

Fracture of toner due to paper swelling

LORRAINE C. VANDER WIELEN, JOEL C. PANEK, AND PETER H. PFROMM

EFFECTIVE DEINKING OF PHOTO-copies and laser-printed paper has proven elusive, principally because of the properties of the toners that are used to form the image on these papers. 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 a porous structure rather than a continuous film. In this work, we consider the toner and paper as a two-layer composite consisting of a toner polymer on a cellulosic substrate, as illustrated in **Fig. 1**. In this simplified context, the events in the repulping process that lead to the breakup of the toner layer can be more clearly understood.

The first step in deinking of wastepaper is repulping, wherein 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, as seen in **Fig. 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 from the slurry is influenced by their size and shape as well as their degree of retention to fibers (2-7). The size of toner particles in the repulped slurry is related to the composition of the toner, the nature of the printing process used to apply

the toner, 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 fractures into smaller particles when a mechanical stress acting on the toner exceeds the toner's fracture strength. The stress acting on the toner originates from swelling of the paper and from the application of mechanical forces in the repulping step. The magnitude of these stresses varies 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.

ORIGINS OF STRESSES AND TONER STRENGTH

Paper swelling

When toner-printed paper is immersed in water, the paper readily swells in response to water sorption. The water has virtually no effect on the toner. Because the toner is fused to the paper surface, it resists swelling of the paper, which creates mechanical stress in the toner. The toner can respond to the stress by detaching from the paper, cohesively fracturing, or remaining attached, as seen in **Fig. 3**. The response is determined by the cohesive strength of the toner and the strength of the adhesion between toner and paper. When the stress exceeds the cohesive strength of the toner, the toner fractures into smaller pieces.

ABSTRACT

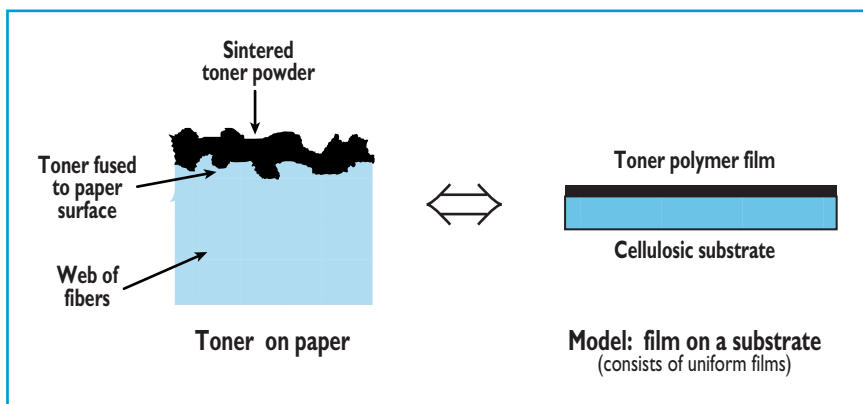
Efforts to improve the deinking of toner-printed paper have been hampered by an incomplete understanding of the mechanisms occurring during the recycling process. These mechanisms are difficult to study because of the complexity of the toner-paper system. To analyze the initial step of repulping, this work focused on the fracture of the toner layer that occurs when the paper swells upon immersion in water. Toner-printed papers were immersed in water (no mechanical agitation) and examined with a light microscope at 40× magnification. Sheet swelling caused significant fracture of toner for sheets soaked in water below the toner's glass-transition temperature (T_g). Above the T_g , where the toner changes from a brittle to a rubbery material, fracture was virtually nonexistent. The pH of the soaking medium had no significant effect on the swelling-induced toner fracture. The effect of temperature was also apparent when the toner-printed sheets were repulped. Repulping below the T_g produced a greater number of smaller particles compared with repulping above the T_g . The results show that paper swelling below the T_g produces large particles that are then broken into smaller particles by the mechanical action of the repulping process.

Application:

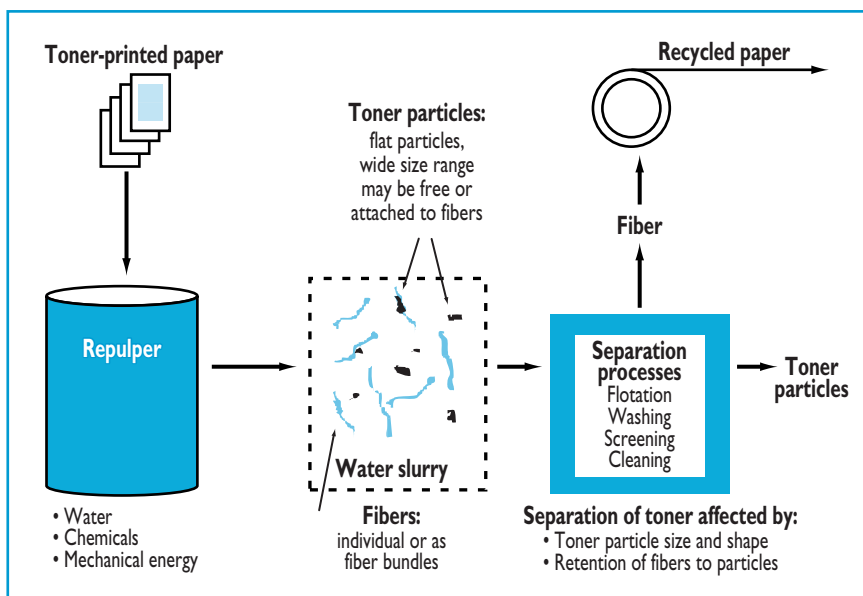
Shows that the particle size distribution of polymeric toners in a recycled furnish is affected by the temperature of the repulping operation and the material properties of the toner.

Mechanical action of the repulper

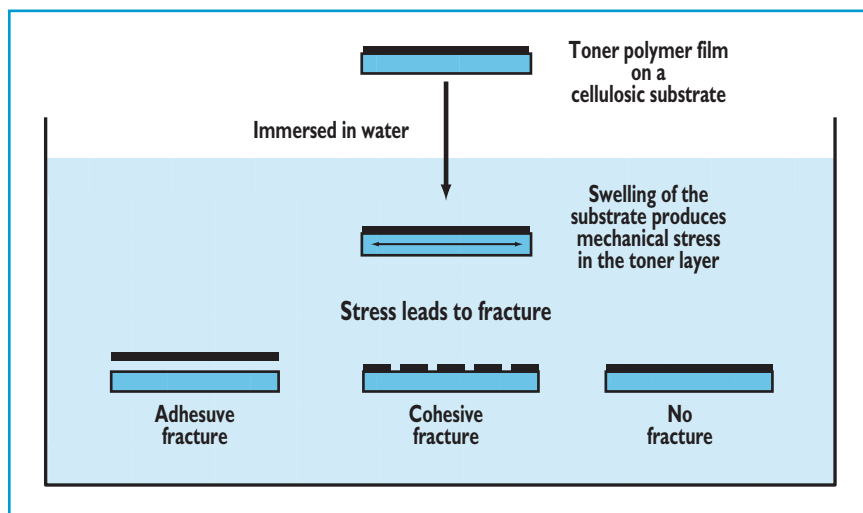
A second mechanism leading to fracture of the toner is the application of mechanical energy during repulping. The mechanical forces in a repulper include direct mechanical



1. Cross-sectional views of toner on a paper surface and of toner/cellulose model



2. Deinking process for toner-printed papers



3. Response of toner film to stress produced by swelling of cellulosic substrate upon immersion in water

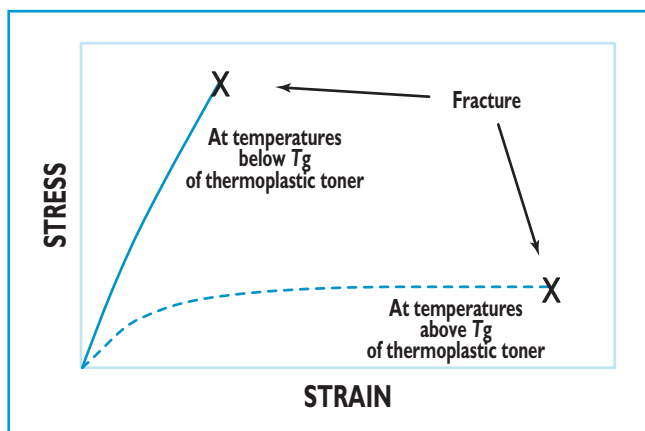
forces (paper-hitting rotors), fiber-fiber shear forces, shear stress from differences in flow velocity, attrition, and mechanical shearing between two plates (10). Higher consistencies and longer pulping times produce a greater number of smaller particles because of the forces acting on the toner (2-4, 7, 8). The degree of toner fracture is influenced by the magnitude of these forces and the strength of the toner layer.

Fracture strength of toner

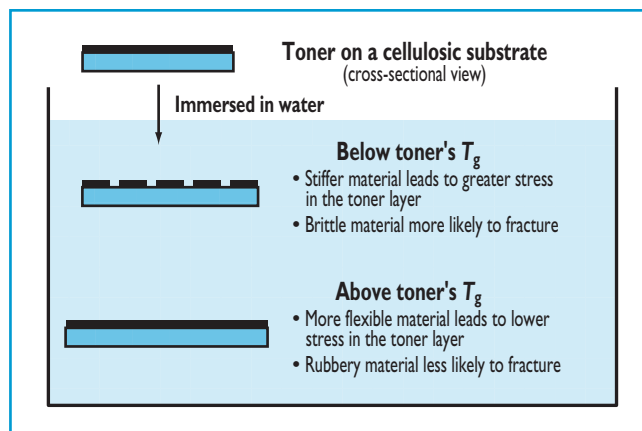
The fracture strength of the toner is determined by its material properties and physical structure. In this work, we are addressing the material properties, although it is recognized that the physical structure, particularly the thickness and the porosity of the layer, plays a very significant role (4).

Toner consists of a polymer binder (55-90%) and pigment (5-40%), as well as other additives. The material properties of a toner are largely determined by the polymeric binder. Polymer binders are sensitive to temperature, which can have a significant effect on the properties of the toner, as seen in Fig. 4. Below the glass-transition temperature (T_g) of the polymeric binder, toner behaves as a brittle solid. It is stiff and resists stress but fractures at relatively low strains. Above the binder T_g , toner becomes rubbery. It is flexible and shows little resistance to stress, elongating significantly before fracture. Figure 5 shows that the brittle toner below its T_g will preferentially fracture.

This work examines the effects of paper swelling (during the initial immersion step in the repulper) and the mechanical action during repulping on the fracture of toner into particles. First, we address the effect of temperature and pH on the fracture of toner that occurs when toner-printed paper swells after immersion in water. Next, we investigate the size of toner particles re-



4. Effect of temperature on the stress-strain curve for a typical thermoplastic



5. Effect of temperature on the fracture of toner on a swelling cellulosic substrate

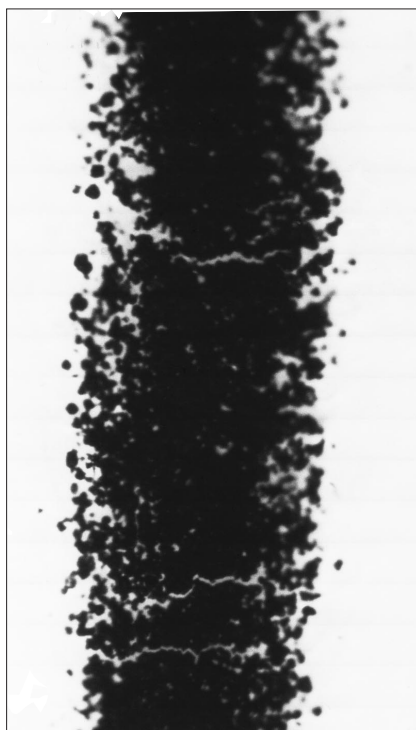
sulting from high-consistency laboratory repulping. The repulping work included an experiment that decoupled the mechanisms of paper swelling and mechanical action.

EXPERIMENTAL

Paper swelling

The toner used for this work (Xerox Dry Ink Plus) consisted of a styrene-acrylate polymer, carbon-black pigment, zinc stearate, and amorphous silica. The T_g of this toner is $56 \pm 2^\circ\text{C}$. 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 10–20 μm 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 $\pm 1^\circ\text{C}$, pH adjusted with hydrochloric acid (6N Baker analyzed) or sodium hydroxide (0.16% VWR brand)]. All samples were immersed for 5 min, removed, and immediately placed under a light microscope at



6. Microscopic photograph (40 $\times$) of swelling-induced cracks in a line of toner. (The toner line is oriented along the cross-machine direction of the paper; cracks occur preferentially along the machine direction of the paper.)



7. Microscopic photograph (40 $\times$) of swelling-induced cracks in a line of toner. (The toner line is oriented along the machine direction of the paper; cracks occur preferentially along the cross-machine direction of the paper.)

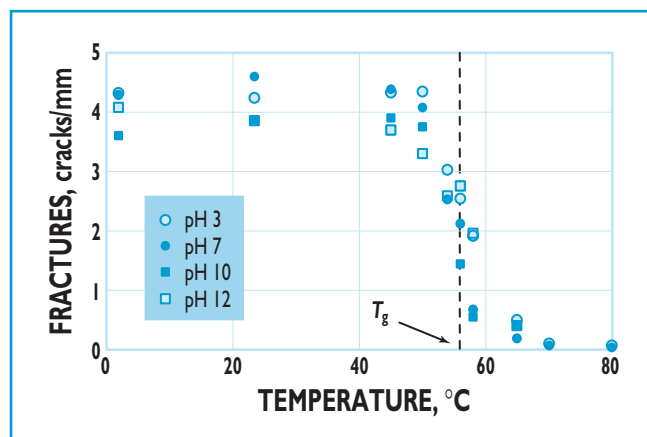
40 $\times$ magnification. Upon submersion in water, cracks in the printed line formed, as seen in Figs. 6 and 7. Fracture is defined here as a crack detected across the width of the line. The distance between cracks was measured using image analysis software (Optimas Corp.). Ten samples

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.

Experiment	SOAKING		REPULPING	
	below T_g	above T_g	below T_g	above T_g
A	...	Brief	...	✓
B	Brief	...	✓	...
C	Extended*	...	...	✓
D	Extended*	...	✓	...

*80 min

I. Experimental conditions for repulping



8. Frequency of fractures in swollen sheets as a function of soaking temperature at four levels of pH

Repulping

Toner-printed samples were repulped at 11% consistency in a 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. A 1.0-kg portion of the printed paper was torn into sections and 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_g . The pH of 6.5 is the natural pH of the system, while pH 11 was obtained by adding aqueous sodium hydroxide. The below- T_g experiments were begun at room temperature (25°C). The temperature increased by 10–15°C during repulping but remained well below the T_g . The above- T_g experiments began at 70°C (water was heated before paper was added). The temperature decreased by 6–7°C during these experiments but did not drop below the T_g . Repulping was done for 10 min on the low setting (900 rpm), with 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 set above the toner's T_g (Experiment A) and one set below the T_g (Experiment B). Both sets were repulped at two pH levels. In the second two sets (Experiments C and D), the paper was allowed to soak in the water for 80 min before being repulped. Experiment C

consisted of soaking the paper in water at room temperature, heating the paper and water above the toner's T_g , and then repulping above the T_g . Experiment D consisted of soaking the paper in water at room temperature and then repulping below the T_g .

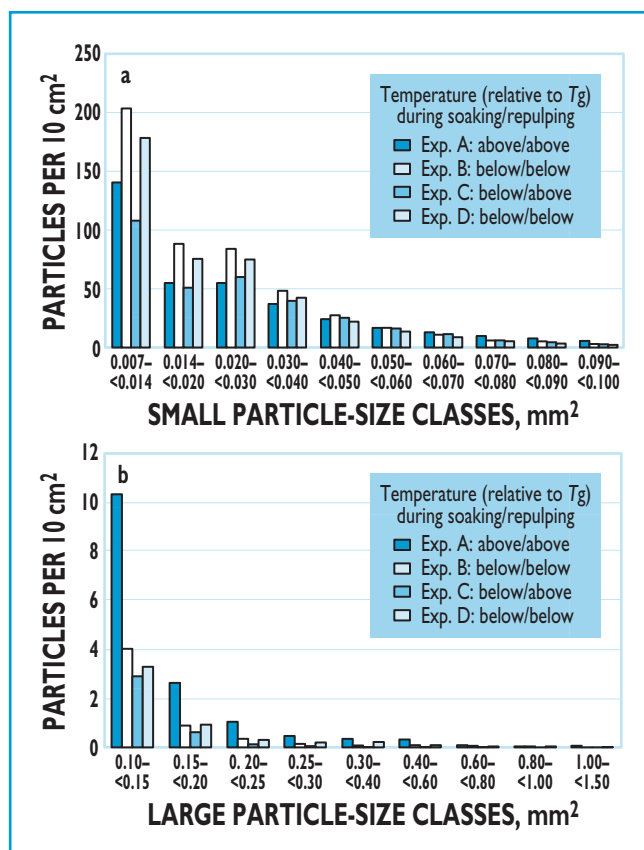
Handsheets were made from pulp samples on a Büchner funnel using grade 415 qualitative filter paper. An image-analysis program (Spec*Scan 200, Apogee Systems, Inc.) was used with a scanner (Hewlett Packard Scan Jet 3C) to measure the black particles appearing in the handsheets. The detected particles were classified into size categories ranging from 0.007 to 1.00 mm². Particles smaller than 0.007 mm² were not reported because they could have slipped through the filter paper that was used to form the handsheets. Image analysis was applied to all but the outer 1.0 cm of the 15.0-cm-diam. handsheets.

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 (Fig. 6) and along its length (Fig. 7), in addition to smaller cracks that were barely detectable.

The photographs indicate that paper swelling fractures the toner. However, it is conceivable that these cracks were already present in the line of toner prior to immersion and were not created by the swelling of the paper. It might be that swelling of the paper simply increased the size of the cracks, allowing them to be seen more easily. Under 40× 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 as those observed at 23.5°C. The fact that samples immersed in water at 70°C did not display significant cracking indicates 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 (Figs. 6 and 7). This appears to be the result of greater cross-directional swelling of the paper, which leads to cracks that

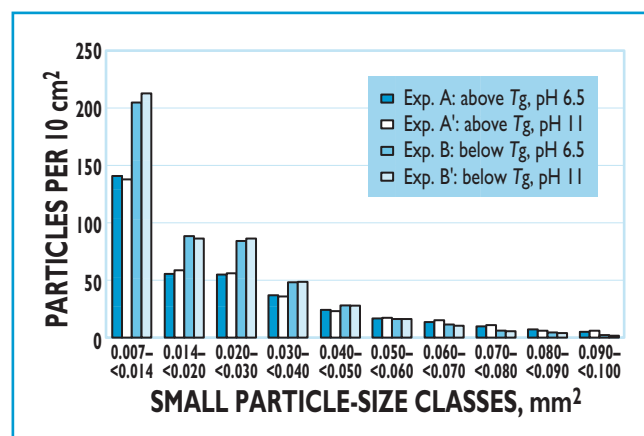


9. Effect of temperature on the size distribution of (a) small toner particles and (b) large toner particles formed upon repulping toner-printed paper in a high-consistency laboratory repulper

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).

Figure 8 illustrates the significant effect that temperature has on fracture. (Fracture is defined as a crack that extends across the width of the printed line.) There is a dramatic decrease in the number of cracks that form as the temperature reaches and exceeds the T_g . 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 in determining the amount of fracture that occurs.

In this system, the pH did not have a significant effect on the amount of fracture induced by paper swelling, as seen in Fig. 8. This indicates that the pH change did not affect the degree of paper swelling or the material properties of the toner. 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



10. Effect of pH on the size distribution of small toner particles upon repulping toner-printed paper in a high-consistency laboratory repulper

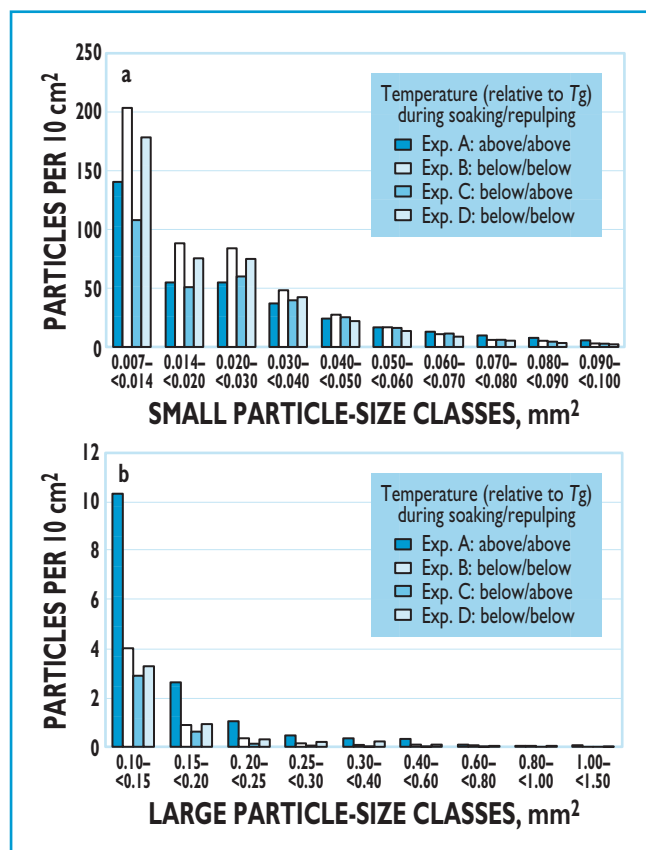
have a significant effect on fiber swelling (12). The effect of pH on the toner will depend on the base polymer. In this case, the toner polymer was inert to changes in pH.

The repulping experiments provided evidence that the effects observed during the paper-swelling experiments can be relevant even after application of the more intense repulping process. The paper swelling experiments showed that more fracture occurred below the T_g than above because the toner is more brittle (Fig. 8). Results for the repulping experiments in Fig. 9 show that a greater number of small particles and fewer large particles are formed below the T_g than above. At temperatures below the toner's T_g , the repulping process breaks the larger, brittle particles into smaller ones.

The results of the repulping experiments in Fig. 10 confirm that pH had no significant effect on particle size. 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 and then repulping it above the T_g . Thus the toner was brittle (below the T_g) in the soaking step and rubbery (above the T_g) 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. This is confirmed 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) in Fig. 11.

The results indicate that the two mechanisms become dominant in different particle size ranges. Paper swelling governs the size distribution of the largest par-



11. Effect of soaking on the size distribution of (a) small and (b) large toner particles upon repulping toner-printed paper in a high-consistency laboratory repulper. (Experiments C and D included a longer soak time below the toner's T_g .)

ticles, while mechanical action breaks the larger particles into smaller ones. Experiment C (soaking below the T_g with repulping above the T_g) resulted in fewer small particles than Experiments B or D (repulping below the T_g), as seen in Fig. 11a. This is because the particles were more rubbery in the repulping step during Experiment C and thus did not break into smaller particles as easily. Fracture occurred during soaking below T_g in all three experiments (B, C, and D); however, the brittle toner broke down to a greater extent when repulping was carried out below the T_g (Experiments B and D). In the same fashion, Experiment C (soaking below the T_g followed by repulping above) resulted in fewer large particles than Experiment A (soaking above the T_g followed by repulping above), as seen in Fig. 11b. This is because the particles were more brittle in the soaking step during Experiment C and broke into smaller particles prior to repulping. Even though the repulping was done at the same conditions for Experiments A and C, the fracture that occurred during soaking in Experiment C 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,

producing only larger particles and essentially no smaller ones. Mechanical action during repulping breaks 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 in these experiments was already quite high, so the swelling fracture mechanism observed here 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 during repulping.

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_g), 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 degree of 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_g). 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 actual toner-paper systems. This will be valuable in determining the effect of toner properties on the particle size distribution. **TJ**

Vander Wielen is a former graduate student, Panek is a graduate student, and Pfromm is an associate professor at the Institute of Paper Science and Technology, 500 Tenth St. NW, Atlanta, GA 30318. Vander Wielen is now a senior project engineer with International Paper – Camden Mill, 1944 Adams Ave., Camden, AR 71701.

The authors thank the Institute of Paper Science Technology and its Member Companies for their support. Portions of this work were used by L.C.V.W. and J.C.P. as partial fulfillment of the requirements for the M.S. degree and Ph.D. degree, respectively, at the Institute of Paper Science and Technology.

Received for review Aug. 13, 1997.

Accepted Jan. 13, 1998.

LITERATURE CITED

1. Borchardt, J. K., Rask, J. H., York, G. A., et al., *Progr. Paper Recycling* 4(4): 16(1995).
2. Johnson, D. A. and Thompson, E. V., *TAPPI 1994 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1291.
3. Berg, S. R., Johnson, D. A., and Thompson, E. V., *TAPPI J.* 80(4): 171(1997).
4. Dorris, G. M. and Sayegh, N. N., *TAPPI J.* 80(4): 181(1997).
5. Snyder, B. A. and Berg, J. C., *Tappi J.* 77(7): 157(1994).
6. Vidotti, R. M., Johnson, D. A., and Thompson, E. V., *Progr. Paper Recycling* 3(3): 39(1994).
7. Pan, R., Johnson, D. A., and Thompson, E. V., *TAPPI 1995 Recycling Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 37.
8. Vidotti, R. M., Johnson, D. A., and Thompson, E. V., *Progr. Paper Recycling* 2(4): 30(1993).
9. Borchardt, J. K. and Lott, V. G., *TAPPI 1995 Recycling Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 17.
10. Fallows, J. D., *TAPPI 1992 Deinking Seminar Notes*, TAPPI PRESS, Atlanta, Session 2-1.
11. Stamm, A. J., *Wood and Cellulose Science*, Ronald Press, New York, 1964, pp. 239-47.
12. Lindström, T. and Carlsson, G., *Svensk Papperstid.* 85(3): R14(1982).