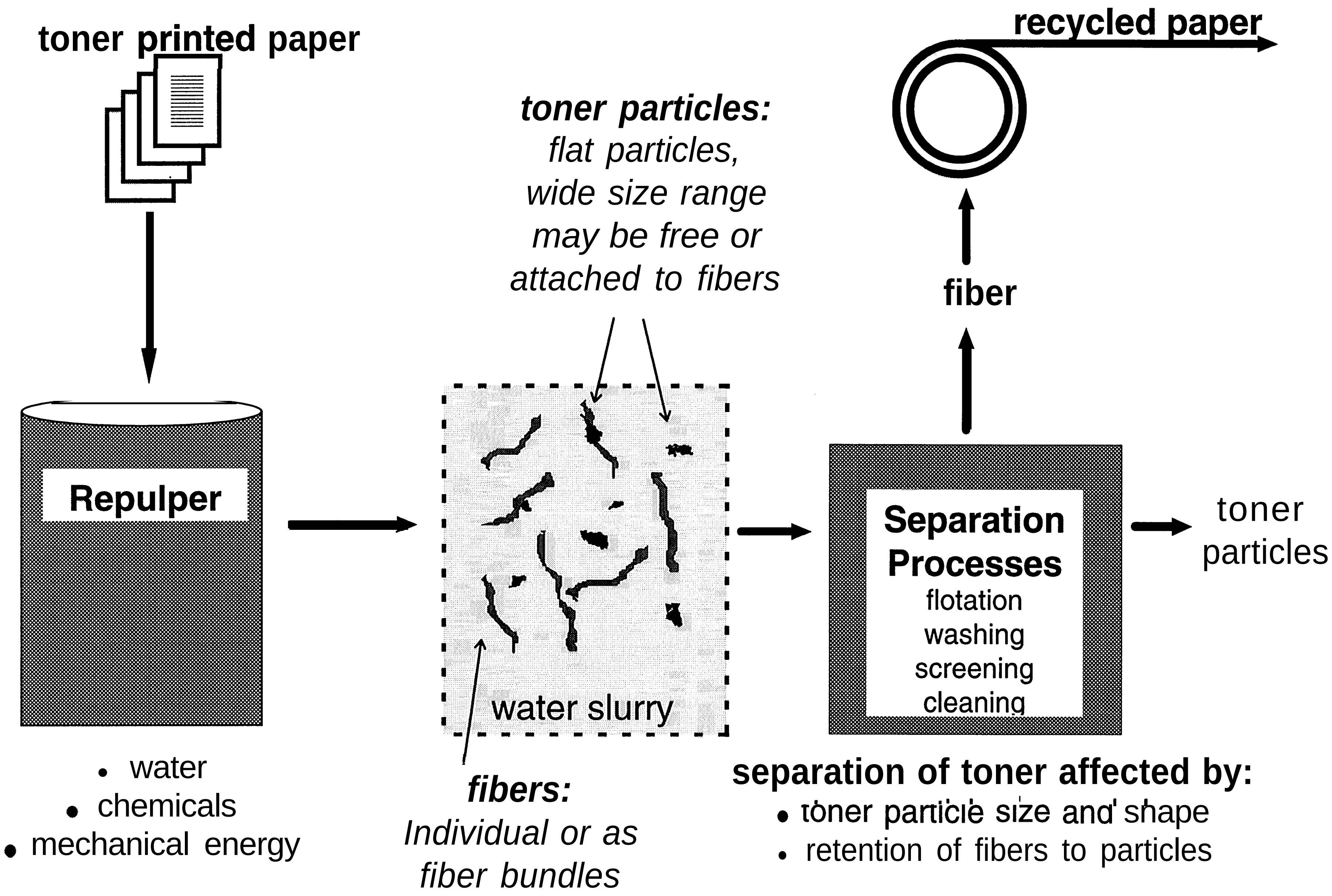
I. Experimental Conditions for Repulping.



toner on paper
(cross-sectional view)

model: film on a substrate
consists of uniform films

1. Schematic diagram of toner on a paper surface. In this work, we are considering the toner on paper as a polymer film on a substrate.



toner printed paper

Repulper

- water
- chemicals
- mechanical energy

toner particles:
flat particles,
wide size range
may be free or
attached to fibers

water slurry

fibers:
Individual or as
fiber bundles

Separation Processes
flotation
washing
screening
cleaning

toner particles

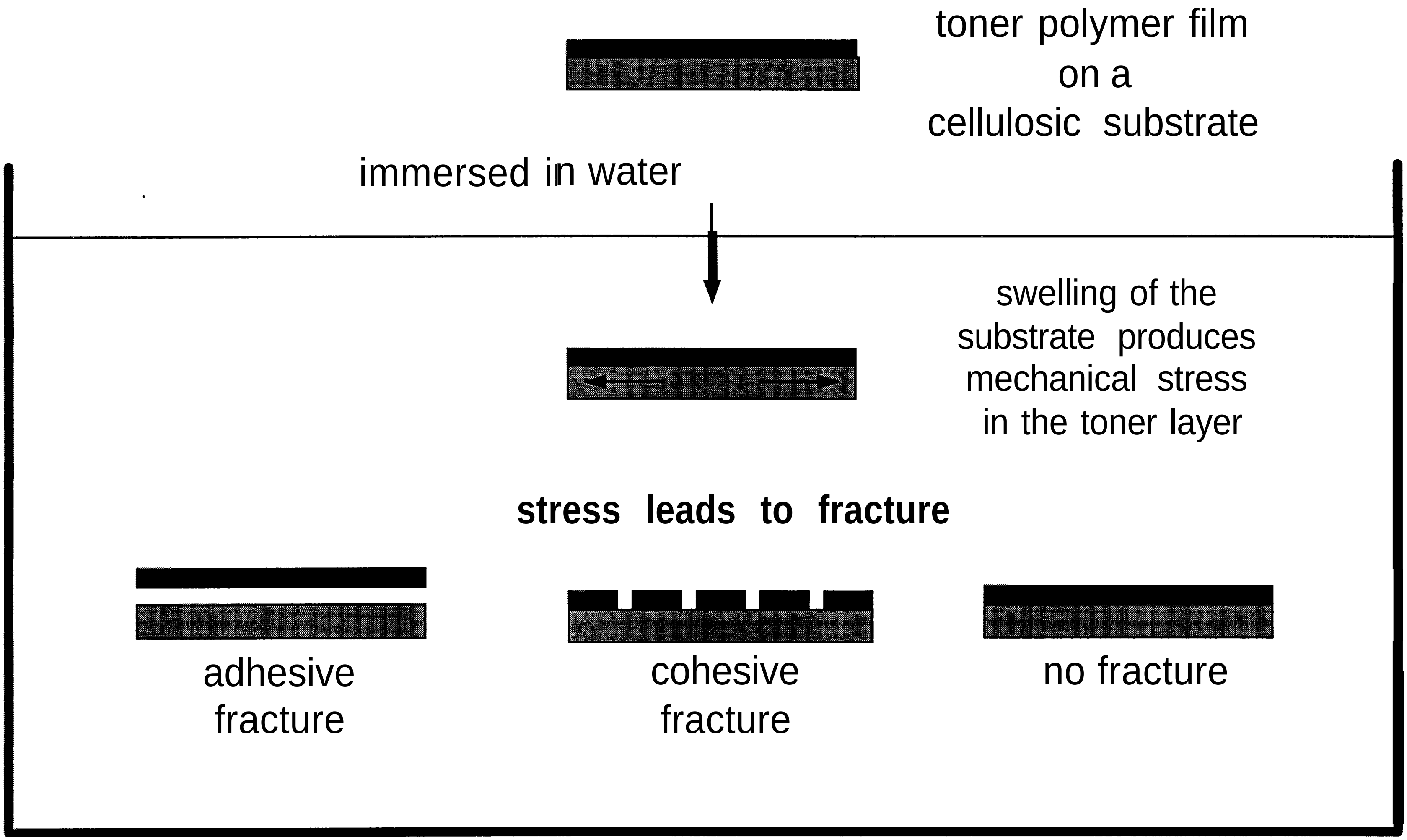
fiber

recycled paper

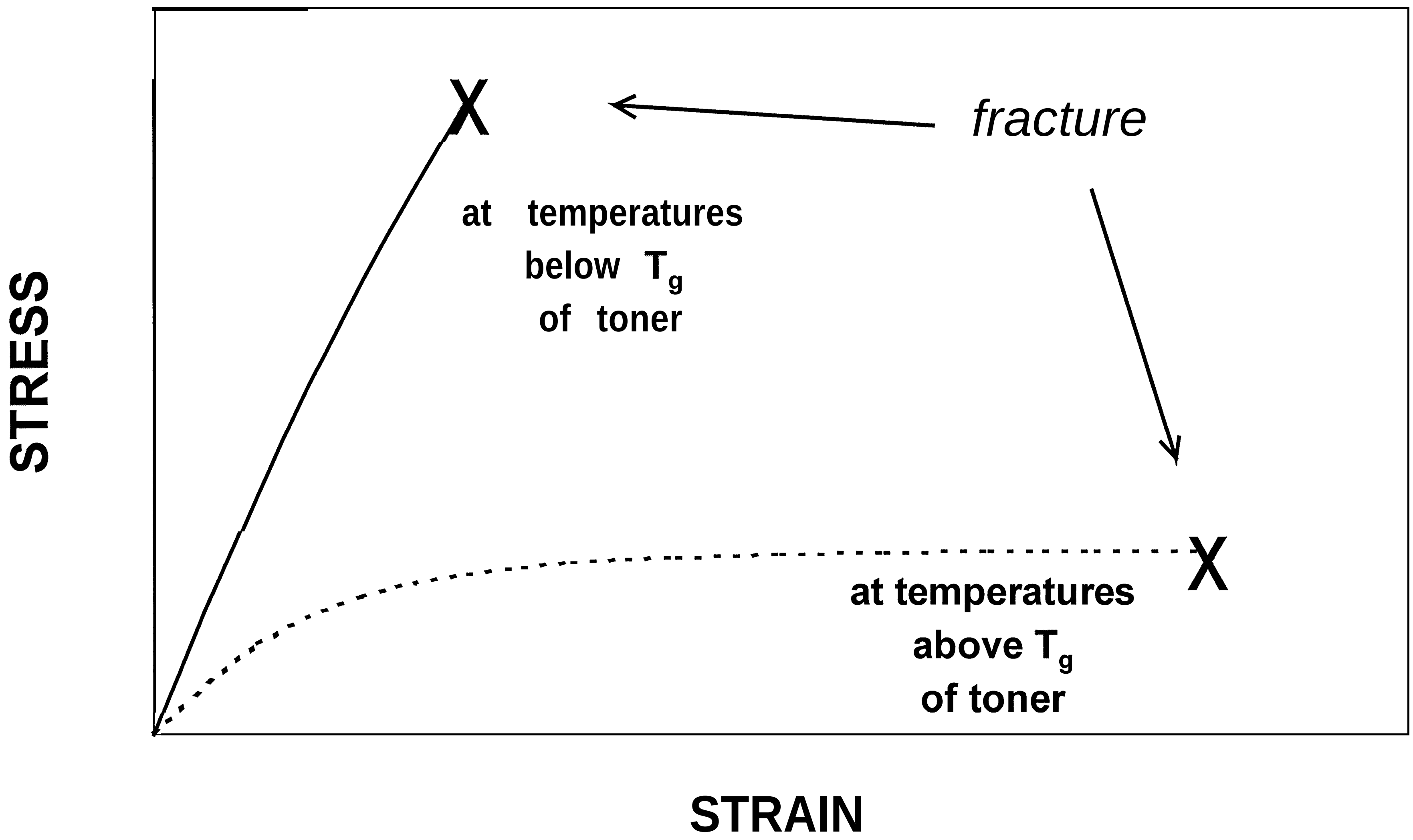
separation of toner affected by:

- toner particle size and shape
- retention of fibers to particles

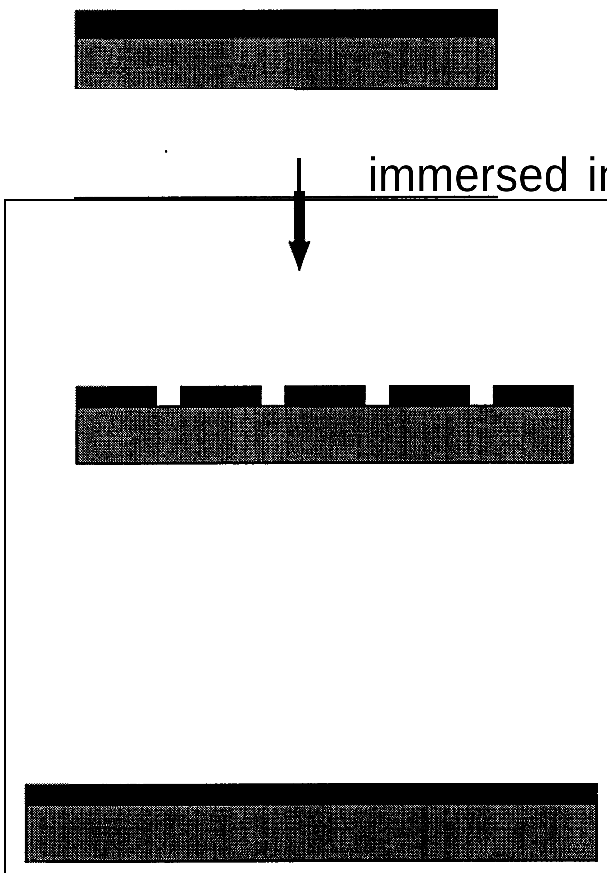
2. Repulping produces a fiber slurry with flat toner particles with a wide size distribution. The size and shape of these particles affect their separation.



3. The fracture of toner on paper composite upon immersion in water. Fracture occurs due to an increase in stress in the toner layer.



4. The effect of temperature on the stress-strain curve of a typical thermoplastic.



Toner on a cellulosic substrate

(cross-sectional view)

immersed in water

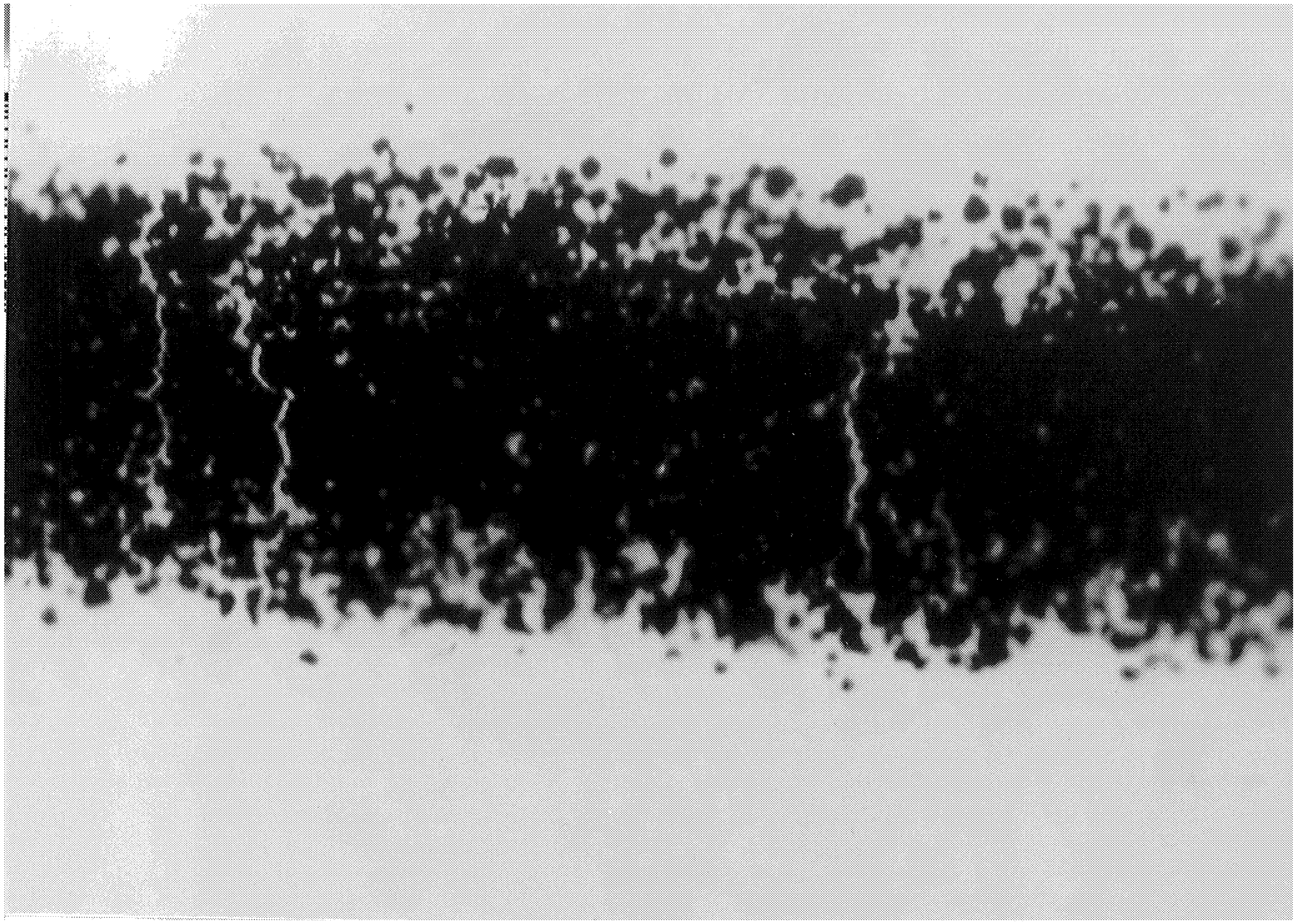
Below toner's T_g

- stiffer material leads to greater stress in the toner layer
- brittle material more likely to fracture

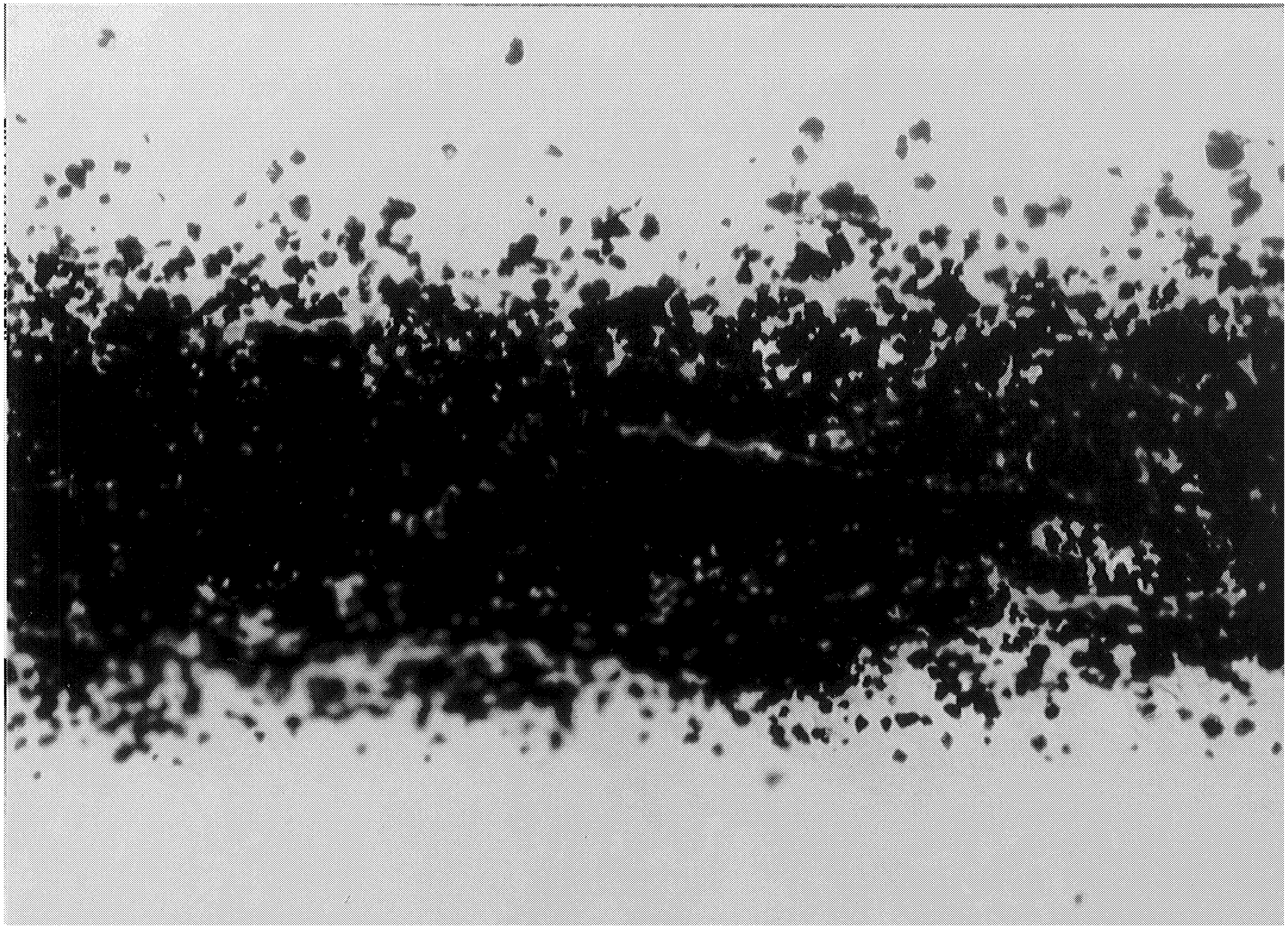
Above toner's T_g

- more flexible material leads to lower stress in the toner layer
- rubbery material less likely to fracture

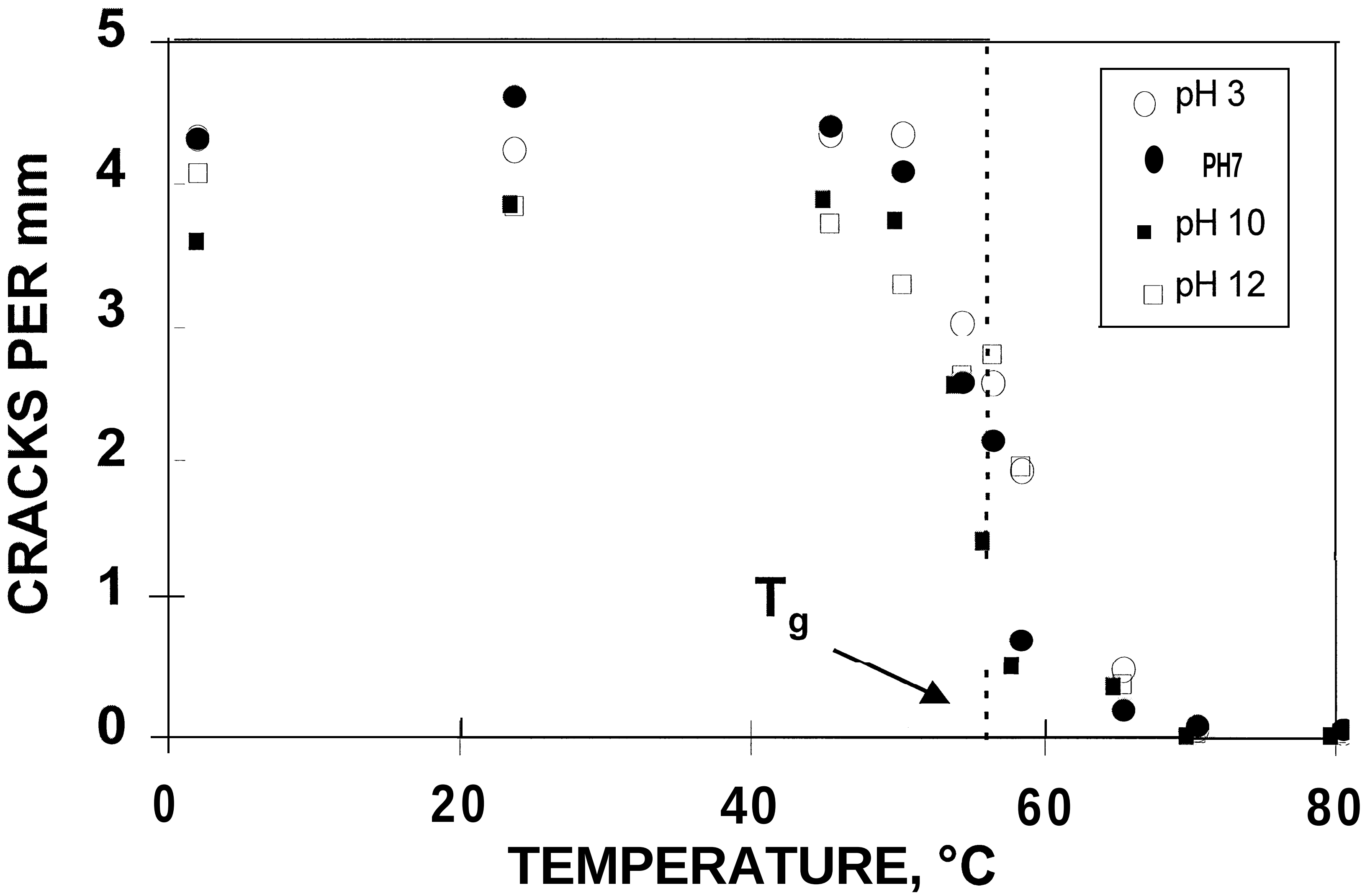
5. **The effect of temperature on the fracture of toner on a swelling cellulosic substrate.**



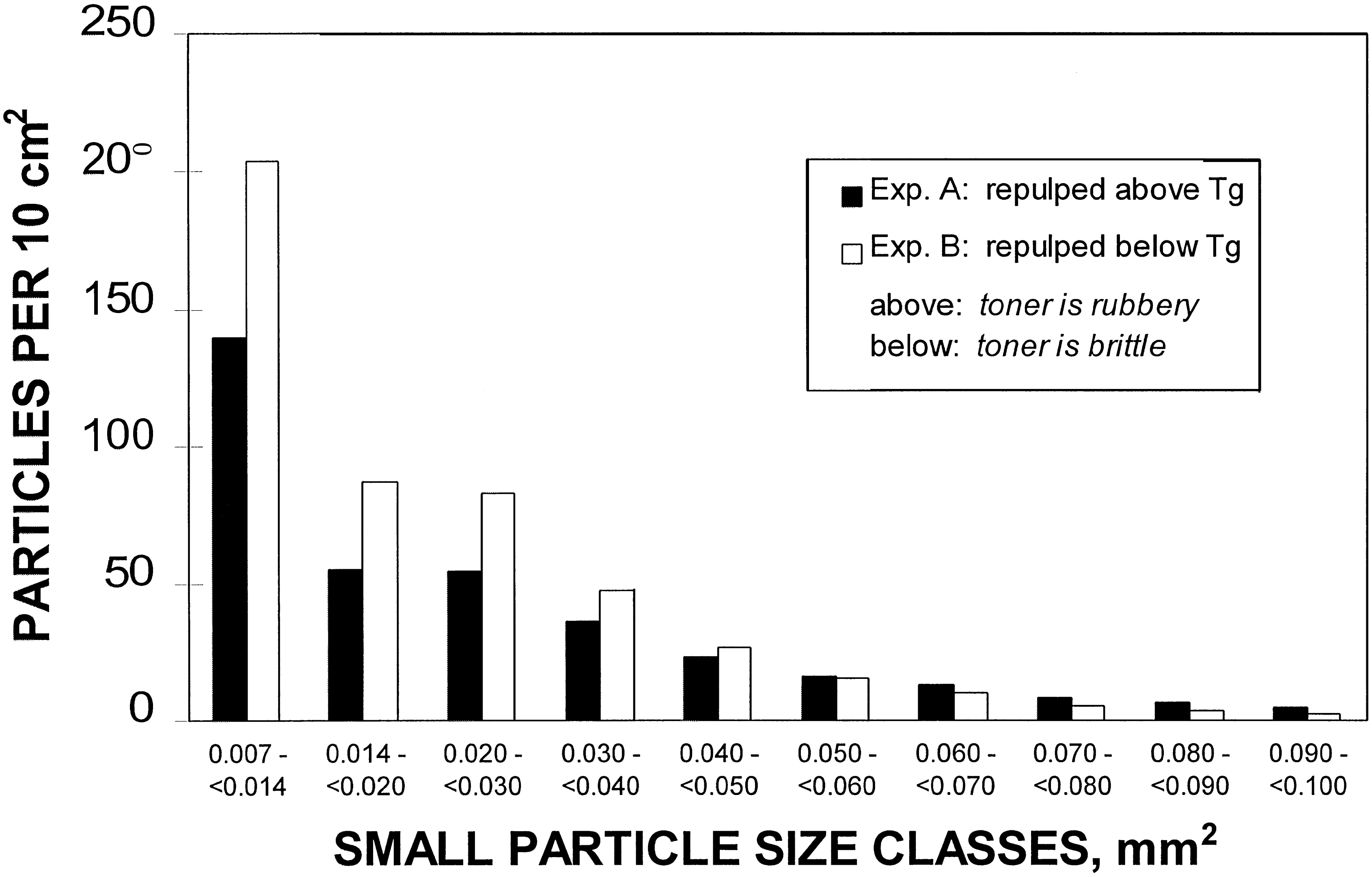
6. Microscopic photograph (40X) of cracks that form in a line of toner due to paper swelling. The line is oriented along the cross-direction of the paper. The cracks are observed to occur preferentially along the machine-direction of the paper.



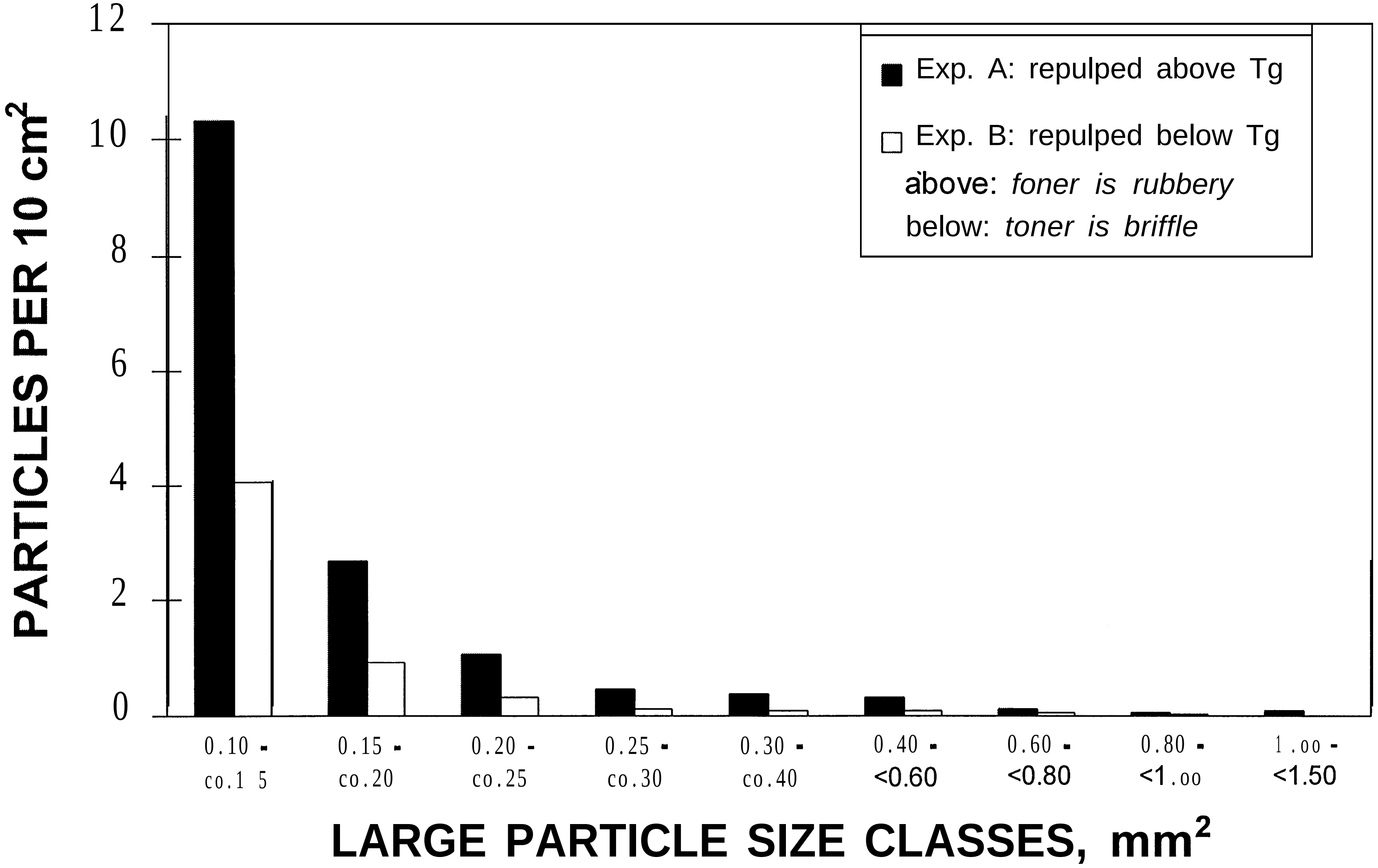
7. Cracks in a line of toner that is oriented along the machine-direction of the paper, Again, the cracks occur preferentially along the machine-direction of the paper.



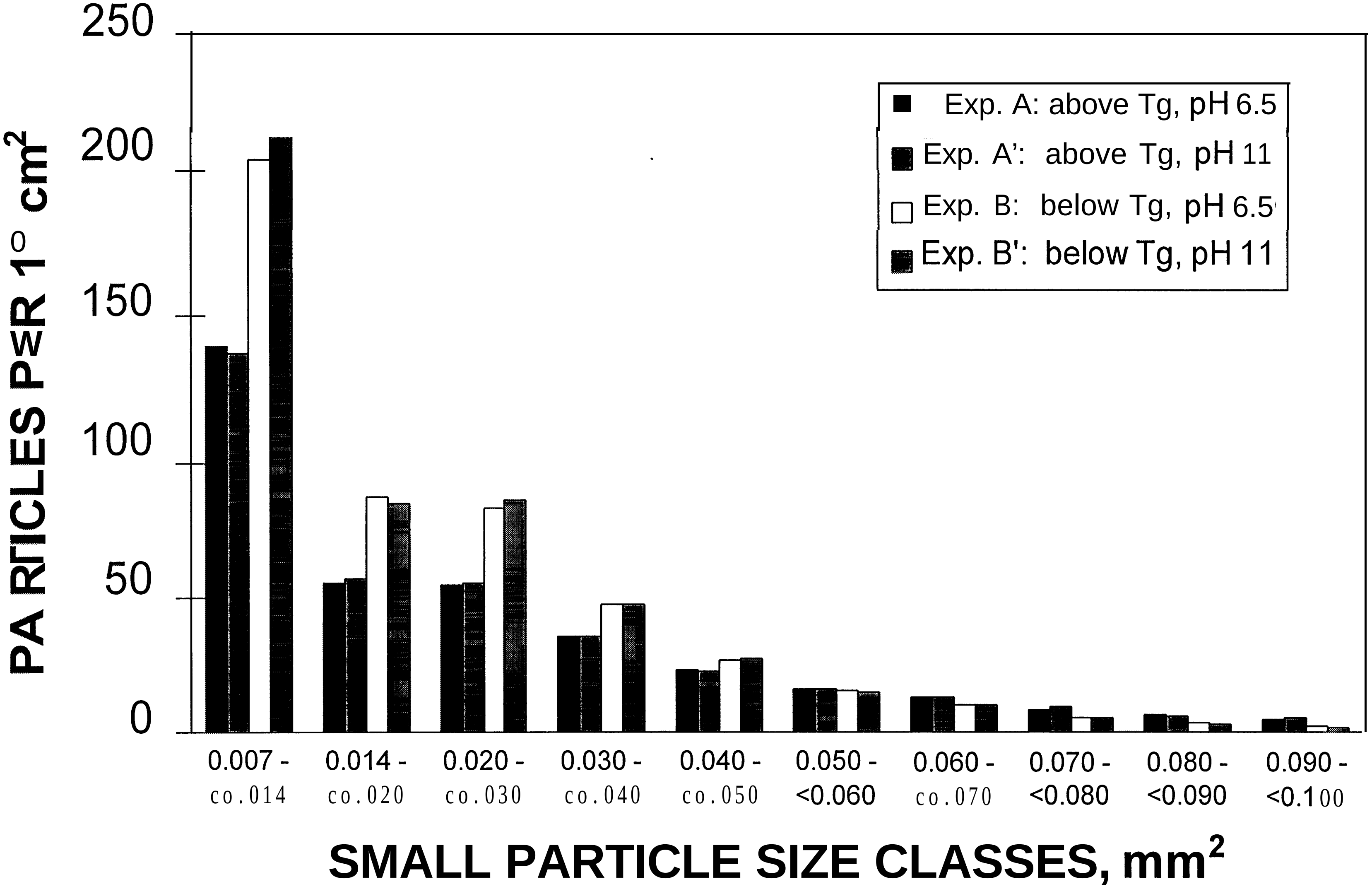
8. Number of fractures per millimeter that were observed in lines of toner due to paper swelling. Fracture is defined as a crack that extends across the width of the line. A significant change in the amount of fracture is observed at the glass transition temperature (T_g) of the toner.



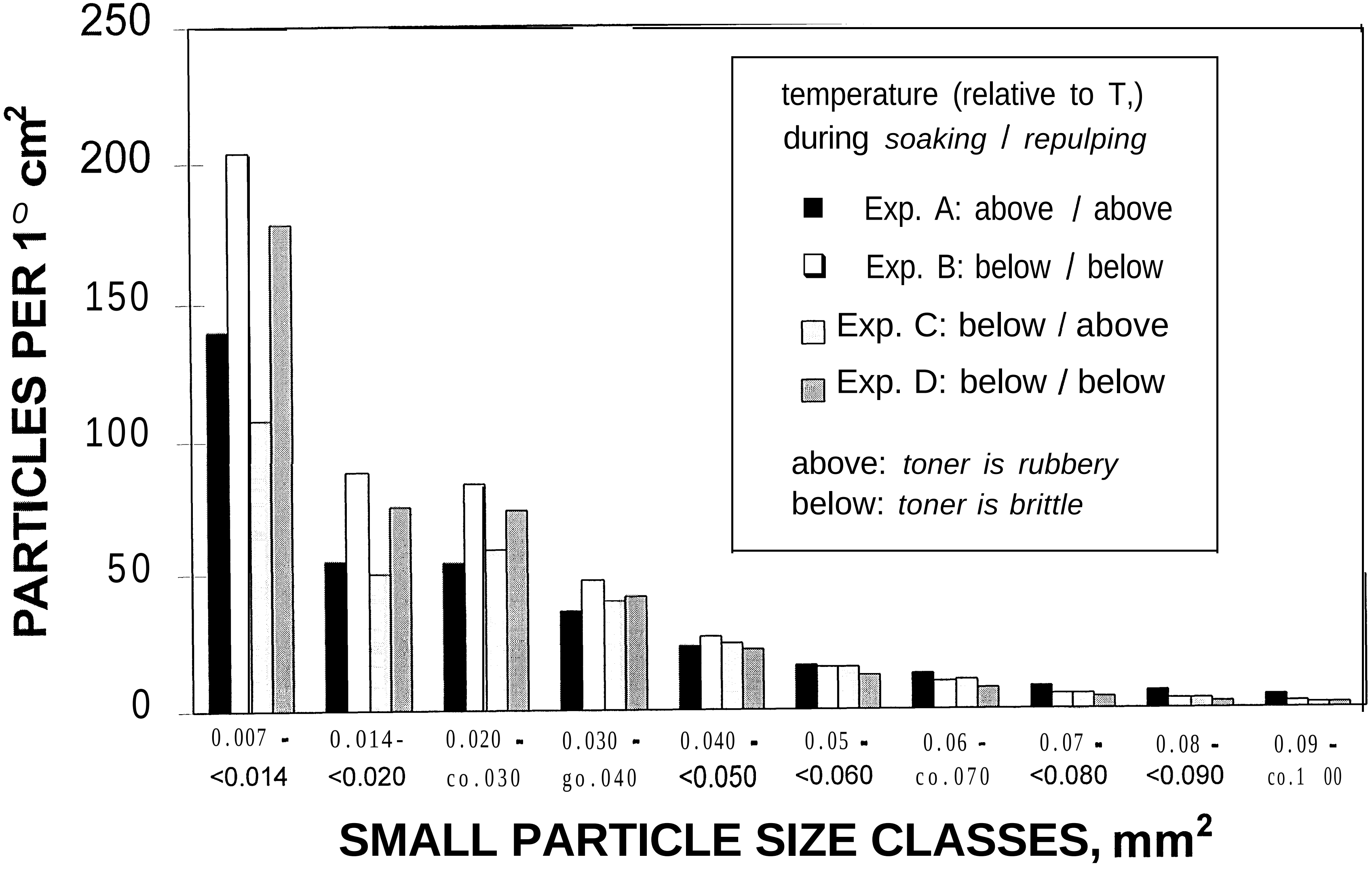
9. The effect of temperature on the size distribution of the smaller toner particles formed upon repulping toner-printed paper in a high-consistency laboratory repulper.



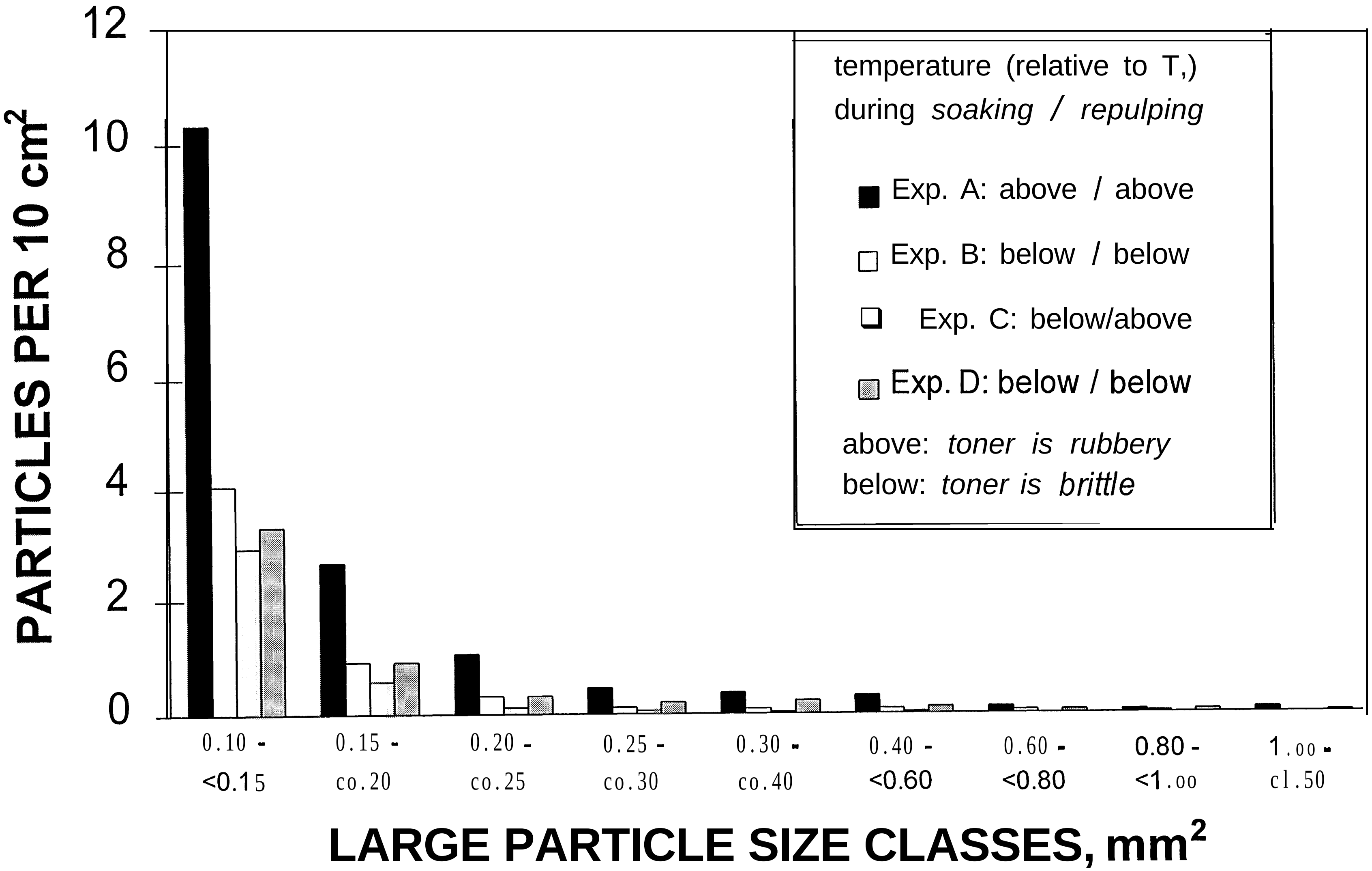
10. The effect of temperature on the size distribution of the larger toner particles formed.



11. The effect of pH on the size distribution of toner particles. The original experiments, A and B, were repulped at the natural pH. Experiments A' and B' were adjusted to pH II.



12. The effect of soaking on the size distribution of the smaller toner particles. Experiments C and D included a longer soak time below the toner's T_g. Experiment C was then repulped at a temperature above the toner's T_g, while Experiment D was repulped below the toner's T_g.



13. The effect of soaking on the size distribution of the larger toner particles.