PEER REVIEWED

Role of polymers in deinking mixed paper

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ABSTRACT

Discarded paper contains plastics, ink, fillers, and coatings. All of these contaminants must be separated from the fibers that are useful for papermaking. In the conventional process, the plastics are removed by hand before the discarded paper is reused. The procedure increases the cost of the raw material.

New investigations show the benefit of keeping the plastics in the furnish and using them as attributes in deinking. In the process, the polymers are transformed into scavengers for ink and other colloids after exposure of the discarded paper to a pulping liquor containing mineral spirits and sodium silicate. Deinking occurs when the ink and colloid-loaded plastics are removed from the clean fibers by screening.

This study reveals that the joint action of mineral spirits and sodium silicate is paramount for the transformation of the surface properties of the polymers and for the attachment of colloids to the surface-modified plastics. The data indicate that ink removal is temperature dependent. Adhesion of particles does not significantly affect the glass transition temperature and the FTIR spectra of the plastics.

Application:

This work demonstrates that mixed paper can be used without initial segregation of plastics. These polymers can play an important role in deinking the furnish.

In 1995, 215 millions tons of municipal solid waste was discarded, and paper products made up about 38% of that estimated amount *(1)*. Because of environmental concerns and the fact that paper and paperboard constitute the largest portion of the materials discarded each year in the country, the paper industry is now pressed to recover and use more discarded paper as a source of fibers for making new products. As more companies begin to use and compete for the best grades of discarded paper, the possibility of a shortage of good secondary fiber sources is increasing. These sources are the well presorted and characterized grades at the high end of the waste stream.

If the fiber shortage occurs, the survival of many industries (mainly those that rely on postconsumer discarded paper as a raw material for their mills) will depend on their ability to efficiently process furnishes of a very low quality. These include mixed household and bulk mail papers (direct mail, catalogs, and magazines). Currently, there is no indication of an approaching shortage of bulk mail. A recent study *(2)* shows that bulk mail paper constitutes approximately 60% of the total weight of discarded paper that is not currently being recycled. Most of the material is still landfilled or incinerated, despite the legislative effort to promote recycling. This is because there is no efficient process for reclaiming fibers from mixed papers.

The nature and the continuously changing chemical composition of contaminants within the furnish require the application of an efficient and economical process to make bulk mail paper a valuable resource. The absence of such a process is a major hurdle to recycling mixed paper. Essentially, a change is needed in the way that the aforementioned material is recycled.

One new way of recycling mixed paper may start with an attempt to answer this question *(3)*: Can the undesirable contaminants be used as if they were "valuable attributes" of the furnish, and can they "actively participate" in the deinking of wood pulp fibers?

A query of this kind suggests that the cleaning process that is currently used in the industry should be re-evaluated. Certainly, if the most-feared contaminants (i.e., plastics) can be used to deink discarded paper, this would be beneficial to the mill operator. Such a change in the way that recycling is approached would allow any mill to decrease the costs associated with the sorting and deinking operations. The recovery of wood fibers from bulk mail paper will then become a very viable venture *(3)*.

Following a new thread of ideas, a novel process for treating mixed discarded paper is being developed. In the new process, the solid polymer contaminants are transformed into scavengers for ink and hydrophobic colloidal particles (i.e., clay, titanium oxide, alum, and precipitated calcium carbonate that is liberated during the discarded paper pulping). In this procedure, mineral spirits (a mixture of low-molecular-weight hydrocarbons) and sodium silicate are simultaneously added to the liquor used to pulp paper. Exposure to the solution alters the properties of the polymer contaminants and the colloids. Subsequently, the plastics retain more ink and colloidal particles than they otherwise would (**Fig. 1**). Deinking is achieved when the ink and colloid-loaded poly-

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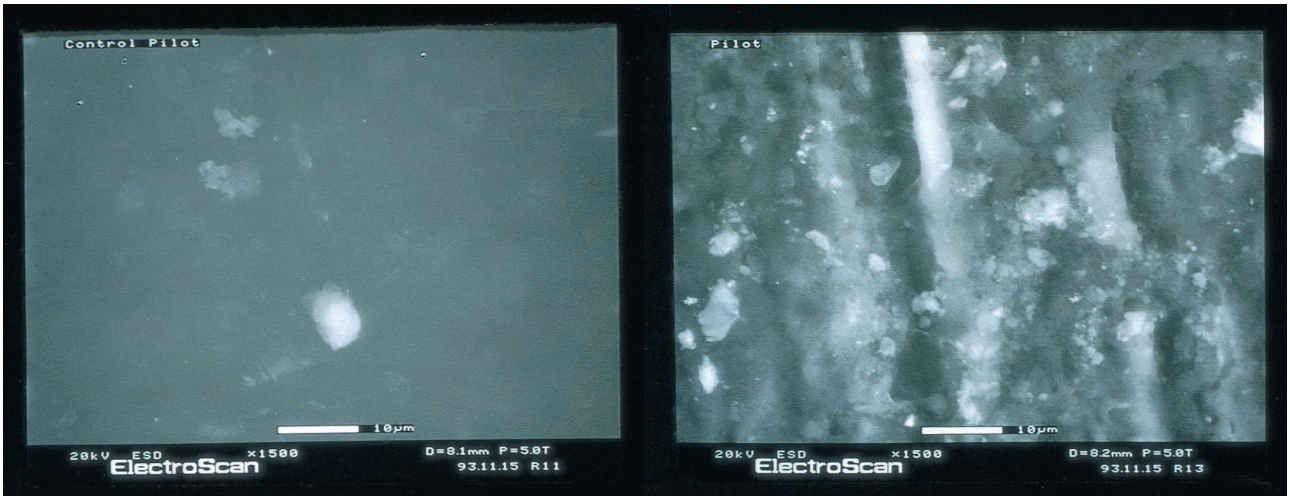


1. Environmental scanning electron photomicrographs of plastic films rejected to the screen during pulp cleaning. Samples obtained from discarded paper treated without (left) and with (right) mineral spirits and sodium silicate. The bottom picture shows the particles retained on the surface of the polymer.

mers are separated from the clean wood fibers by screening. The obtained pulp is very clean and would not require further deinking by conventional methods (i.e., flotation and washing).

Because fillers and coating components are also retained on the plastics, the process has the potential to significantly reduce the volume of sludge that would be generated during the recycling process. The data obtained during the laboratory experiments were confirmed on a large scale in the pilot mill trials. The information obtained during the investigations was presented in subsequent publications *(3–5).*

Since retention of particles (of ink and other colloids) on the plastic surfaces is the keystone of the new process, this paper is devoted to investigating the role of polymers in deinking. The study evaluates the efficiency of deinking as a result of pulping conditions and a change in composition and structure of the polymers exposed to various treatments.

LITERATURE REVIEW

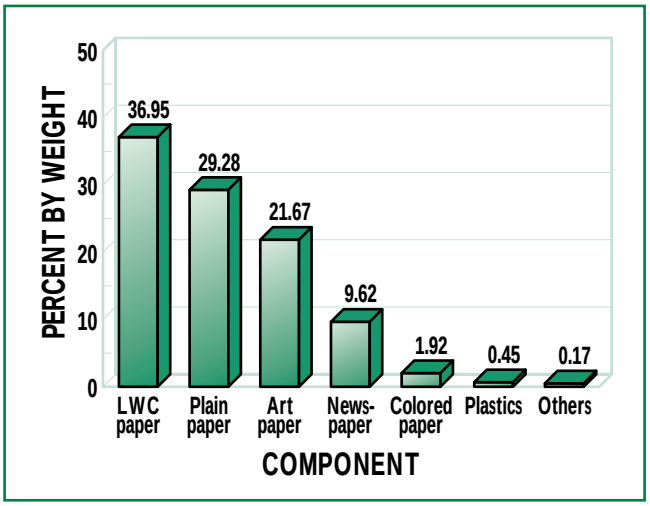
The conventional deinking processes (screening, cleaning, flotation, washing, and the combination of these operations) are not able to efficiently treat low-quality mixed papers. Several attempts to improve the deinking of these furnishes have been made. After separation of the plastics, most investigators have added a variety of solids and chemicals to the pulp to remove ink particles from the furnish. Depending on the type of interactions occurring between the additives and the ink, the process could be classified as adsorption *(6–11),* agglomeration *(12–19),* and dissolution *(20–33).*

In the adsorption processes, the collecting solids are selected from materials having a strong affinity for the ink particles. Solids having a hard, relatively inactive surface are rendered more effective as collectors by coating them with sticky or viscous oils and gums and waxes, which adhere to the surface. The collecting solids are added to the slurry obtained after pulping of the recovered paper with a caustic solution containing peroxide and a suitable surface-active agent or soap in the temperature range of 30–50°C. Deinking occurs when the ink-coated collectors are recovered from the pulp by screening, sedimentation, or magnetic separation. In these processes, mineral spirits (or other solvents) are not used as a component of the pulping liquor. A typical example of deinking by adsorption is described in the Canadian patent issued to Puddington, Sparks, and Sexton in 1977 *(6).*

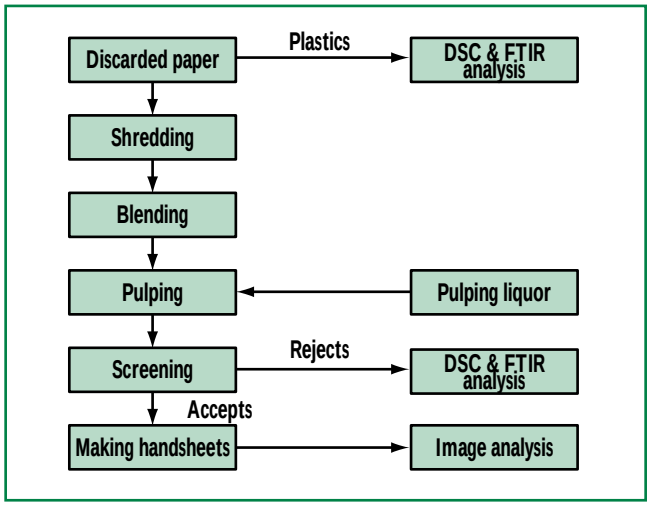
The agglomeration processes use soap flakes in suspension, or placed on carriers, to deink the furnish. The flakes are obtained by precipitating solutions of metal soaps of fatty or bituminous acids with solutions of salts of alkaline earths. The papers are impregnated with surfactants and alkalis and then pulped in the presence of an organic hydrocarbon compound and the highly adsorptive flakes. The ink and flake agglomerates are separated from the clean fibers by latent vortex action.

In dissolution processes, the discarded paper is exposed to large amounts of organic solvents to dissolve the ink and soluble organic contaminants. In most cases, the solvents are used in conjunction with surfactants to increase their effectiveness. Deinking occurs when the fibers are separated from the solvent by filtration. Other investigations used organic solvents along with specially designed equipment to deink discarded paper.

A U.S. patent issued to Weyerhaeuser in 1981 *(10)* and a subsequent publication *(11)* describe the case of a dissolution process wherein a collecting solid is added to the pulp



2. Weight distribution of materials present in mixed paper



3. Representation of the experimental procedure

slurry to remove the ink. The solid has a solubility parameter similar to that of the toners so that the softened toner is slightly soluble in the collector. In the process, the paper is pulped to form an aqueous slurry. The pulp is heated to a temperature of 38–75°C, and collecting chemicals and collecting solids are then added to the slurry. The selection of the solid collectors to use in deinking depends on the specific chemical composition of the toner. The materials of choice consist of vinyl, acetate, urethane, and olefin polymers in the form of beads, prills, and sheets. The collecting chemicals were primary and secondary, saturated and unsaturated aliphatic alcohols (C_8 to C_{22}), and saturated aliphatic hydrocarbons (C_7 through C_{28}).

The work described in this paper is an improvement over the previous investigations. First, it uses the furnish's mixture of polymeric contaminants as valuable attributes for deinking, and the raw material is processed without a prior separation of the plastics. Second, it does not target a specific type of ink. It relies on the joint action of minerals spirits, sodium silicate, and the mixture of plastics to remove all types of inks (toners, flexographic, and gravure) and other colloids (i.e., clay, TiO_2, and calcium carbonate) that are present in the furnish [Fig. 1 *(4)*]. Finally, it uses conventional equipment; no new capital investment is required.

EXPERIMENTAL APPROACH

Materials

A typical sample of mixed papers contained coated and uncoated sheets printed with offset, gravure, and flexographic inks and toners. Plastic films and other synthetic fibers were commingled with the papers. **Figure 2** shows the weight distribution of the various materials present in a typical sample of discarded paper.

The polymeric compounds present in the furnish were analyzed by using a Mattson Galaxy 4020 Fourier transform infrared spectrometer (FTIR) (Mattson Instruments Inc., Madison, WI) equipped with a Spectra-Tech IR-Plan analytical microscope (Spectra-Tech Inc., Shelton, CT). The thermal behavior of the plastics was characterized by using a Mettler Thermal Analysis System Model TA4000 (Mettler DSC-30, differential scanning calorimeter, coupled to a Mettler TC 11 TA Processor—Mettler Instruments Corp., Highstown, NJ).

The polymers identified in the business bulk mail and mixed papers *(2, 3)* were polyesters, polyethylene phthalates, polyacetates, polyacrylates, polyvinyls, polyacrylamide, polystyrene, butadiene copolymers, polyethylene, and polypropylene. The two major polymers identified in the discarded paper stream were semicrystalline polystyrene and high-density polyethylene.

Methodology

A schematic representation of the experimental procedure adopted during the trial is shown in **Fig. 3**. A batch of unsorted paper (25 kg) was shredded by hand into 3-in. x 3-in. pieces and then mixed by using a 4-ft-diam. tumbling blender for 2 hours. Very large pieces of plastic films and sheets made of synthetic fibers were discarded; all the other polymeric contaminants were kept in the experimental sample.

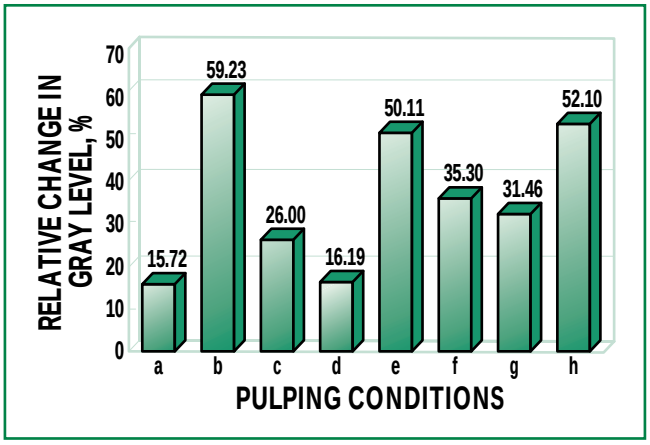
The furnish was pulped in accordance with the following method. Mixed discarded papers (1 kg) were placed in an Adirondack Formax 1800H high-consistency laboratory pulper (Adirondack Machine Corp., Glens Falls, NY). An aqueous liquor (9 L) was added to the content of the pulper, and the machine was operated for 10 min. The impeller was rotated at a frequency of 10 Hz. **Table I** shows the pulping conditions adopted in the different trials. The pulping liquor contained sodium hydroxide, hydrogen peroxide, sodium silicate, and mineral spirits.

At the end of the operation, the slurry was diluted by adding water to the contents of the pulper, and then the stock was flushed out of the machine by turning the impeller for a few seconds. The obtained pulp was screened by using a vibrating screen equipped with a 0.015-in. slotted plate (Valley Iron Works Co., Appleton, WI).

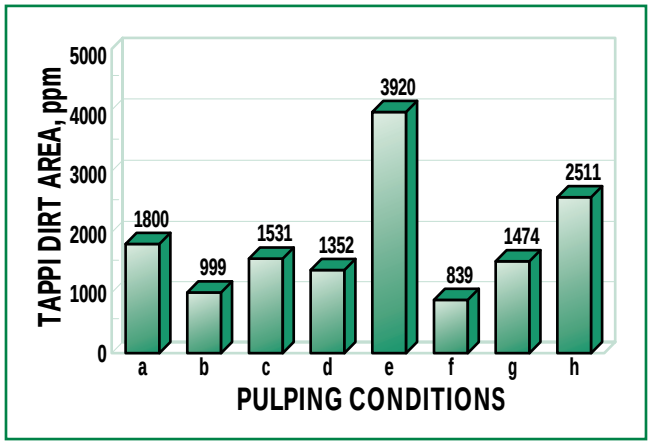
Experiment	Pulping temp., °C	Pulping liquor	Other conditions
a	25	3% NaOH, 1% H_2O_2, 1.22% Na_2SiO_3, 1% M.S.*	10% consistency, 10 min, 10 Hz
b	50	Same as above	Same as above
c	60	Same as above	Same as above
d	70	Same as above	Same as above
e	50	0.3% NaOH, 1% H_2O_2, 1.22% Na_2SiO_3, 1% M.S.	Same as above
f	50	3% NaOH, 1% H_2O_2, 3.66% Na_2SiO_3, 1% M.S.	Same as above
g	50	3% NaOH, 1% H_2O_2, 1.22% Na_2SiO_3, 0.6% M.S.	Same as above
h	50	3% NaOH, 1% H_2O_2, 1.22% Na_2SiO_3, 1.4% M.S.	Same as above

*M.S. + mineral spirits

I. Pulping conditions adopted in the investigation



4. Relative change of gray level as a function of pulping conditions for polystyrene films present in mixed papers. The pulping conditions are defined in Table I; change in gray level is evaluated with respect to a clear polystyrene film (control).



5. TAPPI dirt area (in ppm) for ink particles remaining in the screened pulp as a function of pulping conditions. The pulping conditions are defined in Table I.

The polymers rejected to the screen were collected, dried at room temperature, and then analyzed by using a Fourier transform infrared spectrometer coupled to an infrared microscope. The thermal behavior of the plastics was characterized by using the differential scanning calorimeter.

After the trials, the composition of the ink-loaded plastics was analyzed by using the FTIR microscope. A control of the same type as the specimen was then selected. The pair of samples, about 1 in. x 0.5 in. in size, was used in determining the efficiency of the ink retention on the surface of the plastics. The ink retention was determined by comparing the relative change in gray level of the ink-loaded polymer substrates to the same property for the clear plastics taken as controls. The relative changes of gray level were determined as percent variations in luminescence values of white light from black to white. The measurement was carried out using an 8-bit monochrome system (Optomax V HR image analyzer—Optomax Inc., Hollis, NH).

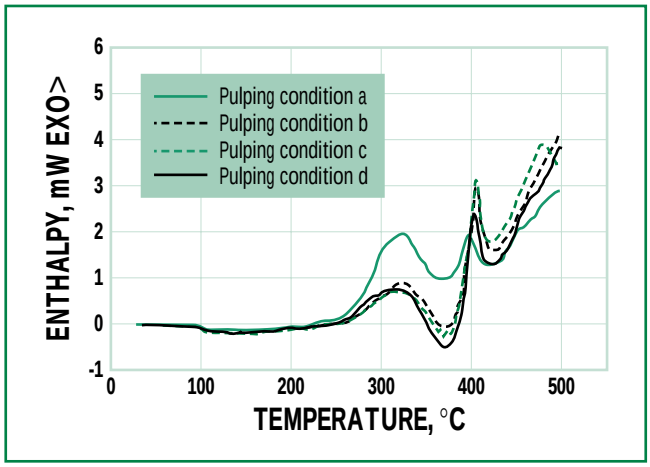
Furthermore, handsheets were made from the screened pulp fibers in accordance with Tappi Test Method T-220, and the amount and size of residual dirt particles were determined by using an Optomax V HR image analyzer *(5)*.

RESULTS

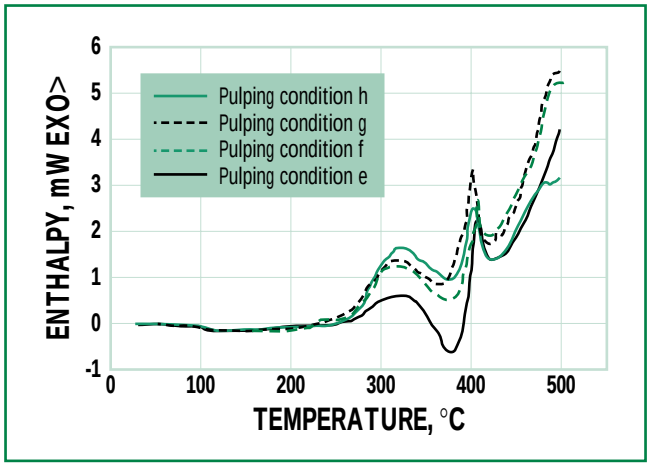
Role of polymers in adsorbing and removing inks

The change in the gray level of the plastics rejected to the screen during wood fibers recovery is directly related to the amount of ink adsorbed by the polymers. The examination of the data indicates that, between the two major polymers found in the waste stream, polystyrene displays a more pronounced change in gray level after adsorption of ink from the furnish. Polyethylene does not show a significant change in gray level. In the experimental procedure adopted (low-ash-content paper and low amounts of flexographic and gravure inks), polystyrene removes more inks than polyethylene.

Figure 4 shows the relative change of the gray shade for samples of ink-loaded polystyrene rejected to the screen during recycling of paper. Examination of the results indicates that adsorption of ink particles by the



6. DSC thermograms of polystyrene films rejected from pulp obtained from mixed paper. Vibrating flat screen used. Pulping conditions are defined in Table I.



7. DSC thermograms of polystyrene films rejected from pulp obtained from mixed paper. Vibrating flat screen used. Pulping conditions are defined in Table I.

plastics exposed to mineral spirits, sodium hydroxide, and sodium silicate depends on the temperature of the liquor. Ink retention corresponding to more than a 50% change in gray level occurs at about 50°C. These changes are associated with the experimental conditions b, e, and h in Fig. 4.

Adsorption of ink by the polymer substrate increases significantly when the amount of mineral spirits increases from 0.6 to 1.0%. A slight decrease in retention is observed when the furnish is exposed to a liquor containing 1.4% mineral spirits. Optimal deinking occurs with a 1% addition of mineral spirits. Sodium silicate, used in conjunction with mineral spirits, affects the adsorption of particles on the surface of the polymers. The adsorption of ink decreases when the sodium silicate concentration changes from 1.22 to 3.66%; reduction of the amount of sodium hydroxide from 3.0 to 0.3% also decreases the adsorption of particles.

KEYWORDS
Adsorbents, bibliographies, deinking, hydrocarbons, low grade materials, materials, mixed waste papers, plastics, polymers, screening, sodium silicate, solid wastes, sorbents, waste papers.

Maximum ink adsorption is observed when paper is pulped at 50°C by using a liquor containing 1% mineral spirits, 1.22% sodium silicate, 3% sodium hydroxide, and 1% hydrogen peroxide (Fig. 4, experimental condition b). This condition also yields a pulp containing the second smallest dirt size. This result is also consistent with previous findings *(3, 4)*. Note that when a higher concentration (i.e., 3.66%) of sodium silicate is used, the size of the residual particles of ink is the smallest (**Fig. 5**, experimental condition f). However, the corresponding change in gray level (with respect to the control) for the plastic exposed to the liquor, and adsorption of ink, is only about 35%.

Similarly, sodium hydroxide seems to affect the size of the ink particles. For example, the use of a pulping liquor containing 0.3% sodium hydroxide does not yield a product with a low dirt particle size. These observations are not well understood. Further investigations are needed to explain the findings.

Change of polymer composition and structure during paper pulping

The DSC thermograms of the rejects to the screen are shown in **Figs. 6** and **7**. An examination of these curves indicates that the glass transition temperature (approximately 100°C) and exothermal temperatures (about 320 and 400°C) were not changed by exposing the plastics to different pulping conditions. However, with the exception of the material exposed to 1.4% mineral spirits, most pulping liquor composition and temperatures did not significantly change the FTIR spectrograms of the plastics when compared to the spectra of the standards. The data analysis shows that polystyrene has a glass transition temperature of 100°C, and the exothermal peaks are at about 320 and 400°C.

A plot of the correlation coefficients of the FTIR spectra as a function of treatment condition is shown in **Fig. 8**. Note that only polystyrene exposed to a pulping liquor containing 1.4% mineral spirits has a low correlation with respect to the standard. The data indicate that exposure to the pulping liquor does not alter the bulk chemical composition of the plastics. This is also confirmed by examining the FTIR data for the samples of polystyrene exposed to various pulping liquors (**Fig. 9**).

CONCLUSION

Pulping conditions play an important role in deinking by use of polymer scavengers. The composition and the temperature of the liquor affect the retention of ink on the surface of the plastics. Ink particles are effectively removed by the plastics during recycling. However, the size of the

particles remaining in the cleaned pulp is not controlled only by retention on the surface of the polymers.

Addition of mineral spirits in conjunction with sodium silicate leads to retention of ink particles on the surface of the polymers. An optimum temperature for the pulping process is 50°C. Maximum retention is obtained with a liquor of the following composition: 1% mineral spirits, 1.22% sodium silicate, and 3% sodium hydroxide.

The glass transition temperature of polystyrene does not change upon exposure to the pulping liquor. However, the intensity of the exothermic transitions changes after exposure to the liquor. The value of the correlation coefficients of the FTIR spectra for polystyrene depends on the liquor composition. However, the change of these quantities does not correlate with the observed gray level for the plastics rejected to the screen. **TJ**

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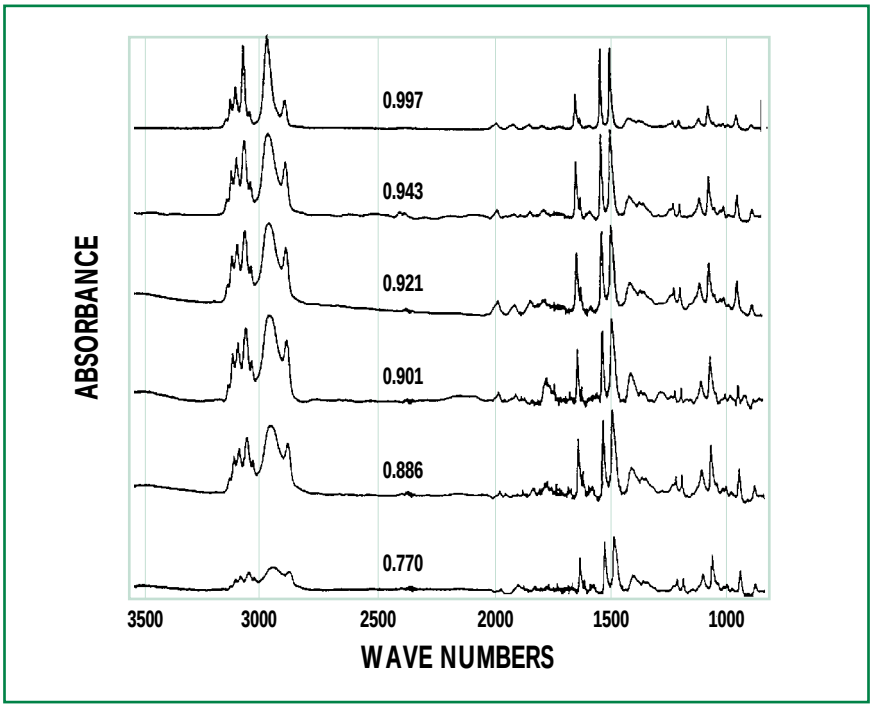
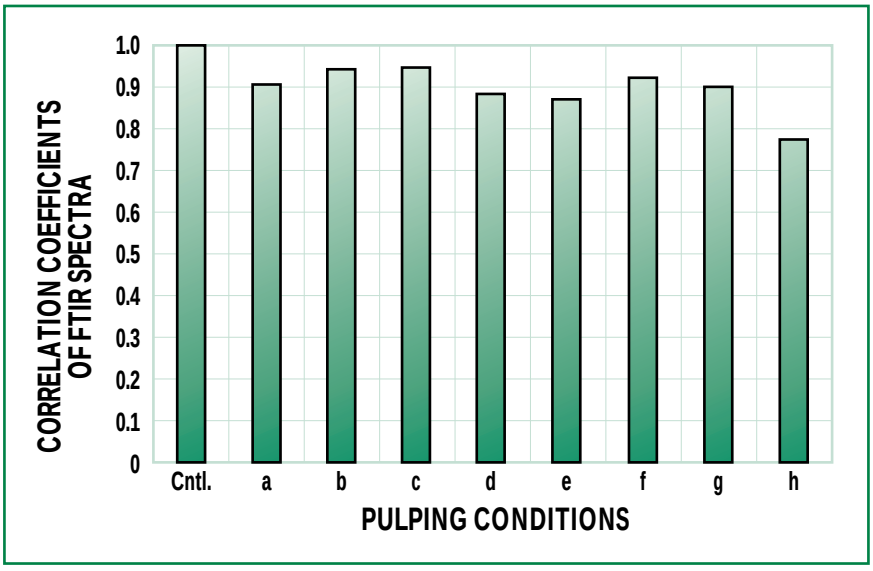


8. Correlation coefficients of the FTIR spectra of the control (clear plastic) and the ink-loaded polystyrene films rejected from the pulp obtained from the mixed paper. Wavenumber range 800–3600. Vibrating flat screen used. Pulping conditions are defined in Table I.



9. FTIR spectrograms of polystyrene films rejected when screening the pulp obtained from mixed paper. The specimens have different correlation coefficients of the FTIR spectra with respect to the control (clear polystyrene film). The pulping conditions are defined in Table I.

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