Utilization of Waste Leather Shavings as Filler in Paper Making

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ABSTRACT: Leather industry generates large amounts of wastes, most of them are burned causing environmental pollution. This study aims to use these wastes as filler in bagasse pulp before sheet formation, as a novel method. Leather shavings were subjected to multistage disintegration to prepare powder, then treated with different monomers and applied in paper sheets. The formed sheets exhibit a considerable improvement in some of their properties such as tear, water resistance, air permeability, and thermal stability. Only breaking length was affected by adding untreated and treated leather shavings. Consequently, the resulting paper sheets have potential for application in wrapping and packaging industries. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1713–1719, 2010

Key words: filler; FTIR; mechanical properties; polystyrene; recycling

INTRODUCTION

Fibrous raw materials for pulp making are divided into three main categories: wood fibers that constitute about 75% of all the fibrous raw material supply of pulp mills, reclaimed waste paper about 20%, and remaining 5% are nonwood fibers.[1]

For the increasing demands coupled with increasing shortage and higher prices of wood, nonwood fibers gained their importance as raw material for pulp production in countries poor in wood sources. Among the many nonwood fibers, e.g., bagasse, bamboo, and straws, utilized for paper pulp manufacture, sugar cane bagasse distinguishes itself as being one which promises to become a major fibrous raw material because it is easily available from sugar mills and its fiber lengths are comparable with those of hard woods. It is a fibrous, low-density material with a very wide range of particle sizes.

Partial replacement of paper pulps with other natural or synthetic fibers has been studied for preparing some specialty papers or for preparing papers with less expensive fibers (every 1% increase in fillers decreases the cost by 2.5 \$/ton).

One of the most significant problems of the leather industry is waste generation. About 30% of leather substance processed in tanneries is rejected, mainly after shaving process, in the form of protein wastes containing about 10–15% chromium (III). These wastes are mainly deposited and burned causing hazards to the environment.[2]

The most often proposed technological solution of the waste leather shavings problem is the utilization in secondary or artificial leathers designed for foot wear, fancy goods, or nonwoven fabrics as substrates for leather like materials.

Another trend of utilization of wastes is to detanne or recover chromium III compounds and processing the recovered collagen into gelatin, adhesive, or protein hydrolyzate.[3,4]

The recovered gelatin can be used in cosmetics, sizes, printing inks, and photography. The protein hydrolyzate due to its high-nitrogen content can be possibly used as fertilizer or additive to fodders, whereas the recovered chrome can be used in tanning process.[5]

In the last few years, studies were directed to utilize the wastes of chrome shavings as a filler of rubber.[6] Chrome tanned waste collagen was used beside silica[7] or as leather powder.[8]

During literature survey on mixing leather shavings and bagasse pulp together as they exist in big amount without considerable usage, no results were found. Therefore, this work proposed a novel method by adding leather shavings to bagasse pulp before sheet formation. The shavings waste was disintegrated into powder and treated with different monomers then applied in papermaking. The

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resulting paper sheets were evaluated through mechanical, physical, and thermal properties. This partial replacement of pulp fibers has two benefits: reducing the cost of paper industry and consuming a part of leather shavings that cause environmental problems.

EXPERIMENTAL

Raw materials used

- Unbleached bagasse pulp produced from Egyptian sugarcane bagasse at Edfo pulp, Upper Egypt, beaten to 30 SR° in a valley beater.
- Waste leather shavings supplied by medium-sized tannery located in Misr-Elkadima region, Cairo, Egypt.
- Styrene, ethyl acrylate, and butyl acrylate monomers from "Merck- Schuchadt."

Treatment of leather shavings

Waste leather shavings were subjected to multistage disintegration to prepare a powder then sieved through 0.3 meshes. The resultant leather powder was divided into four parts: untreated leather powder, leather powder treated with styrene, ethyl acrylate and butyl acrylate monomers individually. The treated samples were filtered and dried at 60°C for 2 h in an air oven and sieved again through 0.3 meshes and are then ready for addition to pulp.

Paper manufacture

The paper sheets were prepared according to SCA-Std[9] after addition of different concentrations of untreated and treated leather shavings using the SCA Model sheet form (Alorentzen & Wetter). After sheet formation, the sheet was pressed for 4 min using a hydraulic press according to standard (SCAN: 5 kgf/cm^2). Drying of the sheet was made using a rotating drum at 60°C ± 5°C (SCAN) for 2 h. The sheets were then placed for conditioning before subjecting them to tests. Table I shows the different sheets compositions used.

TABLE I
Sheet Composition

Series	Sheet pulp composition
I	Bagasse pulp + untreated leather shavings
II	Bagasse pulp + leather shavings treated with styrene
III	Bagasse pulp + leather shavings treated with ethyl acrylate
IV	Bagasse pulp + leather shavings treated with butyl acrylate

Paper testing

- Breaking length and tear: according to German standard methods.[10]
- Water retention: ASTM D2402-90.[11]

Air permeability

The permeability of paper sheets was tested on "Toyoseiki permeability tester- Japan," at a pressure of 12.7 mm water.

Infrared spectra

IR spectra were carried out using FTIR Nexus 670 infrared spectrometer, Nicolet (USA) over range 400–4000 cm^{-1} with resolution of 4 cm^{-1}, KBr disk technique was applied at NRC, Egypt.

Thermogravimetric analysis

Thermal analysis of treated and untreated samples were carried out from 50 to 450°C under nitrogen atmosphere at heating rate 10°C/min with TGA Perkin Elmer.

RESULTS AND DISCUSSION

In this work, different concentrations of untreated and treated leather shavings were added to bagasse pulp. Five sheets were prepared for each concentration and tested for breaking length, tear factor, water retention, and air permeability. TGA and IR studies were carried out for the optimum concentration in each series.

Characterization of leather shavings

Leather chrome shavings for this study were subjected to different analysis such as:

Physical properties

The physical properties of chrome shavings determined and presented in Table II.

Organic constituents

The main component of leather shavings is protein or amino acid crosslinked with small amount of chrome. Amino acid has C, N, and H as main components, which are presented in Table III.

TABLE II
Physical Properties of Untreated Chrome Shavings

pH	3.5
Moisture %	12
Ash %	14

TABLE III
Organic Constituents of Chrome Shavings

Element	C	H	N	S
Percent	32	5	11	2

Effect of addition of leather shavings on characteristic properties of bagasse paper sheets

Effect of addition of leather shavings on the breaking length

The effect of addition of untreated leather shavings and leather shavings treated with different polymers on the breaking length of bagasse paper sheets is shown in Figure 1.

From Figure 1, it can be seen that by increasing the percentage of untreated and treated leather shavings in the bagasse paper sheets, there was a decrease in the breaking length in all samples. This may be due to the reduction in fiber-to-fiber bonding as a result of the interference of leather shavings with bagasse fibers. It is clear that the deterioration in breaking length was the least in case of addition of untreated leather shavings (10% decrease at 25% leather shavings content). There is also a slight deterioration in the breaking length of paper sheets loaded with leather shavings treated with butyl acrylate monomer (decrease of 11.5%) because of its high-chain length and low T_g value, which makes leather fibers softer and more elastic than the leather shavings treated with other polymers. On the other hand, leather shavings treated with styrene monomer showed a significant decrease in breaking length (up to 40% decrease) because fibers treated with styrene have hard characters due to high T_g value of styrene monomer (95°C)[12] so it would mostly produce brittle fibers. The breaking length of paper sheets loaded with leather shavings treated with ethyl acrylate resisted deterioration from 5 to 20% leather shavings content as it decreased only about 5% from its original breaking length value, but a significant decrease occurred at 25% leather shavings content thus losing 35% of the breaking length at 5% leather shavings content.

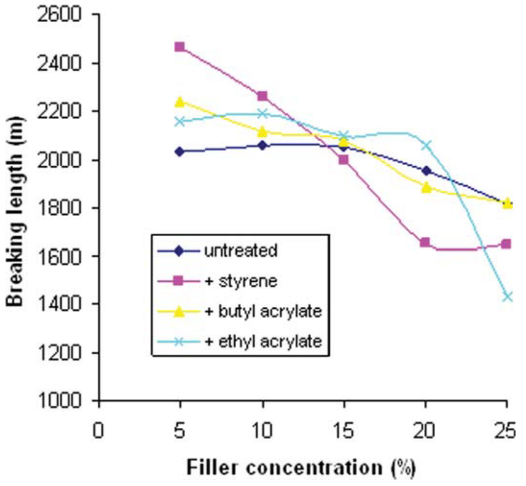


Figure 1 Effect of addition of different series concentrations on breaking length. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of addition of leather shavings on tear factor

Figure 2 shows the effect of addition of untreated and treated leather shavings on tear factor of bagasse paper sheets. From Figure 2, it is clear that for all samples, the tear factor gradually increased by increasing the concentration of leather shavings and had maximum value at 25% leather shavings content. The increase in tear factor was 20–35% in all samples. This may be due to the fact that tear resistance is strongly dependent on fiber length; whereas breaking length is influenced to a much smaller extent.[13] Therefore, this increase in tear factor may be due to the higher length and strength of leather fibers than that of bagasse pulp fibers. Sheets containing stronger fibers have a higher tear strength because more work has to be done when more fibers are pulled out and not broken.[14,15] The highest tear factor was detected in case of addition of leather shavings treated with ethyl acrylate.

Effect of addition of leather shavings on water retention

The water resistance value is the most widely measured parameter of the fiber swell ability in water. Water retention of pulp is directly proportional to the amount of the disordered region in fibers (amorphous). The used pulp is unbleached and contains

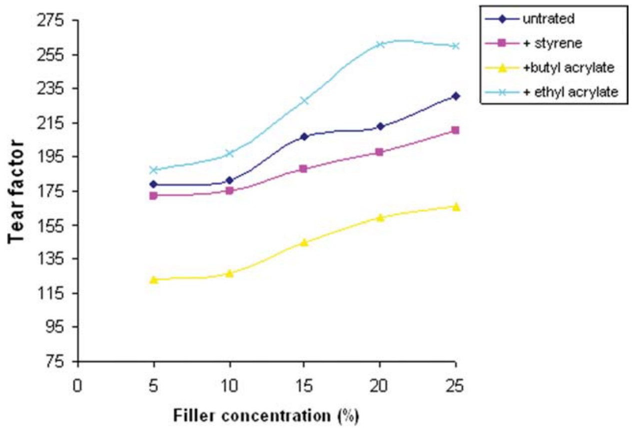


Figure 2 Effect of addition of different series concentrations on tear factor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

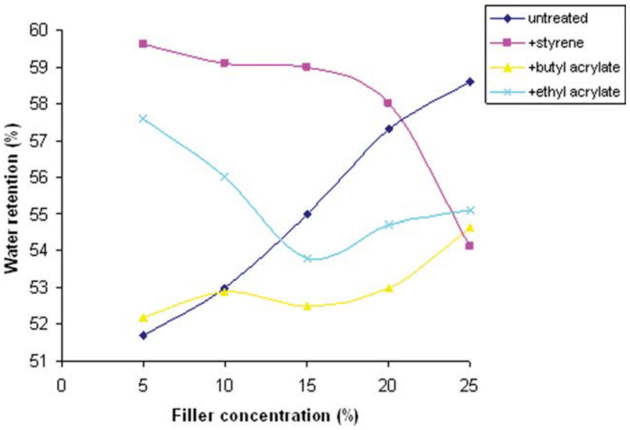


Figure 3 Effect of addition of different series concentrations on water retention. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lignin, which is considered a highly disordered matter. On the other hand, leather shavings fibers are more ordered substances, especially those treated with ethyl and butyl acrylate. The effect of addition of different concentrations of untreated and treated leather shavings on water retention of paper sheets is shown in Figure 3. From Figure 3, it is noticed that all bagasse samples loaded with leather shavings had water retention values less than blank (without leather shavings). Improved water resistance may be correlated to the ability of the polymers to form a protective layer at the interphase, which prevents the diffusion of water molecules into paper sheets. It is also clear from Figure 3 that as the concentrations of untreated leather shavings and leather shavings treated with butyl acrylate and ethyl acrylate increased, water retention of samples increased too. This is due to their hydrophilic character. But in case of leather shavings treated with styrene, the water retention decreased because of its known hydrophobic character. It can be concluded that the addition of leather shavings reduced the water retention of paper sheets, which is a good character in paper packaging.

From all previous results (breaking length, tear factor, and water retention), the optimum filler concentrations were selected in each series. They were 15, 10, 15, and 20% in case of loading bagasse pulp with untreated leather shavings, leather shavings treated with styrene, butyl acrylate and ethyl acrylate respectively. Air permeability, IR spectra, and thermogravimetric analysis were tested for the previously mentioned samples.

Effect of addition of leather shavings on air permeability

The air permeability tests of paper sheets were carried out and the results are presented in Table IV.

TABLE IV
Air Permeability Values of Paper Sheets Filled with Different Leather Shavings Treatments

Series	Air permeability (cm^3/cm^2 s)
Blank	1.82
I	1.243
II	2.19
III	0.928
IV	0.724

From Table IV, it can be noticed that air permeability of all paper sheets loaded with treated leather shavings decreased than the blank one (the improvement in air permeability was 30–70%). This decrease is probably due to the increase in fiber length of leather shavings than bagasse fibers, therefore the pores between cellulose fibers were partially blocked. But in case of leather shavings treated with styrene, the air permeability increased; may be due to the rigid film formed around leather fibers making them poor in homogeneity and compatibility with bagasse fibers, thus increasing the pores between them leading to increase in air permeability.

IR spectra

Infrared spectroscopy is probably the method most extensively used for the analysis of functional groups. The infrared spectra of bagasse pulp (blank) and bagasse pulp loaded with untreated and leather shavings treated with different monomers were carried out and presented in Figure 4.

Figure 4 shows symmetric stretching vibration of OH groups in the region 3200–3500 cm^{-1}, which

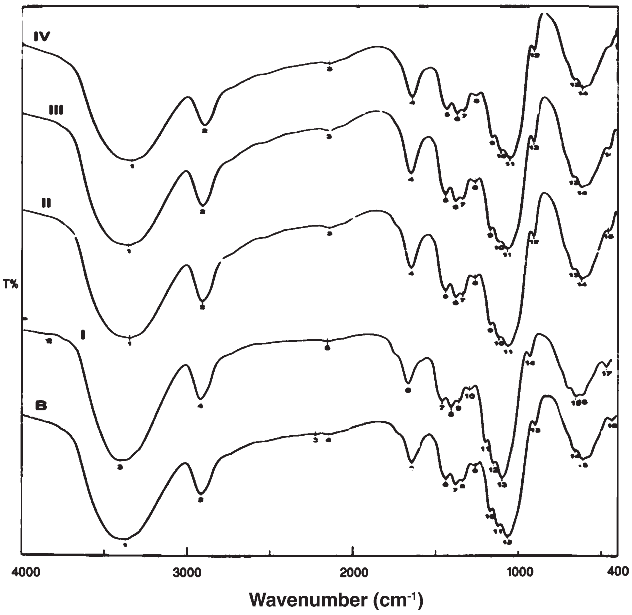


Figure 4 IR spectra of (B) blank of sample and different series.

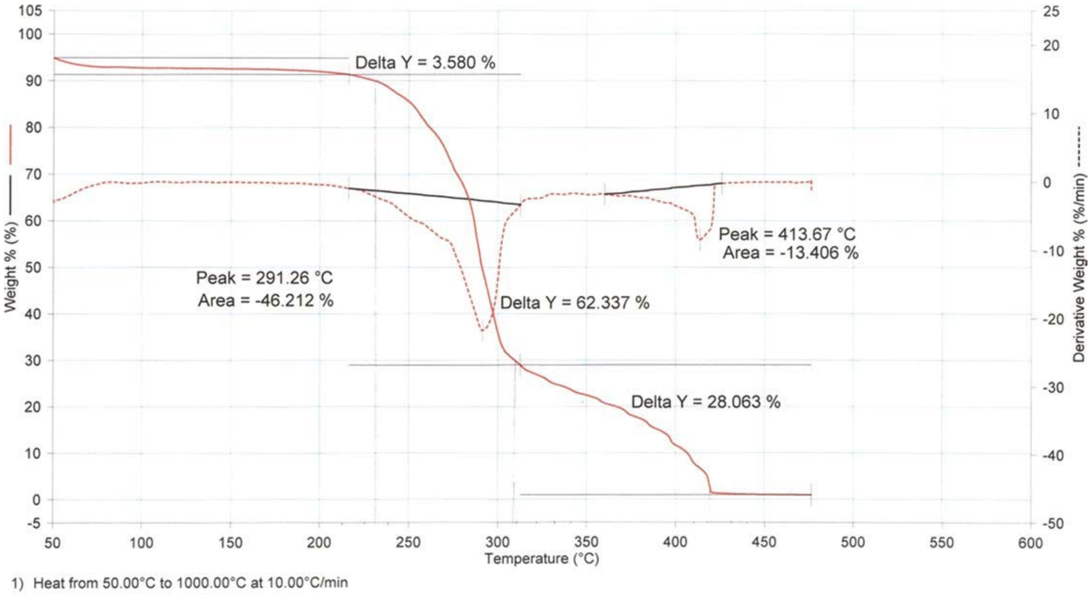


Figure 5 TGA of blank sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

overlaps with stretching vibration of NH. These two groups are present in both bagasse pulp and leather shavings so it appeared as a broad band. IR absorption peaks for the sample in the region 2880–2920 cm^{-1} may result from the stretching vibration of C—H of both pulp and leather shavings. The absorption band in the region 1620–1650 cm^{-1} is characteristic to C=C of the two sample components. Band at 1630 cm^{-1} is related to the C=C stretching. Bands in the range 1300–1430 cm^{-1} with medium intensities are characteristic to C—O stretch of amino acid, which is the main component of leather shavings. IR also shows the characteristic absorption bands at the range 1000–1200 cm^{-1} related to C—O stretching vibration.

From Figure 4, it was found that all samples had the same bands because they have the same characteristic groups but with increasing intensity of bands than blank. This may be explained either that the interaction between leather shavings and bagasse fiber was physical so that there was no chemical interaction (bonds) between them or there was a chemical reaction producing the same functional groups. The composition of samples could also

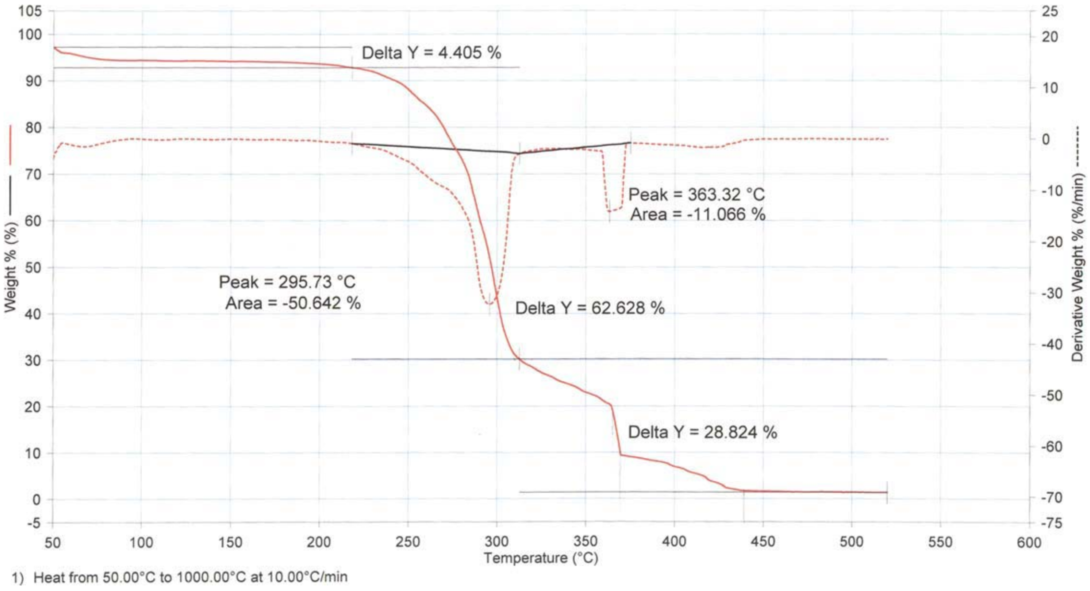
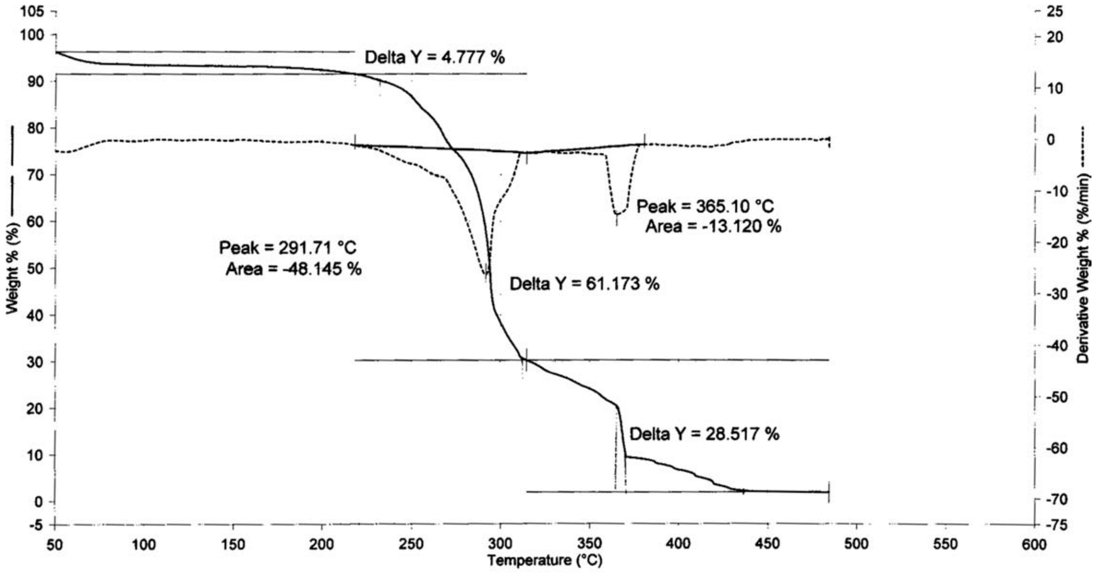


Figure 6 TGA of series I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



1) Heat from 50.00°C to 1000.00°C at 10.00°C/min

Figure 7 TGA of series II.

influence the intensity of the bands as the percentage content of fillers was high reaching 25%.

Thermogravimetric analysis

Thermal behavior for blank, pulp loaded with untreated leather shavings and pulp loaded with leather shavings treated with styrene are presented in Figures 5–7. It is clear that there are three main degradation stages. The first stage represents dehydration and volatilization of low-molecular weight substances, the second stage is the main degradation stage, and the third stage is the carbonization stage. According to the analysis by Broido and coworkers,[16] thermal degradation of cellulose starts at about 217°C with endothermic intermolecular water elimination to produce anhydrocellulose, whereas endothermic tar formation predominates at higher temperature (about 277°C). The anhydrocellulose undergoes further exothermic pyrolysis to form char and gases.

To account for the effect of the above treatments on thermal resistivity of the samples toward thermal degradation, the loss percentage mass in the samples against the temperature is plotted in Figure 8. It can be noted that, in case of blank sample (bagasse pulp only) the loss in weight is 10% at 230°C, 70% at 310°C and tends to be steady at 420°C. In case of TGA for pulp loaded with untreated leather the loss in weight is 10% at 230°C, 70% at 310°C and a new phase appeared due to the presence of leather shavings starts to decompose at 360°C, the curve tend to be steady at 437°C, this raising in decomposition temperature resulted in more stability, while TGA of pulp loaded with styrene has the more thermal stability it loss10% of its weight 240°C and 70% of weight at 313°C and a new phase appeared at 365°C and starts to be steady at 440°C. From the previous data, leather shavings addition contributes to improve thermal resistance of pulp paper and the addition of styrene increase this improvement due to its benzene ring which need more raising in temperature to be broken.

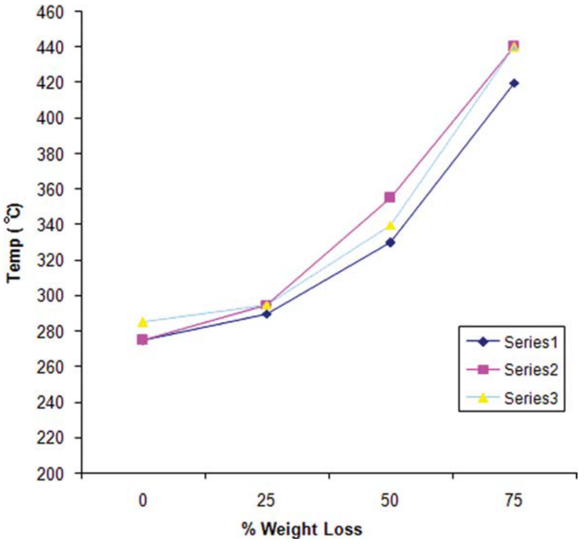


Figure 8 Thermal stability of different series, where series I is blank, series II is pulp loaded with leather shavings treated with styrene, and series III is pulp loaded with untreated leather shavings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSION

The above study can be summarized as follows: waste leather shavings was disintegrated into powder and treated with different monomers then added as fillers in bagasse pulp.

1. Paper sheets filled with untreated and treated leather shavings had higher water resistance.
2. Tear factor increased by increasing filler percentage, while breaking length decreased due to decrease in fiber-to-fiber bonding.
3. All samples had improved thermal stability.
4. All samples (except samples filled with leather shavings treated with styrene) had lower air permeability.

The leather shavings succeeded in application as filler in bagasse pulp aiming at reducing the cost of paper making, minimizing environmental pollution caused from burning leather shavings and improving some properties of paper sheets making them suitable in usage in wrapping and packaging industries.

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