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INFLUENCE OF ETHOCEL POLYMER (EC) LOADED WITH INORGANIC NANOPARTICLES (ZNO-NPS) ON THE CHEMICAL AND PHYSICAL PROPERTIES OF WOODEN PAPER

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Abstract:

The paper aims to determine the effectiveness of ethocel polymer, zinc oxide nanoparticles, and ethocel/ZnO nanocomposite for the consolidation of wooden paper pulp. Aged paper samples were treated with ZnO (0.5%,1%), ethocel (0.5%,1%), and ethocel loaded with ZnO NPs. The treated paper samples with the selected consolidated materials were submitted to artificial aging to evaluate their aging behavior. Visual examination, studying the paper morphology by SEM microscopy, FTIR-ATR analysis, colorimetric measurements, and determining the tensile properties were performed to study the morphological or chemical change that could occur due to consolidation or artificial aging. The data revealed that the consolidation treatment enhances the chemical stability of wood paper pulp. The data of yellowness and brightness reveals that the most effective treatment for decreasing the yellowness of aged paper is ZnO NPs, regardless of the effect of nano zinc on enhancing brightness properties; it has also been able to improve yellowness value. The results showed that ethocel loaded with nano zinc gave a noticeable improvement in the tensile properties of the aged wood pulp.

1. Introduction

Paper and paperboard, used for writing, printing, and other graphic purposes, are made primarily from bleached wood pulp obtained by mechanical, semi-chemical processes. Historical papers are very sensitive, especially if exposed to improper conditions. Papers with sensitive dyes or inks, pigments, and dyes degrade under daylight conditions with strong UV and IR radiations [1]. Wooden paper pulp was first developed in the early 1800_s. It is used for making newsprint. Wood is converted into pulp by the mechanical method to produce fibers for paper manufacturing. Wood pulp papers contain short paper fibers, which can cause weakness in wood pulp paper due to its high lignin content that causes paper acidity, darkening, and staining. High acidity can also lead to brittleness and discoloration of paper artworks [2]. Cellulose ethers and their properties were studied to select the appropriate concentrations for paper materials. Cellulose derivatives are widely used for paper conservation treatments, such as paper mending, strengthening, and resizing [3]. Recently, nanomaterials have been successfully tested for organic material conservation and consolidating and protecting artifacts from damage. Many nanoparticles are utilized to preserve the organic material and can cover the material's surface to create a self-cleaning system and preserve the original appearance of the treated samples. They also decrease and prevent air pollutants' deposition. ZnO NPs inorganic nanoparticles are widely used to coat the surface with self-cleaning, UV protection, and antifungal characteristics [4]. Some researchers studied the effect of thermal and light aging on treated paper samples by cellulose ethers. They reported changes in physical, chemical, and mechanical properties. Moreover, ethocel loaded with inorganic nanoparticles (ZnO NPs) may be interesting as an innovative material for wooden paper consolidation [5,6]. Many nanoparticles are utilized to preserve the organic material and can cover the material's surface to create a self-cleaning system and preserve the original appearance of the treated samples [7,8]. They also decrease and prevent air pollutants' deposition. ZnO NPs inorganic nanoparticles are widely used to coat the surface with self-cleaning, UV protection, and antifungal characteristics [9,10]. Nanomaterials have high surface reactivity due to their large surface area [11-13]. ZnO possesses high photocatalytic efficiency and has a high response to UV light which significantly activates the interaction of ZnO with bacteria. ZnO nano-

particles show the phototoxic effect which produces reactive oxygen species, essential for biological applications [14-16]. Zinc oxide nanoparticles have profound applications in almost every field because they are easy to prepare, inexpensive and safe for the human being. However, ZnO nanoparticles are in the scientific spotlight because of their unique properties such as semiconducting property, piezo-electric property, optical property, antibacterial property, anti-fungal and wound healing property and UV filtering property, high catalytic and photochemical activity [17,18]. Zinc oxide (ZnO) nanoparticles (NPs) have been used for many purposes, such as wear proofing for rubber composites, strong UV absorption in cosmetics and sunscreen, antimicrobial agents, and UV blocking and deodorant in the textile industry, Zinc oxide NP_s with cotton fabrics or paper sheets showed good antimicrobial properties. Zinc oxide NPs have a good self-cleaning function on surfaces when applied in the presence of UV light, where it prevents dust or dirt accumulation on the surface [19-21]. One of the most important properties of ZnO NPs is their ability to inhibit the growth of various bacterial and fungal strains, both in solution or on the surfaces [22,23]. Zinc oxide nanoparticle have also used as coating for different substrates. For a material to be considered super hydrophobic it must possess a certain roughness, with hierarchical structures in the micro and nano meter scale. Also, it is worth mentioning the ability of zinc oxide to form UV absorbing and anticorrosion coatings [24-26]. ZnO was considered for many industrial applications due to its ability to act as anticorrosive protection [27,28]. The research aims to evaluate the effect of thermal and UV light aging on the behavior of wood paper pulp treated with ethocel (EC) and zinc oxide (ZnO) nanoparticles. The treated aged samples were evaluated by visual examination, FTIR spectroscopy, and surface morphology with SEM microscopy.

2. Materials and Methods

2.1. *Samples preparation*

Ethylcellulose E200 (Ethocel) from Kremer, USA. and Zinc oxide nanoparticles (ZnO-NPs) from Sigma Aldrich, Mo St. Louis, USA. Ethyl cellulose and ZnO NPs prepared with two concentrations were as follows: 0.5% & 1% of ethyl cellulose (ethocel) in isopropanol alcohol was prepared by adding 0.5 & 1 g of ethocel to 100 cm of isopropanol alcohol. ZnO NP was prepared with the same concentration of ethocel, and ethocel/ZnO was prepared by mixing ethyl cellulose with ZnO nanoparticles with the same ratio under the magnetic string. Wood pulp paper was prepared in the Egyptian National Library and Archives (Corniche El Nile, Cairo). It was beaten to 40 °SR in a beater following the standard method (SCA). The prepared paper sheets wei-ghed about 80 g/m^2 and were prepared using a leaf casting machine according to paper sheet manufacturing.

2.2. *Treatment process*

The consolidants (*EC and Ethocel nanocomposites*) were applied with soft brush on the surface of paper samples, fig. (1).

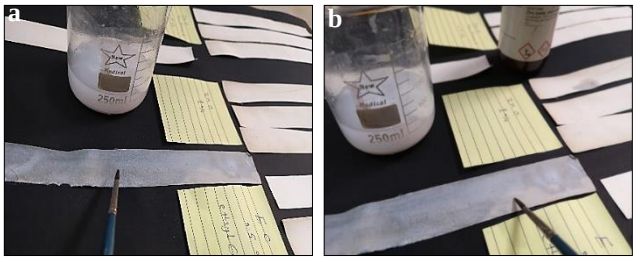


Figure (1) paper samples prepared for the experimental study; **a.** Ethocel, **b.** Ethocel nanocomposites.

2.3. *Accelerated aging*

The paper samples (wood pulp) were thermally aged at 70°C and 65% RH in an environmental chamber for 12 days following the (TAPPI) standard test method T 544 cm-08. According to Feller, the thermal testing for cellulose ethers of thermal stability is essentially based on the degradation rate [29]. Therefore, heating paper for 72 hours at 100 °C gave results like the ones resulting after 25 years of natural aging in many museums and archives at normal environmental conditions. The treated samples were subjected to thermal aging to test their stability

2.4. *Testing and analytical methods*

A professional portable LCD digital microscope with MP digital zoom 100-1000 was used to detect the appearances changes of the treated samples after consolidation. Furthermore, it was used to distinguish the behavior of Ethocel and EC nanocomposite on aged paper samples. The morphological study of the treated and untreated samples was investigated by SEM (JEM-1230 electron microscope, JEOL Ltd., Tokyo, Japan, operated at 60 Kv). It was used to determine consolidation materials' behavior and penetration index into paper material. Also, it was used to determine the ability for the re-binding and adhesion between cellulose chains in the paper support both in the untreated and treated samples. Optimatch 3160 (SDL Company) was used to measure the treated and untreated samples before and after thermal aging at the National Institute of Standards (NIS) in Cairo, Egypt. The detected color values under the CIE lab were presented to evaluate the behavior of (EC) polymer and (EC) nanocomposite. FTIR spectroscopy was used to detect any changes that might occur in paper composition due to post-consolidation treatments or thermal aging [30]. The ATR FTIR spectra were collected using Nicolt 380 with a TGS detector under transmission mode in the range of 4000-400 wavenumber. The test of elongation and tensile strength was carried out to detect the strength properties of treated and untreated samples before and after thermal aging using SDL Atlas, Boras, H5K, Sweden following the (TAPPI standard T 494) in the Metrology Lab, NIS.

3. Results

3.1. *USB digital microscope*

USB digital microscope results proved those different features among the untreated aged paper samples and treated samples as noted in fig. (2).

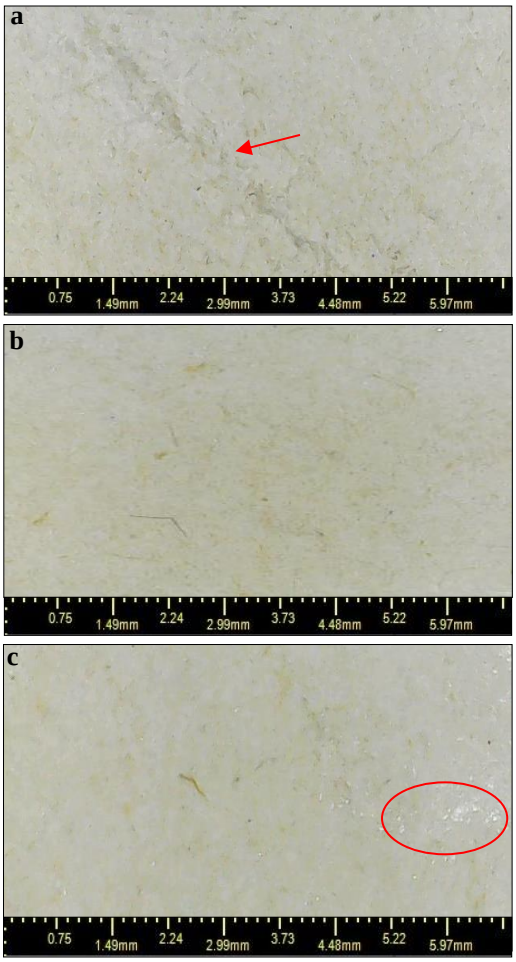
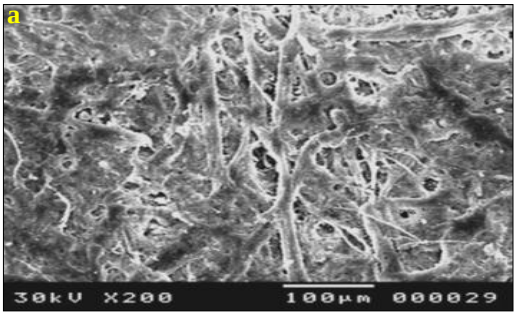


Figure (2) paper samples' surfaces before and after consolidation; **a.** aged untreated paper sample, **b.** sample treated with ZnO nanoparticles, **c.** sample treated with EC polymer and EC nanocomposites (glossiness on the outer surface could be seen).

3.2. *SEM characterization*

A microscopic investigation was performed to assess the efficiency of the consolidation treatments in terms of the presence of reinforcing material into paper structure. The evaluation was undertaken by comparison between a control sample and treated samples with EC solutions. Expected behavior of the consolidation treatment, the fiber has become more interfered with each other in addition to a noticeable increase in fiber width was noted, the examined samples Figure (3) summarized the consolidant penetration through the paper structure [31].



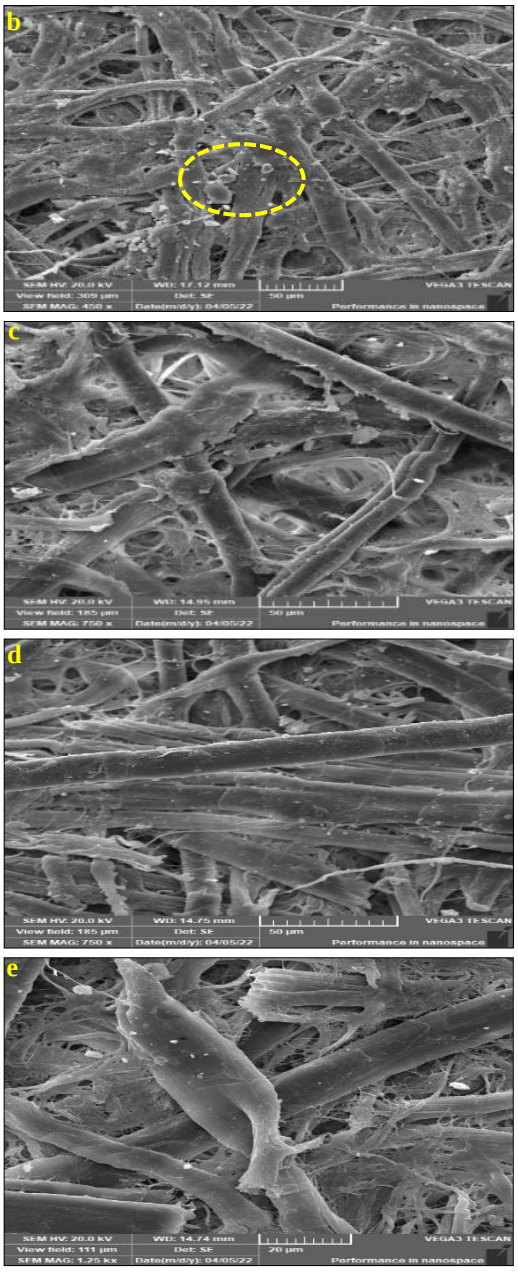


Figure (3) SEM micrographs of the aged paper samples; **a.** weakness, gaps and erosions between fibers, **b.** samples treated with ZnO nanoparticles, where, good penetration of nanoparticles could be noted, **c.** sample treated with Ethocel (EC 1%), where. the treated material did not penetrate inside the walls of the fiber but deposited on the outer surface, **d.** distribution of nanocomposites between gaps, the surface became more integrated in addition to a noticeable increase in the fiber width, **e.** the samples after thermal aging, where, gaps and erosion due to the heat effect could be seen

3.3. *Color change investigation*

Previous studies reported that paper yellowing could be recognized as a sign of the chromosphere groups resulting from the oxidation process during artificial or natural aging of the cellulose molecule, tab$_s$. (1-a & b). Paper yellowness is caused by the hydrolysis process, photoreaction, and thermal degradation. As a result of these physical and chemical

influences, a loss in molecular weight and a decrease in the degree of crystallinity appeared [32,33].

Table (1) Yellowness and brightness values before and after thermal aging

Samples	Yellowness	Brightness
Ref.	14.89	46.72
Treated sample with ZnO NPs 0.5%	14.67	48.50
Aged treated sample with ZnO NPs 0.5%	14.65	47.32
Treated sample with ZnO NPs 1%	16.14	43.00
Aged treated sample with ZnO NPs 1%	16.39	43.14
Treated sample with EC 0.5%	14.85	46.77
Aged treated sample with EC 0.5%	15.03	46.63
Treated sample with EC 1%	17.81	36.28
Aged treated sample with EC 1%	18.08	35.92
Treated samples with EC/ZnO 0.5%	14.61	38.95
Aged treated sample with EC/ZnO 0.5%	20.04	31.00
Treated samples with EC/ZnO 1%	16.74	40.69
Aged treated sample with EC/ZnO 1%	17.50	38.47

Table (2) CIE Lab values of treated and untreated paper samples.

Samples	L*	a*	b*	ΔE
Ref. (untreated)	82.94	1.46	9.14	-
Treated sample with ZnO NPs 0.5%	91.75	0.66	7.33	**9.03**
Aged treated sample with ZnO NPs 0.5%	92.89	0.17	8.00	**1.41**
Treated sample with ZnO NPs 1%	89.66	0.98	7.35	**6.97**
Aged treated sample with ZnO NPs 1%	90.63	0.92	6.57	**1.25**
Treated sample with EC 0.5%	88.69	1.21	8.46	**5.80**
Aged treated sample with EC 0.5%	87.98	0.69	10.93	**2.62**
Treated sample with EC 1%	88.89	1.31	8.56	**5.98**
Aged treated sample with EC 1%	88.94	0.75	10.83	**2.34**
Treated samples with EC/ZnO 0.5%	89.71	1.27	8.61	**6.79**
Aged treated sample with EC/ZnO 0.5%	90.55	0.46	10.02	**1.83**
Treated samples with EC/ZnO 1%	92.38	0.61	6.70	**9.79**
Aged treated sample with EC/ZnO 1%	92.55	-0.07	9.61	**2.99**

3.4. *FTIR analytical results*

Utilizing FTIR spectroscopy, the interactions and the behavior of EC polymer were recognized in paper composition by detecting the functional groups of the cellulose molecule. By comparing FTIR ATR spectra of untreated aged and aged treated samples, fig. (4), aged paper represented a wide and strong OH stretching band that appeared at 3640 cm^{-1} and 2930 cm^{-1} stretching of alkyl groups of the cellulose molecule [34,35]. A sharp peak that appeared is attributed to the stretching vibration of C=O appeared at 1720 cm^{-1}. The peaks that appeared at 1185 cm^{-1} and 1125 cm^{-1} are attributed to the C-O stretching vibration. The region was attributed to CH bond stretching (cellulose crystallization spectrum) increased from 1375 cm^{-1} to 1380 cm^{-1}. The region of C=C increased from 1428 cm^{-1} to 1462 cm^{-1}. The peak intensity of C-O-H also increased dramatically from 1119 cm^{-1} to 1159 cm^{-1}, and C-O from 1043 cm^{-1} to 1056 cm^{-1} [36].

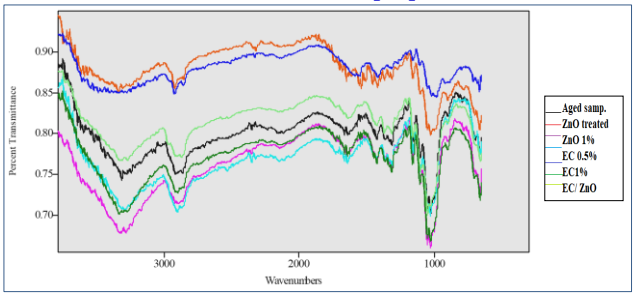


Figure (6) FTIR spectra of paper samples treated with selected consolidants.

3.5. *Measurement of the tensile strength*

According to tab. (3), the tensile strength was higher in the samples treated with EC 0.5 and 1% compared with those treated with zinc oxide. The treated sample with EC recorded a tensile strength of about 61.1%. It can be observed that the nanocomposites treated samples improved the behavior of the tensile breaking strength at an increase of (3%) compared to the untreated samples.

Table (3) Tensile strength and breaking factor before and after aging

Sample	Tensile Strength N/mm^2	Elongation %
Ref.	55.6	1.30
Control after aging	43.25	1.17
Treated sample with ZnO NPs 0.5%	78.2	1.26
Aged treated sample with ZnO NPs 0.5%	74.3	1.19
Treated sample with ZnO NPs 1%	80.4	1.28
Aged treated sample with ZnO NPs 1%	67.41	1.24
Treated sample with EC 0.5%	61.1	1.14
Aged treated sample with EC 0.5%	49.8	1.07
Treated sample with EC 1%	63.3	1.21
Aged treated sample with EC 1%	51.4	1.08
Treated samples with EC/ZnO 0.5%	73.4	1.27
Aged treated sample with EC/ZnO 0.5%	62.56	1.22
Treated samples with EC/ZnO 1%	90.5	1.32
Aged treated sample with EC/ZnO 1%	82.1	1.26

4. Discussion

Digital microscope observations showed the appearance of paper samples before and post consolidation treatment, the aged samples showed darkness on the surface and tiny cracks was noted on the external surface, fig. (2-a). Samples treated with EC showed an improvement on paper morphology, less gloss and no color change was detected, indicating the effectiveness of EC polymer for enhancing aged paper properties. While in case of EC nanocomposites we notice a slight glossiness in the outer surface, after aging a slight color change was observed. SEM investigations were carried out to detect the changes that may occurs post-consolidation treatments and to assess the behavior of EC polymer and ZnO NPS into the paper composition. Cellulosic fibers commonly decay thermally over degradation, and oxidation due to the heat effect, As well as the breakdown of cellulose chains and hemicelluloses [37-39]. Figure (3) showed the surface morphology of paper samples before treatment and after thermal aging. SEM results for the untreated samples revealed that there is remarkable change in the morphological structure of wood pulp due to thermal ageing process, additionally; the occurrence of cracks in paper fiber as shown in fig. (3-c). The investigation of wood pulp paper treated with ethocel polymer and ethocel/ZnO nanocomposites has shown an improvement in the morphology of wood fibers compared with untreated samples; it is clear the regular distribution of the nanocomposites on the outer surface [40,41]. The adhesion of small masses of ZnO nanoparticles with cellulose molecule is obviously seen. While in the case of EC nanocomposites a noticeable white mass distributed over the paper surface. The SEM micrograph of thermally aged treated samples, it revealed that the paper surfaces showed smooth appearance, clear regular grain and the fibers has become more interfered together as shown in fig. (3-d & e). The results obtained by FTIR ATR analysis; the spectra revealed characteristic absorption bands attributed to cellulose bands are detected in the wave number regions in the range between 3600-2800 cm^{-1} and 1650-400 cm^{-1}. These peaks corresponding to microcrystalline cellulose bands. The FTIR peaks were observed

at wave number range of 3640-2900 cm^{-1} is attributed to O-H and C-H bonds in polysaccharides. The observed peak at 3330 cm^{-1} corresponds to hydrogen bonding vibrations in cellulose. The aged paper represents a wide and strong OH stretching band appeared at 3640 cm^{-1}, and 2930cm^{-1} stretching of alkyl groups of cellulose molecules. A sharp peak that appeared is attributed to the stretching vibration of C=O appeared at 1720 cm^{-1}. The peaks that appeared at 1185 cm^{-1} and 1125 cm^{-1} are attributed to the C-O stretching vibration. In addition, the results after consolidation treatment with ZnO, and EC/ZnO appeared strong at 3434 cm^{-1}, also a sharp peak appeared at 1425 cm^{-1} which is due to CH bands indicating to crystalline structure, while the band at 900 cm^{-1} is attributed to the amorphous region in cellulose structure, but after treatment appeared sharp at 1429 cm^{-1}, The CH_2 stretching band represents to the degree of crystallinity of cellulose molecule which increased due to polymer interaction. The chemical bonding of cellulose chain clearly observed from the band at 2351 cm^{-1} resulting of CH deformation [42, 43]. After thermal aging a noticeable increase in the CH_3 stretching band intensity, the amorphous area decreased indicating the increase of cellulose crystallinity due to the interaction between cellulose molecule and polymer nanocomposite, an observable shifting in the OH stretching band corresponding to the hydrogen bonding was also detected in the treated samples after aging. The data concluded that the consolidation treatment enhances the chemical stability of wood paper pulp [45]. The data of yellowness and brightness reveals that the most effective treatment for decreasing the yellowness of aged paper is ZnO NPs, regardless of the effect of nano zinc on enhancing brightness properties; it has also been able to improve yellowness value. The control untreated sample and treated samples were subjected to thermal aging [46,47]. The change in the degree of yellowing of paper samples represented in the **Δ b*** values the data showed that the ZnO nanoparticles reduced the degree of yellowing. The value of yellowness of untreated and treated samples varied from 14.89 to 20.04, but in the case of ethocel polymer the changes in yellowing varied from moderate to significant effect. The data presented in tab. (2) showed the Lightness values of all treated paper samples, the treated samples with ZnO 1%. Paper samples treated with zinc oxide nanoparticles ZnO NPs and cellulose polymer nanocomposite EC ZnO 1% showed the least darkening with a lightness (**L***) value of 92.89 & 92.38. A significant decrease in the values of **a***, b* indicates that the consolidation treatment reduced the paper yellowness [48,49]. The total color values increased in the high concentrations of the consolidating agents after aging, the influence of aging was more notable when using EC/ZnO 1% rather than the using of 0.5%. The total color difference (ΔE) values in samples treated with EC/ ZnO in two concentrations was 6.79 and 9.79**,** considered a strong difference. After exposing the sample to aging, the percentage of color changes was 1.83 and 2.99, which means very acceptable percentage of color change. The results also revealed that lowest values were observed in the treated samples with ZnO in two concentrations 0.5% & 1% proving that adding using ZnO enhanced the optical properties of aged paper [50]. The tensile strength for the treated samples with nanocomposites EC + ZnO at 0.5 wt% was slightly higher than the treated sample with ZnO nanoparticles (about 1%). For the treated samples with Ethocel (EC) and EC nanocomposites, the tensile strength was 6.4 and 7.3 % higher than the aged un treated samples respectively. Hence, these shows good penetration and interaction between the –OH groups of the cellulose molecule and the –OH/C=O groups of cellulose ethers (Ethocel). Moreover, several researchers mentioned the improvement of the mechanical properties of paper materials after consolidation treatments with cellulose ethers, due to better interactions and better adhesion. The tensile strength has been increased, due to the symmetrical dispersion of the cellulose fibers and Ethocel nanocomposite [51,52]. Aged untreated samples showed 22.2% lower tensile strength and 10% lower breaking factor compared to the treated samples with ethocel. Treated samples with Ethocel nanocomposites (EC/ZnO) showed 8% higher tensile strength, tab. (3) and 1% higher breaking factor with regard to untreated samples. Thermal deterioration of paper leads to reduce the tensile strength. It has been discussed in previous studies that cellulose submits to cross linking during thermal aging [53,54]. Heat aging is mainly occurring in terms of chemical bonding and chain detachment; Hydrogen linking between cellulose chains or the creation of covalent bridge which attach or link chains together [55]. The creation of these interactions between the chains reinforces tensile strength and reduces the elasticity with regard to the treated samples the reduction in tensile strength values for all treated samples after thermal aging was less than the untreated aged samples. The tensile strength of paper fibers is moderately increased up after consolidation this may be due to complex molecule of cellulose [56].

5. Conclusion

The reinforcing material can be evaluated by its behavior and penetration into the paper structure, which can be assessed by physical analysis. The enhancement of the mechanical properties can be determined by performing tensile breaking tests. To evaluate the efficiency of ethocel polymer for enhancing the mechanical properties of wood paper pulp. Untreated and treated aged wood pulp paper was submitted to thermal aging and then was characterized using SEM and analyzed using FTIR spectroscopy. According to the findings of SEM, colorimetric measurements, and FTIR analysis, samples treated with Ethocel/ZnO 1% nanocomposite led to better results regarding tensile properties compared to ethocel polymer at the same concentration. Paper brightness revealed a remarkable decrease for all treated samples; the highest decrease was observed for those treated with ethocel polymer. The results of the tensile strength of the treated samples illustrated that ethocel polymer enhanced the aged paper's mechanical characteristics because of good penetration within the paper. According to the results, ethocel polymer revealed good results in achieving unremarkable color change, enhanced by adding ZnO nanoparticles, especially at a concentration of 1%. The high concentration also gave good bonding and cohesion between paper fibers.

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