Recycling potential of printed thermomechanical fibers for newsprint

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ABSTRACT

In earlier investigations of repeated recycling of TMP, only some of the individual papermaking processes, such as wet pressing, drying, and calendering, have been discussed. The result in many of these investigations has been an increased or unchanged tensile strength.

In this study, a TMP has been recycled for five complete cycles, including a printing step and a deinking step. This implies an addition of ink material into the system. Chemical changes in the TMP fiber are significant. Hydrophilicity of the fiber surface increases, measured as charge and oxygen-to-carbon ratio (O/C).

The produced sheets show an increased surface roughness and a decreased tear and tensile index. Obviously the printing step, the ink, or its components obstruct the interfiber bondings in the sheet-forming operation.

Application:

More investigation is required to confirm the negative effects of a printing stage on recycling.

THE EFFECT OF REPEATED RECYCLING has been studied in several investigations. However, most of the published results have focused on chemical pulps. Repeated recycling of low-yield chemical pulps causes a dramatic loss of tensile and burst strength in paper *(1–7)*.

Only a few studies have focused on the effect of recycling on mechanical fibers. In contrast to studies of chemical pulps, these studies do not show any distinguishable loss in the bonding capacity of dried fibers. Physical properties, such as tensile and burst strength, are increased or unaffected by recycling *(1, 6, 8–10).* This is believed to be the result of an increased level of fiber bonding, and it is suggested that the mechanism behind these improved bondings is the more-flattened and thereby more-flexible fibers *(1, 6).* This has been explained by a slight delignification that takes place during deinking. In another study, it was not possible to detect any fiber flattening in spite of increased density and strength *(11).* The specific energy input in the first preparation of the thermomechanical pulp (TMP) fibers has been shown to have a profound effect on the papermaking properties of pulps during recycling *(12).* This is explained by large differences in the fiber length distribution and in the character of the fractions generated at different energy input levels, and by the fact that different fiber fractions behave differently during recycling.

Surface roughness for recycled TMP sheet has been noted to increase after recycling *(10).* Conflicting results, however, have been reported, where an increased smoothness was detected *(13).*

The use of deinking chemicals, such as alkali and peroxide, contributes to better bonding of TMP fibers by making them more hydrophilic on the surface. This has been explained by the removal of extractives and an increase in the amount of carboxylic groups *(9, 10).* Furthermore, it has been shown that the carbohydrate and lignin composition in TMP does not change substantially on recycling with water or with standard deinking chemicals *(9).*

The influence of recycling seems to involve a combination of changes in both fiber morphology and fiber chemistry.

Less is understood about the influence of the use of recycled fibers in printing operations. There is some justification for suspecting that the moistening and drying that take place in printing and various finishing operations also may have some effect on the fibers. None of the earlier studies has included a printing step in each cycle. One investigation has focused on the influence of a printing step, but only on chemical pulp and with printing only in the first cycle. The conclusion from that work was that the interfiber bonding was reduced and that the ink itself obstructed the fiber–fiber bonding *(14).*

The aim of our study was to assess the changes taking place in TMP during recycling involving deinking, calendering, and printing. With the present experimental work, we have tried to fill some of the existing gaps in the literature. Loss of fines from the recycling loops was restricted to that from the flotation step.

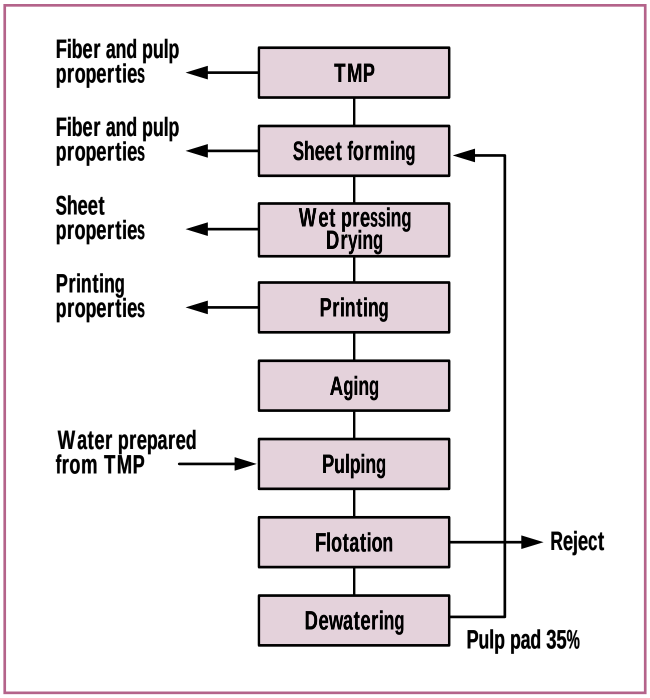
EXPERIMENTAL

Raw material

The raw material was undried virgin TMP for newsprint from the SCA Ortviken mill. Material properties were 102 mL CSF and 62% ISO brightness.

Recycling procedure

The recycling consisted of forming handsheets from the virgin TMP in a



1. Flow diagram of the recycling procedure

HOBART LABORATORY PULPER	
Time, min	5 at speed 1, 20 at speed 2
Temperature, °C	45–50
Pulp consistency, %	10
NaOH, %	1
Na-silicate, %	2
EDTA, %	0.5
Soap, Berocell 8000P, %	1
H_2O_2, %	1
Water hardness, °dH	20
DEGUSSA FLOTATION CELL	
Volume, L	10
Pulp consistency, %	1
Time, min	15
REJECTS REMOVED IN FLOTATION STAGE, %	
Cycle 1	10.5
Cycle 2	5.5
Cycle 3	3.4
Cycle 4	1.2

I. Pulping and flotation procedure

Nips, steel/fiber	2
Load, kN/m	50
Speed, m/min	10
Steel roll temperature, °C	21

II. Calendering conditions

sheet former with circulation of the backwater, pressing, and drying of the sheets; five weeks storage at room temperature; calendering; printing; aging for three weeks at room temperature; deinking of the aged sheets; and dewatering of the pulp before the next sheet forming (see **Fig. 1**). The sheets were pulped in laboratory-prepared backwater, as described in the next section. The grammage of the sheets for printing and cycling was 80 g/m², and the sheets were prepared with circulation of the backwater to avoid fines loss. The pH was adjusted to 7 before sheet forming.

The pulping and flotation procedure is described in **Table I**.

Preparation of the water for pulping

A quantity of 1.5 kg unprinted virgin newsprint was pulped in a Lamort laboratory pulper at 10% consistency and a temperature of 45°C for 25 min. The pulp was then diluted with warm water (45°C) to 4% consistency and then left to stand for 20 min before dewatering in a centrifuge. New water was prepared for every cycle from the same unprinted paper. The chemical oxygen demand (COD) of the prepared water was 390 mg/L.

Calendering

Five weeks after sheet forming, the sheets were treated in a Küster laboratory calender under the conditions shown in **Table II**.

Pulp and paper testing

The handsheets used to test paper properties (65 g/m²) were prepared in a handsheet former with circulation of the backwater. The first seven sheets were discarded. **Table III and Table IV** show the test methods that were used for the pulp and paper testing, respectively.

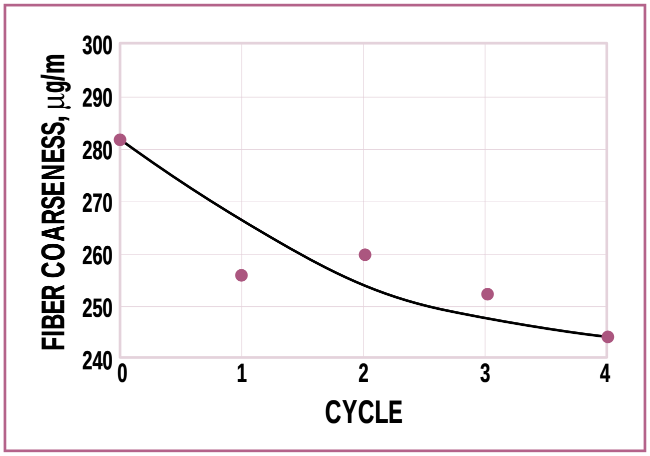
Water retention value. The water retention value (WRV) gives the weight fraction of water retained by wet pulp after the pulp has been subjected to centrifugation at 3000 g for 15 min. During centrifugation, the pulp (1 g dry pulp) is placed in a cylindrical copper holder with a wire mesh (100-mesh) soldered to the bottom. The value given is the mean value of four determinations.

Charge. The fiber charge was measured by polyelectrolyte titration using polybrene as the adsorbing polymer *(15)*.

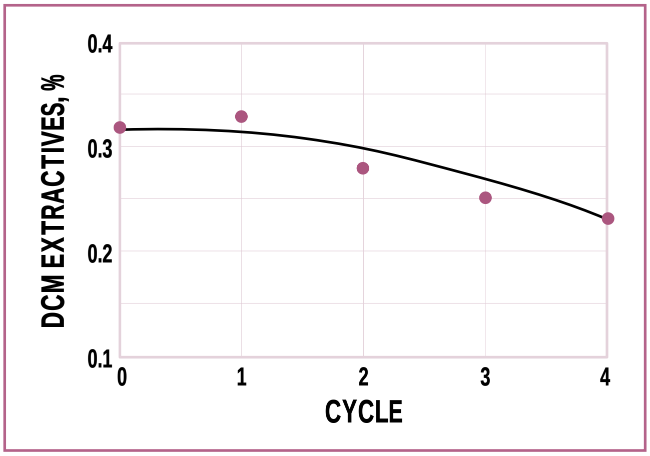
Fatty acids and resin acids. The amount of fatty and resin acids was measured by gas chromatography (GC) after esterification of the dichloromethane extract with trimethylanilinehydroxide.

The GC determination was done using a Hewlett-Packard 5890 Gas Chromatograph equipped with a flame ionization detector (FID) and a DBS column (30 m, 0.32-mm ID). Split injection was at 280°C. The GC was working at an initial temperature of 175°C, rising to 200°C in increments of 10°C/min.

Scanning electron microscopy. Surfaces of the sheets, before and after the first cycle, were examined with a scanning electron microscope (SEM), Stereoscan 360, Cambridge Instruments Ltd., Cambridge, U.K.



2. The coarseness of the fibers, measured by the Kajaani method, decreases with recycling.



3. Recycling decreases the amount of DCM-extractable material in the TMP.

Freeness, CSF	SCAN-M 4:65
Ash content at 575°C	SCAN-C 6:62
Amount of fines	BDDJ, wire 125P (76 µm)
Fiber length, coarseness	Kajaani FS100
DCM extract	SCAN-C 7:62

III. Methods for pulp testing

Preparation of handsheets	ISO 65 g/m², circulation of the backwater
Sheet density	SCAN-P 7:75R
Tear index	SCAN-P 11:73
Tensile index, stretch at break	SCAN-P 38:80
Bending stiffness, resonance method	SCAN-P 64:90
Surface roughness	Optical profile tester
Brightness, ISO	SCAN-P 3:93
Y-value, *L*a*b**	SCAN-P 3:75R
Opacity, *s, k*	SCAN-P 8:93

IV. Methods for paper testing

Printing

Two strips were cut from every sheet after calendering. They were printed on both sides on a Prübau laboratory printing machine with mineral oil-based, cold-set offset ink. The printing roll was modified to produce print over 50% of the surface. The total printed area was about 34% of the total paper surface.

Printing properties — color demand. The color demand of the sheet was measured in the Prübau laboratory printing machine with mineral oil-based, cold-set offset ink and presented as color demand at color density $D = 1.1$ g/m².

Contact angle

Distilled deionized water was used to measure the contact angle on the strips from the laboratory sheets. Eight or more measurements were made on each sample. Measurements were also made on sheets aged for 12–16 weeks at room temperature.

The contact angles were measured using a DAT 1100. This equipment, from Fibro System AB, consists of an automatic drop applier and a high-speed video camera connected to a personal computer. The video camera records up to 50 pictures/second with a shutter speed of 1 ms. An image-analyzing program is used to find the height and base of the drop. These values then are used to calculate the contact angle. The contact angle used for assessment is taken after 1 second.

Electron spectroscopy for chemical analysis (ESCA)

The ESCA measurements on the laboratory sheets were performed with an AXIS HS spectrometer from Kratos Analytical using a monochromized A1 Kα X-ray source. Measurements also were made on sheets aged for 12–16 weeks at room temperature as well as on extracted sheets. The extractions were made according to SCAN-C 7:62, with the exception that the amount of pulp was lower. The O1s and C1s signals used to estimate the O/C (oxygen to carbon) atomic ratio were collected at a pass energy of 80 eV, and the high-resolution spectrum used to estimate carbons with different levels of oxidation was collected at a pass energy of 20 eV. All samples were measured in three different areas.

RESULTS

Effect on fiber properties

The effect of the recycling treatment on freeness, WRV, and fines content is shown in **Table V**. The changes are most evident during the step from virgin pulp to once-recycled pulp. The freeness was increased, which could be caused by a certain loss of fines, even if losses were avoided. However, no changes could be detected in the amount of fines. Another explanation for the increased freeness could be less

Cycle	CSF, mL	WRV, %	Ash content, %	Fines, %	FIBER Length, mm	FIBER Coarseness, µg/m
0	102	132	0.54	17.7	1.49	282
1	158	124	1.01	18.1	1.53	256
2	152	130	1.40	16.1	1.54	260
3	164	126	2.05	17.5	1.47	252
4	142	136	3.16	17.0	1.48	244

V. Pulp properties for the recycled TMP fibers

Cycle	Total charge, µeq/g	DCM extractives,%	Fatty acids, mg/kg	Resin acids, mg/kg
0	56.2	0.32	474	44.9
1	81.3	0.33	462	12.1
2	83.5	0.28	337	7.5
3	95.2	0.25	343	7.5
4	112.3	0.23	283	12.7

VI. Chemical properties for the recycled TMP fibers

Cycle	O/C	C–O	O–C–O	C–C	O–C=O
0	0.39	42	8	48	2
1	0.51	54	10	34	1
2	...	...	...	...	...
3	...	...	...	...	...
4	0.60	63	12	25	1

VII. The effect of recycling on the surface properties measured by ESCA. The composition is given as atomic %.

Cycle	O/C	C–O	O–C–O	C–C	O–C=O
0	0.61	59	13	26	3
1	0.64	65	13	20	2
2	0.63	66	13	20	2
3	0.65	68	13	18	1
4	0.65	66	14	19	1

VIII. The effect of recycling on the surface properties of the extracted sheets measured by ESCA. The composition is given as atomic %.

Cycle	O/C	C–O	O–C–O	C–C	O–C=O
0	0.35	38	12	47	3
1	0.40	53	10	35	2
2	0.44	60	10	29	1
3	0.57	59	12	27	1
4	0.60	61	13	25	1

IX. The effect of recycling on the properties of the aged sheets measured by ESCA. The composition is given as atomic %.

swollen fibers after drying and thus better drainage. In some investigations, the freeness has decreased due to recycling, and this has been explained by an increase in the fines content *(1, 9)*.

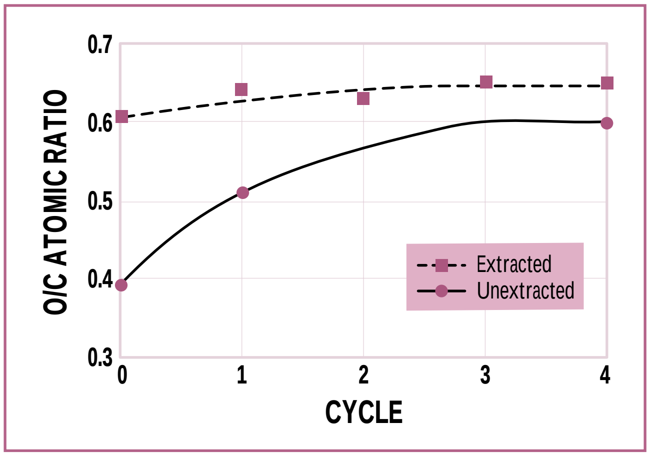
Some recent results have demonstrated that the specific energy consumption in the first preparation of the mechanical pulp has a significant impact on the freeness development in recycling *(12)*. High energy input produces low-freeness pulp that contains more short fibers than a pulp produced with a lower energy input. Moreover, the chemical character of the different fiber fractions depends on the energy input. This was explained by the heterogeneous physical and chemical character of the mechanical pulps. Also, an increase or decrease in freeness can be achieved, depending on how the pulp is treated in the recycling simulation process. The difference in the character of the obtained fiber fractions may explain the contradictions in published recycling results.

Table V also demonstrates the effect of recycling on the fiber length and fiber coarseness. In this work, as in many others, the effect on the fiber length is small. However, the fiber coarseness does decrease (see **Fig. 2**). In one publication, it has been suggested that a delamination mechanism may be the explanation behind thinner fiber walls and thus lower fiber coarseness *(11)*.

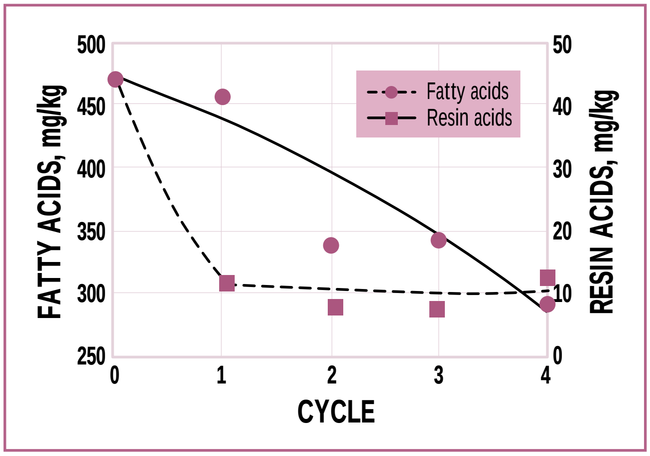
Effect on chemical composition

The amount of extractives decreases, and the greatest changes are observed after the first cycle (see **Fig. 3 and Table VI**). This correlates with the surface characterization by means of ESCA, where the amount of carbon bonded to only carbon and/or hydrogen (C–C) decreases, and the oxygen-to-carbon ratio (O/C) increases (see **Fig. 4 and Table VII**).

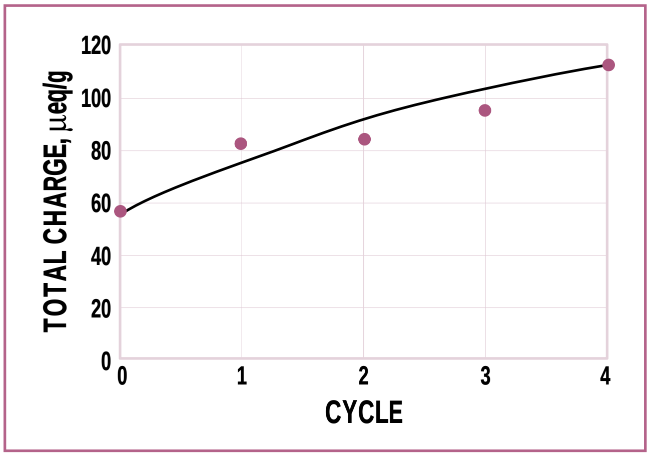
This suggests that the amount of extractable material on the fiber surface is decreased. Hence, the lower total amount of extractable material reduces the opportunities for finding such material on the fiber surface. The oxygen-to-carbon ratio increases only marginally with recycling when the samples are extracted, which fur-



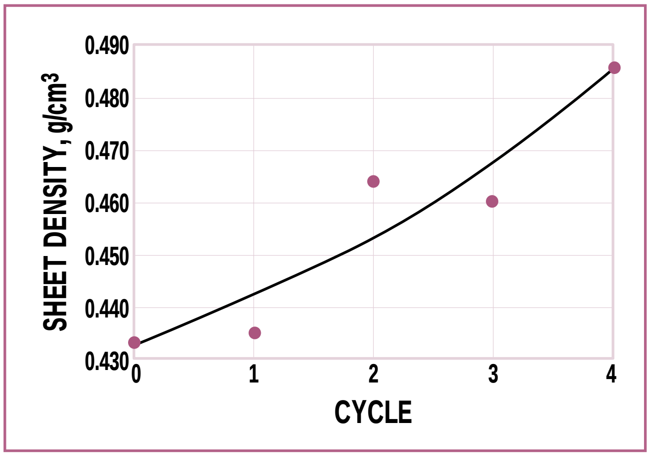
4. The effect of recycling on the oxygen-to-carbon ratio (O/C) of the unextracted and extracted sheets



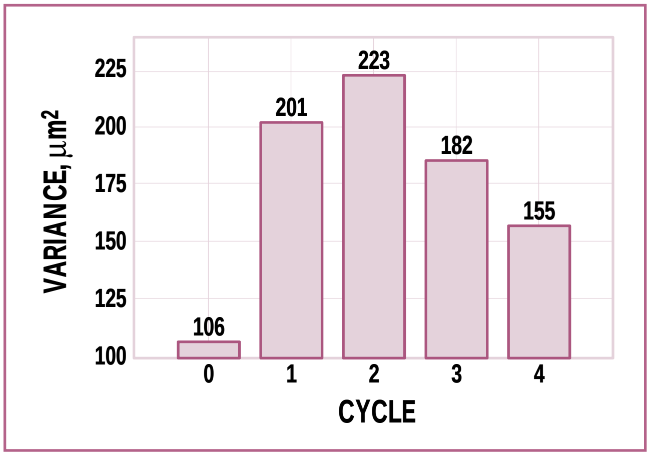
5. Removal of the fatty acids and resin acids from the TMP during recycling



6. The total charge of the pulp is increased by recycling.



7. The density of the sheet is increased by recycling TMP.



8. The effect of recycling on the surface roughness of the sheet as measured by an optical profile tester

ther supports the hypothesis that the underlying cause is the removal of extractives (see Fig. 4 and **Table VIII**). It also can be noted that O/C decreases as a result of aging for the first cycles, while it remains at a high level for the last (see Table VII and **Table IX**). This indicates that extractable material migrates from the bulk to the surface when the total amount of extractives is high in the first cycles.

The amount of fatty acids decreases more slowly than the amount of resin acids (see **Fig. 5**). This can be an effect of the addition of fatty acids to flotation and the poor solubility of the calcium soaps. The retention caused by surface chemical factors in sheet forming is also higher for fatty acids than resin acids *(16)*.

The total charge of the pulp is considerably increased by recycling in spite of a decrease in the extractives content (see **Fig. 6**). The charge probably originates mainly from carboxylic groups. These groups are created by hydrolysis of pre-existing esters or lactones within the hemicellulose fraction of the pulp *(17)*. The alkali treatment causes peeling of the polysaccharides, which generates metasaccharinic acid end groups. Furthermore, the hydrogen peroxide treatment increases the

Cycle	Density, g/cm^3	Tensile index, N·m/g	Stretch at break, %	Tear index, $mN{\cdot}m^2/g$	Bending stiffness index, $N{\cdot}m^7/kg^3$
0	0.433	41.6	2.03	6.78	1.12
1	0.435	36.9	1.81	6.94	1.12
2	0.464	34.6	1.76	6.79	0.94
3	0.460	38.0	1.78	6.76	1.08
4	0.485	36.2	1.82	6.51	0.66

X. Mechanical properties for the recycled TMP fibers

Cycle	Contact angle at 1 s (Fresh sheet), deg	Contact angle at 1 s (Aged sheet), deg	Color demand in printing, g/m^2
0	29.3	81.5	0.80
1	37.0	54.5	0.93
2	...	44.5	1.05
3	42.8	43.6	1.10
4	43.2	45.2	1.14

XI. Results from the contact angle measurements for unaged and aged sheets and the color demand of the unaged sheet in printing

Cycle	Brightness, %	*Y*-value, %	L^*	a^*	b^*	Opacity, %	*s*-value m^2/kg	*k*-value m^2/kg
0	62.4	72.2	90.6	–0.1	13.7	95.8	77.4	3.3
1	57.3	64.5	85.3	–1.7	9.6	97.8	56.7	5.1
2	58.6	68.2	86.1	–2.3	9.7	96.5	58.4	5.2
3	58.6	67.3	85.7	–2.3	8.9	97.2	56.5	4.7
4	58.4	67.7	85.9	–2.3	9.3	96.1	53.8	4.3

XII. Optical properties for the recycled TMP fibers

amount of carboxylic groups due to oxidation of the pulp components, primarily lignin. The small increase in O/C of the extracted pulps also may be an indication that oxidation occurs in the lignin or carbohydrates. In contrast to the increased total charge, the amount of carbons with three oxygen bonds (O–C = O) (e.g., carboxylic acid, carboxylate and/or ester groups) decreases. Similar results have been obtained by other authors *(10).* However, note that only a thin surface layer of the fibers is analyzed by ESCA.

KEYWORDS

Chemical properties, deinking, extractives, fibers, graphic arts, mechanical properties, mechanical pulps, newsprint, physical properties, printing, printing papers, properties, reclaimed fibers, recycling, refiner mechanical pulps, surface properties, tear strength, tensile properties, tensile strength, thermomechanical pulps, wettability.

Effect on sheet and surface properties

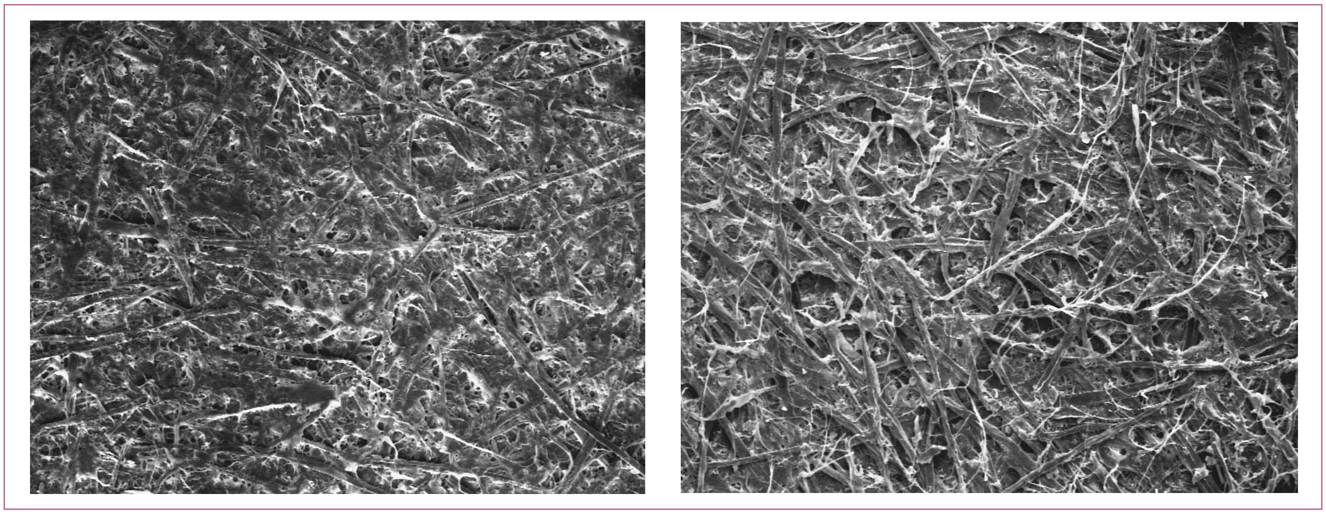
The sheet density increased due to recycling (see **Fig. 7**). In spite of the improved density, the tensile strength decreased after the first cycle (see **Table X**). The first drying of the fibers decreased the stretch value, but no further decrease took place during the following three cycles. The sheet stiffness was not significantly affected until during the last cycle, when an increase also was detected in the sheet density.

The surface roughness of the sheet as measured with an optical profile tester *(18)* showed an increased value with cycling, but after three cycles, the roughness decreased (see **Fig. 8**). The increased roughness also is obvious from studies of the sheets in the SEM, where a much more open surface structure may be observed after the first cycle (see **Fig. 9**). The increased surface roughness also must provide the explanation behind the increased color demand in printing (see **Table XI**).

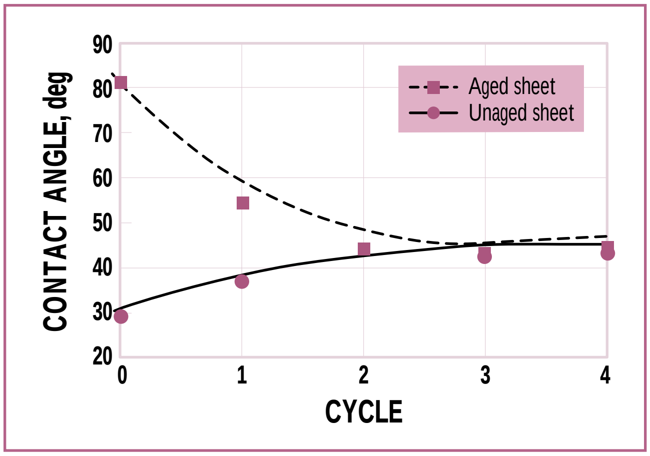
The increased density provides one explanation for the lower *s*- value caused by recycling, as shown in **Table XII**. The amount of fines remains constant, and the decreased *s*-value therefore cannot be explained in this way. However, the chemical treatment during recycling probably gives a more even fiber surface, which scatters light less than the original TMP fiber prepared by mechanical means.

In spite of the lower *s*-value, the opacity was increased by recycling. This is possible because of simultaneous changes in the *k*-value and the reflectance factor, R_0. The increase in the *k*-value is most probably caused by the remaining ink particles, indicated also by the lower L^*-value, while R_0 is probably increased due to the poorer bonding ability of the fibers.

The water contact angle of newly produced sheets increased due to recycling (see **Fig. 10**). This also has been observed in another study, where a printing step increased the advancing contact angle *(19).* In contrast to the ESCA results, this may suggest that the fiber surfaces become more hydrophobic. The observed larger contact angle may arise from the increased surface roughness. There also has been some hydrophobic material strongly located on the surface, thus increasing the contact angle but not affecting the ESCA measurements to the same extent. Furthermore, the aged sheets show a larger contact angle for the first cycles. The difference between a newly produced sheet and an aged sheet decreases with cycling and,



9. Scanning electron micrograph of the sheet surface before (left) and after (right) the first cycle



10. The effect of recycling on the water contact angle of the unaged and aged sheet

after the third cycle, they reach the same contact angle level. This might be an indication of migration of extractives from the bulk to the fiber surface, when the extractives content is high during the first cycles.

CONCLUSIONS

In spite of an increased total charge, increased oxygen-to-carbon ratio, decreased extractives, and an increased sheet density caused by recycling, the paper sheet shows an increased surface roughness and a small decrease in the tensile index.

The increased contact angle and the decreased amount of carbons with three oxygen bonds are the only results in this study that indicate a more hydrophobic surface. This could explain the deteriorated strength properties obtained by recycling.

This effect of printing seems to outweigh the effect of improved fiber bonding from repeated recycling that earlier investigations have demonstrated.

Several stages in the performed recycling procedure can influence these results, e.g., the printing process, the chemistry of the ink, and variations in the calendering process.

This investigation on TMP is the first that includes all essential process steps in the recycling process for graphic papers. **TJ**

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