Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 633

Effect of Temperature and pH on the Fracture of Toner Due to Paper Swelling

L. Vander Wielen, J.C. Panek, and P.H. Pfromm

January 1997

Submitted to
1997 TAPPI Recycling Symposium
Chicago, Illinois
April 14–16, 1997

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and

- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

EFFECT OF TEMPERATURE AND pH ON THE FRACTURE OF TONER DUE TO PAPER SWELLING

Lorraine Vander Wielen
Graduate Student

Joel C. Panek
Graduate Student

Peter H. Pfromm
Assistant Professor

Institute of Paper Science and Technology
Atlanta, GA 30318

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 system. To analyze the initial step of repulping, this work studied the fracture of the toner layer resulting from paper swelling only.

Observations of toner-printed paper upon immersion in water showed that significant fracture of toner can occur due to paper swelling. Below the glass transition temperature of the toner, fracture was evident. Above this temperature, fracture was virtually nonexistent. This is due to the change of the toner from a brittle to a rubbery material. The pH did not affect the fracture.

INTRODUCTION

Effective deinking of photocopies and laser-printed paper has proven elusive, largely due to the characteristics of the polymer-based toner, which produces the image. Toner can be considered as a thermoplastic fused onto the surface of paper, and acts as a brittle, hydrophobic solid under ambient conditions. The goal of deinking wastepaper is to separate the toner from the paper fibers so that the fibers can be reused.

The first step in deinking of wastepaper typically consists of disintegrating the paper by immersing the furnish in water and applying mechanical forces. This produces a fiber slurry from which the toner can be more easily removed in subsequent separation processes. In this slurry, toner is primarily found as plate-like particles, which are more or less detached from the fibers [1, 2]. The ability to remove these toner particles from the fibers has been shown to be affected by their size and shape, as well as the retention of fibers to the particles [3-6]. These characteristics vary significantly enough to affect deinking efficiency.

The size of the toner particles resulting from repulping has been shown to be affected by the composition of the toner, the printing process used, and the deinking conditions [3-8]. It has been suggested that these factors affect the cohesiveness of the printed layer, and that it is the cohesiveness that determines the size. Dorris and Sayegh [3] proposed an apparent layer thickness to quantify the cohesiveness of a print layer. They showed that the particle size resulting from repulping increases with increasing apparent layer thickness.

To further study the factors that determine the size of toner particles in repulping, we chose to investigate the initial step of immersion of toner-printed paper into water. Specifically, we examined the breakup of a continuous character of toner into smaller fragments that occurs upon immersion.

One of the mechanisms occurring when toner-printed paper is immersed in water is the swelling of the paper due to water sorption. The paper readily swells; 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 it may remain attached (Figure 1). The response is determined by the cohesive strength of the toner and the adhesive strength of the toner to the paper. When the cohesive strength of the toner is exceeded, the toner will fracture into smaller pieces.

Thus, the toner particle size is determined by the stress in the toner layer and strength of the toner. The stress in the toner is determined by the degree of swelling of the paper, the stiffness of the materials, and the geometry (described below). The strength of the toner is determined by its material properties and its physical structure. Therefore, it is important to know whether the stiffness and the strength of the toner change significantly with process conditions, such as temperature and pH.

The temperature can have a significant effect on the properties of the toner. Toner consists of a polymer binder (55-90%) and pigment (5-40%), in addition to other additives. Below the glass transition temperature (T_g) of the polymeric binder, the toner behaves as a brittle solid. It shows a high resistance to stress, but fractures at relatively low strains. When the T_g is exceeded, the toner behaves as a rubbery material. It shows little resistance to stress, but stretches significantly before fracturing.

The objective of this work is to determine the effect of temperature and pH on the fracture of toner. This will lead to a better understanding of the factors controlling the size and shape of toner particles in a deinking process.

LAMINATE MODEL

The stress in the toner may be quantified by modeling toner on paper as a two-layer composite. The stresses in the composite due to hygroexpansion of the paper are as follows:

$$\sigma_T = E_T(\varepsilon_0 - \kappa z) \qquad (1)$$

$$\sigma_P = E_P\left(\varepsilon_0 - \kappa z - \varepsilon_H\right) \quad (2)$$

Where σ_T is the average stress [MPa] in the toner; σ_P is the average stress in the paper; E_T and E_P are the moduli [MPa] of the toner and paper, respectively; ε_0 is the midplane strain; κ is the curvature [mm^{-1}]; z is the distance [mm] from the midplane; and ε_H is the hygroexpansive strain (swelling) of the paper. A balance on the forces in the system gives the following equation:

$$\sigma_T = \frac{\varepsilon_H}{\left[\frac{1}{E_P}\frac{h_T}{h_P} + \frac{1}{E_T}\right]} \quad (3)$$

Where h_T is the thickness of the toner layer, and h_P is the thickness of the paper. This shows that the stress in the toner can be predicted from the thickness of the layers, the moduli of the materials, and the degree of hygroexpansion of the paper.

EXPERIMENTAL

The toner used for this work consisted of a styrene acrylate polymer, carbon black pigment, zinc stearate, and amorphous silica. A pattern of lines was photocopied onto standard copy paper. 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. Fracture is defined here as a crack detected across the width of the line as seen in Figure 2. The lines were photocopied onto twenty-pound alkaline copy paper that had been stored at 50% relative humidity. For uniformity of the results, the data reported here were collected using lines printed along the cross direction of paper only.

The fracture of the toner was observed using a light microscope at 40X magnification. The samples were immersed in water for 5 minutes, removed, and immediately placed under the microscope to obtain an image. Upon submersion in water, cracks in the line formed, as seen in Figure 2.

The distance between cracks was measured using image analysis software. The average number of cracks per millimeter was calculated from these measurements.

The toner-printed paper was submerged in water at various temperatures and four different pH levels. The temperature was controlled (+/- 1°C) using water baths. The pH was adjusted using sodium hydroxide (0.16% VWR) and hydrochloric acid (6N Baker analyzed).

RESULTS AND DISCUSSION

Cracks in the toner layer are detected when the sample is immersed in water. However, it is possible that these cracks may already be present prior to immersion, rather than created from paper swelling. The cracks may have formed in the photocopier or from handling of the paper. Swelling of the paper may simply increase the size of the cracks and allow the cracks to be seen more easily.

Cracks in the toner were not apparent under 40X magnification prior to immersion in water, but became visible after being submerged in 23.5°C water. These cracks were no longer detectable when the sample was dried. These results indicate that the cracks are visible only when the paper is in the swollen state.

On the other hand, samples that were initially immersed in 70°C water showed very few cracks relative to the samples that were initially immersed in 23.5°C water. If the cracks were already present, these samples at 70°C should show a similar number of cracks. Thus, it is likely that pre-existing cracks were not significant in the samples, and that the fracturing was due to swelling of the paper.

The number of cracks formed from submerging toner-printed paper in water of various temperatures and four pH levels are shown in Figure 3. The dramatic step change in this curve clearly shows the significant effect that the temperature has on the fracture, specifically, whether the temperature is above or below the glass transition temperature (T_g) of the toner. The T_g of the toner studied here is 56+/-2°C. At temperatures below the T_g, many fractures were observed. Above the T_g, little to no fracturing was observed.

The change in fracture behavior can be explained by the change in the properties of the toner. Below the T_g of the toner, the stress that develops due to swelling of the paper is significant enough to fracture the toner. Above the T_g, the rubbery material stretches with the swelling paper, rather than fracturing.

The experiment was repeated using water at pH 3, 7, and 12. The results showed that the pH had no significant effect on the incidence of toner fracture upon immersion in water. This indicates that the pH has no significant effect on paper swelling or the strength of the toner in this system.

The orientation of the print relative to the paper affected the observed fracture pattern. For lines that were printed along the cross direction of the paper, the cracks that formed were mainly machine directional. This can be seen in Figure 2, where the cracks that formed were perpendicular to the direction of the lines. On the other hand, lines printed along the machine direction showed longer fractures along the machine direction, and little cross-directional fracture. This is shown in Figure 4, in which the cracks that formed were primarily along the direction of the line.

Because the cracks formed primarily along the machine direction, the fracture of the lines appears to be the result of greater cross-directional swelling of the paper. Machine-formed paper swells from 1.2 to 3.0 more times in the cross direction than in the machine direction due to fiber orientation and dried in stresses and strains [9].

The average crack length created by fracturing below the T_g was 255 μm with a standard deviation of 106 μm. This compares with reported toner particle sizes of 40 to 400 μm resulting from repulping [10]. There are also a number of smaller particles on the order of the toner particle size due to scattering of toner during the photocopy process. Toner particles from paper repulped at a higher temperature are expected to be larger, due to decreased fracture. Borchardt and Lott showed that the size of toner particles increased by 48% with a pulping temperature above the T_g of the toner [8].

CONCLUSIONS

These results show that paper swelling alone causes significant fracture of toner below the glass transition temperature of the toner. The cracks that form are oriented primarily along the machine direction of the paper due to greater hygroexpansion of the paper in the cross direction.

Below the glass transition temperature, solid toner is brittle and cohesively fractures due to an increase in stress in the non-swelling toner. However, above the T_g of the toner, the toner becomes 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 affect the strength of the toner or the paper swelling.

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 particle size distribution. A study of toner fracture in a model composite is underway at IPST.

REFERENCES

1. Johnson, D.A.; Thompson, E.V. "Fiber/Toner Detachment Studies: Repulping and Flotation of Laser Printed Paper. Part I" *Proc. 1994 TAPPI Pulping Conf.* pp. 1291-1299.

2. Borchardt, J.K.; Rask, J.H.; York, G.A.; Cathie, K. "Microscopic Analysis of Toner-printed Paper After Pulping" *Progress in Paper Recycling* 4(4):16 (Aug. 1995).

3. Dorris, G.M.; Sayegh, N.N. "The Role of Print Layer Thickness and Cohesiveness on Deinking on Toner-Printed Papers" *Proc. 1994 TAPPI Pulping Conf.* pp. 1273-1289.

4. Snyder, B.A.; Berg, J.C. "Effect of Particle Size and Density in Flotation Deinking of Electrostatic Papers" *Tappi J.* 77(7):157 (1994).

5. Vidotti, R.M.; Johnson, D.A.; Thompson, E.V. "Repulping and Flotation Studies of Photocopied and Laser-Printed Office Paper. Part II. Flotation" *Progress in Paper Recycling* 3(3):39 (May 1994).

6. Pan, R.; Johnson, D.A.; Thompson, E.V. "Fiber/Toner Detachment Studies: Repulping and Flotation of Laser Printed Paper. Part II." *Proc. 1995 TAPPI Recycling Symp.* pp. 37-45.

7. Vidotti, R.M.; Johnson, D.A.; Thompson, E.V. "Repulping and Flotation Studies of Photocopied and Laser-Printed Office Waste Paper. Part I: Repulping and Image Analysis" *Progress in Paper Recycling* 2(4):30 (Aug. 1993).

8. Borchardt, J.K.; Lott, V.G. "Deinking Toner Ink Containing Furnishes. Part 3. Are Microscopic Ink Particles Formed on Pulping?" *Proc. 1995 TAPPI Recycling Symp.* pp. 17-36.

9. Stamm, A. Wood and Cellulose Science. The Ronald Press Co. 1965. pp. 238-247.

10. Scott, W.E.; Gerber, P. *Tappi Journal* "Using Ultrasound to Deink Xerographic Waste" 78(12):125 (1995).

ACKNOWLEDGEMENTS

The authors would like to thank the Institute of Paper Science and Technology and its Member Companies for their support. Portions of this work were used by L.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.

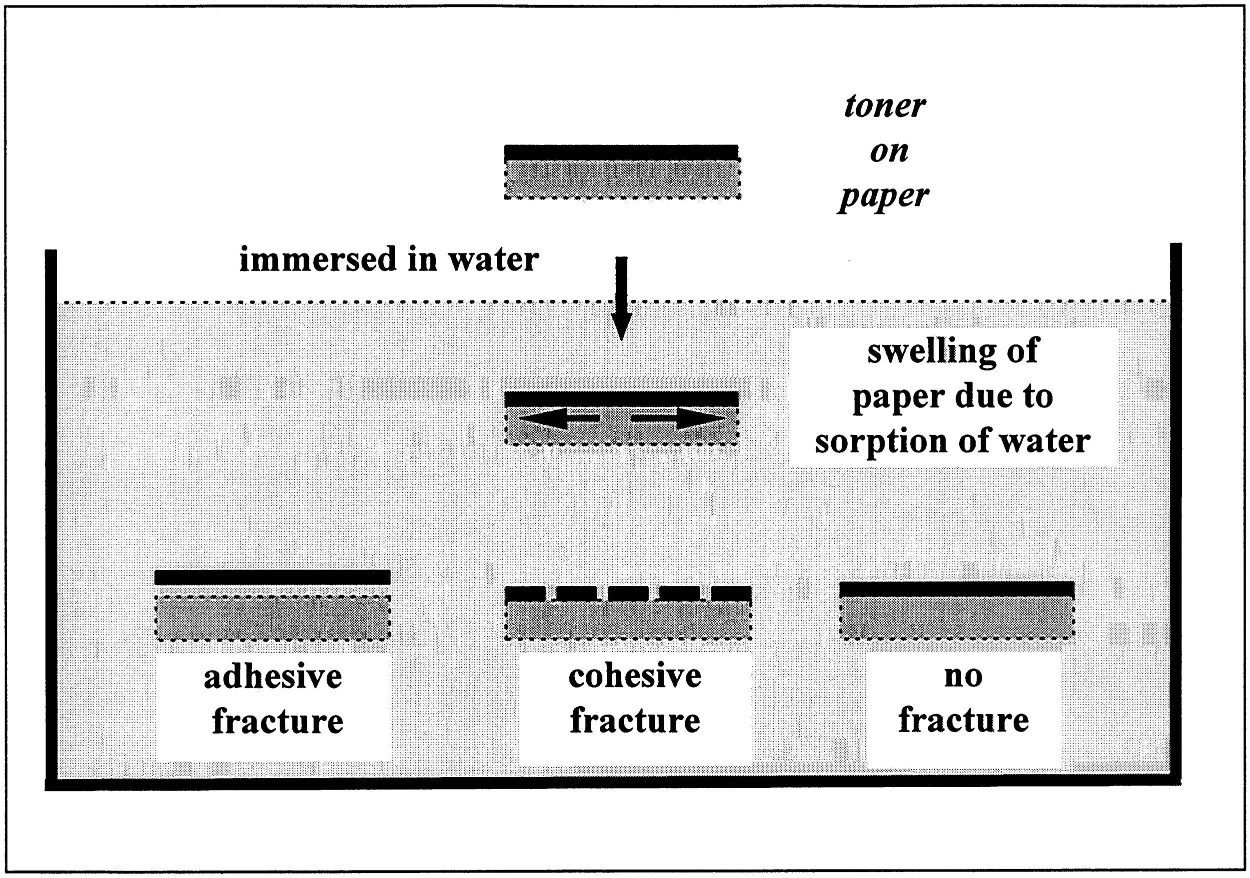

Figure 1: Model of fracture modes of toner when toner-printed paper is immersed in water.

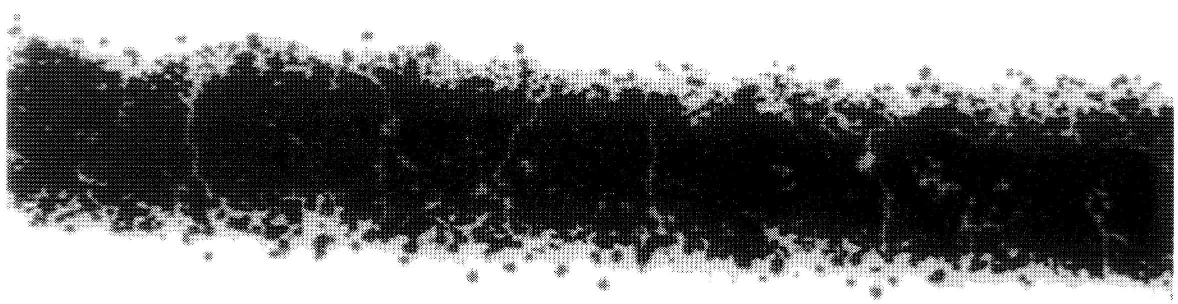

Figure 2: Fractures in toner layer form upon immersion of toner-printed paper in water due to the hygroexpansion of paper. Line is oriented in the cross direction of the paper.

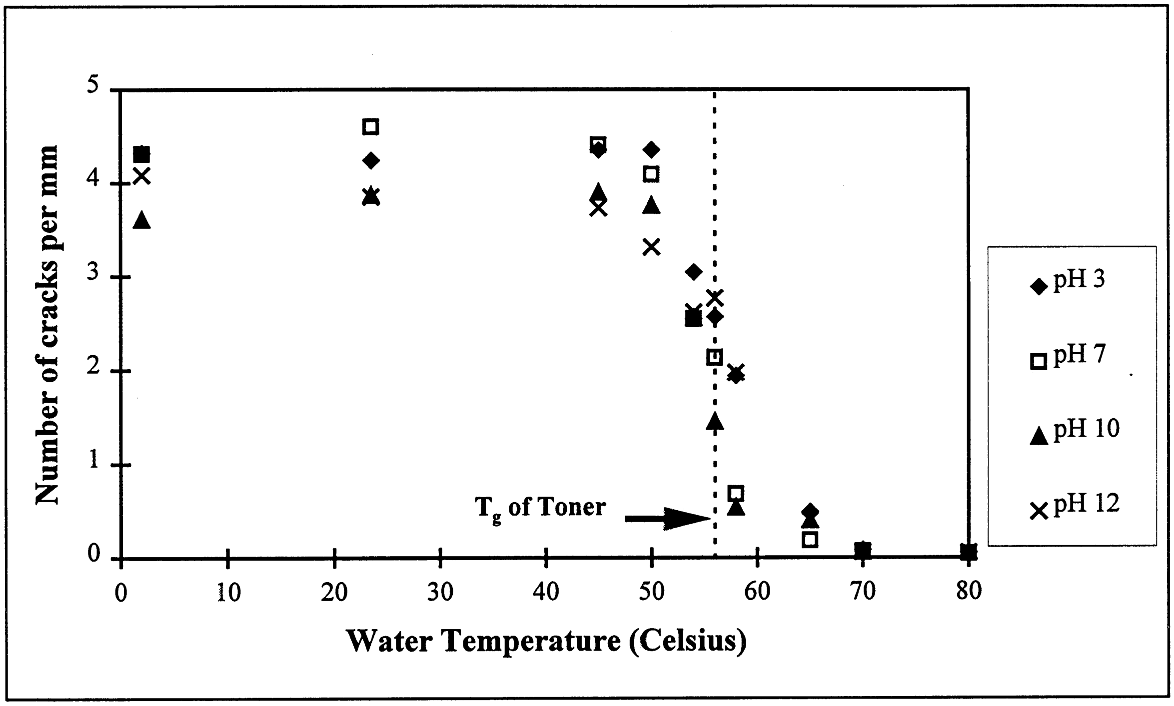

Figure 3: Number of fractures per millimeter observed in toner resulting from immersion of toner-printed paper in water. A significant change in the occurrence of fracture is seen at the glass transition temperature of the toner.

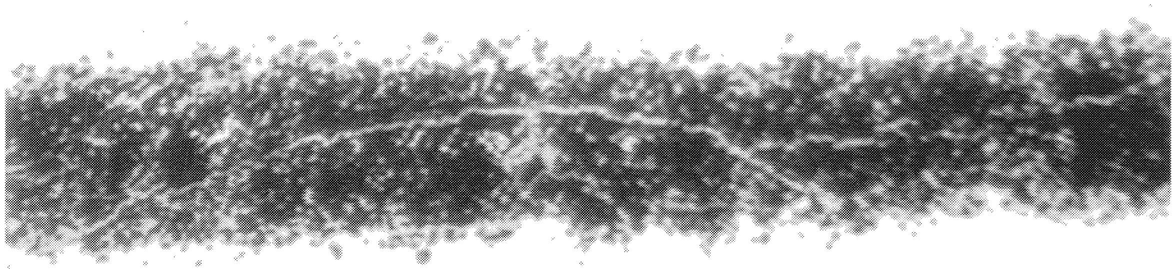

Figure 4: This line was printed in the machine direction of the paper. The cracks that formed are aligned primarily in the machine direction. Comparison with Fig. 2 shows that the cracks were aligned primarily with the machine direction in both cases.