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A technique for selective placement of carboxylic acid groups on kraft fibers is described. Topochemistry of acidic groups was confirmed with a novel scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDS) technique. Paper strength testing indicates that selective placement of acidic groups on or near a fiber outer surface can substantially increase the fiber-to-fiber specific bond strength.

INTRODUCTION

Chemical pulps contain carboxylic acid groups from hemicellulose retained through the pulping and bleaching processes. Certain bleaching agents, such as ozone, oxygen, and peroxide, can increase the carboxylic content through direct oxidation of cellulose. Carboxylate groups can have a large impact on final sheet strength. The effect of these weakly acidic groups on a fiber's ability to swell is well known [1]. Recently, however, the literature has indicated that the introduction of acid groups onto the surface of pulp fibers might be affecting sheet strength by increasing the specific strength of the fiber-fiber bonds. This has been suggested by several authors working with mechanical pulps modified by oxidation or sulfonation [3-5] as well as by one author working on oxygen delignification of kraft pulps [6]. In none of these experiments, however, was the concentration of surface acid groups deliberately changed in a controlled manner. The purpose of this study was to carry this out to examine the contribution of acid groups on fiber surfaces to paper strength. Pulps were prepared with different acid group distributions across the cell wall, but the same total acid content. In this way the contribution of surface acid groups was decoupled from the contribution of uniformly distributed acid groups.

APPROACH

In designing the procedure for the introduction of acid groups, several constraints were considered. It was essential that the overall pulp properties should be retained, and the cellulose should not be degraded. For these reasons, oxidation was ruled out, as was the use of lignin containing pulps. A bleached kraft pulp was chosen, and carboxylic acid groups were introduced using a halo-acetic acid reaction to form carboxymethyl cellulose [7]. Either chloroacetic acid, or the more reactive iodoacetic acid, was used.

To produce surface substitution, the fibers were first dried from water. This caused the cell wall to become inpervious [8], so that in a non-swelling medium the reaction occurred primarily with fiber surfaces. To produce bulk subsitution, solvent exchange dried fibers were used as a starting material. Solvent exchange drying retains some of the

wet fiber structure [9], allowing penetration of reactants into the cell wall. The bulk substituted pulp was subjected to a restrained drying cycle from water prior to testing. In this way, all three pulps experienced one restrained drying cycle from water prior to production of sheets for strength testing, giving all pulps a similar drying history.

The substitution topochemistries were confirmed using an SEM-EDS technique developed for this study. The carboxylic acid groups in the pulps were deprotonated and ion exchanged to the calcium form. The treated fibers were freeze dried, imbedded in Epox 812, and sectioned on an ultramicrotome with a diamond knife to 400 nm. The calcium ions acted as a tracers by tagging the carboxylate groups and allowing for detection with EDS. Cation tagging of carboxylic groups has been used previously to increase contrast in transmission electron microscopy [10]. The calcium peak/background ratio of x-ray counts was taken to be proportional to carboxylic concentration. The electron beam was scanned across fiber cell walls and peak/background ratios for calcium were determined at five relative positions. Five line scans per fiber were taken and three fibers from each treatment were examined.

RESULTS AND DISCUSSION

The results of an SEM-EDS study are shown in Figure 1 which the peak/background ratios for the relative positions across the fiber cell walls. Position 1 is adjacent to the lumen and Position 5 is adjacent to the cell outer wall. The distribution of carboxylic groups is uniform across the cell wall for the blank and bulk substituted fibers. Surface substituted fibers show carboxylic enrichment of the lumen and outer cell wall surfaces.

The modulus of elasticity of the handsheets was measured to determine if pulp preparation affected the stress transfer in the sheets. The modulus was plotted against soft platen apparent density as shown in Figure 2. There was no affect of fiber treatment in the plot, indicating that the various treatments did not introduce fiber deformations that would alter stress transfer in the sheets. With this knowledge tensile strength can be used as an indication of fiber-fiber bond strength. Tensile strength is plotted against scattering coefficient as shown in Figure 3. At the same scattering coefficient, the surface substituted sheets are 45% stronger. The clear implication of this observation is that surface enrichment of carboxylic groups results in an increase in specific bond strength. This result was confirmed using the Scott-Bond test. Scott-Bond strength is dependent on specific bond strength, and has been used to measure increases in specific bond strength caused by addition of starch [11,12]. Figure 4 contains the plot of Scott-Bond strength against light scattering coefficient. Here, again, the surface enriched pulp has the highest strength at any level of scattering coefficient, being about 50% higher.

This work demonstrates that the topochemistry of chloroacetic acid substitution of kraft pulp fibers can be influenced by the degree of swelling of the fibers. If the fiber cell wall is in a dry collapsed state, the substitution occurs primarily at the fiber surface. If the fiber is in a more expanded state, then the substitution occurs uniformly across the cell wall. Carboxylic enrichment of fiber surfaces results in improved paper strength

properties when compared to bulk carboxylation or no treatment at all. These results imply that specific acidic group topochemistries could be engineered in pulp fibers to yield superior final products. A promising approach to this goal would be to evaluate commercial oxidative bleaching agents, such as ozone, peroxide, or oxygen to determine if these technologies could produce desired acidic group topochemistries.

CONCLUSIONS

The chloroacetic acid substitution technique detailed here can produce distinct acidic group topochemistries in kraft pulp. Carboxylate topochemistries were confirmed using a novel SEM-EDS technique. Carboxylate enrichment of fiber surfaces resulted in differences in tensile and Scott-Bond strengths which could be explained by an increase in fiber-to-fiber specific bond strength. Carboxylic enrichment of the interior of the fibers did not affect specific bond strength. The differences in sheet strength imply that unique products could be designed if a desired acidic group topochemisry could be built into pulp.

EXPERIMENTAL

Materials

The solvents were anhydrous and all reactants were ACS reagent grade and used without further purification.

Pulp

The long fiber fraction (>35 mesh) of a unbeaten, never-dried OZE bleached commercial kraft pine was the starting material for this study. The pulp was converted into the sodium form according to the procedure described by Scallan [1]. The pulp was then dried using either a six step solvent exchange process (water/methanol/toluene % volume: 75/25/0, 25/75/0, 0/100/0, 0/100/0, 0/100/0, 0/0/100), or formed into sheets (couched, not pressed) and dried under restraint in rings.

Chloroacetic Acid Substitution

All reactions occurred at 1.5% consistency in an 87% isopropanol and 13% methanol solution containing 0.15% excess weight percent KOH. The surface substituted pulp was prepared by heating at reflux for one hour a mixture of restraint dried pulp in the alcoholic alkali solution containing 0.6 weight percent chloroacetic acid and 1.2 weight percent KI. The bulk substituted pulp was prepared by first immersing solvent exchanged dried fibers in isopropanol containing 0.13 weight percent chloroacetic acid. These fibers were then heated at reflux for one hour in the alcoholic alkali. The blank (control) pulp was prepared by heating at reflux for one hour a mixture of restraint dried pulp in the alcoholic alkali solution (no chloroacetic acid). Final carboxylic acid contents

determined with conductometric titration [13] to be 72 meq/kg for the blank pulp and 144 meq/kg for both substituted pulps.

SEM-EDS

The samples were analyzed on a JEOL JSM-6400 SEM with a Link exL EDS. The EDS detector had a 40° incline and was operated in beryllium window mode. The accelerating voltage was 15 kV, sample tilt was 20°, and the working distance was 39 mm. A mount for viewing thin sections in the SEM was prepared by attaching a machined carbon grid holder over a 4 mm hole in an aluminum stub. The hole was coated with carbon paint and trapped electrons passing through the sample in the mount.

Handsheets

The three pulps produced (Blank, Bulk, Surface) were dispersed with a British disintegrater and converted to the calcium form. Tappi standard handsheets were produced, with the exception that wet pressing pressures of 25, 50, 100, 200, and 400 psi were used to change bonded area. The sheets were dried under restraint in rings.

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FIGURE 1. PEAK/BACKGROUND RATIOS ACROSS CELL WALLS

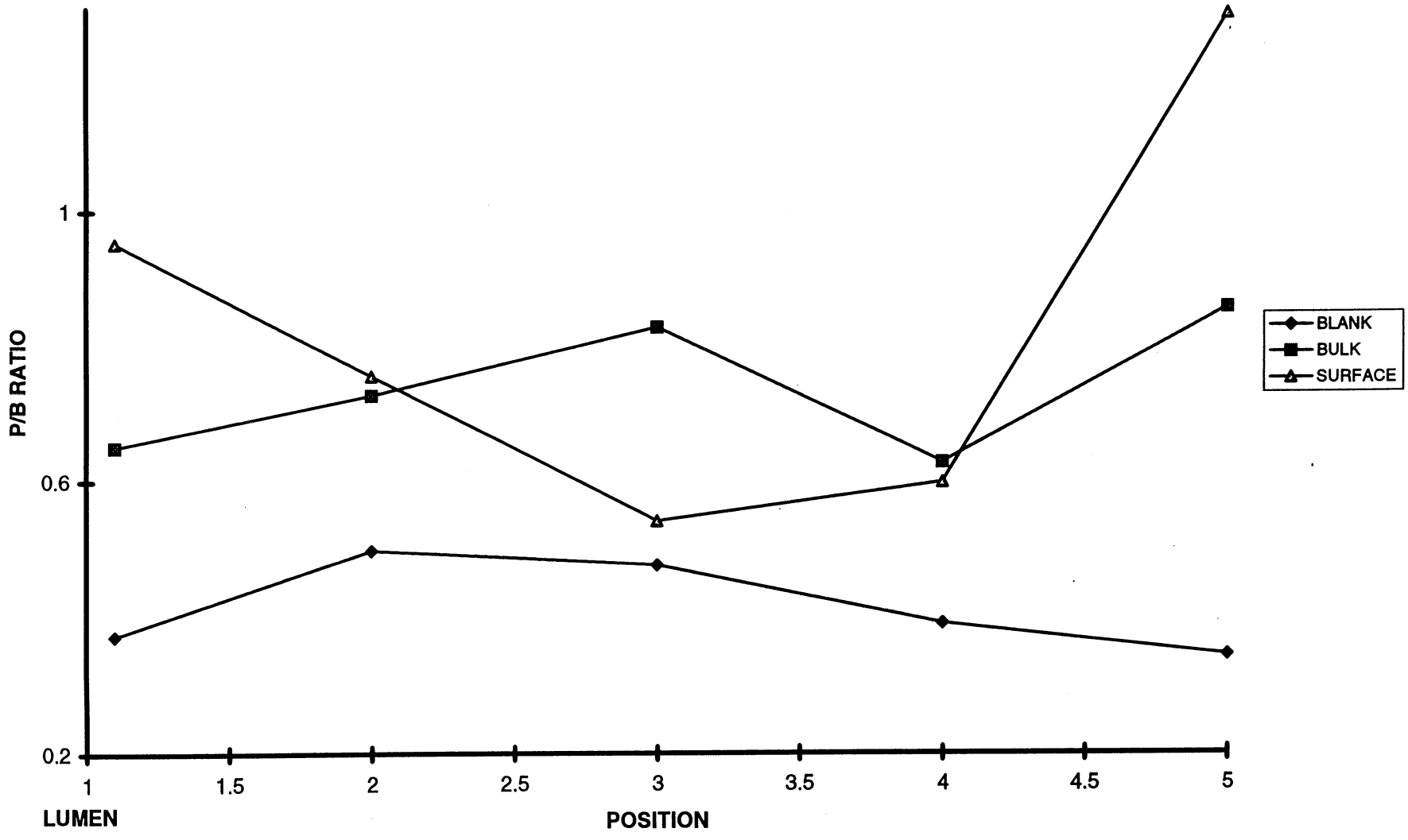

FIGURE 2. MODULUS OF ELASTICITY VS. DENSITY

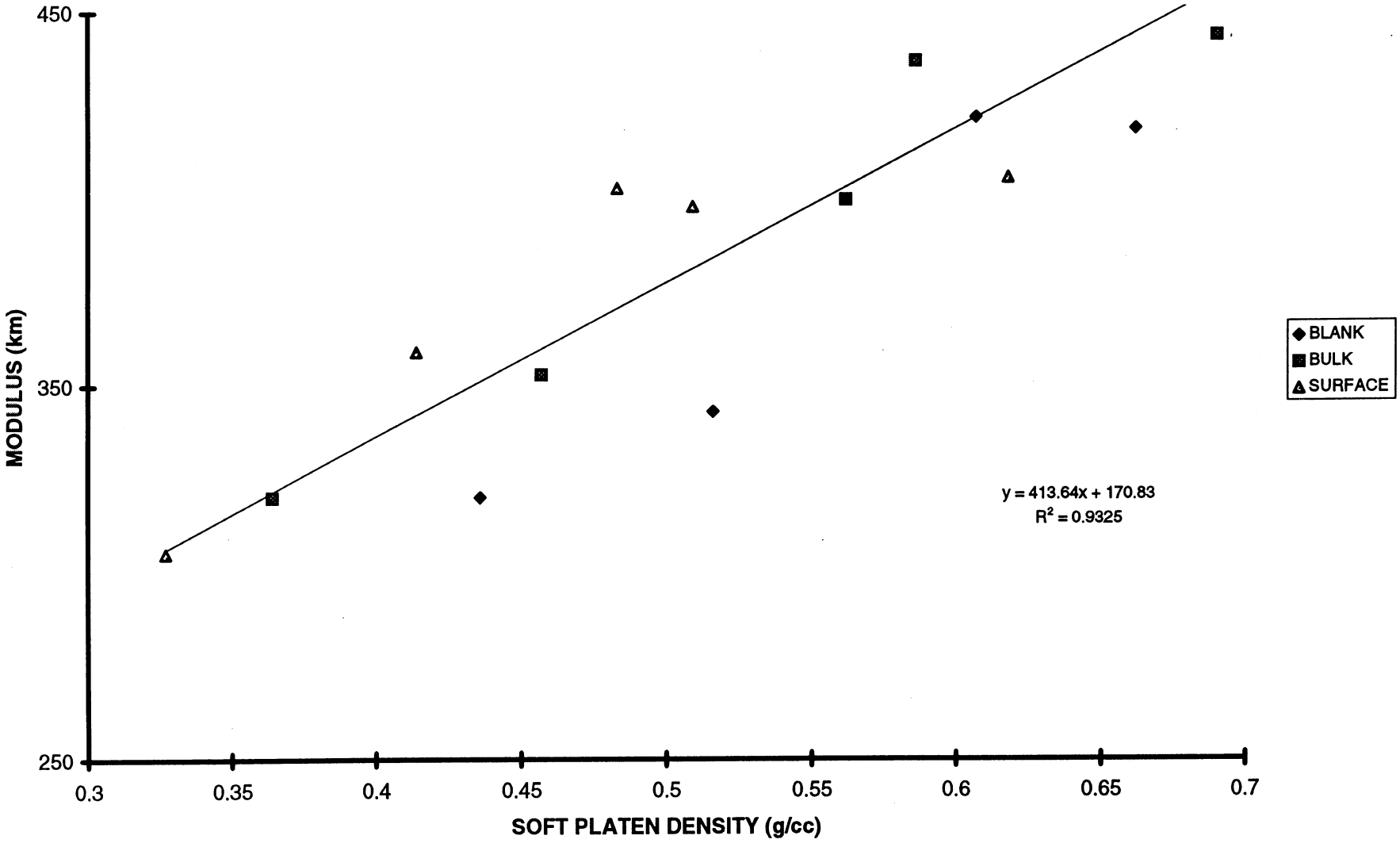

FIGURE 3. TENSILE STRENGTH VS. LIGHT SCATTERING COEFFICIENT.

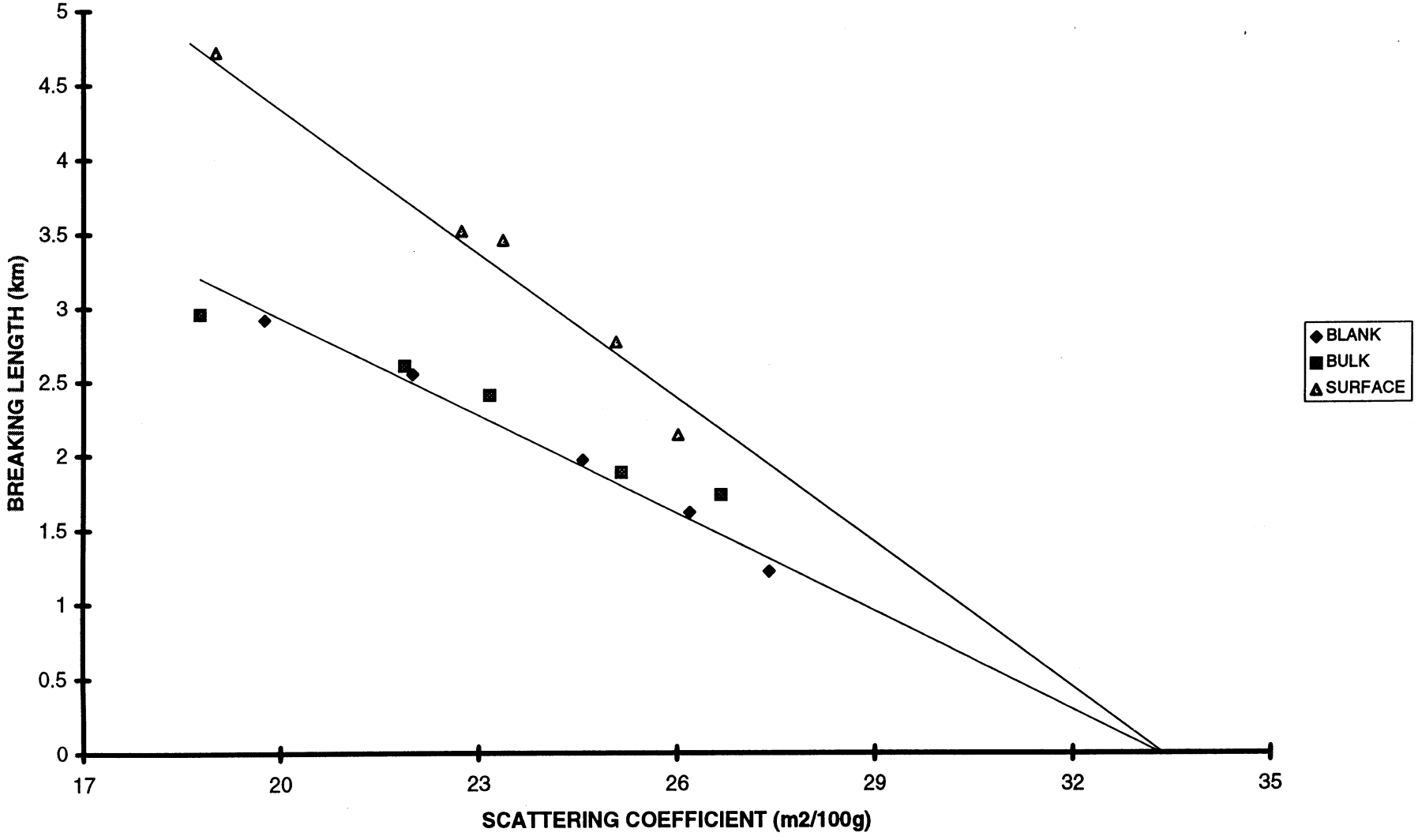

FIGURE 4. SCOTT-BOND VS. LIGHT SCATTERING COEFFICIENT