Surfece Characterization of Naturally Degraded Wood-Free Papers by Near Infrared Fourier-Transform Raman Spectroscopy

Chen, Shaoping
Department of Chemistry, Fujian Normal University

Wu, Zonghua
Institute of Polymer Science, Fujian Normal University

Tanaka, Hiroo
Laboratory of Bioresources Chemistry, Division of Biomaterial Science, Department of Forest and Forest Products Science, Faculty of Agriculture, Kyushu University

https://doi.org/10.5109/24366

出版情報：九州大学大学院農学研究院紀要. 45 (1), pp.163-169, 2000-11. Kyushu University
バージョン：
権利関係：

J. Fac. Agr., Kyushu Univ., **45** (1), 163–169 (2000)

Surface Characterization of Naturally Degraded Wood–Free Papers by Near Infrared Fourier–Transform Raman Spectroscopy

Shaoping Chen*, Zonghua Wu and Hiroo Tanaka**

Laboratory of Bioresources Chemistry, Division of Biomaterial Science, Department of
Forest and Forest Products Science, Faculty of Agriculture,
Kyushu University, Fukuoka 812–8581, Japan

(*Received July 4, 2000 and accepted August 18, 2000*)

Near infrared excited Fourier–transform Raman spectroscopy (NIR–FTR) was applied to non–destructive spectroscopic analysis of the naturally degraded papers. The analytical results reveal that the color of papers was related closely to Raman intensities at 1600 $\mathrm{cm^{-1}}$ band that was assigned to lignin and papermaking additives in the papers. The folding endurances of papers correlated with the intensities at 1097 $\mathrm{cm^{-1}}$ assigned to β–glycosidic linkages of cellulose and hemicellulose and decreased with the increasing storage years. The Raman spectra of the papers illustrate that the α–glycosidic linkages at 1126 $\mathrm{cm^{-1}}$ of hemicellulose and starch were hydrolyzed faster than β–glycosidic linkages during the storage.

INTRODUCTION

Compared to permanence of writing paper made hundreds of years ago, modern paper tends to have a much shorter life expectancy, which has been a serious problem for the preservation of books and documents. It has been estimated that approximately one–third of the 19 million books and pamphlets in U. S. Library of Congress are too brittle for circulation. The permanence of paper has therefore become an important property on which many users base for their choice of paper products.

In the previous work (Wu and Tanaka, 1998), we investigated the effects of sizing agents, starch, and other papermaking additives on the natural deterioration of the books stored for 1–32 years using pyrolysis–gas chromatography (Py–GC). To get better understanding of mechanisms of the natural deterioration, it is important to clarify relations between the paper permanence and various paper constituents during storage. Since a destructive means of determining the paper constituents is not suitable for most of the stored books, a non–destructive means is required. The present study dealt with the application of near infrared excited Fourier–transform Raman (NIR–FTR) spectroscopic technique to the non–destructive determining.

Among vibrational techniques that have been applied to the studies on woody materials (Forsskahl and Jason, 1992; Ono *et al.*, 1998), the Raman spectroscopic technique is advantageous since solid or powder samples can be measured directly. However, conventional Raman spectroscopy using the excitation laser of the visible regions causes a fluorescent emission interfering with the Raman measurement, and

---

* Department of Chemistry, Fujian Normal University, Fuzhou 350007, China

** Institute of Polymer Science, Fujian Normal University, Fuzhou 350007, China causes sample damage due to high energy of the visible laser. Using near-infrared excitation laser dramatically reduced these problems (Parker, 1991). Near infrared laser does not excite υ (O–H) in water much, so that the moisture in sample give little effect on spectra (Edward and Farwill, 1996). Furthermore due to the difference in the selection rule for infrared and Raman spectroscopy, υ (C=C) vibration is only active in Raman scattering which is specific for lignin-derived aromatic skeleton (Agarwal and Atalla, 1994).

MATERIALS AND METHODS

Materials

The paper samples were taken from the books stored in a shelf at ambient temperature and humidity for 1 to 32 years (Wu and Tanaka, 1998). The samples were taken according to JIS P8110 (Japan Industrial Standard).

Measurements of paper properties

Folding endurance of papers was measured according to JIS P8115. To avoid influence of ink color, brightness, L*, a*, and b* values on the unprinted parts of paper samples were measured using a MINOLTA CR-200 photoelectric reflectance photometer.

Raman analyses

Raman measurements of the papers were carried out using a Perkin-Elmer System 2000 Fourier-transform spectrometer fitted with the standard Perkin-Elmer Raman attachment and a Nd:YAG laser (λ=1064 nm). A standard 180° backscatter sampling geometry was used for all of the measurements. The spectra were obtained at a resolution of 4 cm^{-1}, using an accumulation of 50 scans, over the wavenumber range from 3600 to 400 cm^{-1}. The laser power was 600 mW.

RESULTS AND DISCUSSION

Characteristic bands in the Raman spectra of the papers

The Raman spectra of the acidic paper and the neutral paper are shown in Fig. 1, respectively. As a comparison, the spectrum of a handsheet prepared from bleached hardwood kraft pulp without any papermaking additives is also shown in Fig. 1. Though there are not significant differences in the bands of the three Raman spectra, the intensities at 1600 cm^{-1}, 1126 cm^{-1} and 1097 cm^{-1} are quite different. Based on the model compounds (Wu) and the previous papers (Wiley and Atalla, 1987; Agarwal and Atalla, 1994; Conners and Banejee, 1995; Edward and Farwill, 1996; Takayama *et al*, 1997), the main wavenumbers and vibrational assignments for the papers are listed in Table 1.

The bands at near 3300 cm^{-1} are assigned to free and bonded OH groups in the papers. They were weak in the spectra because NIR laser does not excite υ (O–H) much. The band at 2900 cm^{-1} is assigned to stretching vibration of aliphatic CH_2 in cellulose and hemicellulose. This band was chosen as internal standard because the structure is stable against heat and light (Forsskahl and Jason, 1992). The Raman shifts of unconjugated and conjugated carbonyl groups are in the range from 1735 cm^{-1} to 1650 cm^{-1}, and those of

C=C are in the range from 1650 cm^{-1} to 1600 cm^{-1}. The intensity changes at these bands are related closely to color of the papers (Agarwal and Atalla, 1994; Wu and Tanaka, 1997). The strong signals at 1126 cm^{-1} and 1097 cm^{-1} are assigned to glycosidic linkages of cellulose, hemicellulose and starch in the papers. The bands at 788 cm^{-1}, 698 cm^{-1} and 636 cm^{-1} belong to calcium carbonate and clay, respectively.

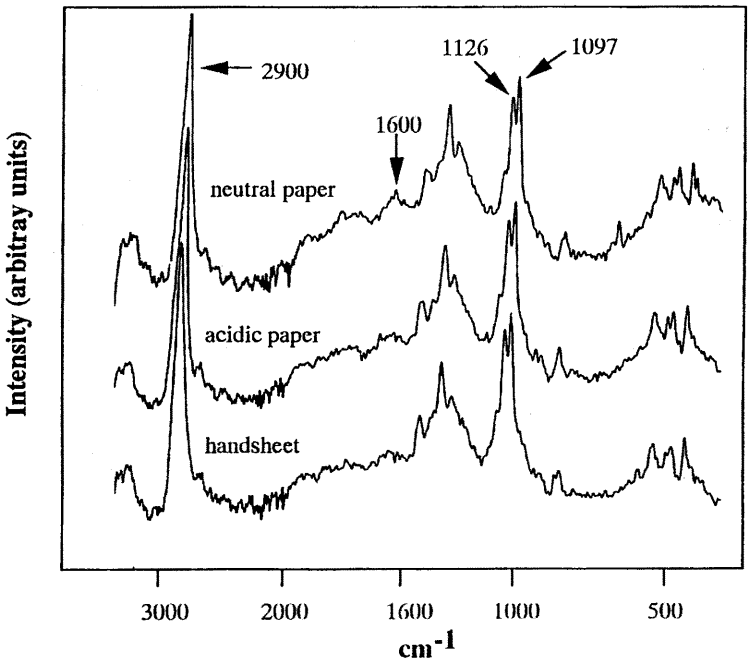

Fig. 1. Raman spectra of a neutral paper, an acidic paper and a handsheet prepared from bleached hardwood kraft pulp.

Table 1. Wavenumber and vibrational assignments for the naturally degraded wood-free papers.

Wavenumber (cm^{-1})	Mode	Approximate decription of vibration mode
3300	υ (OH)	free, bonded
2900	υ (CH$_2$)	holocellulose
1735	υ (C=O)	unconjugated
1650	υ (C=O)	conjugated
1600	υ (C=C)	lignin, papermaking additives
1381	δ (CH$_2$)	holocellulose
1341	δ (CH$_2$)	holocellulose, starch
1126	υ (COC)	α-, β-glycosidic linkages
1097	υ (COC)	β-glycosidic linkages
997		alum
788		calcium carbonate
698		calcium carbonate
636		clay

Bands related to color of the papers

The permanence of paper refers to the retention of significant usage properties, particularly color and folding endurance, over prolonged periods. So the attention in this study was paid on the relations between Raman intensities at the characteristic bands and the two paper properties. It is generally accepted that unconjugated and conjugated carbonyl groups in paper constituents are one of main reasons for discoloration of woody materials (Agarwal and Atalla, 1994; Wu and Tanaka, 1994, 1997). But lignin in the wood–free papers was a minor component (Wu and Tanaka, 1997; 1998), and the Raman spectra of the papers demonstrated that the changes in the range from 1735 cm^{-1} to 1650 cm^{-1} were small. These results illustrate that the unconjugated and conjugated groups were not main groups responsible for discoloration of the papers.

It can be seen from the Raman spectra of the papers that the difference in the intensities at 1600 cm^{-1} is significant. The band assignments in Table 1 show that rosin and papermaking additives such as polyacrylamides in the papers contribute to this band. Therefore, the papermaking additives may be considered to be responsible for discoloration of the papers.

The color of samples from the books stored for 1 to 32 years was investigated in terms of brightness, L* (lightness), a* (red, green, or gray), and b* (yellow, blue, or gray) values. The analytical results showed that the changes in L* and a* values of the papers were small during the storage, but large losses in the brightnesses and significant increases in the b* values of the papers were observed. The statistics demonstrate a smaller brightness (Fig. 2) and a larger b* value (Fig. 3) correlated with a larger intensity ratio of I_{1600}/I_{2900}. These facts revealed that the papermaking additives contributing to the band at 1600 cm^{-1} would result in large discoloration of the papers during the storage. This is in good agreement with the results determined by Py–GC (Wu and Tanaka, 1998).

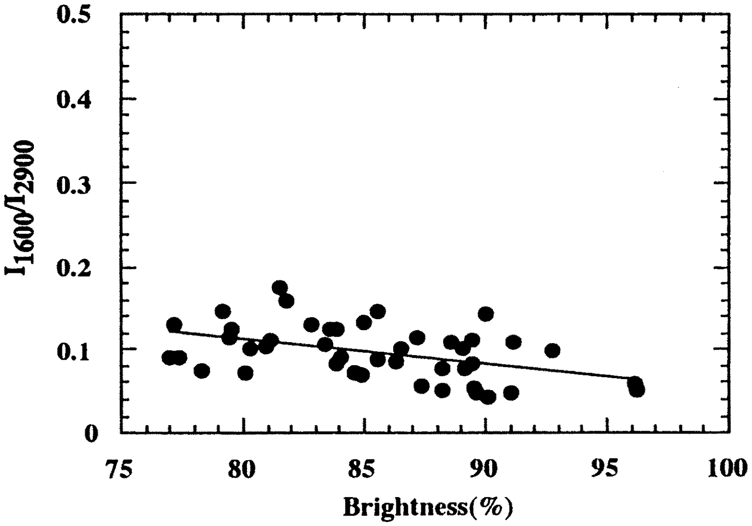

Fig. 2. Relationship between brightnesses of the papers and the Raman intensities at 1600 cm^{-1}.

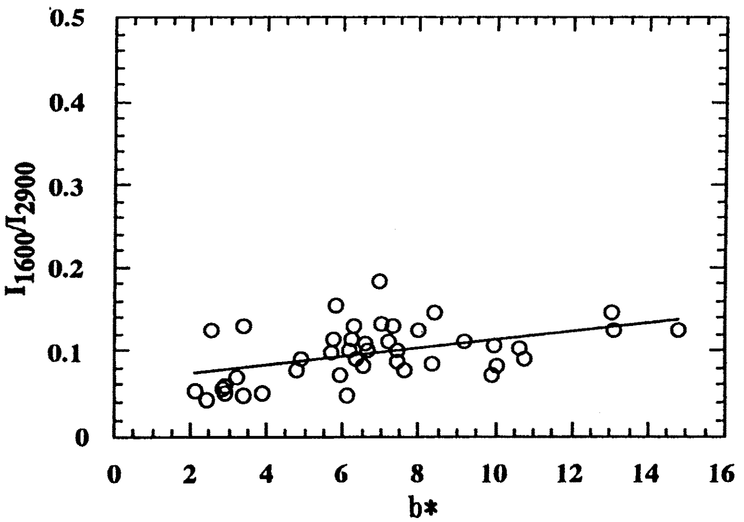

Fig. 3. Relationship between the yellownesses (b*) of the papers and the Raman intensities at 1600 cm^{-1}.

Our recent study illustrated that rosin and other papermaking additives greatly influenced the color of wood-free papers (Wu and Tanaka, 1997).

Changes in glycosidic linkages of the papers during storage

As shown in Fig. 4, the intensities at 1907 cm^{-1} of the acidic papers decreased gradually with increasing storage years. Since the intensities reflect the polymerization degrees of cellulose on paper surfaces (Agarwal and Atalla, 1994), the decrease in the Raman intensities at 1907 cm^{-1} illustrates that the cleavage of β-glycosidic linkages on the paper surfaces proceeded gradually during the storage. In the previous paper (Wu and Tanaka, 1998), we reported that the folding endurances of the papers declined with increasing storage years. Thus the Raman spectra suggests that the cleavage of β-glycosidic linkages due to acidic hydrolysis during the storage may be a main reason for the losses in the mechanical property of the acidic papers.

Similar to I_{1097}/I_{2900}, the intensity ratio of I_{1126}/I_{1097} also shows a decreasing trend with the increasing storage years (Fig. 4). As shown in Table 1, the band at 1126 cm^{-1} is assigned to symmetric stretching of α- and β-glycosidic linkages in carbohydrates. Among the carbohydrates of the wood-free papers, only hemicellulose and starch contain α-glycosidic linkages in their molecules. The decreases in the intensity ratio of I_{1126}/I_{1097} with increasing storage years means that both of α- and β-glycosidic linkages were hydrolyzed gradually due to acid, and the cleavage of α-glycosidc linkages proceeded faster than that of β-glycosidic linkages during the storage. Luner and Usuda suggested that the hydrolysis of hemicellulose in paper is a more important factor than that of cellulose for the deterioration of paper. The Raman spectra of the papers here demonstrate that the decreases in α-glycosidc linkages of hemicellulose and starch were

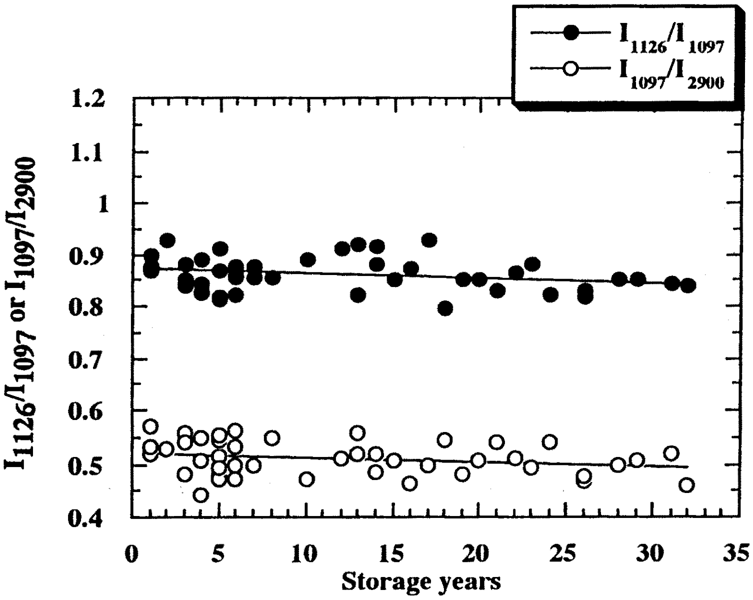

Fig. 4. Relationship between the storage years of the acidic papers and the Raman intensity ratios.

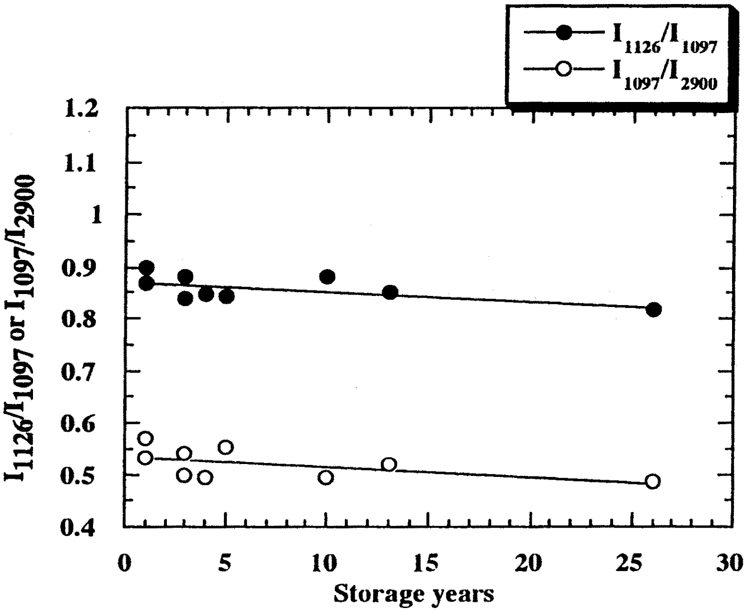

Fig. 5. Relationship between storage years of the neutral-alkaline papers and the Raman intensity ratios.

related deeply to folding endurances of the papers.

It is worthy to note that both intensity ratios of I_{1097}/I_{2900} and I_{1126}/I_{1097} in the Raman spectra of neutral–alkaline papers decreased with the increasing storage years (Fig. 5). Based on the statistics between the folding endurances and the intensity ratios as shown in Figs. 4 and 5, it is obvious that the cleavages of α– and β–glycosidic linkages in the neutral–alkaline papers were as fast as in the acidic papers during the storage. In our knowledge, if a paper is neutral or alkaline, it will have good permanence. But the analysis results in the Raman spectra suggest that chemical additives in neutral–alkaline papers may also cause serious deterioration of the papers.

Besides the bands described above, the band at 1080 cm^{-1} assigned to oxycellulose, and bands at 1300 and 900 cm^{-1} relate to crystallinity of cellulose were reported to affect the fiber strength (Edward *et al.*, 1996). But there was no clear relationship between these bands and the folding endurance of the papers.

REFERENCES

Agarwal, U. P. and R. H. Atalla 1994 Raman spectral features associated with chromophores in high–yield pulps. *J. Wood Chem. Techn.*, **14**: 227–234

Conners T. E. and S. Banerjee 1995 *Surface analysis of paper.* CRC Press, New York, pp152–181

Edward, H. G. M., E. Eills, D. M. Farwill, and R. C. Janaway 1996 Preliminary study of the application of Fourier transform Raman spectroscopy to the analysis of degraded archaeological linen textiles. *J. Raman Spectroscopy*, **27**: 663–667

Forsskahl, I. and J. Jason 1992 Sequential treatment of mechanical and chemimechanical pulps with light and heat. *Nordic Pulp Paper Res. J.*, **7**(2): 48–54

Luner, P., 1969 Paper permanence. *Tappi*, **52**(5): 796–802

Ono, T., K. Sonda, K. Ito, M. Shibata, T. Kato and Y. Otake, 1998 Non–destructive determination of hemicellulosic neutral sugar composition in native wood by Fourier transform Raman spectroscopy. *J. Wood Chem. Techn.* **18**(1): 27–41

Parker F. S. 1991 *Application of infrared, Raman, and resonance Raman spectroscopy in biochemistry.* Plienum Press, New York, London

Takayama, M., *et al.*, 1997 Fourier transform Raman assignments of guaiacyl and syringyl maker bands for lignin determination. *Spectrochimica Acta A*, **53**: 1621–1625

Usuda, M. 1984 The current trend of book preservation and the mechanisms of degradation of paper. *Japan Tappi*, **38**(1): 48–54

Wiley, J. H. and R. H. Atalla 1987 Band assignments in the Raman spectra of celluloses. *Carbohydrate Res.*, **160**: 113–129

Wu, Z. H., M. Sumimoto and H. Tanaka 1994 A novel approach to improve brightness stability of H_2O_2–bleached high–yield pulps by addition of radical scavengers to the pulping process. *Holzforschung*, **48**(5): 400–404

Wu, Z. H. Unpublished data

Wu, Z. H. and H. Tanaka 1997 Study on mechanisms of the natural deterioration of wood–free papers by FT–NIR. *Proceeding of the 47th Annual Meeting of the Japan Wood Research Society*, P. 328

Wu, Z. H. and H. Tanaka 1998 Permanence of wood–free papers: Papermaking additives in naturally degraded wood–free papers. *J. Wood Sci.*, **44**: 111–115