Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 943

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May 2002

Submitted to
TAPPI Journal

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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CORONA DISCHARGE AMPLIFICATION OF ACID GROUP TOPOCHEMISTRY

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Corona discharge can be used to modify fiber charge, which is known to impact fiber swelling and fiber-to-fiber bonding.

ABSTRACT

Corona discharge treatment is known to result in the surface oxidation of plastic and polymeric materials. In this study, thermomechanical pulp (TMP) fibers were corona treated at various treatment dosages. Scanning electron microscopy (SEM) revealed the creation of pinholes at higher dosages, with no observable fiber degradation at lower dosages. Electron spectroscopy for chemical analysis (ESCA) indicated that corona treatment provides significant increases in carboxylic acid groups on the fiber surface with increased treatment dosages. SEM and ESCA indicated that at lower dosages, acid group increases as high as 65% at the surface of TMP fibers could be attained with no observable fiber damage.

INTRODUCTION

It is widely known that fiber charge is critical to fiber and paper properties. Fiber charge impacts interactions between fibers and process chemicals (1,2) as well as fiber-to-fiber bonding (3-10). In TMP, the majority of charge is attributed to the carboxylic acid groups found in hemicellulose, while a small portion of the ionizable groups are contributed by extractives and lignin (6). The presence of acid groups is important to pulp properties, since bulk acid groups are known to impact fiber swelling (3), while surface acids have a direct impact on specific bond strength (4).

Corona discharge treatment applies a high voltage between two electrodes. As electrons move through the air, a plasma containing many highly oxidative species, including ozone, excited and ground state oxygen atoms, and dioxygen radicals, is created (11). Corona discharge treatment generates free radicals in substrates placed in the gap between the two electrodes, and results in the oxidization and increased surface energy of plastic and polymeric surfaces (12).

Corona discharge technology has been widely applied to increasing the adhesive bond between flat surfaces, such as plastic and polymer laminates, and to the adhesion of inks and laminates to the surface of cellulose, paper, and wood (11-17). Corona discharge has also been used to oxidize wood and paper so as to improve the adhesion of paint and glue (18,19). The wettability of and bonding between layers of cellulose films, such as cellulose acetate and cellophane, have also been enhanced via corona discharge treatment (20,21).

ESCA has been applied to illustrate increases in the ratio of oxygen to carbon (O/C) on pulp fibers. When newsprint was corona treated, the increased O/C ratio was accompanied by increases in the coefficient of friction of the paper (22). Increases in carbonyl and carboxylic acid groups in sheets of various corona treated pulps have also been detected using ESCA (23). In addition, SEM has been applied to the analysis of corona treated materials. When SEM was used to inspect corona treated Whatman filter paper for physical damage, losses of fibrils were reported after one minute of treatment, while fiber damage was reported in samples treated for 10 minutes (24).

In this project, corona discharge treatment at various dosages, each lasting only fractions of a second, was applied. The objective was to significantly modify the acid group topochemistry of TMP fiber surfaces while avoiding fiber damage. The fiber surfaces were analyzed for physical changes using SEM, while ESCA was applied to detecting changes in surface chemistry.

EXPERIMENTAL

Pulp Preparation

A softwood thermomechanical pulp was used for this work. Since significant differences in acid group topochemistry may be found among TMP fines and fibers, only long fibers were used so as to reduce variability in the starting material. The Bauer-McNett long fiber fraction (14P/28R) with a freeness of 742 mL (25) was acetone extracted, hot disintegrated at 30,000 rpms (26), and formed into TAPPI standard handsheets (27). The handsheets were conditioned at 50% relative humidity (28) prior to corona discharge treatment on a Pillar Sheet Treater at levels from 0 to 111 $W/m^2/min$.

SEM Analysis

SEM analysis was performed on a JEOL JSM-35C Scanning Electron Microscope (SEM) to qualitatively compare corona discharge treated and control samples. The samples were oven dried, then sputter-coated with carbon in the Anatech Limited Hummer V sputter coater. A 15 kV electron beam was used to analyze all samples. Image analysis was done using NIH Image Version 1.61 software on a Mcintosh Quadra 650 computer, operating system 7.6.1. Images were collected at 1280 x 960 pixels.

Surface Chemistry

The corona treated and control sheets were stored for 21 days at TAPPI standard conditions (28) prior to surface analysis. A 1.5 mm x 0.6 mm section from the center of each sheet was degassed overnight to remove all residual moisture. ESCA was performed on a Physical Electronics 5802 Multitechnique instrument with a monochromatic Al K_α x-ray source and analyzed by probing with a beam to a maximum depth of 5.0 nm from the surface of the sheet. The resulting spectra were used to characterize surface chemistry by integrating the areas under characteristic photoelectron peaks, with detection limits of approximately 0.1 atomic %. **Figure 1,** generated from a corona treated TMP sample, graphically illustrates characteristic Gaussian peaks, the distances between which correspond to characteristic shifts of known species.

INSERT FIGURE 1 HERE

Figure 1. Carbon 1s (1s orbital) curve fit for a corona treated TMP sheet.

Samples were analyzed in triplicate using individually treated sheets, as well as a single sheet sampled from three different locations. The statistical significance of surface analysis data was confirmed by performing t-tests with 95% confidence intervals.

Conductometric titrations were performed to characterize the total acid content of untreated and corona treated samples based on published methods (29,30). The acid groups bound to pulp fibers can be in a salt or protonated forms (7), which can be cation exchanged. To prepare for conductometric titrations, the pulps were water-soaked for 24 hours then stirred with 300 mL of 0.10 M hydrochloric acid (HCl) to liberate the fibers and convert the pulp to the protonated form. The pulp was then washed with deionized water and dispersed into 250 mL of 0.001 M sodium chloride (NaCl) and 1.5 mL of 0.1 M HCl. The resulting solution was titrated with a standardized 0.05 M NaOH solution as conductivities were measured. The total acid groups were extrapolated from plots of the resulting data.

RESULTS

SEM Analysis

When corona treated sheets formed from TMP long fibers were SEM analyzed, no visible difference in the surfaces of corona discharge treated and untreated fiber surfaces at treatment levels below 56 $W/m^2/min$ were observed. Above this level, pinholing was observed, as illustrated in **Figure 2.** Although the SEM work of past authors suggests a reduction in fibrils on the surface of Whatman filter papers (24), it was not observed in this case (**Figures 3 and 4**). However, since only TMP long fibers were utilized, there were few fibrils or fines available for observation, as described in **Figures 3 and 4**. Also, a gentler treatment was applied in this study. While the duration of treatment in the past study was greater than or equal to one minute (24), the duration of treatment in this study amounted to fractions of a second.

INSERT FIGURE 2 HERE

Figure 2. SEM image of pinhole created upon corona discharge treatment of TMP sheet at 111 W/ft^2/min at 240X.

INSERT FIGURE 3 HERE

Figure 3. SEM image of TMP sheet after corona treatment dosage of 55.5 W/m^2/min at 600X.

INSERT FIGURE 4 HERE

Figure 4. SEM image of untreated TMP sheet at 600X.

Surface Chemistry

A corona treatment dosage of 56 $W/m^2/min$ provided statistically significant increases in acid groups without causing observable fiber damage. Statistical significance of the ESCA data was determined by performing t-tests with 95% confidence intervals using methods described by Rees (31). ESCA revealed dramatic increases in acid groups at the surface of TMP fibers with increased corona treatment dosages, as illustrated in **Figure 5.** This observation was accompanied by decreases in carbon bonded to another carbon or hydrogen and small increases in carbonyl carbons. No significant difference was seen in the amount of carbon bonded to a single oxygen before and after corona discharge treatment.

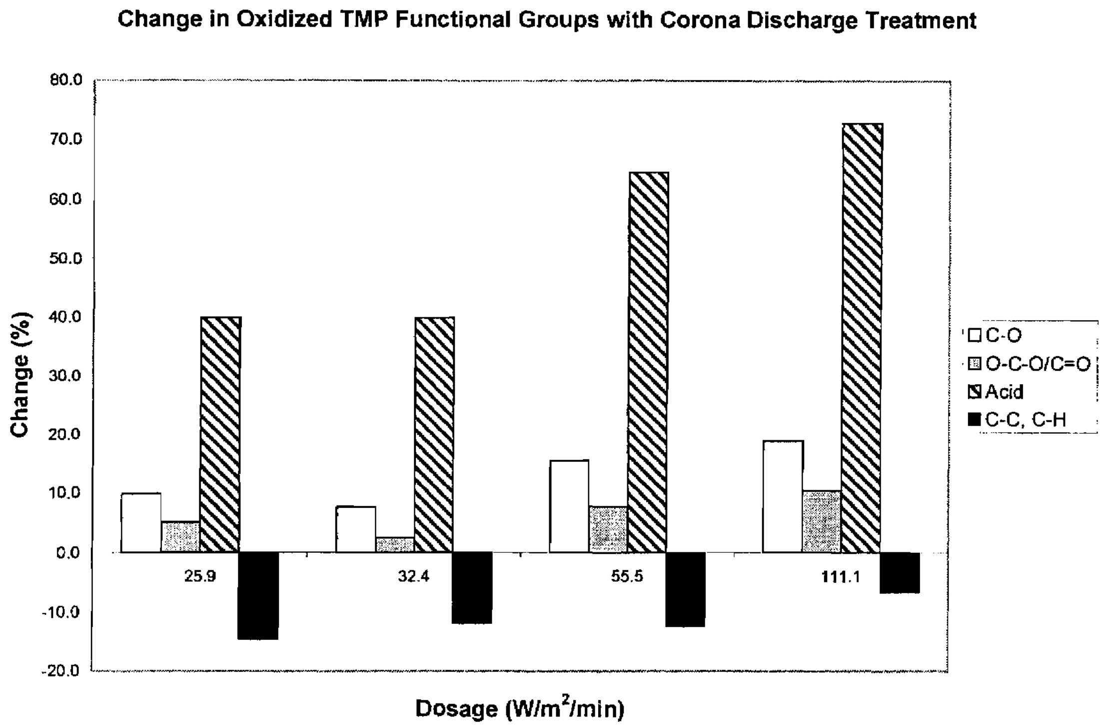

Figure 5. ESCA studies of TMP sheets indicate that acid groups increase significantly due to corona discharge treatment.

When conductometric titrations were performed, the corona treated and untreated $60g/cm^2$ sheets showed no statistically significant difference in total acid groups. This is believed to be a result of using fibers which naturally contain many interior and exterior carboxylic acid groups. These acid groups are likely to have overwhelmed the effect of increasing acid groups only on those fibers at the surface of the handsheet, in an ultra-thin layer only at the outer surface of each exposed fiber.

CONCLUSIONS

Corona discharge treatment provides a significant increase in acid groups at the fiber surface without the application of chemicals. The ability to control surface charge by mechanical means offers possibilities for flexibility to those seeking to modify fibers with minimal chemical consumption. By controlling treatment dosages, the surface charge of fibers may be modified without imparting physical damage.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the member companies of the Institute of Paper Science and Technology. Portions of this work are being used by L. Vander Wielen as partial fulfillment of the requirements for graduation from the Institute of Paper Science and Technology. L. Vander Wielen is a Ph.D candidate and Professor A.

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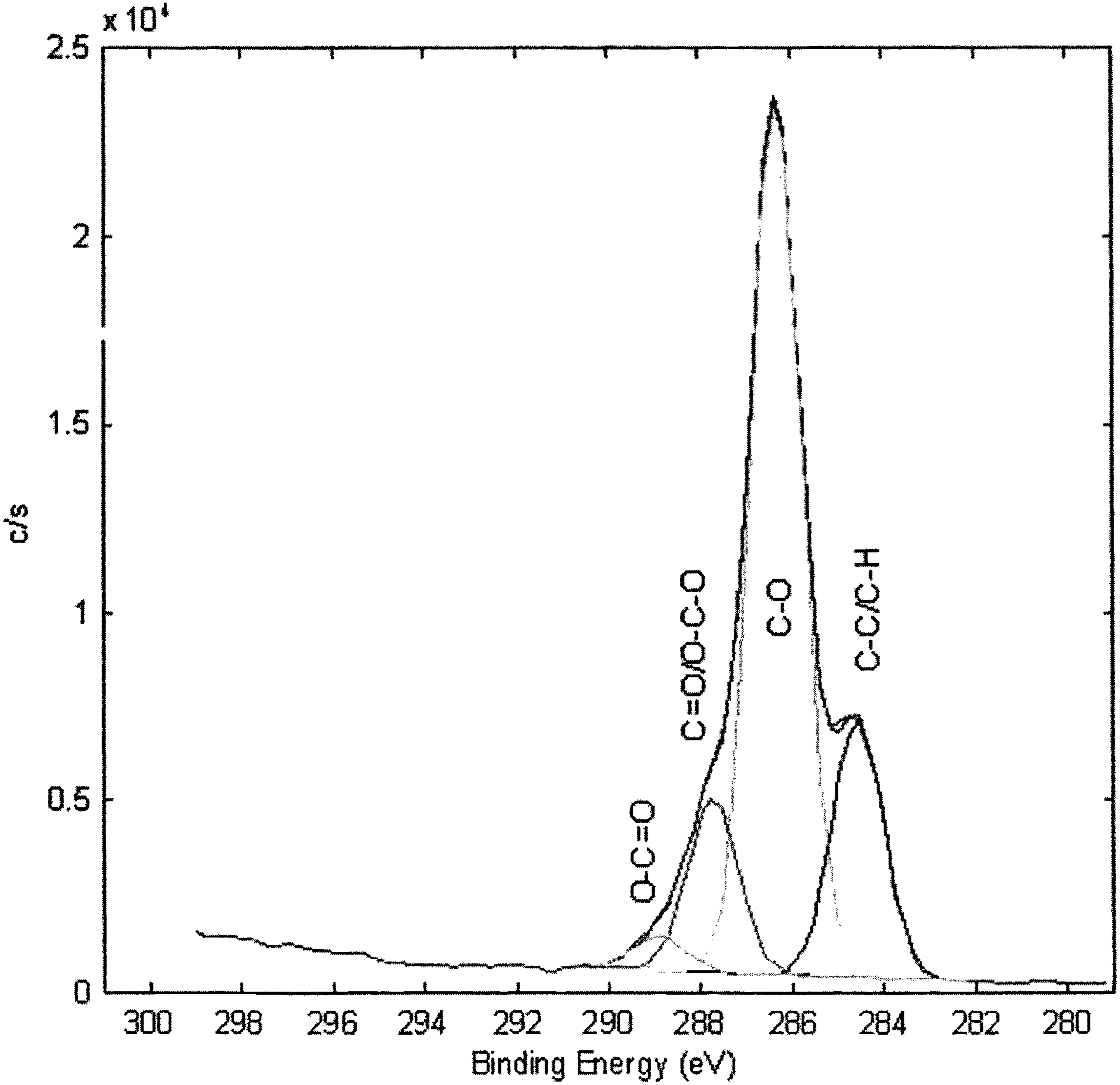
x 10⁴
2.5
2
1.5
1
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c/s
O-C=O
C=O/O-C-O
C-O
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284
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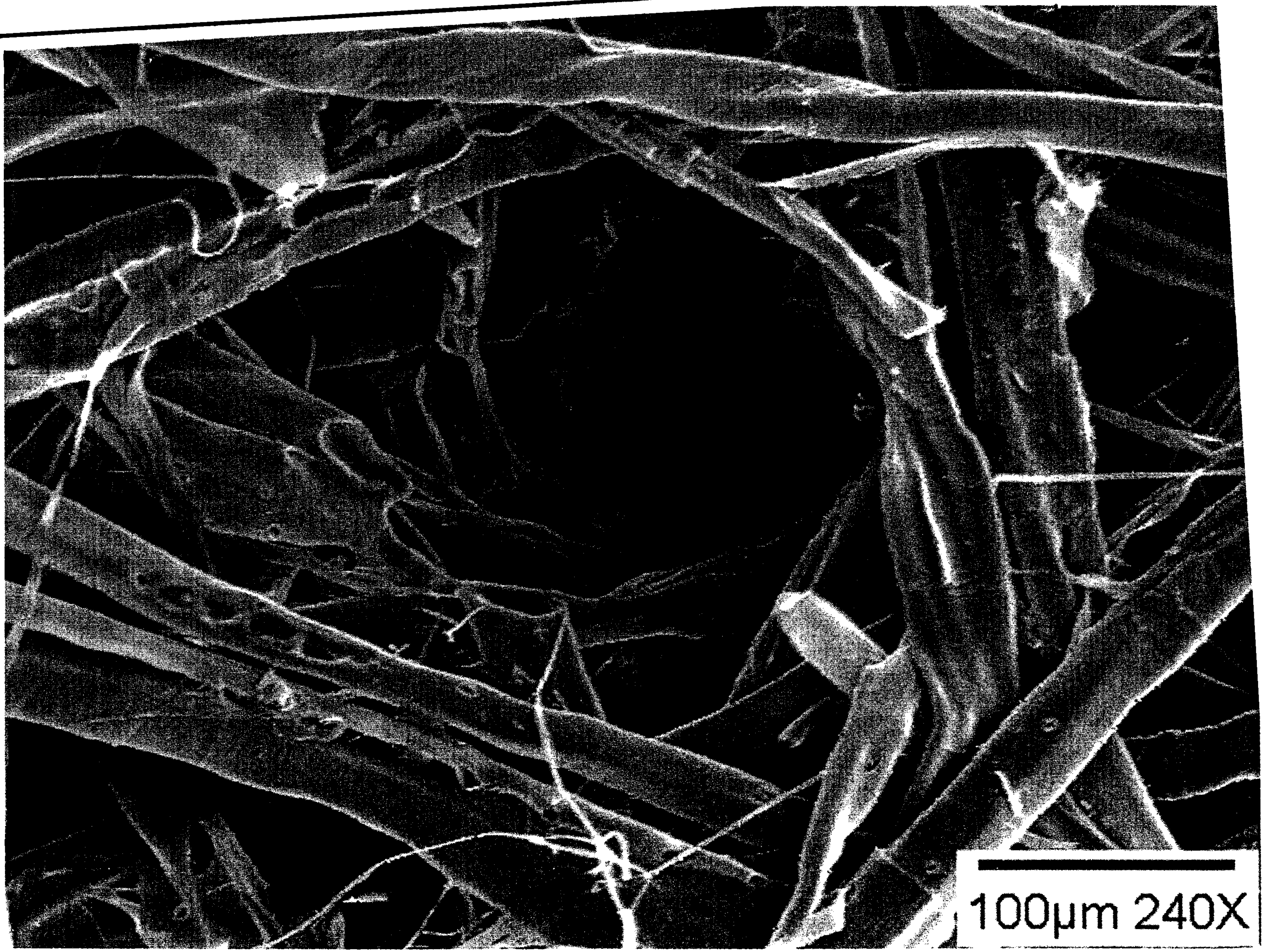
280
Binding Energy (eV)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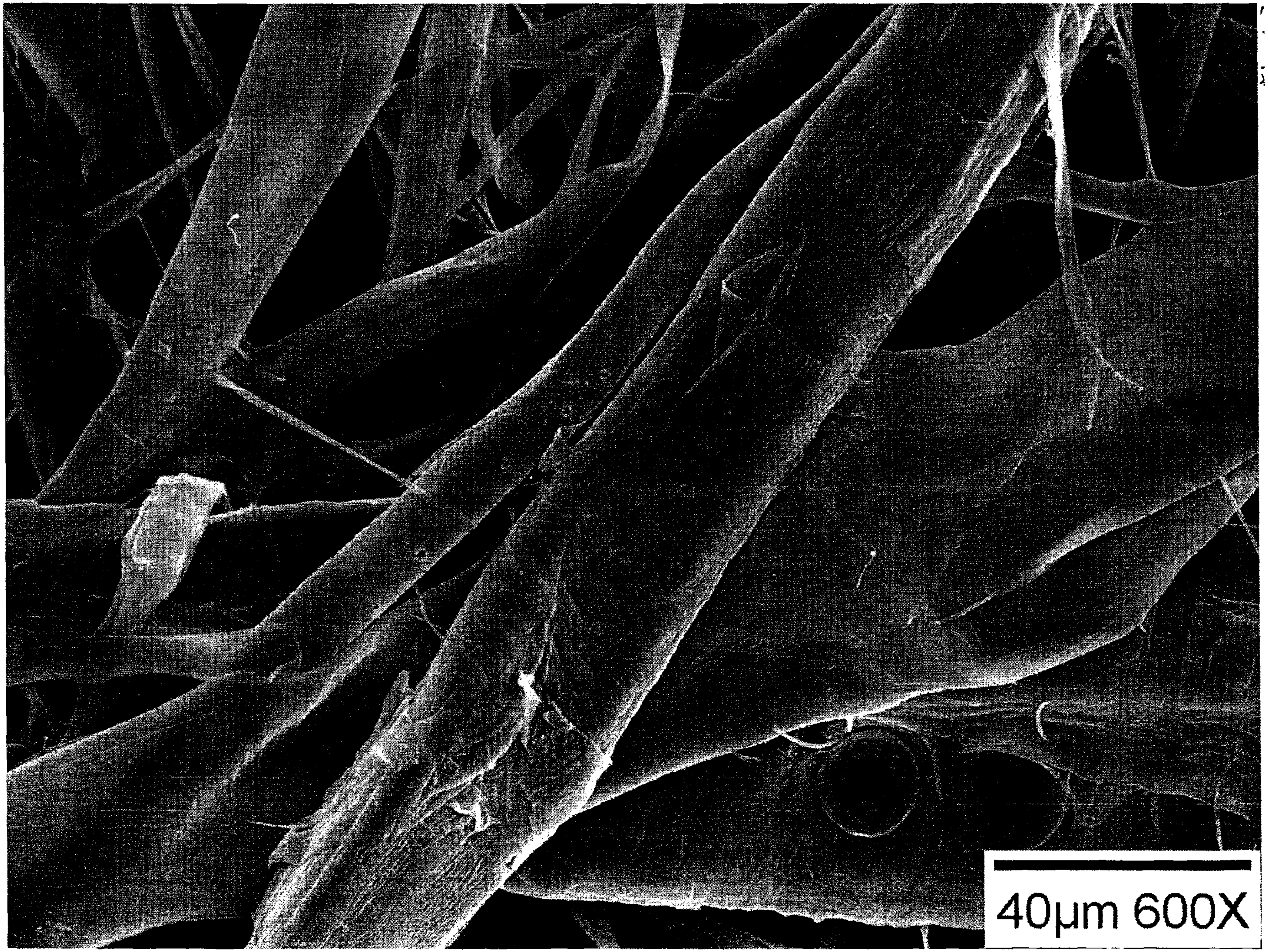
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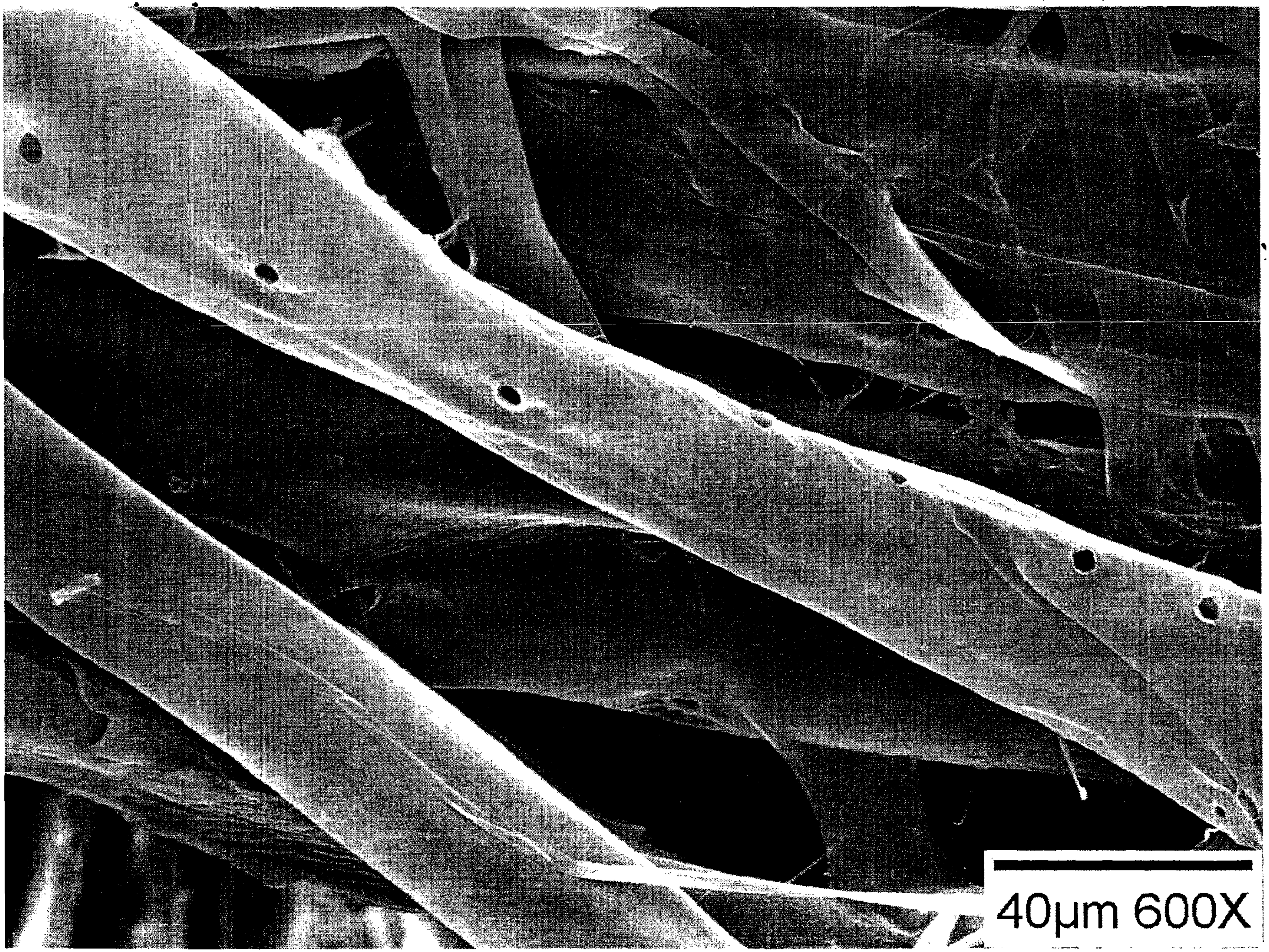
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