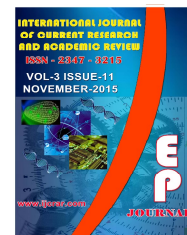




## International Journal of Current Research and Academic Review

ISSN: 2347-3215 Volume 3 Number 11 (November-2015) pp. 42-59

[www.ijcrar.com](http://www.ijcrar.com)



### Investigations on Paper Making Raw Materials and Determination of Paper Quality by FTIR-UATR and UV-Vis DRS Spectroscopy

R. Pavithra<sup>1\*</sup>, S. Gunasekaran<sup>2</sup>, E. Sailatha<sup>1</sup> and S. Kamatchi<sup>1</sup>

<sup>1</sup>Spectrophysics Research Laboratory, PG & Research Department of Physics, Pachaiyappa's College, Chennai – 600 030, India

<sup>2</sup>St. Peter's Institute of Higher Education and Research, St. Peter's University, Avadi, Chennai – 600 054, India

*\*Corresponding author*

#### KEYWORDS

Additives,  
FTIR-ATR,  
UV-Visible  
DRS / DTS,  
Paper quality

#### A B S T R A C T

Paper is a properly processed collection of cellulose fibre, generally obtained from wood and non-wood materials. Certain additives are added to enhance the paper quality during the paper making processes. Monitoring the removal of lignin, extractives and the presence of additives in the enhancement of the paper quality was done by using Fourier Transform Infrared – Universal Attenuated Total Reflection (FTIR-UATR) technique in the Mid IR region. An attempt has been made to find the quality of papers for printing with respect to their coatings by using FTIR-ATR and Ultraviolet (UV) - Visible Diffuse Reflectance (DRS)/Diffuse Transmittance (DTS) spectroscopic techniques. The print quality of paper is determined with respect to the spectral response of coating and sizing agents by FTIR-ATR technique. UV-Visible spectroscopy is also deployed to find the print quality of papers of same density from their UV-Visible spectral response exhibited in Reflectance and Transmittance mode. The employed spectroscopic techniques are extremely reliable and well recognized fingerprinting method in the quality analysis of papers.

#### Introduction

Being an old discovery, paper still holds its place in documentation and information sharing media. Beyond the commercial importance, documentation and printing need papers of fine quality. Manufacturers of papers are always seeking for betterment in the production of paper by eliminating the

unappealing substances, causing porous and dullness to the paper. Majorly, pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood and agricultural residues. In developing countries, about 60% of cellulose fibers originate from non-wood raw materials such

as bagasse, cereal straw, bamboo, jute, etc (Gullichsen, 2000). The main steps in pulp and paper manufacturing are: Raw material preparation and handling, Pulp manufacturing, Pulp Washing and Screening, Chemical recovery, Bleaching, Stock Preparation, and Papermaking (Bajpai, 2012).

Raw material for paper is chosen according to its application. Cellulose fibers, the main constituents of papers, generally isolated from hard and soft woods. Soft wood cellulose fibers are used in the making of paper, where strength is required. The hard wood fibers are shorter than soft wood fibers and afford bulk, smoothness and opacity. They used to produce printing and writing paper. The cellulose fibre grade is different for different species and it decides the strength of the tree. In order to reduce cutting down trees, agricultural wastes i.e. non-wood materials are introduced in the making of paper. In India, Certain percentage of cellulose fibres from sugarcane bagasse plays substitute for wood cellulose fibres in the making of paper.

Considering paper making, debarked wood made into wood chips and it is cooked with active cooking chemicals, this reduces wood into fibres. Krafting is a commonly adopted process in pulping; it is also known as sulphate process. Papers obtained from chemical pulping are known as wood free or lignin free papers. Lignin, a brown colour phenolic polymer, acts like a glue in holding cellulose fibers together and other extractives are usually removed in chemical pulping. Bleaching aims for pulp whitening and isolation of cellulose. Maximum effort has taken to remove lignin and other extractives, removal of these delays discolour of paper. Bleaching of pulp fibres is a complex process involving formation of many chemical reactants.

In addition to cellulose fibres, paper contains certain amount of additives like fillers, pigments, metal ions (Proniewicz et al., 2001). Similarly, some additives are added to enhance the quality of paper, the significance of adding additives is, when an additive is distributed on the fibers it forms an insoluble network around and through the fiber contacts of paper. If additive added paper is rewetted, this network prevents fiber separation, thus preserving some fraction of the original dry strength (Herbert, 1995).

The deployment of sizing agent in paper making is to change the absorption characteristics of the paper. The amphiphilic nature of sizing dodges liquid to not to penetrate or to spread through and also allows inks and paints to remain on the surface of the paper. The retention of sizing on the surface of paper exhibits the efficiency of sizing (Champ and Ettl, 2000; Johansson et al., 2004; Ravnjak et al., 2007). Alike, fillers and coating aid sizing on paper, these enable a smooth finish on papers and make papers more suitable for printing. The opacity of a paper can be increased by coatings, instead of pulp fibres.

Apart from coating polymers, few chemicals are also included in the paper making. These chemicals should be eliminated thoroughly, once the fulfillment of their roles, few such are flocculants, deflocculants, dewatering and bleaching agents.

While making paper by kraft (Sulphate) pulping, maximum effort has been taken to remove other compounds rather than cellulose and it can be monitored at the end of every step by FTIR-ATR technique. Spectroscopic approaches are being widely used to differentiate the wide categories of cellulosic, proteinaceous and regenerated

natural fibres and the many different types of synthetic fibre (Howell and Davis, 1991).

Fourier Transform Infrared spectroscopy belongs to vibrational spectroscopy, characterizes molecules with respect to the vibrations of functional groups present in it. It can also be used in the determination of molecular structure of a material qualitatively and quantitatively.

Vibrational spectroscopy has wide spectrum of techniques for materials characterization including conventional or Transmission Fourier Transform Infrared (FTIR), FT Raman and Attenuated Total Reflectance in FTIR spectroscopy. These methods have been employed for the study of textile fibres, to study their state of deterioration and also to confirm processing and dye treatments (Garside and Wyeth, 2000).

In FTIR spectroscopy, among far and near, the middle Infrared (IR) region i.e.,  $4000 - 450\text{cm}^{-1}$ , is most commonly employed, as it covers most of the vibrational transitions. The mid IR region is further divided two regions as high frequency and low frequency region.

The finger print region between  $1450$  and  $900\text{cm}^{-1}$ , mostly deformation and few stretching vibrations of the functional groups of the material are characterized in this region, is highly used in the structural determination of a molecule.

In general, the obtained peak position in FTIR spectra depicts the corresponding vibration with respect to the effective mass of vibrating group atoms and the adjacent atoms in the molecule. The FTIR absorbance spectra could be characterized by the position, optical density or absorbance, half width and the shape of the peaks. The materials investigated are

analyzed with reference to the existing IR database, so that the determination of chemical composition of the test material has been done with ease.

The conventional transmission Infrared technique involves, hard sample preparation and time consumption, all these issues are addressed by an advanced Attenuated Total Reflectance spectroscopy (Coates and Sanders, 2000).

Thus, the paper samples and the chemicals involved in paper making can be well characterized by using FTIR-ATR technique. The cellulosic fibres, ligno-cellulosic fibres and other polymers viz., Cationic Poly Diallyl Dimethyl Ammonium Chloride (PDADMAC), Cationic Polyacrylamide (CPA), Anionic Polyacrylamide (APA), Alkyl Ketene Dimer (AKD), Polyamide

Bases like Nylon 6, Nylon 66 possess  $C_1$  symmetry and Calcium Carbonate possess  $D_{3h}$  (Bhagavantam and Venkatarayudu, 1939), so all the vibrational modes are active in infrared spectroscopy. FTIR-ATR technique is a reliable technique in the quality and coating analysis of papers used for printing and papermaking raw materials.

The left out information by Infrared spectroscopy in the analysis of finding the best coated side of paper has overcome by Ultraviolet-Visible (UV-Vis) Diffuse Reflectance spectroscopy.

The ultimate aim of the work is to analyze the quality of papers with respect to the sizing and coatings on the paper, by using dynamic spectroscopic tools with advancements. FTIR-ATR and UV-Vis DRS/DTS are deployed to learn the quality of papers.

## **Materials and Methods**

### **Materials**

The raw materials involved in paper manufacturing viz., ground wood chips, ground sugarcane bagasse (herein after referred as 'bagasse'), dry unbleached wood pulp, unbleached bagasse pulp, bleached wood pulp, bleached bagasse pulp and papers procured from a reliable leading manufacturers of papers in Tamil Nadu, India, were analyzed in the Mid IR region of 4000 - 450cm<sup>-1</sup>. Alike, additives and chemicals used in paper making process as dewatering agents, sizing agents and fillers, namely, Cationic Poly Diallyl Dimethyl Ammonium Chloride (PDADMAC), Cationic Polyacrylamide (CPA), Anionic Polyacrylamide (APA), Alkyl Ketene Dimer (AKD), Polyamide Bases like Nylon 6 (NY6), Nylon 66 (NY66) and scraped paper (S), provided by the manufacturers, suspected to have traces of unappealing residuals of the chemicals employed were also investigated by single bounce FTIR-UATR technique. From the manufacturers, it is learnt that Calcium Carbonate (CaCO<sub>3</sub>) is used as fillers in the production of papers, so precipitated CaCO<sub>3</sub> is also compared with the scraped paper (S) by using FTIR-UATR technique.

As provided, PDADMAC, CPA, APA and AKD were liquids, whereas NY6, NY66 and S, were solids. A few ten microlitre of sample PDADMAC was placed on the IRE crystal and FTIR spectra was recorded. Alike CPA, APA, AKD, NY6 and NY66 were analyzed but APA and AKD subjected to laminar air flow to remove the water thoroughly. As water is a good absorbent of infrared radiation (IR), it affects the actual spectral response of the test material and dominates in the FTIR spectrum of test material. For solids, ensured as moisture

free, force is applied by force gauge on the samples to provide good optical contact with the Internal Reflectance Crystal.

Commercially available coated papers viz., P1, P2, P3 and P4 of various shades i.e., P1, a cream white paper of 80GSM and P2, P3, P4, true white papers of 80GSM procured from various sources were admitted to FTIR-UATR and UV-Visible DRS/ DTS investigations. All spectral measurements were carried out at room temperature and measured several times to ensure the experimental reproducibility conditions. These Spectroscopic facilities are availed from Sophisticated Analytical Instrumentation Facility (SAIF-SPU), St. Peter's University, Avadi, Chennai - 600 054, India.

### **FTIR-UATR Technique and Spectral Measurements**

The FTIR-UATR spectral measurements were carried out by using PerkinElmer Spectrum-Two FTIR spectrometer with Attenuated Total Reflectance accessory having highly reliable, chemical inert, single bounce diamond as its Internal Reflectance Element (IRE), makes ATR as Universal Attenuated Total Reflectance (UATR). The Attenuated Total Reflectance spectroscopy utilizes total internal reflection phenomenon. When the angle of incidence of the IR beam from source is greater than the critical angle, all incident IR radiations are completely reflected at the interface, results in total internal reflection. Not limiting it with interface, a short existing IR bubble appears on the surface of the Internal Reflectance Element (IRE) crystal, is known as evanescent wave and it could be absorbed by the test material, when it comes into contact with IRE. This evanescent wave, a bubble of infrared, protrudes to 0.5 – 5μ beyond the crystal surface. The depth of

penetration of infrared radiation from denser IRE into the test material depends on refractive indices of the materials to be investigated and the wavenumber of the infrared radiation.

Single bounce UATR reduces sample quantity used for measurement. The solid test material placed on crystal must be provided limited force so that large pressure can be generated to offer good optical contact between the test material and IRE. Hence, single bounce of total internal reflection is well enough to study the infrared absorption. No force is needed for liquids, as vicinity of IRE has small retention to make liquid to settle on it.

In regions of the infrared spectrum, where the test material absorbs energy, the evanescent wave will be attenuated or altered. This attenuated IR radiation of evanescent wave is passed back to the main stream of internally reflected IR beam, which then exits the opposite end of the crystal and it is detected by the detector in IR spectrometer. The system generates an infrared spectrum.

The spectral recordings were done at 16 scans with resolution of  $4\text{cm}^{-1}$ . All the test materials investigated were placed on the crystal of 2mm surface area with single bounce reflection has  $350\text{cm}^{-1}$  as its cutoff wavenumber; suitable pressure is given to solids to make good optical contact with the diamond, whereas for liquids, no external pressure is given. These spectra were subtracted against the background of air spectrum. After every scan, the crystal is cleaned with isopropyl alcohol soaked tissue and a background of new reference air was taken to ensure the crystal cleanliness. The Spectra and the average spectra are constructed using the software 'Spectrum',

provided with FTIR Spectrum Two spectrometer.

### **UV-Visible Spectral Measurements**

The UV-Visible region in the electromagnetic spectrum is deployed to characterize materials and is known as Electronic spectroscopy, generally used to find the electronic properties and the light absorption characteristics of the materials. Absorption of UV- Visible radiation is associated with excitation of electrons in molecules, from lower to higher energy levels and the absorption also depends on the sample concentration. In common, UV-Visible spectra have only a few broad absorbance bands compared to infrared spectroscopy. The limitation of measuring only homogenous solution and transparent solids is overcome by measuring solids, pastes and gels using Diffuse Reflectance Spectroscopy accessory in the UV-Visible spectrometer. It can measure reflected and scattered radiation from test material with integrating sphere. The integrating sphere helps to study the transmittance and reflectance properties of liquids and solids. The integrating sphere enables garnering the light emerging from the test material in arbitrary direction, thus the Diffuse Reflectance Spectroscopy (DRS) or Diffuse Transmittance Spectroscopy (DTS) can be achieved.

When placing the test material at the entrance port of the sphere, transmitted light enters the sphere through the test material is collected and measured by the detector, known as Diffuse Transmittance. Similarly, placing the test material at the exit port of the sphere reflects the UV-Visible radiation by the test material is collected and measured at the detector in Diffuse Reflectance.



The transmittance spectra obtained can be converted into their equivalent absorbance spectra for convenience. Alternatively, the reflectance spectra obtained can be converted to Kubelka – Munk (K-M) spectra, K-M based on two constants that characterize the absorption and scattering per unit layer thickness of the medium. Kubelka and Munk suggested a system of differential equations, based on the light propagation (Vesna Džimbeg et al., 2011). The insensitiveness of reflectance mode towards the increase in the thickness of the material is conquered by Kubelka-Munk theory. K-M theory helps to get the typical absorption spectrum of the test material.

An Ultraviolet-Visible spectrometer with integrating sphere is employed in the quality analysis of papers is PerkinElmer Lambda 35 UV-Vis Spectrometer with UV WinLab software. The spectral recordings carried out in the wavelength range of 200 nm to 1100 nm at slit width of 2nm for papers. Spectra of papers were recorded after making proper auto zero, a blank or a background correction. For Diffuse Reflectance and Diffuse Transmittance, provided highly diffusing Polytetrafluoroethylene (PTFE) white standard is placed at the exit port of the integrating sphere and the auto zero is made, this is subtracted with the spectra of the test material automatically. For Diffuse Transmittance, the white standard is kept at the exit port of the sphere throughout the measurement even after auto zero and the test material is placed at the entrance of the sphere, so that diffuse transmitted light is collected at the detector without exiting the sphere. Papers were cut into 5x5 cm pieces and clamped in front of the integrating sphere for DTS measurements. In Diffuse Reflectance, once after auto zero is made, the standard is removed and the sample holder with proper cut papers are placed in the 8° specular included holder for placing

sample holder and standard, it helps to collect specular reflection. It helps to collect the specular reflection arise in the test material. The two sides of each paper are admitted to UV-Vis measurements.

## **Results and Discussion**

The analyses focus more on qualitative studies of Lignocellulosic fibres, Cellulosic fibres, Chemicals involved in paper making and different brands of coated papers by employing FTIR-UATR and UV-Visible DRS/DTS spectroscopic techniques. In Fig.1, the FTIR spectra of ground bagasse powder, dry unbleached bagasse pulp and dry bleached bagasse pulp are given and the removal of lignin is studied. In Fig.2, the FTIR spectra of ground Eucalyptus wood, dry unbleached wood pulp and dry bleached wood pulp are given and the removal of lignin and extractives from cellulosic fibres are monitored. Fig. 3 shows the FTIR spectrum of a paper made up of 60 and 40% of bagasse and eucalyptus wood pulps.

The chemicals and additive polymers are expected to have their impact on paper were studied by FTIR-UATR technique and is shown in Fig. 4, each chemical or coating polymer is compared with the FTIR spectrum of paper to having the traces of chemical residues.

The FTIR spectrum of scraped paper (S) suspected to have the traces of chemical residues is also compared with FTIR spectrum of precipitated Calcium Carbonate and is represented in Fig. 5. The FTIR spectra of two sides (A &B) of papers of same density (Gram per Square Meter (GSM)) but various shades, procured from various sources are represented in Fig. 6. The average FTIR spectrum of each paper

was overlaid and compared in low frequency region as shown in Fig. 7.

The UV-Visible spectra of papers in Diffuse Reflectance and Diffuse Transmittance modes are given in Fig. 8 and Fig. 9, two sides of each paper represented as A and B is compared. The overlaid average spectra of Reflectance and Transmittance are shown in Figs. 10 and 11. The overlaid average Kubelka – Munk spectra of all papers are presented in Fig. 12. Fig. 13 shows the overlaid average transmittance spectra of all the four papers.

### **FTIR Band Assignments**

FTIR band assignments of Lignocellulosic and Cellulosic bands are based on comparative analysis of spectra of elementary carbohydrates. The FTIR spectral signatures of Lignocellulosic, cellulosic fibres and a finished paper are represented in Figs. 1, 2, 3 respectively and Table 1 provides more information about the appearance and the disappearance of the spectral bands. As per observations, the spectral impressions are explicit in the high frequency region of FTIR spectra and exhibit unique spectra in the finger print region. The region between 1450 – 900 $\text{cm}^{-1}$ , known as finger print region, is also the most significant region in resolving the complexity of cellulose (Socrates, 1980).

In the FTIR spectra of Cellulosic, Lignocellulosic fibres and in paper, a broad band appeared in the region around 3340  $\text{cm}^{-1}$  is due to the asymmetric and symmetric O-H stretching. Weak bands arise around 2900  $\text{cm}^{-1}$  is of asymmetric C-H stretching. IR Absorption of symmetric  $\text{CH}_2$  stretching band is appeared around 2850  $\text{cm}^{-1}$  is due to the aromatic methoxyl and methylene groups in lignin, the disappearance of this band occurs, after the removal of lignin. A

medium weak intensity band observed at around 1730  $\text{cm}^{-1}$  is due to the stretching vibration of unconjugated C=O in xylans and it is not seen in the cellulosic fibres once the lignin is removed (Rodrigues, 1998; Boeriu et al., 2004).

Sharp but weak absorption bands in the 1604  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$  are due to the stretching vibration of conjugated C=O of xylans (Boeriu et al., 2004) and the bending vibration of adsorbed water. The band 1604  $\text{cm}^{-1}$  due to lignin is not found after the cooking process. Bands appeared in 1513  $\text{cm}^{-1}$  in bagasse and 1504  $\text{cm}^{-1}$  in Eucalyptus wood are due to aromatic skeletal vibration of lignin, the disappearance of these bands ensure the removal of lignin. The appearance of bands 1466  $\text{cm}^{-1}$  in bagasse and 1461 $\text{cm}^{-1}$  in wood are due to the asymmetric deformation of C-H in lignin. A weak intense band around 1430  $\text{cm}^{-1}$  is the cause of C-H asymmetric deformation. The C-H symmetric deformation vibration is noticed in the region of 1370  $\text{cm}^{-1}$  and  $\text{CH}_2$  wagging is noticed around 1320  $\text{cm}^{-1}$  of cellulose (Garside and Wyeth, 2000; Boeriu et al., 2004). The region from 1230-1250  $\text{cm}^{-1}$  is remarkable with the presence of lignin and hemicellulose, may occur due to the in plane deformation of C-OH in polysaccharides. The removal of lignin is witnessed by the presence of the band at 1202  $\text{cm}^{-1}$  in bagasse pulp and 1204  $\text{cm}^{-1}$  in wood pulp and paper due C-O stretching. A sharp band around 1160  $\text{cm}^{-1}$  depicts the asymmetric stretching of C-O-C and ring breathing of C-C of cellulose. It is also observed that lignin also has C-O ester group stretching vibration in this region. A band around 1105  $\text{cm}^{-1}$  is for C-O-C stretching vibration of glycosidic bond which combines a carbohydrate molecule to another group of same or to other group (Proniewicz et al., 2001, Boeriu et al., 2004). After the removal of lignin, the pulps

and papers show a new sharp band at around  $1050\text{ cm}^{-1}$  appears like doublet with  $1030\text{ cm}^{-1}$  seems to be a stretching vibration of C-OH of  $2^\circ$  alcohol of cellulose (Pandey, 1999). A strong peak around  $1030\text{ cm}^{-1}$  leads to the stretching vibration of C-OH of  $1^\circ$  alcohol of cellulose and this could be observed only after the removal of lignin and other extractives. A split in the vibrational bands observed between  $1030\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  due to the stretching of C-O are more distinct in Eucalyptus wood than in Sugarcane bagasse. This shows that the cellulose content in wood is higher than any of its non-wood counterpart. Generally, the bands below  $900\text{ cm}^{-1}$  are complex modes and assigned to be the deformation vibrations of CCC, CCO, COC, OCO and COH are expected. A band observed near  $895\text{ cm}^{-1}$  is due to the in plane stretching vibration of C-O-C. A weak band seems to exhibit a shoulder around  $870\text{ cm}^{-1}$  may due to the surface enhancing agents employed while paper making. A band at  $663\text{ cm}^{-1}$  is due to out of plane deformation of C-H functional group. Appearance of a new band around  $610\text{ cm}^{-1}$  is due to the deformation of C-C-C in cellulose. A sharp band appeared around  $560\text{ cm}^{-1}$  is due to the out of plane vibration of C-H functional groups. The remaining bands observed in the spectra may due to overtones and combinations of the fundamental modes.

The disappearance of spectral bands around,  $2850\text{ cm}^{-1}$ ,  $1730\text{ cm}^{-1}$ ,  $1510\text{ cm}^{-1}$ ,  $1466\text{ cm}^{-1}$ ,  $1230\text{-}1250\text{ cm}^{-1}$  and  $831\text{ cm}^{-1}$  after cooking and bleaching of Lignocellulosic fibres and the appearance of new bands after the cooking and bleaching processes at  $1200\text{ cm}^{-1}$ ,  $1050\text{ cm}^{-1}$  and  $560\text{ cm}^{-1}$  are clearly visualized by using FTIR spectra. Lignin, a glue binds the cellulosic fibers together, the elimination of lignin leads cellulose to vibrate freely and upraise of new bands are found in the spectra of cellulose fibres and

papers obtained from FTIR technique. After pulp bleaching, intensity or optical density of the cellulosic fibres increases with the absence of lignin and hemicellulose. Hence the appearance and the disappearance of distinctive peaks in cellulose fibers were well explained by FTIR spectroscopy.

Once after pulping, paper manufacturers concentrate more on enhancing the surface of paper according to its need and necessity. Considering the quality of paper in the aspect of printing, the retention of any chemicals rather than fillers, sizing and coating agents are not allowed to settle down on the surface of the paper. FTIR analysis was employed in the detection of few chemicals and additives involved in paper making and they were compared with a scraped paper, suspected of having traces of unappealing polymers are shown in Fig. 4. In Fig. 4a, a comparison of FTIR spectral signatures of coated paper and S were made and the deviations of bands in the regions of  $1428\text{ cm}^{-1}$ ,  $875\text{ cm}^{-1}$  and  $713\text{ cm}^{-1}$  from the recognized paper to the test material S are witnessed. The investigation was started with the assumption that the deviated fundamental modes of vibration from coated paper may due to the polymers used in paper making.

It is observed from the spectra represented in Fig. 4 that the paper S under test may exhibit the traces of few additives used as flocculants, dewatering agents, sizing agents, coating and fillers. A strong vibrational mode observed in the finger print region at  $1428\text{ cm}^{-1}$  in S sample may due to asymmetric deformation of methyl/methylene group of the polyamide bases viz., AKD, NY6 and NY66, while a band at  $875\text{ cm}^{-1}$  may constantly represent the in-plane bending vibration of C-H functional groups in Polyamide Bases E and F. The band located at  $713\text{ cm}^{-1}$  may due to



the C-H out of plane bending vibration of Alkyl Ketene Dimer, a sizing agent (B). Hence, the appearance of the vibrational modes rather than cellulose may be due to the vibrational bands of additive polymers AKD, NY6 and NY66. The vibrational bands appeared at  $1428\text{ cm}^{-1}$ ,  $875\text{ cm}^{-1}$  and  $713\text{ cm}^{-1}$  are not due to unappealing chemicals employed in paper making are obviously due to the surface enhancing agents. Though the comparisons made on paper were inadequate, so sample is also compared with Calcium Carbonate, filler used in paper making is represented in Fig. 5.

The AKD cannot be easily detected while calcium carbonate shows strong absorption bands at about  $1415\text{ cm}^{-1}$  and  $874\text{ cm}^{-1}$  (Gorassini et al., 2008). Fig. 5(a) shows the FTIR spectrum of Calcium Carbonate and Fig. 5(b) clearly depicts the FTIR spectrum of 'S' having traces of Calcium Carbonate. The filler tend to interact with pulp components and deposit on their surfaces (Cadotte et al., 2007). An attempt has been made to differentiate the spectral responses of the Precipitated Calcium Carbonate filler from the cellulose fibers by using FTIR-ATR spectroscopic technique. A band observed in  $1472\text{ cm}^{-1}$  is due to the asymmetric stretching of  $\text{CO}_3$  and in paper S, it is sensed in  $1428\text{ cm}^{-1}$ , a red shift is noticed due to the interaction of filler with fibres. The appearance of a band at  $1080\text{ cm}^{-1}$  is due to symmetric stretching of  $\text{CO}_3$ . A band at  $872\text{ cm}^{-1}$  is due to the asymmetric deformation vibration of  $\text{CO}_3$  and a band at  $713\text{ cm}^{-1}$  is due to symmetric deformation of Carbonate in Calcium Carbonate is found in scraped paper S (Kazuo Nakamoto, 2009). It is witnessed that the domination of surface enhancing agents are on the paper. With respect to the spectral behavior of the surface enhancing agents, an attempt has been made to find the quality of different commercial papers of same density but

different shades by using FTIR-ATR spectroscopic technique and shown in Fig. 6. FTIR spectra were recorded for two sides (A&B) of all four papers and are reliable in the surface analysis of papers. There are no remarkable differences observed in A and B sides of papers, both sides are alike because the evanescent wave protrudes through paper is absorbed by the cellulosic fibres and the surface enhancing agents like fillers. So, the average spectrum of A and B sides of each paper was taken and overlaid in Fig. 7.

The average FTIR absorption spectra from  $2000\text{ cm}^{-1}$ -  $450\text{ cm}^{-1}$  of A and B sides of papers P1, P2, P3 and P4 are given in Fig. 7. Optical density of remarkable bands around  $1428\text{ cm}^{-1}$ ,  $875\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$  due to the sizing & coating agents and fillers in the finger print region were considered in the quality analysis of paper. The peak intensity of the key bands in paper P2 is highest of all and is more suitable for printing, compared to other three papers. Paper P4 also has better retention of fillers on its surface; other two papers have less retention of fillers and sizing agents are visualized from the overlaid FTIR spectra.

Though the quality of paper is well determined by the FTIR-ATR spectroscopic technique, finding a best coated side on paper is quite challenging. To overcome the drawback of finding the best coated side on paper UV-Visible Diffuse Reflectance and Diffuse Transmittance spectroscopy is employed.

### **UV-Vis Spectral Analysis**

From Fig. 8, the differences in the A and B sides of each paper namely P1, P2, P3, P4 are identified with respect to the spectral impressions exhibited in the UV-Vis DRS spectra.

**Table.1** FTIR band assignments of Lignocellulosic, Cellulosic fibers and a finished Paper

Wavenumber (cm <sup>-1</sup> )							Vibrational Band Assignment
Bagasse	Unbleached Bagasse Pulp	Bleached Bagasse Pulp	Eucalyptus wood	Unbleached Wood Pulp	Bleached Wood Pulp	Paper	
3338	3332	3332	3338	3338	3337	3332	v O- H
2917	2890	2894	2892	2898	2896	2899	v C- H
2854	-	-	2857	-	-	-	v CH <sub>2</sub>
1734	-	-	1738	-	-	-	v C=O of xylans
1604	1646	1641	1650	-	1644	1644	δ O-H/v C=O
1513	-	-	1504	-	-	-	Skeletal vibration
1466	-	-	1461	-	-	-	δ C-H
1423	1433	1433	1424	1430	1426	1428	δ <sub>asy</sub> C-H
1370	1373	1370	1370	1370	1373	1370	δ <sub>sym</sub> C-H
1316	1319	1315	1324	1315	1316	1316	CH <sub>2</sub> wagging
1240	1249	1251	1231	-	-	-	Out of plane δ C-OH
-	1202	1202	-	1204	1204	1204	v C-O
1160	1164	1161	1159	1161	1161	1162	v <sub>asy</sub> C-O-C ring breathing
1104	1106	1106	1108	1106	1106	1107	v C-O-C of glycosidic bond
-	1053	1053	1048	1055	1055	1054	v C-OH of 2° alcohol / v C-O
1033	1031	1031	1033	1031	1031	1030	v C-OH of 1° alcohol / v C-O
992	991	1000	988	1003	1001	999	ρ C-H
896	897	896	897	894	897	895	v C-O-C/ Glucose ring stretch
831	-	-	835	-	-	871	In-plane bending of C-H
711	715	715	710	710	704	711	δ C-O-C/ δ C-C-C
663	658	655	666	661	661	663	Out – of plane bending of C-H
-	607	613	-	610	613	614	δ C-C-C
583	583	580	591	582	582	578	Out of plane deformation of C-H
563	559	559	558	559	559	558	Out of plane deformation of C-H
523	522	524	527	520	520	522	Out of plane deformation of C-H

**Fig.1** FTIR spectra of (a) ground bagasse powder, (b) dry unbleached bagasse pulp, (c) dry bleached bagasse pulp and the inset spectra of region 1800 cm<sup>-1</sup> 450 cm<sup>-1</sup>

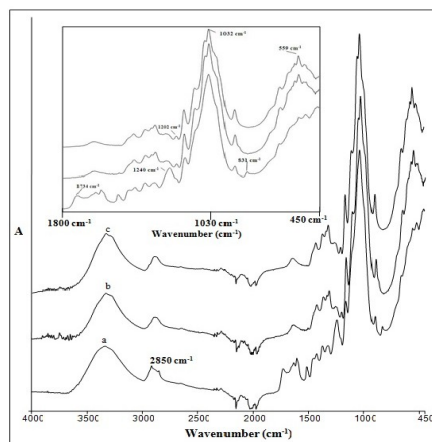


Fig.2 FTIR spectra of (a) ground Eucalyptus wood (b) dry unbleached wood pulp, (c) dry bleached wood pulp inset spectra of the region between 1800cm<sup>-1</sup> and 450cm<sup>-1</sup>

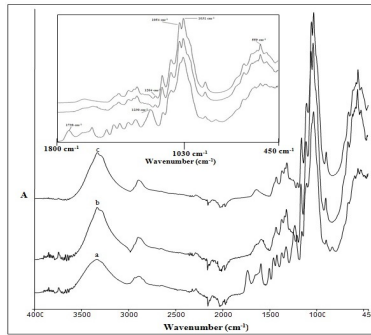


Fig.3 FTIR spectrum of a finished paper made up of bagasse and eucalyptus wood pulps

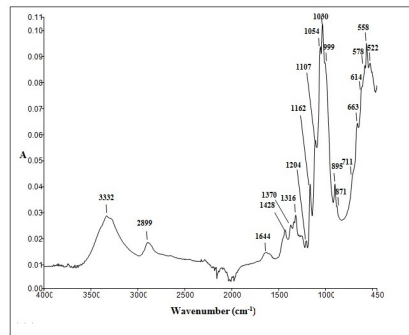


Fig.4 Overlaid FTIR Spectra of S with finished paper and the additives in paper making

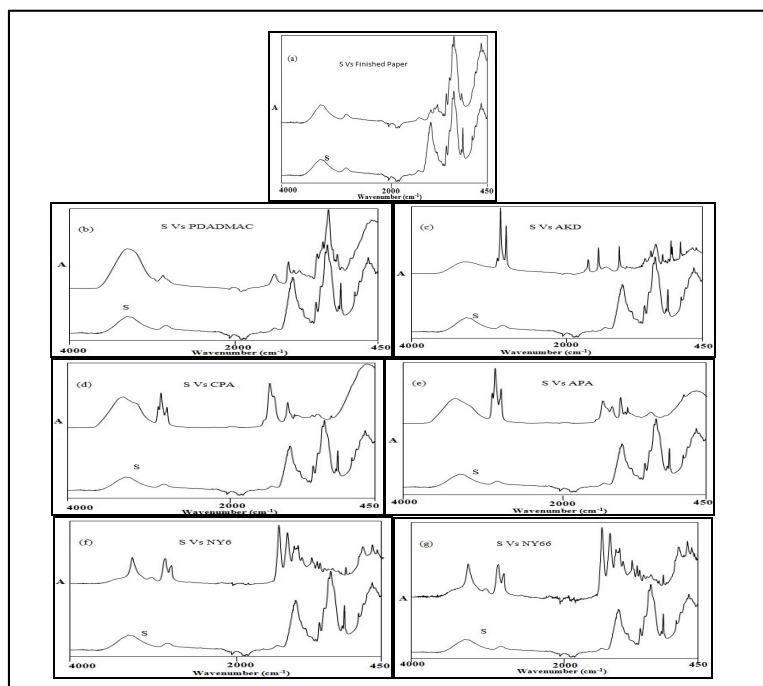


Fig.5 Overlaid FTIR Spectra of Sample S and Calcium Carbonate at the region from 2000cm-1 to 450 cm-1

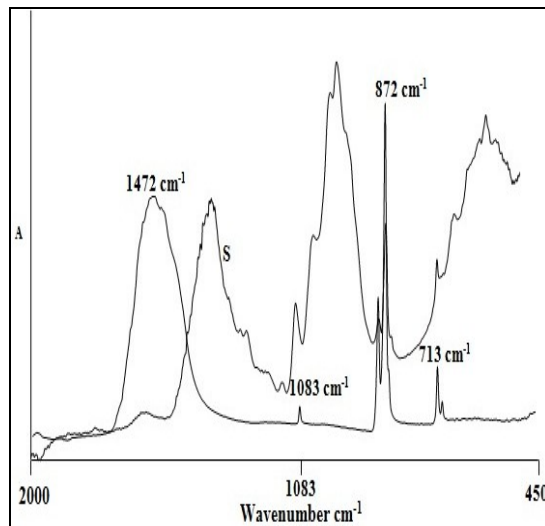


Fig.6 Overlaid FTIR Spectra of A (black) and B (Red) sides of different types of papers at the region of 2000cm-1 to 450cm-1

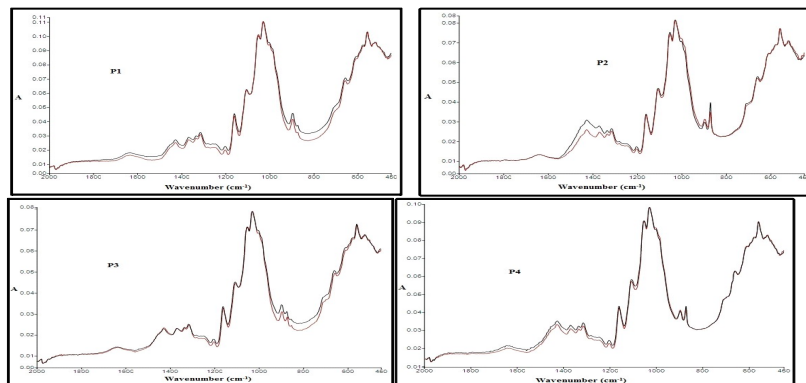
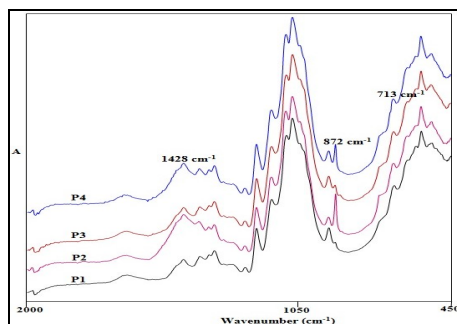
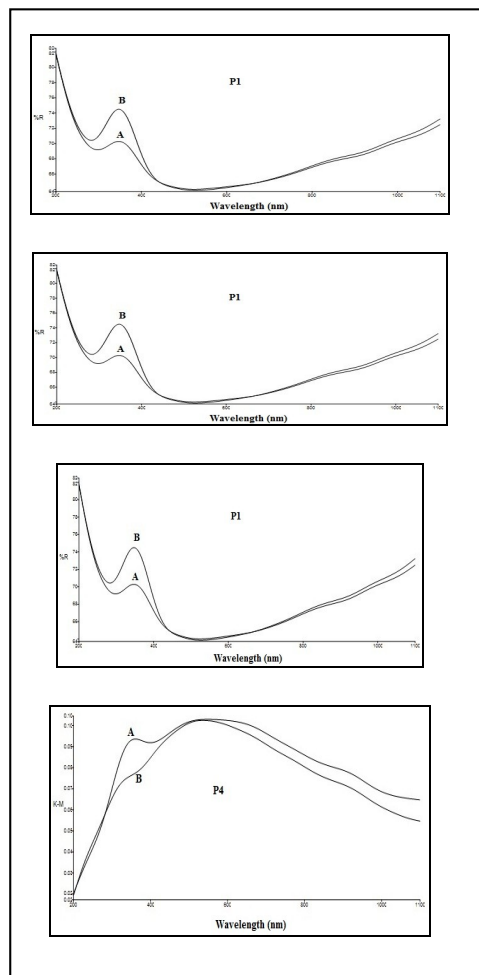


Fig.7 Overlaid Average FTIR spectra of different brands of papers from the region of 2000 cm-1 – 450 cm-1



**Fig.8** Overlaid UV-Vis Diffuse Reflectance Spectra of A and B sides of different brands of papers



**Fig.9** Overlaid Average UV-Vis DRS Spectra of A and B sides of different brands of papers

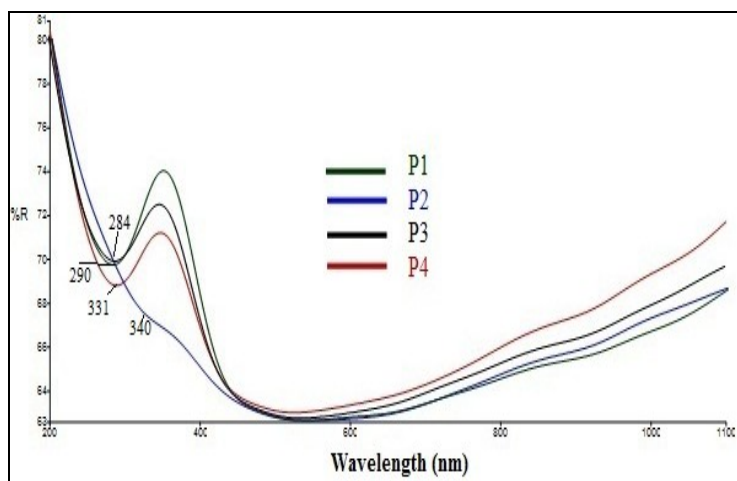




Fig.10 Overlaid K-M spectra of A and B sides of papers P1, P2, P3 and P4

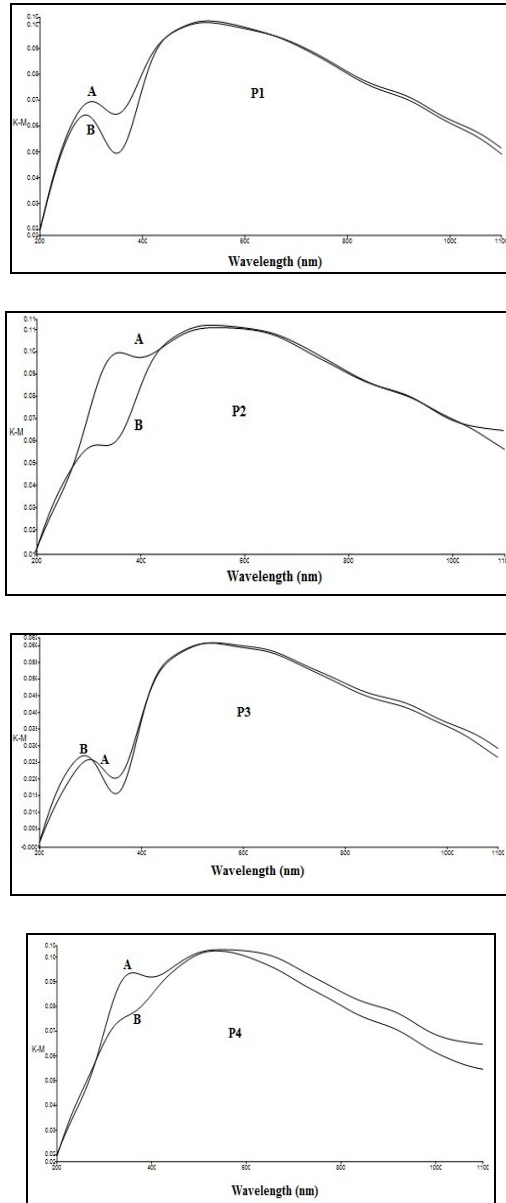


Fig.11 Overlaid Average K-M Spectra of A and B sides of different brands of papers

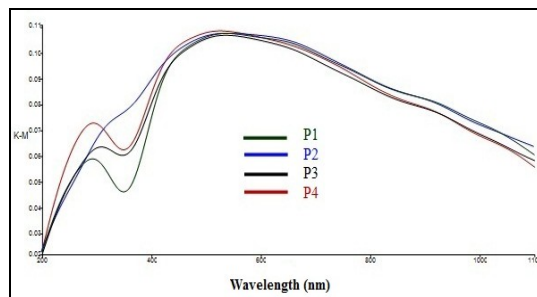


Fig.12 Overlaid Diffuse Transmittance UV-Vis spectra of A and B sides of different branded papers

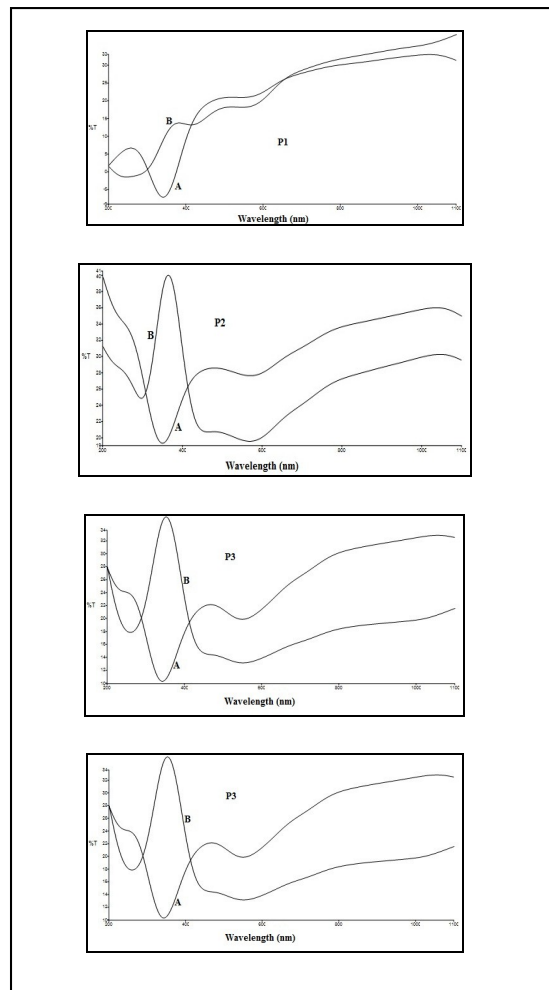
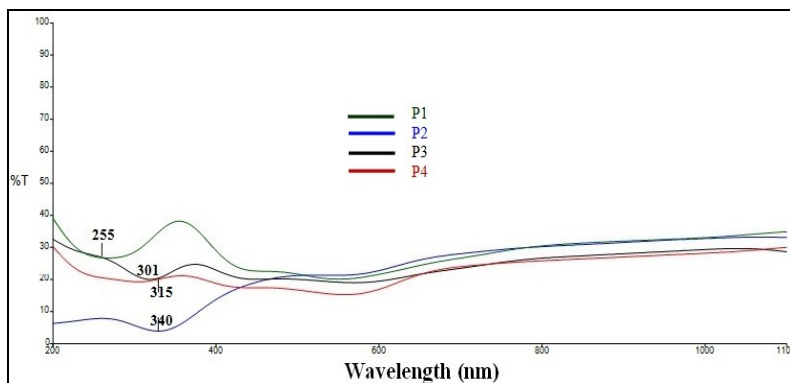


Fig.13 Overlaid average Diffuse Transmittance Spectra of A and B sides of different brands of papers



In general, the coated papers have less reflectance than the uncoated papers, the reflectance of B side of all the four papers are higher than A side of papers (Silva Gril et al., 2012). In dependence to the wavelength, it is observed that the reflectance seen in the UV-Visible DRS spectra are due to the optical brighteners used in paper making for paper whitening. The maximum absorption around 280 nm – 320 nm are due to the filler  $\text{CaCO}_3$  employed, downward peaks of the reflectance and transmittance spectral bands are the maximum absorbed wavelength and the wavelength of the B side of the papers is found in the shorter wavelength region due to the partial free electronic transition of fillers employed. The maximum wavelength observed in the A side of paper is found with a small shift towards the longer wavelength (red shift) due to the restricted electronic transition of the fillers bound to the cellulose fibres, as pure cellulose fibre did not exhibit proper UV-Vis absorption characteristics. Once the paper undergone coating, it suppresses the effect of optical brighteners and is proved with the analysis on A sides of papers. The UV-Visible DRS spectra of A side of papers exhibit low reflectance and red shift of absorption of maximum wavelength, a downward peak, observed in the reflectance spectra due to the bonding of surface enhancing agent with the cellulosic fibers. The whole reflectance of B side is higher than A side, it ensures the presence of surface enhancing agent on B side is quite lesser than A side of each paper. It is understood from the overlaid average spectra of papers given in Fig. 9 that papers P2 has lower reflectance than all other papers and paper P4 has second lower reflectance than P1 and P3. Since the papers considered are coated, the reflectance value does not exceed 100%. The obtained results from reflectance spectra are further fortified with the Kubelka-Munk (K-M) spectra of

papers, overlaid average K-M spectra are shown in Fig.10. The obtained reflectance spectra is converted to K-M and is maximum for paper P2 than P4, due to the absorption of the surface enhancing agents; it shows the higher quantity of surface enhancing agents than other papers. The reassurance of the presence of surface enhancing agents is well executed by the K-M spectra from reflectance spectra shown in Fig. 11.

It is learnt from the transmittance spectra of A and B sides of Papers shown in Fig.12, side B of papers transmit UV-Vis radiation more than side A of papers. The overlaid average transmittance spectra is scheduled to depict in Fig. 13, from the spectra, paper P2 has lower transmittance than all other papers and paper P4 has second lower transmittance than P1 and P3.

The lower transmittance ensures the presence of coating agents by the absorption of UV- Vis radiation and the transmittance is restricted by the coatings on the surface of the papers. The spectral results also show that the opacity of the paper is not increased by the addition of the cellulose fibers but the addition of coatings.

The lower reflectance and transmittance depicts the good absorbance of the UV-Vis radiation by the surface enhancing agents. Hence, the lower reflectance and transmittance exhibited by papers are rich in surface enhancing agents and it is observed vice versa in K-M spectra of papers.

Consequently, it is learnt that FTIR-ATR and UV-Vis DRS, DTS spectroscopic techniques should be employed in the paper making industry in the production of finely coated papers used for large scale offset and digital printing.

## Conclusion

With the help of spectral signatures exhibited in FTIR-ATR spectroscopic technique, the removal of lignin and the extractives are ensured in the isolation of cellulose fibers from wood and sugarcane bagasse. Different commercial brands of papers of same density are also analyzed using FTIR-ATR spectroscopy and the better quality of paper is found with respect to the infrared absorption of surface enhancing agents employed. The difficulty in finding the better coated side of paper has overcome by UV-Visible Diffuse Reflectance and Diffuse Transmittance Spectroscopy. The suppression of the bands observed due to Calcium Carbonate fillers in reflectance and transmittance confirm the better coated side of papers and the raise in the intensity of K-M spectra of paper confirms the quantity of surface enhancing agents in paper P2 compared to other papers. The average DRS and DTS spectra helped in finding the quality of paper with respect high opacity.

## Acknowledgement

Authors would like to thank Sophisticated Analytical Instrumentation Facility (SAIF-SPU), St. Peter's University, Avadi, Chennai-600 054, India, for providing instrumentation facility to carry out spectral measurements.

## References

- Bajpai P., 2012. *Biotechnology for Pulp and Paper Processing*, Springer Science + Business Media.
- Bhagavantan S. and Venkatarayudu T., 1939. *Proc. Indian Acad. Sci.*, A9, 224.
- Boeriu C.G., Bravo D., Gosselink J. A. Richard, van Dam E. G., 2004.

Characterization of structure dependent functional properties of lignin with infrared spectroscopy, *Industrial crops and products*, 20, 205-218.

- Cadotte M, Tellier M., Angeles Blanco, Elena Fuente, Theo G. M. van de Ven and Jean Paris, 2007. *Flocculation, Retention and Drainage in Papermaking: A Comparative Study of Polymeric Additives*, 85, 240-248.
- Champ, S. and Ettl, R., 2004. The dynamics of alkyl ketene dimer (AKD) retention, *J. Pulp Paper Sci.* 30(12), 322.
- Coates J. and Sanders A., 2000. A Universal Sample Handling System for FTIR Spectroscopy, *Infrared Spectroscopy*, 12(5), 12-22.
- Garside P., Wyeth P., 2000. Characterization of Plant fibres by Infrared Spectroscopy, *Polymer Preprints* 41, 1792-1793.
- Gorassini A., Calvini P., Baldin A., 2008. *Fourier Transform Infrared Spectroscopy (FTIR) analysis of historic paper documents, Multivariate Analysis and Chemometry Applied to Environment and Cultural Heritage*, second ed., *Mediterraneum Meeting*.
- Gullichsen J, 2000, *Fibre line operations*. In: Gullichsen J, Fogelholm CJ (Eds.) *Chemical Pulping – Paper making science and technology*, Fapet Oy, Helsinki, p 137, Book 6A.
- Herbert H. Espy, 1995. The mechanism of wet-strength development in paper – a review, *Tappi*, 78, 90-99.
- Howell H.E. and Davis J.R., 1991. Qualitative Identification of fibres using NIR spectroscopy, *Textile Chemist and Colorist*, 23, 69-73.

- Johansson, L.S., Campbell, J.M., Koljonen, K. and Kleen, M., 2004. On surface distributions in natural cellulosic fibers, *Surf. Interface Anal.*, 36, 706.
- Pandey K.K., 1999. A study of chemical structure of soft and hardwood and wood polymers by FTIR Spectroscopy, *J. Appl. Polym. Sci.*, 71(12), 1969-1975.
- Proniewicz L.M., Paluszkiewicz C., Aleksandra W.B., Halina M., Barański A., Konieczna A., 2001. FT-IR and FT-Raman study of hydrothermally degraded cellulose, *Journal of Mol. Struc.*, 596, 163-169.
- Ravnjak, D., Plazl, I. and Moze, A., 2007. Kinetics of colloidal alkylketene dimer particle deposition on pulp fibers, *Colloid Polym. Sci.*, 285, 907.
- Rodrigues J., Faix O., Pereira H., 1998. Lignin Content of Eucalyptus globules wood, *Holzforschung*, 52, 46-50.
- Kazuo Nakamoto, 2009. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, sixth ed. John Wiley and Sons Publications, New Jersey.
- Silva Gril J., Gunde M.K., Rozalia S., Diana G. S., 2012. FTIR and UV-Vis analysis of classic and recycled papers, *Papripar*, LVI/4.
- Socrates G., 1980. *Infrared Characteristic Group Frequencies*, First ed. John Wiley and Sons Publications, New Jersey.
- Vesna Džimbeg, 2011. Kubelka-Munk Theory in Describing Optical Properties of Paper, *Technical Gazette*, 18, 117-124.