Characterization and Aging of Biotreated Kraft Bagasse Pulp

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ABSTRACT: Strains of bacteria [*Pseudomonas flurescens* (Pf1 and Pf2); *Bacillus subtilis* (B)] were used for treatment of kraft bagasse pulp. Both of the bacterial treated kraft bagasse pulp (BKBP) and control (C) pulp samples were chelated with EDTA and then bleached with hydrogen peroxide. The effect of aging on paper brightness was investigated. The brightness change due to aging for both control sample and bleached bacterial treated (BBKBP) pulp are 19.38% and (5.99%–15.35%), respectively. The crystallinity index (CrI) is calculated for both control sample (C) and BBKBP via X-ray diffraction patterns. It was found that the CrI for BBKBP was increased by 4.46% compared with the control (C) sample. The relative intensity and assignment of absorption bands for BKBP) were studied via FTIR spectra. Pyrolytic behavior of the different samples was investigated by thermal gravimetric analysis and derivative thermogravimetric techniques. Calculations of the mass loss were used to elucidate the rate constant of decomposition and the activation energy. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1887–1894, 2007

Key words: bacterial treatment; hydrogen peroxide bleaching; paper aging; X-ray diffraction; FTIR spectra analysis; thermogravimetric analysis

INTRODUCTION

The use of agro-based materials as alternate raw materials to wood for pulp production has been steadily increased in recent years due to increasing restraints on forest harvesting.[1] The average annual increase in agro-based fiber pulp capacity is now more than triple the average annual increase in wood capacity, at 6% versus 2% for wood, on a worldwide basis.[2] There are a wide variety of agro-based materials that can be utilized for pulp production, such as straw, bagasse, and bamboo.

Pulping process is generally divided into two broad classes—chemical and mechanical—which produce substantially different fiber characteristics. The choice of the process depends on the end application of the pulp and the raw material. In many papermaking operations, a combination of chemical and mechanical pulp is used to obtain the desired paper characteristics.

Biopulping is defined as the treatment of wood chips with lignin-degrading microorganism prior to pulping. Lignocellulosic materials, biopulping, biobleaching, and pulp modifications represent biotechnical applications with the greatest potential in terms of cost reduction, energy consumption, process improvement paper quality, and decrease in environmental impacts.[3]

There have been only a few studies on wood treatment with bacteria as compared to fungi.[4,5] The potential advantages of using bacteria instead of fungi are possibly shorter treatment times due to higher growth rates, more convenient inoculation, and more economic inoculum preparation techniques.[6]

Lignin-containing paper has excellent retention of mechanical properties upon accelerated aging in the dark; there is no correlation between loss of brightness and the mechanical strength. Ultraviolet irradiation of lignin-containing pulp causes formation of phenoxy radicals in the lignin, and these phenoxy radicals are further oxidized by either alkoxy or peroxy radical to *o*-quinines and other chromophores. Thus, lignin should inhibit auto-oxidative degradation of cellulose.[7] Lignin content in the range of 0–28% does not result in greater loss of strength properties upon aging.[8]

Pyrolytic methods are commonly used in the analysis of agro-based materials and its component.[9] Thermogravimetry (TG) and derivative thermogravimetry (DTG) is a simple technique for studying the pyrolytic behavior of materials. The mass loss occurring during slow heating under an inert atmosphere can be measured. Activation energy and volatilization rates for cellulose materials could be determined.[10] FTIR spectroscopy technique has been used to investigate the fine structure characteristics of bacterial treated kraft bagasse pulp (BKBP).

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In the first part of this work, the effects of bacterial treatment on the brightness and hand sheet mechanical strength properties of a kraft bagasse pulp were studied.[11] The present study describes the susceptibility of bacterial treatment to brightness reversion. The X-ray diffraction patterns of control and bleached bacterial treated kraft bagasse pulp were studied (BBKBP). The relative intensity and assignment of absorption bands for BKBP were calculated. Also, pyrolytic behaviors of different samples were investigated.

EXPERIMENTAL

Material

Unbleached kraft bagasse pulp was provided by Edfo Mill, Egypt [15% NaOH, 5% Na_2S (as N_2O), 0.05% anthraquinone (AQ)-based on raw material i.e. (oven dry pulp) at 160°C for 2 h and 1 : 6 liquor ratio]. The raw material has the following analysis according to Tappi standared methods: α-cellulose 64.0% T 203 om-83, pentosane 27.5% T 223 om-84, and lignin 4.8% T 222 om-88. Pure chemicals of laboratory grads were used.

Methods

Strains of bacteria [*Pseudomonas flurescens* (Pf1 and Pf2); *Bacillus subtilis* (B)] were evaluated for their bleaching and improvement strength properties of kraft bagasse pulp. These strains were obtained from plant pathology department, National Research Centre, Egypt. The used strains were cultivated under aseptic conditions. Bacterial growth was prepared by growing each tested strain into conical flasks (250 mL) containing 100 mL of autoclaved nutrient broth medium (NBM). NBM is a specific media for abundant growth of bacteria. The inoculated flasks were incubated at 30 ± 2 °C for 48 h using incubator shaker. The bacterial inoculum was adjusted as 6×10^6 CFU. CFU is colony for unit, which is used as a rate for determining microbial count in different substances.

Bleaching sequence

Each of the bacterial treated and untreated [control (C)] pulp samples were chelated, before bleaching with hydrogen peroxide. The conditions for chelation were as follows: start pH of 5.5, 3% consistency, 1% ethylene diamine tetra-acetic acid at 50°C for 30 min. After chelation, the pulp received a water wash at 1% consistency. The peroxide bleaching of the bacterial treated and untreated kraft bagasse pulp was carried out in sealed polyethylene bag at 80°C, for 2 h, with 2% H_2O_2, 1% $MgSO_4{\cdot}7H_2O$, 2% NaOH, and 3% Na_2SiO_3, and 10% consistency. All bleaching pulps were thoroughly washed after filtration with distilled water till neutrality, and then, the peroxide bleaching is repeated. The kraft bagasse pulp was disintegrated to SR degree of about 40 according to SCAN-C 19 : 65. The bleached pulps were used to make five physical hand sheets according to Tappi test method T 205 om-88. ISO-brightness was determined with Hunter lab instrument Color/Difference Meter D25-2, using MgO as standard white. All ISO-brightness values are the average of five hand sheets, and each hand sheet was read 10 times (five times at each site).

Paper aging

The thermal aging test was performed according to Tappi test method T453 pm-85 at 105°C for 2 h. Hand sheets were removed and conditioned in the same room for several hours, before reading the brightness.

Analysis

FTIR spectra analysis

Infrared spectra were recorded by Jasco FT/IR, Nicolet, and model 670. The samples were measured as thin films using the diffuse reflectance mode of IR spectroscopy. The unit cell used is model no. 0030-099 and serial no. 0207-003. The CO_2 of air, moisture oxygen and H_2O of air were eliminated by measuring the background spectra before every sample. Bands are in the region from 4000 to 400 cm^{-1}, detectors are DTGS.

Thermogravimeteric analysis

TG was recorded by Perkin–Elmer Thermal Analysis Controller AC7/DX TGA7, using a heating rate of 10°C min^{-1} in nitrogen atmosphere.

X-ray diffractions

The crystallinity index (CrI) calculated from X-ray diffraction patterns of untreated (control) and treated samples were recorded by DIANO 800 (USA). Co. Kx radiation $\lambda = 1.75$ Å. The CrI was determined from Eq. (1), as proposed by Segal et al.[12]

$$\mathrm{CrI} = [(I_{002} - I_{\mathrm{am}})/I_{002}] \quad (1)$$

RESULTS AND DISCUSSION

Effect of thermal aging on paper brightness

The main goal of this work is to study the thermal aging effect on the susceptibility of bacterial treated pulp to brightness reversion. Table I shows the effect

TABLE I
The Effect of Bacterial Treatment on Brightness Value for Aged Paper and on Crystallinity Index of BBKBP

Sample	Brightness before aging (%)	Brightness after aging (%)	Change (%)	Crystallinity index, CrI (%)
C	64.00	51.60	19.38	87.91
Pf1-20 days	65.90	60.56	8.10	88.15
Pf2-20 days	67.60	63.55	6.35	91.83
B-20 days	68.70	61.70	10.19	88.43
Pf2-10 days	66.10	62.20	5.99	–
Pf2-30 days	67.50	61.55	6.74	–
Pf2-40 days	68.00	57.56	15.35	86.35

of bacterial treatment on the aged paper brightness value of the BBKBP. It is clear that the brightness decreased sharply in case of the aged control sample, where it decreased slightly in case of the aged bacterial treated pulp. The brightness change due to aging for both control sample and bacterial treated pulp are 19.38% and (5.99%–15.35%), respectively. On the same conditions, treatment with Pf1, Pf2, and B strains for 20 days results in a slight brightness reduction for Pf2-20 compared with Pf1-20, B-20 strains and control samples. It has been reported that, in bleached kraft pulps, the aging reactions are predominantly related to the transformation of polysaccharides.[13–15] The thermal yellowing of chemical pulps has been reported to be influenced by the chemical composition of the pulp, i.e., the contents of lignin, hemicellulose, metal ions, carbonyl, and carboxyl groups.[16] Thermal yellowing has been related to the content of hexenuronic acid[17]; pulps with a high hexenuronic acid content being less stable on heat treatment. Also, it was found that the transition metal ions, such as Fe^{2+}, Fe^{3+}, Cu^{2+}, or Mn^{2+} present in the bleached pulps in trace amounts, have been associated with a faster brightness loss.[14] From the same table, it is clear that treatment with Pf2 strain for different incubation times from 10 to 40 days results in an increase in brightness reduction after the thermal aging, as the incubation time increased. These results are in agreement with those of Sykes,[18] and so bacterial treatment of unbleached kraft bagasse pulp followed by alkaline hydrogen peroxide bleaching results in a small brightness change after thermal aging compared with control sample, while the brightness change after thermal aging of the pulp increased with increasing the incubation time.[19,20]

X-ray Diffraction

The mechanism of the bacterial degradation of crystalline cellulose is still poorly understood because of the complexity of the substrate. In nature, cellulose is insoluble in most solvents; it is fibrous and composed of both crystalline and amorphous regions. The CrI and surface area has been considered to be important factors for determining enzyme susceptibility. Therefore, in comparison with the CrI of BBKBP and control sample, it was found that, from Figure 1, there is a reasonable relationship between the CrI and the bacterial treatment; at the same time, from Table I, the CrIs are 87.91% for control sample, and 88.15%, 91.83%, and 88.43% for Pf1-20, Pf2-20 and B-20, respectively. So, one can find that the bacterial treatment increased the CrIs, i.e., increased the ordered region in the cellulose or decreased or removed the amorphous regions in cellulose.[21] Increasing the treatment time of Pf2 from 20 to 40 days of BBKBP decreases the CrI from 91.83% to 86.35%. So, it is clear that the delignification occurring during the processing of the BBKBP alters the structure of lignocellulose; therefore, a change in CrI should be expected. So, the susceptibility of pure cellulose to enzymatic hydrolysis is inversely related to its degree of crystallinity.[22]

Infrared spectroscopy

FTIR spectroscopy is a powerful tool for studying the physicochemical and conformational properties of polysaccharide.[23] The relative absorbance of different bands was determined via the baseline correction method for making a comparative study of the spectra.[24] The band at 1170 cm^{-1} can be attributed to the C—O—C asymmetric vibration. This band has been chosen as an internal standard to determine the relative absorbance.

The IR spectra of (BKBP) is influenced by the spectra of its three main biopolymers, namely lignin, hemicellulose, and α-cellulose. Table II and Figure 2 gives the band positions and the corresponding relative intensities and their assignments for different BKBP for 20 days compared with control sample.[25]

The band at 3460–3412 cm^{-1} is attributed to the hydrogen bonded O—H stretching vibration; its relative absorbance intensity is increased upon bacterial treatment. This may due to the increase in CrI for BKBP samples and, consequently, increase hydrogen bonding.[26]

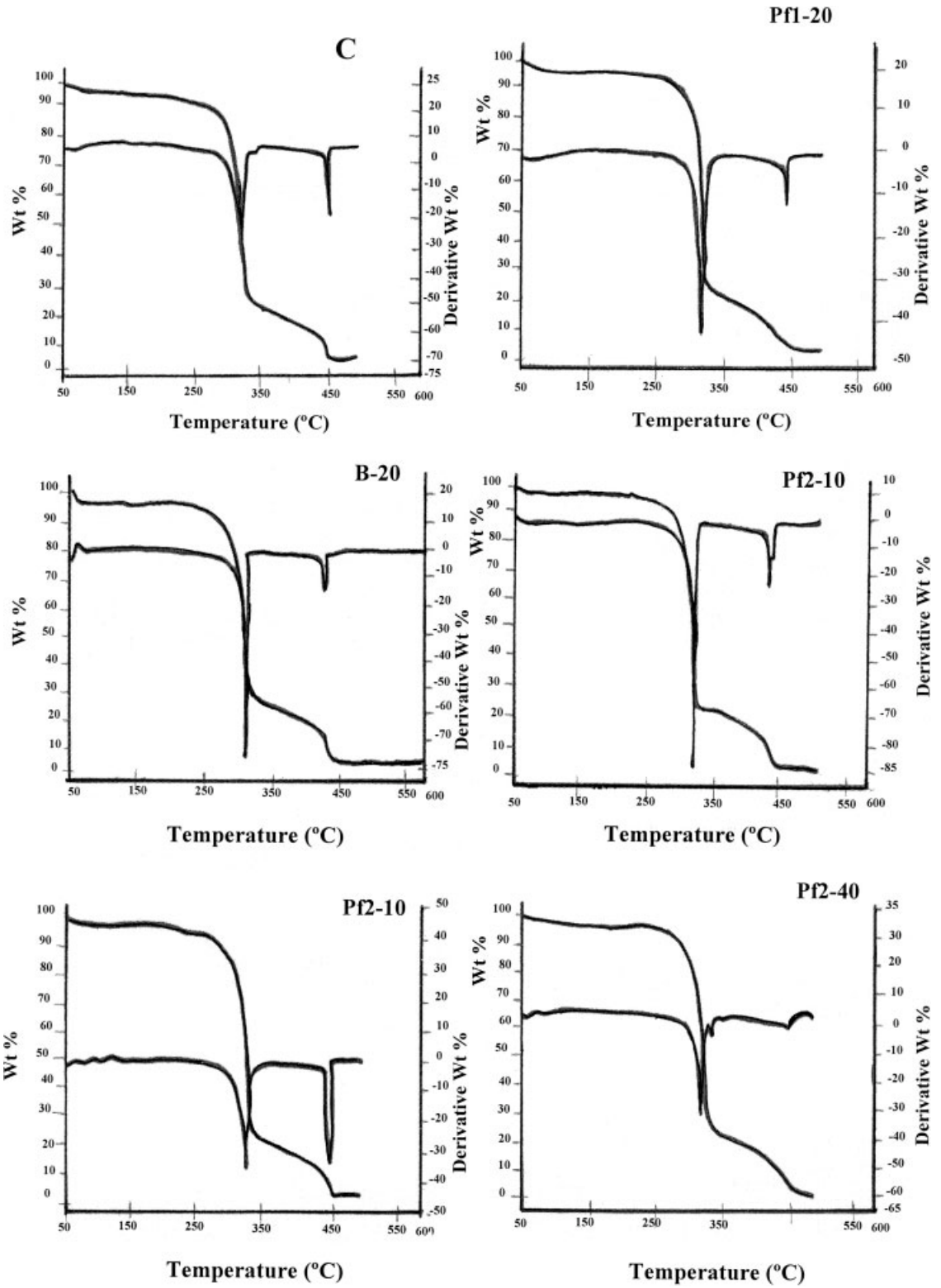

Figure 1 X-ray diffraction of BBKBP; (1) C, (2) B-20, (3) Pf1-20, (4) Pf2-20, and (5) Pf2-40.

The C—H stretching vibration absorbance intensity ratio at 2900 cm^{-1} is slightly increased upon bacterial treatment; this is due to the presence of —CH_2 moieties in the sample. The relative intensities of C—O—O and O—H stretching band at 2138 cm^{-1} were decreased due to the bacterial treatment, which indicate that the peak at 2138 cm^{-1} is associated with internal hydrogen bonding. The absorption band

TABLE II
Infrared Spectra, Relative Intensity, and Assignments of Different Bands of Different BKBP for 20 Days

Band position (cm^{-1})	Relative intensity of samples				Band assignments
	Control	Pf1	Pf2	B	
3460	1.08	1.21	1.22	1.39	O—H stretching vibration (hydrogen-bonded)
2900	2.38	2.43	2.34	2.83	C—H stretching vibration
2138	9.03	7.35	7.03	8.39	C—O—O and O—H stretching
1640	4.08	3.36	3.42	3.83	C—O stretch; in conjugated p-substituted aryl ketones
1430	1.79	1.66	1.25	1.49	Aromatic skeletal vibrations combined with C—H in plane deformation
1370	1.57	1.52	1.64	1.68	Symmetric C—H bending from methoxyl group
1130	0.95	1.00	1.01	0.96	C—O—C asymmetric valence vibration
1043	3.10	3.09	3.09	2.98	C—O ether vibrations, methoxyl, and β-O-4
900	3.72	3.40	3.54	3.55	Out of plane ring stretching in cellulose due to β-linkage

at 1640 cm^{-1} is attributed to the vibration of —C=O stretch; conjugated P-substituted aryl ketones has a marginal decrease in the relative intensity due to degradation in lignin.[27] Microbial lignin degradation has been shown to be an aerobic, i.e., an oxidative process, and so it should proceed via the general pathways of lignin oxidation involving initial electrophilic attack by radical species, followed by heterolytic rearrangements and other transformations.[28] The band near 1430 cm^{-1} due to the aromatic skeletal vibrations combined with C—H in plane deformation has a lower absorbance intensity ratio. This may be related to ring rupture, which is proposed to occur following the coupling of an initially formed phenoxyl radical or cationic radicals with a reactant radical.[29,30]

The 1370 cm^{-1} band, which represents symmetric C—H bending from methoxyl group, exhibits the same or slightly increase in the relative intensity due to the bacterial treatment. The bands near 1162–1125 cm^{-1} assigned to C—O—C asymmetric valence vibration exhibit the same or marginal increase in the absorbance intensity ratio via bacterial treatment. The peaks at 1043 cm^{-1} indicate the stretching vibrations of C—O ether vibrations, and methoxyl and β-*O*-4 give a decrease in the relative intensity upon bacterial treatment. The band at 900 cm^{-1} is attributed to the asymmetric out-of-plane ring stretching in cellulose due to the β-linkage[22] and to the amorphous form in cellulose. Sun et al.[23] reported that the peaks at around 900 cm^{-1} is indicative of the associated hemicellulose. The decrease in intensities of these peaks after the bacterial treatment is referred to the partial removal of the hemicelluloses.

Thermogravimetric analysis

The thermal analysis techniques, such as thermal gravimetric analysis (TGA) and DTG, provide powerful tools to study the behavior of cellulose materials during their thermal degradation. The mass loss method is used to elucidate the rate constant of decomposition and the activation energy.

The analysis was carried out from 50°C to 600°C under nitrogen atmosphere and at a heating rate of 10°C min^{-1}. Samples were also investigated via DTG to prove the identification of the decomposition

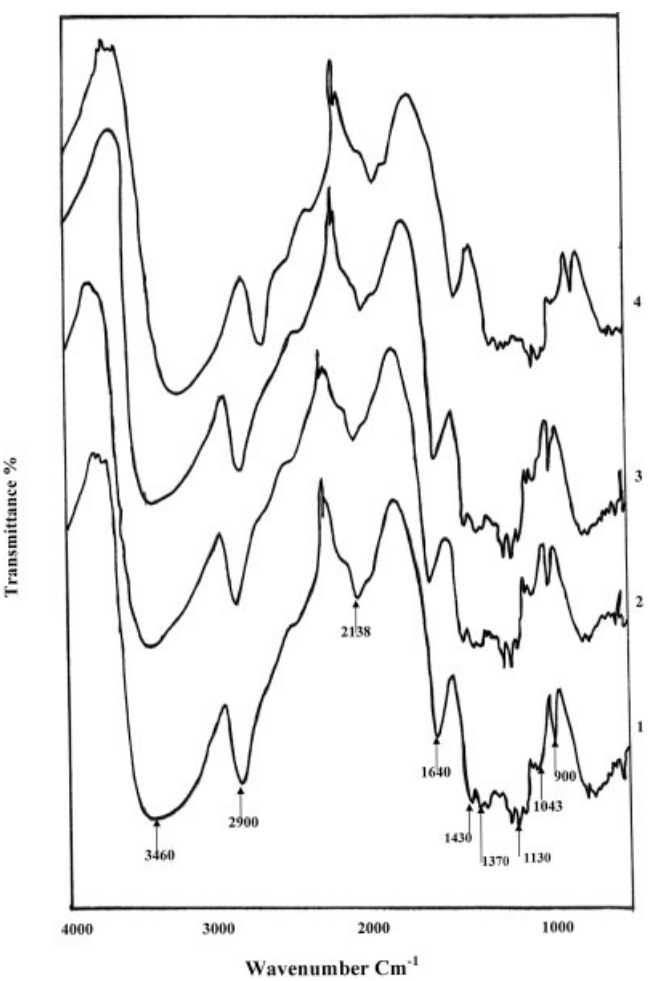

Figure 2 Infrared spectra of different BKBP for 20 days: (1) C, (2) Pf1, (3) Pf2, and (4) B.

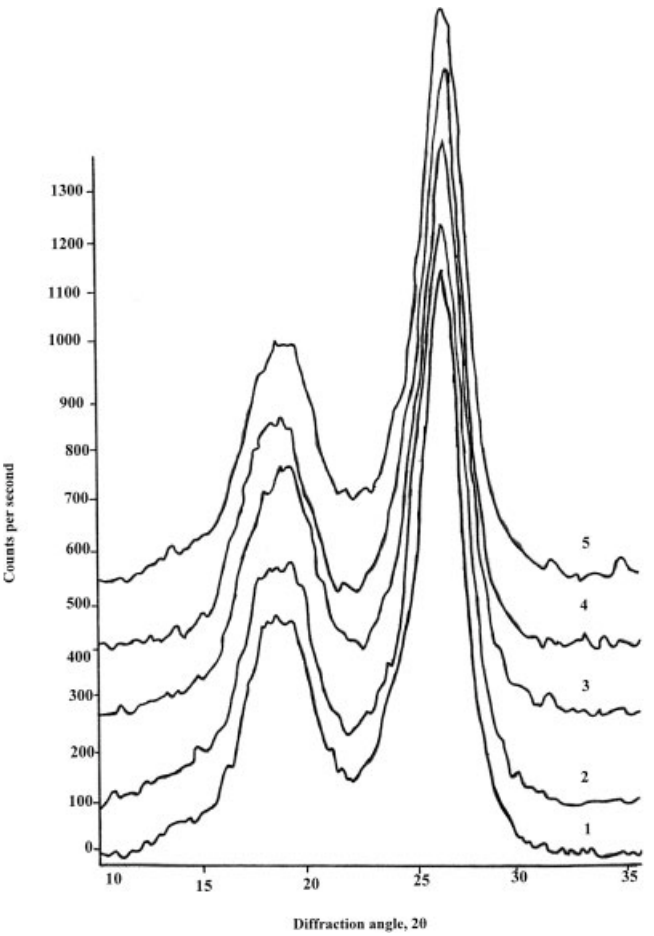

Figure 3 TG and DTG curves for BBKBP.

behavior of the investigated samples. Figure 3 shows the TG and DTG curves of the different samples; it could be seen that, after the moisture content loss and evaporation of the volatile materials at about 255°C the mass of all samples decreases sharply. At about 330°C the main decomposition of the samples amount is about 70% of the total mass. BBKBP shows a complete sharp decomposition to constant masses at 459, 460, 444, 445, 460, and 464°C for C, Pf1-20, B-20, Pf2-10, Pf2-20, and Pf2-40, respectively. DTG curve of BBKBP shows two maximum decomposition peaks at 328°C and 459°C for C, 330°C and 460°C for Pf1-20, 325°C and 444°C for B-20, 329°C and 445°C for Pf2-10, 330°C and 460°C for Pf2-20, and 328°C and 464°C for Pf2-40. These peaks of degradation could be referred to the early dehydration and degradation of the carbohydrate residues, respectively. Table III indicates the decomposition temperature, rate constants, and activation energies of the BBKBP. From the table, it was found that the thermal stability of the BBKBP for Pf1-20, Pf2-20, and Pf2-40 (BBKBP) are the same or less than the control sample.

Calculation of the activation energy

The data obtained from TG curves were analyzed by differential method,[10] in which $\ln\{(W_0 - W_\infty)/(W_t - W_\infty)\}$ is plotted against the time (t), where W_t is the weight after time t, W_0 is the initial weight, W_∞ is the weight of the ash remaining after the final heating. The slope of the obtained line is a rate constant for the thermal decomposition.[10] As shown in Figure 4, plotting $\ln\{(W_0 - W_\infty)/(W_t - W_\infty)\}$ against time under isothermal conditions gave two part lines. The first part, which occurs over the initial 20 min, is due to the loss of water. The second part, straight line portions which cover the following few minutes, is due to thermal decomposition of the samples. This indicates that the loss in weight due to thermal decomposition is a first-order reaction. The calculated reaction rate constants for the second step, straight line portions, i.e., rate constants of the weight loss due to thermal decomposition, were 0.20, 0.24, 0.18, 0.23, 0.19, and 0.23 min^{-1} for C, Pf1-20, B-20, Pf2-10, Pf2-20, and Pf2-40, respectively. The activation energy in the main decomposition temperature region was calculated using Arrhenius equation, the activation energies of control and bleached bacterial treated samples were 171.44, 216.54, 153.49, 209.21, 161.35, and 206.01 kJ mol^{-1} for C, Pf1-20, B-20, Pf2-10, Pf2-20, and Pf2-40, respectively.

TABLE III
Decomposition Temperatures, Rate Constants, and Activation Energies for Bleached BBKBP

Material	Decomposition temperature (°C)	Rate constant (min^{-1})	Activation energy (kJ mol^{-1})
C	328–459	0.20	171.44
Pf1-20days	330–460	0.24	216.54
B-20days	325–444	0.18	153.49
Pf2-10 days	329–445	0.23	209.21
Pf2-20 days	330–460	0.192	161.35
Pf2-40 days	328–464	0.23	206.01

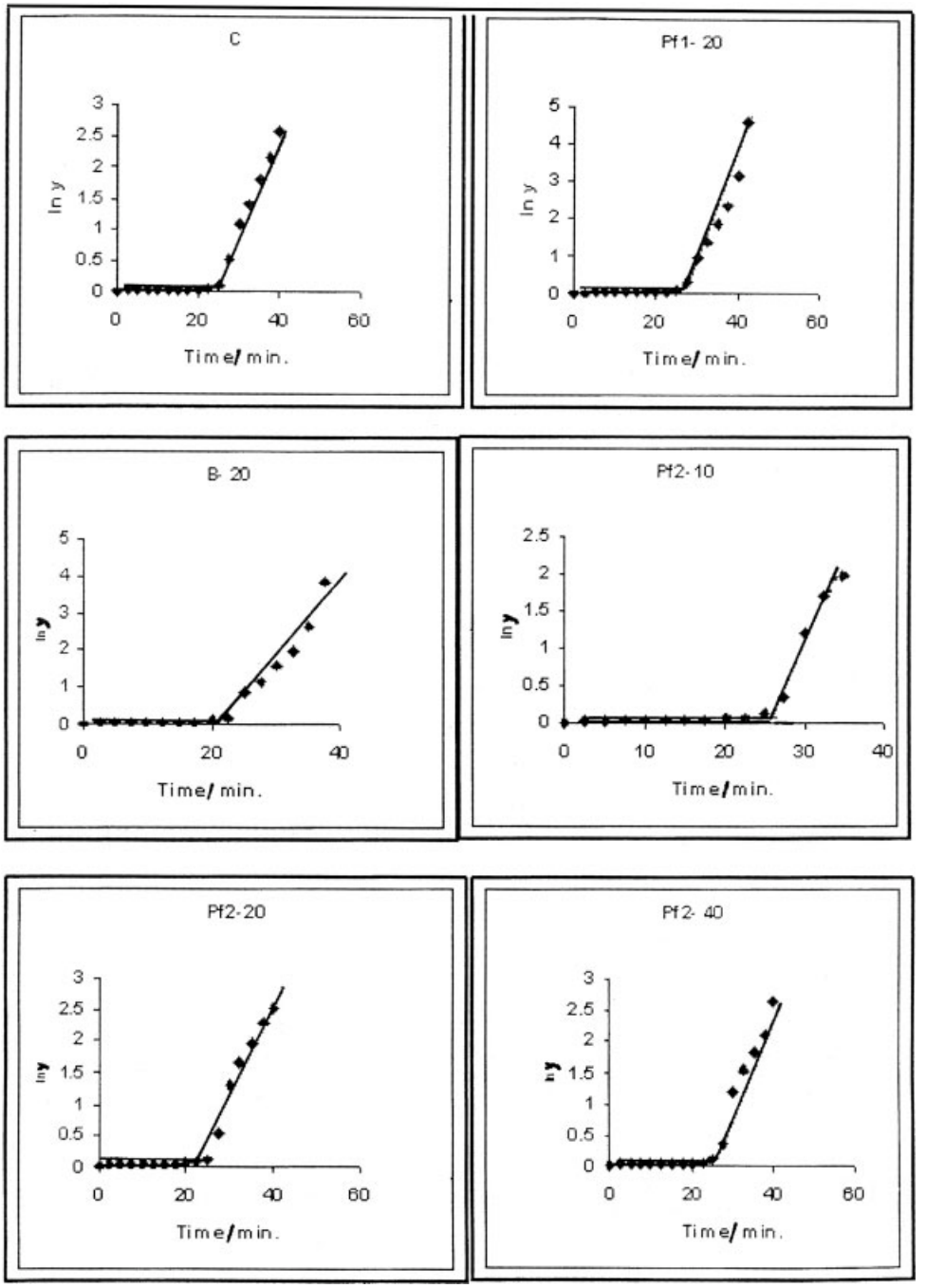

Figure 4 $\ln\{(W_0 - W_\infty)/W_t - W_\infty)\}$ versus time for BBKBP; $y = \{(W_0 - W_\infty)/(W_t - W_\infty)\}$.

CONCLUSIONS

From the results obtained in the present work, it can be concluded that the bacterial treatment results in a paper of more stability on thermal aging compared with the control sample. There is a reasonable relationship between the CrI and the bacterial treatment; the relative absorbance intensities of different bands of BKBP were studied. It is obvious that the microbial lignin degradation can be considered as an oxidative process involving an initial electrophilic attack by radical species, followed by heterolytic rearrangements. The thermal stability, rate constants, and activation energy for control and BBKBP were calculated.

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