FTIR SPECTRUUM OF THE THERMAL AND COLD TREATED PAPER DOCUMENTS, (WITHOUT AND WITH PHOTO TREATMENT)

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The changes in FTIR spectrum of the thermally accelerated, cold treated (without and with photo treatment) bill paper, delivery note paper and paper used for identity card (ID) were investigated. The effect of the treatment on the carboxylic, lignin content and elemental residue was confirmed from the results of FTIR spectrum.

Introduction

Extensive research has been carried out on the thermal behaviour of polymers, since it exercises a significant influence upon phenomena related to thermal deformation, thermal degradation, thermal decomposition, and other heat resisting properties of polymers.(1)

Infrared spectroscopy is one of many available methods of physical measurement which has been widely applied in the field of cellulose chemistry, for instance, it permits the detection of other natural substances in cellulose such as lignin and hemicellulose. Also it aids in the identification of cellulose derivatives, decomposition or

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oxidation products and copolymers. In addition, infra red spectrophotometry. is used in qualitative and quantitative, analysis.[2] Infrared spectra of some wood sections and interpretation of some bands corresponding to the well-known characteristic frequencies of such groups as OH, CH_2 , C = O as well as benzene ring frequencies in lignin was investigated.[3] On the other hand The effect of higher and lower temperatures in addition to ultraviolet radiation on the FTIR spectrum of cellulosic fibers in order to detect its aging have not yet been extensively studied.

The aim of the present work was to study the effect of thermally accelerated aging and cold treatments with and without photo treatment (aging) on the change of FTIR spectrum of some types of paper documents: bill paper, delivery note paper and application paper form used for identity card.

Materials and Methods

Materials:

Bill paper, delivery note paper and application paper form used for identity card (ID) were the same as those used in the previous article.[4]

Methods:

1- Treatments of the paper documents:

One part of the document papers were subjected to thermally accelerated aging in thermostatically controlled oven at 100ºC for 36 hours by suitably hanging them from hooks. Another part of papers were exposed to cold treatment at - 5ºC for 36 hours. Then each treated sample was exposed to UV lamp giving 336 nm wavelengths at 25ºC for 18 hours using controlled cooling system at constant relative humidity (RH) 65± 5%.

2- Chemical analysis:

The carboxyl content (mEq /100g), lignin content and elemental analysis were determined as mentioned before.[5]

3- FTIR measurement *

The changes in the chemical functional groups in the infrared absorption spectra of the treated samples were characterized by using FTIR spectrophotometer (model 1650 Perkin - Elmer).

RESULTS AND DISCUSSION

FTIR spectrum of some paper documents after thermal, cold treatments followed by ultravolt radiation:

A- Bill paper:

In all samples used in this work, the carbonyl band at about 1798-1736 cm^{-1} was greatly reduced in its intensity. This is most probably due to that the carbonyl group crosslinking to a neighboring carbohydrate chain to form a hemiacetal at the expense of the formation of carbonyl group. Thus the band near 1250 cm^{-1} is connected with the C-O stretching mode in the O-C-O group. The effect of thermal, cold treatment followed by photo radiation on the carboxylic content of the paper documents (Table 1) can be confirmed from the results of FTIR spectrum of groups of bands, one near 3400 cm^{-1} of polymeric OH and the other at about 1250 cm^{-1}.

Figure 1b shows the FTIR spectra of the bill peper after thermal treatment. From this Figure it is noted that the band at about 1250 cm-^{1} of O-C-O group disappeared. More effect occured on the function groups when the thermal treated bill peper was exposed to ultraviolet radiation as shown from the disappearance of the band at

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1457 cm^{-1} which correspond to internal deformation of CH_2 group. Also the band of the aromatic ring of lignin at 1516 cm^{-1} became very weak and shifted to 1543 cm^{-1}. This may be attributed to the degradation effect, see (Figure 1c).

On the other hand cold treatment has no effect on the CH_2OH groups, this is because the band at 1457 cm^{-1} of the group remanied in its position without any change in its intensty even when the treated sample was exposed to ultraviolt radiation (Figures 2b, 2c). Also, cold treatment followed by photo treatment is not capable to decompose lignin to which the bands at 1563 and 1543 cm^{-1} are attributed because no significant change in position or intensity of these two bands was observed on comparing the spectrum of the cold treated sample with that of the cold treated followed by ultraviolt radiation.

It must by mentioned that the band at about 1320 cm^{-1} which corresponds to sulphone group was observed in all spectra of bill paper either in intial or treated samples. This may be due to the presence of high residual amount of sulphur (Table 2) that resulted during paper manufacture from rice straw pulp blended with kraft soft wood pulp.

B-Delivery note paper:

(Figure 3b) illustrate FTIR spectrum of the thermally treated delivery note papers. The bands at 2924 and 2858 cm^{-1} corresponding to symmetric and asymmetric stretching vibration of the CH_2 group which appeared as shoulders in the initial sample (Figure 3 a) were changed into one band at 2902 cm^{-1} corresponding to vibration of the CH_2 group. The bands at 1518 and 1582 cm^{-1} in the initial sample disappeared. These bands may be attributed to the stretching vibration of the C = C bonds of the aromatic rings of lignin which decomposed

by thermal treatment due to oxidation. The band at 1458 cm^{-1} which is attributed to the CH_2OH group was shifted to 1432 cm^{-1}. Also, new bands were appeared at 1373 and 1319 cm^{-1} which may be attributed to the deformation vibration of CH_2 group in cellulose and hemicellulose and to sulphone group $>S(=O)_2$ resulted from the oxidation of sulphur residue which remained from pulping process during preparation of paper pulp respectively (Table 2). Exposure the thermal treated sample to ultraviolet radiation led to reduction of the intensty of the band at 1373 cm^{-1} (Figure 3c).

From (Figure 4b) which shows the FTIR spectrum of the cold treated delivery note paper, it is noted that a new weak band was appeared at 1633 cm^{-1} adjacent to the band at 1654 cm^{-1} which may be attributed to bending vibration of absorbed water. Also, the band of the lignin group which appeared in the initial sample at 1518 cm^{-1} appeared as very weak band at 1578 cm^{-1}. The band of the sulphone group at about 1320 cm^{-1} does not appear, this may be attributed to the fact that cold treatment is not capable of oxidizing the sulphur residues even when the sample was exposed to ultraviolet radiation (Figure 4c). As the intensity of the two bands at about 3400 and 1250 cm^{-1} corresponding to OH and O-C-O groups respectively, indicates the carboxylic content of the paper. Thus any increase in their intensity confirm the increase in the carboxylic content of the paper. Thus, from Figures 3, 4 and from the intensity of the two bands corresponding to OH and O-C-O groups, it is clear that the carboxylic content is greater in the thermally treated paper compared to cold treated one. Also, the obtained results revealed that cold treatment had slight effect on lignin comparing to thermal treatment. The spectrum showed reduction in the intensity of the band at 1458 cm^{-1} and a new weak adjacent band appeared at 1442 cm^{-1} which may be attributed to CH_2OH group of cellulose which disappeared after exposing the sam-

ple to phototreatment. Also, photo oxidation of cold treated sample shifted the band at 1654 cm^{-1} of absorbed water to 1639 cm^{-1}.

C - Application paper form used for identity card:

From (Figure 5b) of the thermally treated sample it is noted that the band at 2921 cm^{-1} which corresponds to the stretching vibrations of the CH_2 groups at 2921 cm^{-1} was shifted to 2904 cm^{-1} while, the band at 1637 cm^{-1} in initial sample (Figure 5a) was shifted to 1652 cm^{-1} in case of the thermally treated sample.

The band of lignin at about 1518 cm^{-1} was absent in the spectrum of this type of paper which confirm that this type of paper is free from lignin, as showed from (Table 1).

The intensity of the band at 1436 cm^{-1} was greatly reduced, this give definite information about the effect of the thermal treatment on the CH_2OH group of the cellulose fibers. The band at about 1250 cm^{-1} of O-C-O group was also disappeared by thermal treatment. On the other hand new band was appeared at 1320 cm^{-1} which corresponds to sulphone group. This may be due to oxidation of sulphur residue which present in the sample (Table 2) as a result of pulping process during its preparation from sulphite wood pulp. No significant change was observed on the spectrum of the paper sample when exposed to ultraviolet radiation at 366 nm after thermal treatment (Figure 5c) since, the thermal oxidation was sufficient to give the previous changes in the spectrum of this type of paper and the photo oxidation by ultraviolet radiation is not capable of producing any more significant change.

The results of cold treatment (Figure 6b) revealed an increase in the intensity of the band at 1430 cm^{-1} corresponding to CH_2OH group of cellulose and disappearance of band at 1376 cm^{-1} which

corresponds to -CH bending vibration. Also, the treatment of the sample at lower temperature has no effect on the active CH_2OH group of the cellulosic fibers which is responsible of most chemical reactions, and on oxidation of sulphur residue, therefore the band of the sulphone group disappeared in the spectrum of cold treatment. No clear difference was observed between FTIR spectrum of the sample exposed to photo radiation after cold treatment (Figure 6c) and the spectrum of the sample exposed to cold treatment only.

Also, it is noted from all Figures of the treated bill papers and papers used for identity card that the band at about 1250 cm^{-1} corresponding to O-C-O group was disappeared, although the intensity of OH group was increased due to oxidative cleavage of acetyl linkage and for this reason the results of carboxylic content of both types of papers was decreased when exposed either to thermal or cold treatment even after exposed to ultraviolet radiation (Table 1).

Table (1)
Effect of thermal and cold treatments followed by UV radiation used as accelerated aging on the carboxyl and lignin contents

Conditions	Carboxyl content (m Eq/100g)	Lignin content
Bill paper		
Without treatment	14.8	1.46
Thermat treatment	11.7	1.03
Thermal treatment+UV	11.5	1.00
Cold treatment	13.1	1.40
Cold treatment+UV	12.4	1.30
Delivery note paper		
Without treatment	30.2	2.83
Thermat treatment	36.6	2.41
Thermal treatment+UV	38.0	2.35
Cold treatment	30.7	2.72
Cold treatment+UV	31.8	2.60
Paper used for I.D		
Without treatment	8.6	0.04
Thermat treatment	7.2	-
Thermal treatment+UV	6.1	-
Cold treatment	7.8	-
Cold treatment+UV	7.0	-

Table (2)
Elemental analysis of paper documents

Type of paper documents	N%	CI%	S%
Bill paper	Nil	Nil	3.75
Delivery note paper	Nil	Nil	0.53
Application paper for ID	Nil	Nil	2.60

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التحليل الطيفى بالأشعة تحت الحمراء لأوراق المستندات المعالجة وغير المعالجة ضوئيا بعد تعرضها لدرجات حرارة مرتفعة ومنخفضة

نبيل صفى الدين هشـــام رضـــا

يهدف هذا البحث إلى دراسة تأثير التغيرات التى تحدث فى التحليل الطيفى بالأشعة تحت الحمراء لكل من : أوراق الكمبيالات ، وأوراق مستندات الصرف ، وأوراق الاستمارات المستخدمة لاستخراج بطاقات تحقيق الشخصية المعالجة وغير المعالجة ضوئيا بعد تعرضها لدرجات حرارة مرتفعة ومنخفضة . وقد أثبتت نتائج التحليل الطيفى بالأشعة تحت الحمراء تأثير هذه المعالجات فى محتوى الكربوكسيل واللجنيين ، وكذلك بقايا العناصر لأوراق هذه المستندات .