Effect of Additives on Electrical Resistivity of Pulp Black Liquor-Sawdust Blends

Rasha A. Ahmed, [1] Amal H. Abdel Kader[2]

[1, 2] Kingdom of Saudi Arabia, Taif University, Faculty of science, Chemistry dept., [2]National Research Center, Cellulose and Paper Dept., [1]Forensic Chemistry Laboratories, Medico Legal Department, Ministry of Justice, Cairo, Egypt.

Abstract: *Unlike the large scale paper mills which use the pulp black liquor (PBL) for recovery of chemicals, the small and medium mills usually throw away the black liquor after pulping, leading to pollution problems. Furthermore, sawdust wastes (SDW) produced from factories leads to a big problem. The objective of this study is to determine the effect of natural binders (wax and starch) on the thermal conductivity and electrical resistivity of black liquor-sawdust composites. Surface analysis of samples was studied. Results from Cyclic voltammetry and electrochemical impedance spectroscopy techniques demonstrated that addition of starch and wax increases electrical resistivity of black liquor-sawdust composites.*

***Keywords**: black liquor, natural binders, surface analysis, thermal conductivity, electrochemical impedance.*

I. Introduction

Approximately 7 tones of black liquor are produced in the manufacture of one tone of pulp [1, 2]. Black liquor is an effluent from alkaline pulping of lignocellulosic raw materials, which is an intermediate step in the manufacturing of paper [3]. In large paper mills, the black liquor so produced is combusted, after concentration, in a specially designed boiler to derive energy [4-7]. One of the main ingredients in black liquor is lignin, which is the material in trees that binds wood fibers together and makes them rigid, and which must be removed from wood fibers to create paper [8-12].

The weak black liquor has a solid content of approximately 15% by weight, which is too low for combustion. To raise the solid content in the liquor, it is being evaporated by a sequence of concentrators. When the resulting strong black liquor reaches the recovery unit (boiler or gasifier) it has a solid content of around 75%. Chemically, black liquor is a mixture of several basic elements where the largest fractions are carbon, oxygen, sodium and sulfur.

Sawdust is a by-product from sawmills. Wood chips screening is defined as finely divided wood material which has passed through the screens prior to pulping, *i.e.* wood material smaller than the accepted size for chips. The quality of sawdust depends on the saw type, method of sawing, type of tree used, and the storage method of logs including temperature, moisture and season [13-18]. Thus, sawdust and chips screenings from different mills can be very heterogeneous raw materials.

An adhesive is a substance capable of holding materials together by surface attachment with the ability to sustain the designed load requirement without deformation or failure. For an adhesive to be effective, there are two major characteristic requirements. The adhesive must be capable of impacting adequate bond between the two materials by principle of resistance to load shear, which implies creep static or time independent deformation under sustained load. Other desired requirements are ease of application, reasonable setting time, resistance to moisture, aging, heat and fungal attack, non-staining and gap filling. Traditionally, adhesives of natural origin have been used to repair and adhere black liquor-sawdust material, particularly, starch paste, Arabic gum, and animal glue or gelatin. These adhesives are expected to remain relatively reversible over time. Wax (Fig.1) has been used as an adhesive since the beginning of time. It refers to a class of organic chemical compounds that are plastic (malleable) near ambient temperatures. Characteristically, they melt above 45 °C to give a low viscosity liquid. Waxes are insoluble in water but soluble in organic and nonpolar solvents. Its molecular structure is branched and circular, making it an excellent adhesive. Wax is great gap filler, adheres instantly and is not toxic unless it is burned. It works on any material, porous or non porous. It is acid free and will not wrinkle fine papers. Wax can act as an elastomer, and tackifying agent provides excellent hot-melt adhesive and bond strength, it improves moisture resistance and wettability.

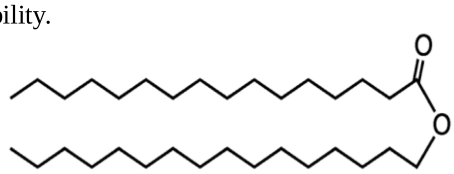

Fig. 1.Wax structure

Starch or amylum, Fig. 2, is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysaccharide is produced by all green plants as an energy store. It is found in many processes either as an adhesive or thickener. The fine, smooth texture, non-staining, non-poisonous nature of starch and the good stability of the product with time makes it a desirable choice particularly for domestic uses.

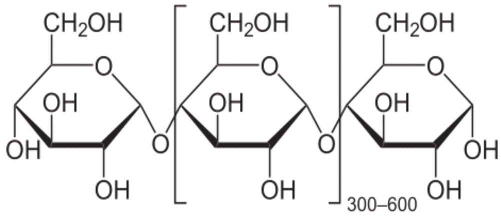

Fig. 2. Starch structure

Electrochemical impedance spectroscopy (EIS) has been used extensively to characterize the electrical properties of desired materials as a function of frequency. The EIS results are used to interpret impedance spectra in terms of resistance and capacitance associated with the physicochemical properties of desired samples [19-25]. To our knowledge, there are very few studies reporting the use of impedance in studying the thermal conductivity and electric resistivity of PBL.

The major purpose of this paper is to study the thermal conductivity and electrical resistivity of two wastes (PBL and SDW), hopping to decrease the pollution problem obtained from these wastes by using them as an active materials for the production of eco-friendly insulating composites using synthetic and natural binders such as wax and starch paste.

First, the morphology of PBL in present and absent of additives was studied using SEM and FT-IR. Secondly, electrochemical impedance and cyclic voltammetry techniques were used to measure the effect of additives on the thermal conductivity and electrical resistivity of the PBL samples.

II. Experimental procedures

2.1.1. Reagent and materials

A waste of pulp black liquor (PBL) from paper industry was provided by paper factory, sawdust waste (SDW) was provided by wood and furniture factories. Three samples were prepared using pulp black liquor waste (PBL) as solid residue after filtration and drying (blank), mixing it with fine sawdust wastes and wax as a binder to produce the second sample (BLSW), finally it mixed with sawdust and natural binder starch paste to produce the third sample (BLSS).

2.1.2. Characteristics of black liquor

The composition of the (PBL) produced during the pulping process in different plants may not be the same, even if the same pulping process is used. However, black liquor consists generally of lignin, hemicelluloses, cellulose, and silica. Minor constituents such as fats, wax, resins, mucilage, and gums. Harada et al., [26] exist in small portions. The elemental analysis of black liquor is 36.4% C, 18.6% Na, 4.8% S, 3.5% H, 2.02% K, 0.24% Cl, 0.14% N, 34.30 % O. [27, 28].

2.2. Instrumental and experimental set-up

The electrodes for the electrochemical studies were fabricated as follows: 10.0 mg of synthesized samples (PBL, BLSW, BLSS) were pressed on an empty electrode with a $1cm^2$ geometrical area. The measurements were carried out with a potentiostat/galvanostat Autolab PGSTAT 73022. EIS measurements were done at an open circuit potential with applied 10 mV sinusoidal perturbations in the 100 kHz to 0.1 mHz frequency range, taking 7 steps per decade. For this purpose, a conventional three-electrode cell was used, composed of Ag/AgCl reference electrode, a platinum wire as the counter electrode, and the empty electrode disc (diameter: 2.5 mm) as the working electrode. The tests were carried in 0.1 M Briton Robinson (B-R) buffer pH 3.5.

Scanning electron microscope (SEM) (Philips, XI 30) was used for characterization of the homogeneity of the coatings where the samples were coated with gold before SEM examination. JASCO 300-E Fourier transform infrared (FT-IR) spectrometer was used to analyze changes in the chemical structure of the samples. The IR spectra were carried out using the potassium bromide pellet technique in the wave number region 4000–400 cm^{-1}.

III. Results and discussion

3.1. Surface morphology

3.1.1. Scanning Electron Microscopy (SEM)

The SEM was done to show the external surface of samples and the interference between composites at different magnifications. Fig. 3(A) shows the SEM images of the blank sample (PBL), where large number of pores and cavities were observed. The cavities on the surface of PBL result in its electric conductivity. After relatively mild mixing of wax and starch was applied to PBL, SEM of BLSW and BLSS samples in Fig. 3B and C, respectively, reveals that both samples are homogenous compact layers in which the pores are filled, and distributed uniformly. The good network of interconnected pores increases the electric resistivity of the PBL due to the presence of wax and starch which act as a great gap filler. It also increases bond strength between black liquor and sawdust wastes.

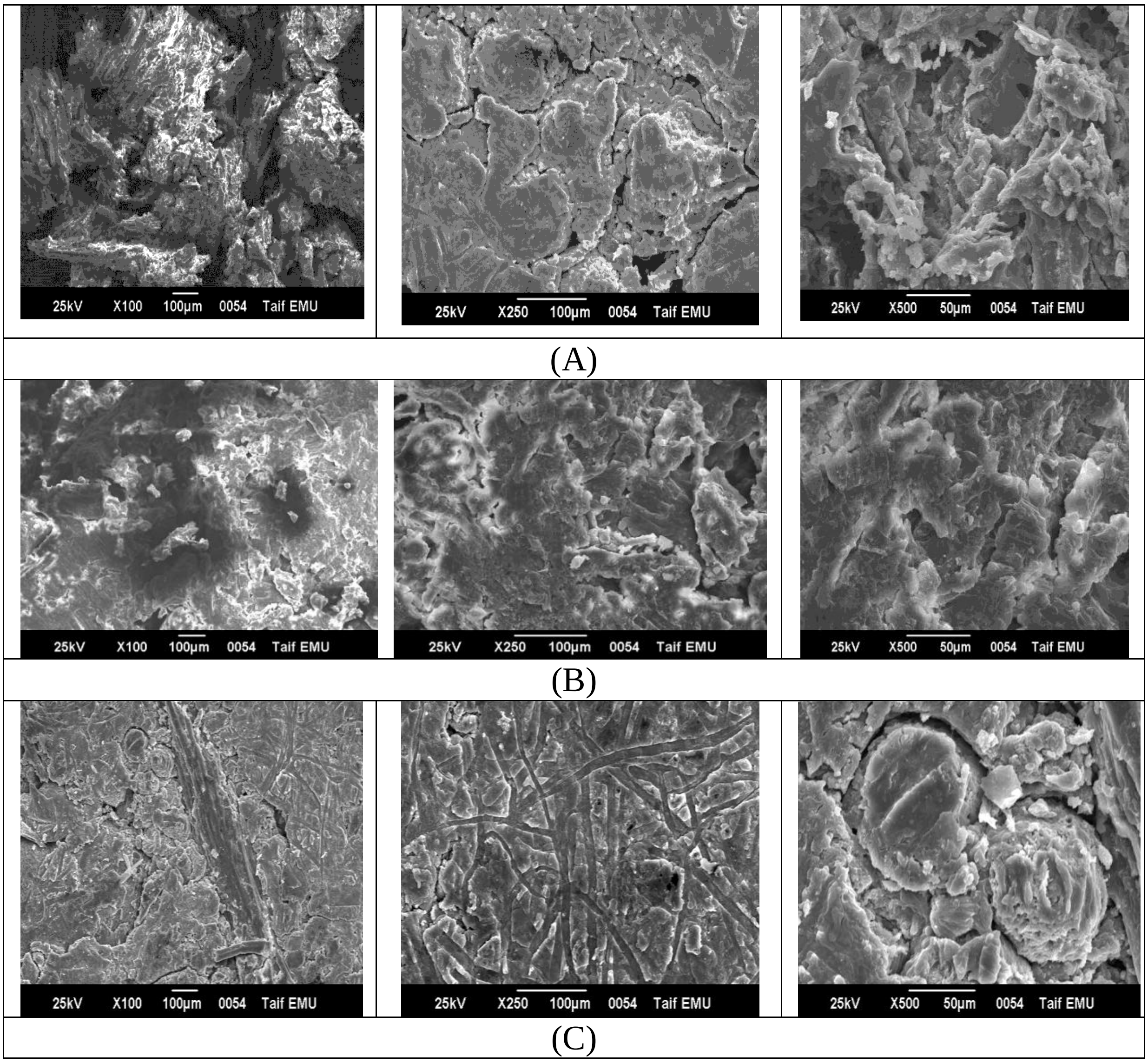

Fig. 3. SEM micrographs showing the surface of PBL(A), BLSW(B), BLSS (C) (magnification 100, 250 and 500 μm).

3.1.2. Comparison of IR Spectra

A full, detailed IR transmission spectrum for the three samples was obtained, and is presented in Fig. 4.

The IR spectrum of PBL Fig. 4(A) shows, the appearance of bands at 1597- 1457 cm^{-1} for the aromatic skeletal vibration of the PBL, The characteristic bands of black liquor were assigned according to the literature, as shown in Table 1.

In contrast, if we look at the IR spectra of BLSW Fig. 4(B), significant features seen include: Appearance of a band at 1222 cm^{-1} which can be assigned to C-O stretching. Progression of weak band at 1118 cm^{-1} for C-OH stretch is noticed. Other frequency present at 782 cm^{-1} for CH_2 rocking assigned to wax structure.

Spectrum of BLSS Fig. 4(C), for the modified black liquor with starch was obtained. The absorption region at 1029 cm^{-1} relates to C–C and C–O stretching modes of the polysaccharide backbone [29, 30]. Appearance of a band at 1380 cm^{-1} assigned to bending modes of O–C–H, C–C–H, and C–O–H angles [30]. Other frequencies, which are not seen before, are observed at 622 and 445 cm^{-1}.

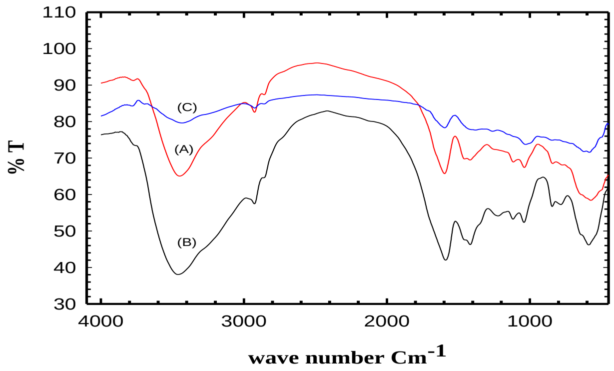

Fig. 4. FTIR spectrum of PBL (A), BLSW (B), and BLSS (C)

Table (1) lists the assignment of the different IR bands of samples.

Maximum band position (cm^{-1})	Band origin
3450-3694	OH stretching (H- bonded)
2924- 2926	CH stretching of methyl or methylene group.
2858	CH vibration of methyl of methoxy group.
1457.9	CH stretching of methyl or methylene group.
1417-1419	CH vibration of methyl group.
1029-1041	OH stretching of primary alcohol.
844	Aromatic C-H out of plane bending.

IV. Electrochemical study

4.1. Electrochemical behavior of the black liquor – sawdust blends

Cyclic voltammetry measurements were performed over a potential range of −2 to 2 V/s) to examine the electrochemical characteristics of black liquor – sawdust blends. Fig. 5(A) shows the cyclic voltammogram of black liquor and sawdust in 0.1 mol L^{-1} B-R (pH 3.4) at 288 K. One anodic broad peak current at −0.12 V with a high charging current during the potential sweep is observed. This attributed to the flow of electric charges through the pulp black liquor (blank), which in turn increases the electric conductivity and decreases resistivity of the sample. The flow of electric charges is expected from the contribution of a high pore diameter of PBL and the conjugated structure of black liquor.

However, Fig. 5(B, C) shows the cyclic voltammogram of black liquor, sawdust with wax and starch, respectively, in 0.1 mol L^{-1} B-R (pH 3.4) at 288 K. In presence of wax or starch, the charged current decreases which attributed to the physical properties of both blends as insulating material which fill the porous film of the black liquor, and retarded the movement of electric charges and thus decreases the current. Generally, the porous structure with a high pores diameters in pulp black liquor sample (PBL) can accommodate more electrolytes and increases electrochemical activation, but the addition of wax or starch to black liquor and sawdust composite decreases their conductivity and becomes more insulation. These data comes in a good agreement with the SEM images.

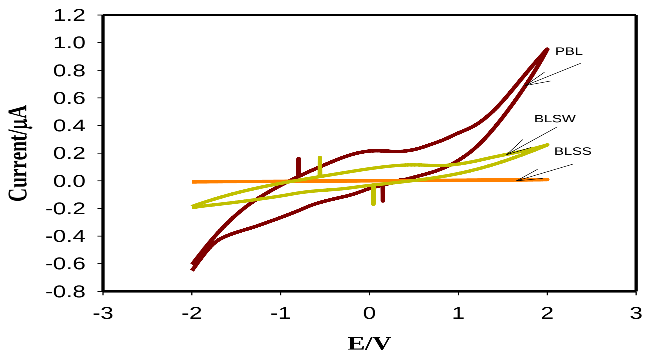

Fig. 5. Cyclic voltammograms of black liquor (PBL), BLSW, and BLSS in 0.1 mol L^{-1} B-R (pH 3.4) at 288 K

4.2. Electrochemical impedance analysis

4.2.1. Effect of additives

To evaluate the effect of wax and starch paste on the conductivity and resistivity of the black liquor composite, electrochemical impedance were investigated in absence and presence of these additives. EIS data were obtained for the black liquor composite electrodes at AC frequency varying between 100 kH_Z and 0.1 mHz at open circuit potential in B-R buffer (pH=3.4) at 318 K. Fig. 6 shows a typical Nyquist plot, that is plot of imaginary part of the modulus *Z'* vs. real one *Z*, for black liquor (PBL) (A), BLSW (B), and BLSS (C). The impedance spectra include semicircles; the large diameter semicircle indicates the higher electron transfer resistance of black liquor sawdust in present of starch paste, in which it confirmed with the cyclic voltammetry technique. However, the diameter of the semicircle decreases in BLSW sample indicating the flow of electric current through that composite. This attributed to wax structure which affected by temperature and permit electron transfer faster than that in starch composite. The presence of starch in PBL perform more stable product. On the other hand, in absence of additives, the diameter of semicircle diminished markedly. Thus, the charge transfer resistance of electro oxidation of pulp black liquor (PBL) increases greatly, and the charge transfer rate is enhanced.

In general, Additives provides excellent adhesive and high bond strength, Moreover they improve electrical resistivity of PBL at room temperature.

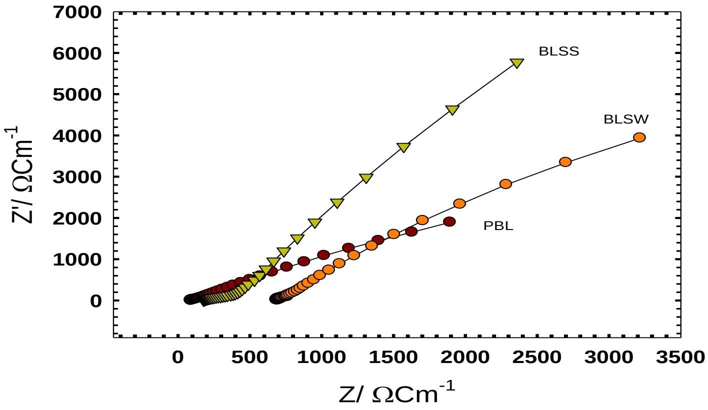

Fig. 6. A typical impedance spectrum for PBL, BLSW and BLSS at 343 K.

4.2.2. Effect of temperature

To evaluate the effect of raising temperature on the conductivity and resistivity of the black liquor composite, electrochemical impedance were investigated at temperature range from 288 K to 343 K for PBL, BLSW, and BLSS. Nyquist plot for pulp black liquor (PBL) at different temperatures is shown in Fig. 7. The large diameter semicircle indicates that the charge transfer rate is sluggish and causes the high resistivity of the composite at 288 K.

However, after rising the temperature, the diameter of semicircle diminishes markedly. Thus, the charge transfer resistance of PBL decreases greatly, and the charge transfer rate is enhanced. The data proves that increasing temperature increases the diameter of these pores and, facilitates the electron transfer across these pores, which make PBL more conductive at higher temperatures. The same behavior is noticed in BLSW, and BLSS. By increasing temperature above 300 K wax melt and separated from its composite causing flow of electricity. However, the more stable BLSS composite retain its behavior to some extent at higher temperature.

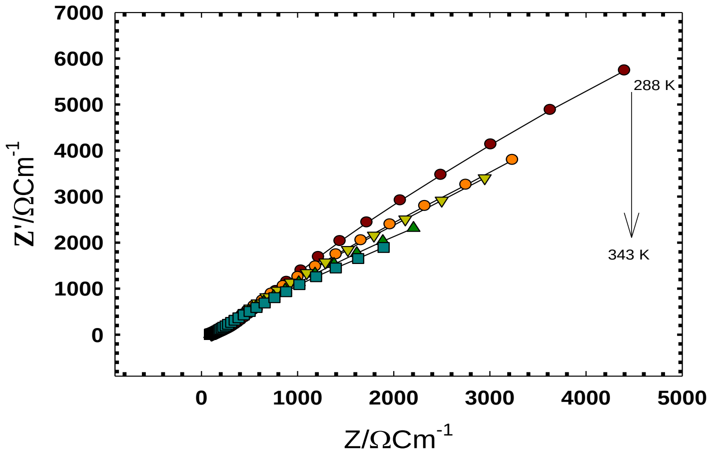

Fig. 7. Nyquist plot for black liquor and saw dust (PBL) at different temperatures

V. Conclusion

In previous references, the morphology and properties of PBL has studied in absence and presence of additives, but the investigations of the porosity as well as thermal conductivity and electrical resistivity of PBL using electrochemical technique are absent. In this paper, the effect of additives (wax and starch) on the porosity, conductivity, and resistivity of PBL-SD has been studied by electrochemical technique, and electrochemical impedance spectroscope, and confirmed by surface analysis.

VI. Acknowledgments

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